TRANSFORMATION GROUPS OF THE THERMODYNAMIC VARIABLES*

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Abstract. A certain class of transformations on the thermodynamic variables E, H, F, G, S, T, P, and V which leave the fundamental equations invariant is investigated and found to form a group of order thirty-two. The quotient group with respect to a normal subgroup of order four gives the octic group obtained by other investigators, the normal subgroup containing trivial but non-excludable transformations. In contradistinction to previous investigators, it is not necessary to use absolute values or a rule of signs. Examples are given of the application of the transformations.

Certain transformations on the fundamental thermodynamic variables will change members of a large class of thermodynamic equations valid for reversible processes into other valid equations of similar form. These transformations have been investigated by Koenig[1] and Buckley[2] and found to form the group of order eight called the octic group. Koenig restricted his transformations to pure substitutions, or permutations, took care of a difficulty in sign by introducing absolute values and a rule of signs, and discussed a geometric method of exhibiting the transformation group. Buckley showed that Koenig's group could be derived in part by Lie's theory of contact transformations, and listed a number of families of thermodynamic equations to which Koenig's transformations apