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Citation: *J. Chem. Phys.* **3**, 715 (1935); doi: 10.1063/1.1749582

View online: <http://dx.doi.org/10.1063/1.1749582>

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A Generalized Thermodynamic Notation

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(Received July 24, 1935)

It has recently been shown by Koenig that, as a result of the symmetry of the fundamental relations of thermodynamics, thermodynamic equations can be grouped into families. In the present paper a generalized notation is described which leads to an elegant method of writing down from one generalized equation all the members of a family; in particular, the signs of the various terms are

very easily manipulated. The question of the number of members of a family is considered, and a method is given for obtaining the generalized equation when any one member of a family is known. Finally the extension of the method to problems of capillarity, magnetization, etc., is shown to be very readily carried out.

DERIVATION OF GENERALIZED FORMULAE

A ONE-PHASE system containing $n-2$ chemical components has n degrees of freedom, provided gravitational, electrical, magnetic, and capillary effects can be neglected. At least one of these degrees of freedom must be extensive.¹

The thermodynamic properties of such a system may, then, be described by means of n extensive variables:

$$X_1 X_2 \cdots X_n.$$

Two of these are S and $-V$, S being the entropy and V the volume; we take $-V$ rather than V purely for convenience in generalizing our equations. For the rest we may take the numbers of moles, the N 's, of any set of $n-2$ independent chemical species.

The internal energy, E , of the system is a function of the X 's, and its partial differential coefficients with respect to each X in turn are the intensive variables of the system:

$$x_r = \partial E / \partial X_r, \quad (1)$$

$$dE = \sum_{r=1}^n x_r dX_r. \quad (2)$$

(2) is usually met with in the form:

$$dE = TdS - PdV + \sum \mu dN,$$

where T is the temperature, P the pressure, and the μ 's are chemical potentials.

Any pair of variables X_r , x_r related by (1) is known as a conjugate pair of variables. A set of

variables containing one member from each conjugate pair is known as a canonical set. Corresponding to the general canonical set of variables:

$$x_1 x_2 \cdots x_p, X_{p+1} \cdots X_n$$

we may define a characteristic function Φ , such that

$$\Phi = E - \sum_{r=1}^p x_r X_r. \quad (3)$$

Differentiating and combining with (2) we get:

$$d\Phi = - \sum_{r=1}^p X_r dx_r + \sum_{r=p+1}^n x_r dX_r. \quad (4)$$

E is the characteristic function corresponding to the canonical set consisting of all the X 's.

Let us take in general a canonical set:

$$Y_1 Y_2 \cdots Y_n$$

and let:

$$y_1 y_2 \cdots y_n$$

be the corresponding conjugate quantities. Then in virtue of (4):

$$d\Phi = \sum_{r=1}^n y_r d|Y_r|. \quad (5)$$

The symbol $|Y_r|$ indicates that Y_r is to be taken with a positive sign when Y_r is an extensive variable and with a negative sign when Y_r is intensive. From (5) we get

$$\partial \Phi / \partial |Y_r| = y_r, \quad (6)$$

where r takes all values from one to n in turn. The next differential coefficients give rise to the generalized form of the Maxwell relations:

$$\frac{\partial^2 \Phi}{\partial |Y_r| \partial |Y_s|} = \frac{\partial y_r}{\partial |Y_s|} = \frac{\partial y_s}{\partial |Y_r|}, \quad (7)$$

¹ Craxford, Gatty and Philpot, *Phil. Mag.* [7] **16**, 849 (1933).

where r and s assume all values from 1 to n subject to the restriction $r \neq s$.

We may next consider relations arising from the use of two characteristic functions simultaneously. Let these be Φ_1 corresponding to the same canonical set as before, and Φ_2 corresponding to the set:

$$Y_1 Y_2 \cdots Y_p, \quad y_{p+1} \cdots y_n,$$

where of course $1 \leq p < n$. It follows at once from the definition of the Φ 's in Eq. (3) that

$$\Phi_2 = \Phi_1 - \sum_{r=p+1}^n y_r |Y_r|. \quad (8)$$

By combination of (8) with (6) we get a generalized relation of the type of the Gibbs-Helmholtz equation:

$$\Phi_2 = \Phi_1 - \sum_{r=p+1}^n |Y_r| \partial \Phi_1 / \partial |Y_r|.$$

Since the $|Y_r|$'s occur in pairs we can write this simply as

$$\Phi_2 = \Phi_1 - \sum_{r=p+1}^n Y_r \partial \Phi_1 / \partial Y_r, \quad (9)$$

or in Jacobian notation as

$$\Phi_2 \Phi_1^{n-p-1} = (-1)^{n-p} \prod_{r=p+1}^n Y_r^2 \frac{\partial(\Phi_1/Y_{p+1}, \Phi_1/Y_{p+2}, \dots, \Phi_1/Y_n)}{\partial(Y_{p+1}, Y_{p+2}, \dots, Y_n)}. \quad (9a)$$

When $p = n-1$, this reduces to

$$\Phi_2 = -Y_n^2 (\partial/\partial Y_n)(\Phi_1/Y_n).$$

By differentiation of (8) with respect to $|Y_s|$ at constant all the other Y 's, we can find the partial derivatives of a Φ when the set of variables taken as independent is not its own set. When $1 \leq s \leq p$, we get

$$\begin{aligned} \frac{\partial \Phi_2}{\partial |Y_s|} &= \frac{\partial \Phi_1}{\partial |Y_s|} - \sum_{r=p+1}^n |Y_r| \frac{\partial y_r}{\partial |Y_s|} \\ &= y_s - \sum_{r=p+1}^n Y_r \frac{\partial y_s}{\partial Y_r}, \end{aligned} \quad (10)$$

using (6) and (7). This result also might be expressed in Jacobian form, for it is of the same form as (9). When $p < s \leq n$, there is only one case of interest, namely, when $p = n-1$ and $r = s = n$. We get

$$\begin{aligned} \partial \Phi_2 / \partial |Y_n| &= \partial \Phi_1 / \partial |Y_n| - y_n - |Y_n| \partial y_n / \partial |Y_n| \\ &= -Y_n \partial y_n / \partial Y_n. \end{aligned} \quad (11)$$

We might introduce more than two Φ 's into the problem simultaneously; but the equations obtained would be mostly of small importance and would be very complicated to deal with except in special cases. There is however one important type of formula in which four different canonical sets of variables are involved; the formula for the difference between constant

pressure and constant volume specific heats is included in this type.

We start from the familiar mathematical identity

$$\left(\frac{\partial y_r}{\partial Y_r} \right)_2 - \left(\frac{\partial y_r}{\partial Y_r} \right)_1 = \left(\frac{\partial y_r}{\partial Y_n} \right)_1 \left(\frac{\partial Y_n}{\partial Y_r} \right)_2.$$

Here the suffix 1 implies that the set of variables corresponding to Φ_1 are to be taken as independent in forming the differential coefficient in question, and 2 implies that the set corresponding to Φ_2 are to be taken as independent. We have assumed too that $p = n-1$. Multiply both sides of this equation by Y_r and use (7); this yields

$$Y_r \left(\frac{\partial y_r}{\partial Y_r} \right)_2 - Y_r \left(\frac{\partial y_r}{\partial Y_r} \right)_1 = Y_r \left(\frac{\partial y_n}{\partial |Y_r|} \right)_1 \left(\frac{\partial |Y_n|}{\partial Y_r} \right)_2.$$

The two terms on the left-hand side can now be dealt with by means of (11), so that we get finally

$$\left(\frac{\partial \Phi_3}{\partial Y_r} \right)_1 - \left(\frac{\partial \Phi_4}{\partial Y_r} \right)_2 = Y_r \left(\frac{\partial y_n}{\partial Y_r} \right)_1 \left(\frac{\partial |Y_n|}{\partial Y_r} \right)_2. \quad (12)$$

Here the canonical set of variables corresponding to Φ_3 differs from set 1 in that y_r replaces Y_r , and set 4 differs from set 2 in the same way.

There is one other result which may be mentioned. Write the Φ corresponding to the general canonical set as $\Phi^{x_1, x_2, \dots, x_p, x_{p+1}, \dots, x_n}$. Then it follows from (3) that

$$\Phi^A + \Phi^B + \Phi^C + \dots = \Phi^{A'} + \Phi^{B'} + \Phi^{C'} + \dots, \quad (13)$$

provided that each variable occurring in the superscripts A, B, C , etc. occurs in the superscripts A', B', C' , etc., the same number of times. A particular case will make this clear. Consider the variables S, V, T , and P . Then

$$\Phi^{SV} + \Phi^{PT} = \Phi^{SP} + \Phi^{VT}$$

or in ordinary notation (following Guggenheim's *Modern Thermodynamics*) $E + G = H + F$.

THE APPLICATION OF THE GENERALIZED FORMULAE

Eqs. (5) to (12) contain in epitome most of the important basic results of thermodynamics. To show how to employ them it will be best to take a couple of examples.

Consider first Eq. (7). Put $n=2$ and take S, V, T , and P as variables. We take as our Y 's any canonical set chosen from among these four variables, say S and P ; then the corresponding y 's are T and V , respectively. The Φ corresponding to the choice of S and P as independent variables is the heat content, H . Thus, allowing for the sign change whenever V appears in an equation, (7) becomes

$$\partial^2 H / \partial |S| \partial |P| = \partial T / \partial |P| = -\partial V / \partial |S|;$$

or, remembering our rule about the interpretation of the symbols $|S|$ and $|P|$,

$$\partial^2 H / \partial S \partial P = \partial T / \partial P = \partial V / \partial S.$$

The other three Maxwell relations arise similarly when we take S and V, T and V , and T and P as independent variables. What is particularly to be remarked about this method is the elegant way in which the plus and minus signs are manipulated.

As a second, more complicated, example, we will take Eq. (12). Once again put $n=2$ and take S, V, T , and P as our variables. For the set 1 of variables we will choose T and P with G as the characteristic function; for set 2, T and V with F ; for set 3, S and P with H ; and for set 4, S and V with E . This choice is in accordance with the requirements of the equation. This gives at once the familiar result for the difference between constant pressure and constant volume specific heats, namely

$$\left(\frac{\partial H}{\partial T} \right)_P - \left(\frac{\partial E}{\partial T} \right)_V = T \left(\frac{\partial V}{\partial T} \right)_P \left(\frac{\partial P}{\partial T} \right)_V.$$

KOENIG'S f_1 FAMILIES OF EQUATIONS

It will be seen that this method affords a very ready way of generating families of thermodynamic equations of the f_1 type considered by Koenig.² We have only to take the requisite generalized formula and make a fairly obvious sequence of substitutions to obtain all the members of a family. The procedure seems to be considerably neater than that of Koenig, who requires a rather complicated series of arrays of characteristic functions and variables in order to make the necessary sequence of substitutions and to obtain equations with the appropriate signs. Moreover, as will be seen later, the present method is more readily extended to other systems than the type so far considered.

To show that the present method of generating families of thermodynamic equations is in every respect as powerful as Koenig's, we must consider how to deduce the generalized formula when a particular case is given. An obvious method is to recapitulate in generalized notation the proof used for the particular case, but this is usually unnecessary.

Let us take for example the equation

$$\partial^2 H / \partial T \partial P = -T (\partial^2 V / \partial T^2)_P.$$

Here the set of variables is T and P and the corresponding Φ is G . There is also an H in the equation; H is the characteristic function of the set S and P . So we take Y_1 for P, y_1 for V, Y_2 for T, y_2 for S , and Φ_2 for H ; we get

$$\partial^2 \Phi_2 / \partial Y_1 \partial Y_2 = Y_2 (\partial^2 y_1 / \partial Y_2^2)_{Y_1},$$

where the sign is still to be adjusted. We now place absolute value signs round every Y and correct the signs of the various terms to agree with the particular case given. We get

$$\partial^2 \Phi_2 / \partial |Y_1| \partial |Y_2| = -|Y_2| (\partial^2 y_1 / \partial |Y_2|^2)_{Y_1}.$$

We can of course omit the absolute value signs when a pair of Y 's occur together; this enables us to write more simply

$$\partial^2 \Phi_2 / \partial |Y_1| \partial Y_2 = -Y_2 (\partial^2 y_1 / \partial Y_2^2)_{Y_1}.$$

² Koenig, J. Chem. Phys. 3, 29 (1935).

This is the equation obtained from (11) by setting $n=2$ and differentiating with respect to $|Y_1|$.

THE NUMBER OF MEMBERS OF A FAMILY

It is of interest to see how many members each family of equations contains. There are obviously as many equations of type (5) as there are Φ 's. Since a canonical set of variables is got by choosing one member from each of the X_r , x_r pairs, and there is a Φ corresponding to each canonical set, there are $2^n \Phi$'s and 2^n equations of this type. Each Φ gives rise to n equations of type (6), so there are in all $n \cdot 2^n$ equations of this type. Similarly, each Φ yields $\frac{1}{2}n(n-1)$ equations of type (7), so there are $n(n-1) \cdot 2^{n-1}$ equations of this type in all.

It is unnecessary to go through each case in detail. The following are the actual results for the rest of the equations:

Eq. (8). $2^{n-1}(2^n-1)$ equations in all. These can be split into groups according to the value of p , that is, according to the number of terms the equation contains. There are $2^{n-1}n!/(p!n-p!)$ equations in each of these groups.

Eq. (9). $2^n(2^n-1)$ equations in all; $2^n n!/(p!n-p!)$ in each group.

Eq. (10). $n \cdot 2^{2n-1}$ equations in all; $2^n n!/(p-1!n-p!)$ in each group.

Eq. (11). $n \cdot 2^n$ equations.

Eq. (12). $n(n-1) \cdot 2^{n-1}$ equations.

For a "closed" system, a system at constant composition, we have $n=2$. Most of the families of equations considered by Koenig are closed-system equations: it is easily verified that inserting $n=2$ into the expressions just given for the number of members of a family leads in each case to the number given by Koenig. Thus there are four Maxwell relations from (7), and eight Gibbs-Helmholtz equations from (9) with $p=n-1$.

For a one-component system, $n=3$. Koenig ignores in his investigation equations in which the μ 's appear as independent variables, so we cannot simply insert $n=3$ in our expressions for the number of members of a family. There are in fact no new equations of type (5). Type (6) yields one new equation for each Φ , so we get the four-membered family

$$\mu = \left(\frac{\partial E}{\partial N} \right)_{SV} = \left(\frac{\partial H}{\partial N} \right)_{SP} = \left(\frac{\partial F}{\partial N} \right)_{TV} = \left(\frac{\partial G}{\partial N} \right)_{TP}.$$

Likewise Eq. (7) yields an eight-membered family.

Most of the equations for systems for which $n>3$ represent nothing more than unnecessary duplication of equations already obtained. Thus for $n=4$ we should get the pair of equations

$$\mu_1 = (\partial E / \partial N_1)_{SVN_2}, \quad \mu_2 = (\partial E / \partial N_2)_{SVN_1}.$$

There are, however, relations like

$$(\partial \mu_1 / \partial N_2)_{N_1} = (\partial \mu_2 / \partial N_1)_{N_2},$$

which are of interest; Koenig's treatment would require a special extension to include such equations.

EXTENSION OF SYSTEMS OF OTHER TYPES

We have so far considered a system for which such things as capillary and electrical work terms can be neglected. But the method can be extended immediately to any system for which there holds an equation of the form of (2).

Thus, for a closed system containing an approximately plane interface

$$dE^* = TdS^* - pdV^* + \gamma dA,$$

where E^* , S^* , and V^* are the surface energy, entropy, and volume, γ is the surface tension, and A is the surface area.³ This equation is of the form of (2), so the generalized Eqs. (5)–(11) are immediately applicable. By way of illustration, let us take the canonical set of variables P , T , and A ; then (7) gives

$$(\partial \gamma / \partial T)_{PA} = -(\partial S^* / \partial A)_{PT};$$

$$(\partial \gamma / \partial P)_{TA} = (\partial V^* / \partial A)_{PT}.$$

Or again, the electrocapillary equation⁴

$$dG = \gamma dA + \Delta \varphi dq$$

(at constant p , T) where $\Delta \varphi$ is the electrical potential difference and q is the quantity of electricity flowing round the external circuit, gives at once

$$(\partial \gamma / \partial \Delta \varphi)_A = -(\partial q / \partial A)_{\Delta \varphi},$$

the Lippmann-Helmholtz equation.

³ Butler, *Chemical Thermodynamics, Part II* (London, 1934).

⁴ Craxford, Phil. Mag. [7] 16, 66 (1933).

As a third example, let us take the equation for closed one-phase systems in a magnetic field

$$dE = TdS - pdV + HdM,$$

where H is the magnetic field and M the magnetic moment.⁵ Typical results which follow from the generalized equations are

$$\begin{aligned} (\partial T/\partial M)_{SV} &= (\partial H/\partial S)_{MV}, \\ (\partial E/\partial M)_{TV} &= H - T(\partial H/\partial T)_{MV}, \\ (\partial \Phi_3/\partial T)_{PM} - (\partial \Phi_4/\partial T)_{PH} \\ &= T(\partial H/\partial T)_{PM}(\partial M/\partial T)_{PH} \end{aligned}$$

(where $\Phi_3 = E + PV$ and $\Phi_4 = E + PV - HM$). The third equation here is the formula for the difference between the constant moment and constant field specific heats, both at constant pressure.

THE INTERNAL ENERGY AS A HOMOGENEOUS LINEAR FUNCTION OF THE EXTENSIVE VARIABLES OF THE SYSTEM

Up to the present we have made no use of the fact that E is a homogeneous function of the first degree in the X 's. From Euler's theorem we get

$$E = \sum_{r=1}^n X_r \partial E / \partial X_r = \sum_{r=1}^n x_r X_r. \quad (14)$$

Differentiating this and using (2) we get the generalized Gibbs-Duhem formula

$$\sum_{r=1}^n X_r dx_r = 0. \quad (15)$$

(15) shows that the canonical set consisting of all the x 's is not an independent set. To give a complete description of the system it is necessary to include at least one X , in order to define the extent of the system.

The Φ corresponding to the canonical set of all the x 's is identically zero, for it is equal to $E - \sum_{r=1}^n x_r X_r$. This Φ might perhaps be excluded from consideration in the earlier part of this paper. But we should not on these grounds exclude $G (= E - TS + PV)$ in the case of a closed system. We must remember that the physical process involved in deriving (14) from (2) is that of increasing the quantity without

altering the state of the system; this is not a possible process for a system at constant all the N 's (i.e., a closed system). In fact the simplest case to which (14) applies is that of a one-component system, with $n=3$.

The formulae obtained with the aid of (14) cannot be treated by the Y notation hitherto adopted, because the distinction between intensive and extensive variables is now of importance in other respects than that of determining the signs of the terms. The results are thus necessarily less elegant, and the families of equations (the f_2^1 families of Koenig) more restricted. In practice (15) is by far the most important equation of the f_2^1 class, so we shall not develop the matter very far.

From (3) and (14) we get

$$\Phi = \sum_{r=p+1}^n x_r X_r. \quad (16)$$

The partial derivatives of Φ in the corresponding canonical set are thus given by

$$\partial \Phi / \partial x_s = \sum_{r=p+1}^n X_r \partial x_r / \partial x_s \quad (1 \leq s \leq p),$$

$$\partial \Phi / \partial X_s = x_s + \sum_{r=p+1}^n X_r \partial x_r / \partial X_s \quad (p < s \leq n).$$

Comparing these expressions with (6) we find that

$$X_s + \sum_{r=p+1}^n X_r \partial x_r / \partial x_s = 0, \quad (17)$$

$$\sum_{r=p+1}^n X_r \partial x_r / \partial X_s = 0. \quad (18)$$

These can be converted further by using (7). We find

$$X_s = \sum_{r=p+1}^n X_r \partial X_s / \partial X_r, \quad (19)$$

$$\sum_{r=p+1}^n X_r \partial x_s / \partial X_r = 0. \quad (20)$$

In (17) and (19), s ranges from 1 to p , and in (18) and (20), from $p+1$ to n . Eq. (18) is of considerable importance, for it is the form in which the Gibbs-Duhem relation is usually applied.

⁵ Stoner, Phil. Mag. [7] 19, 565 (1935).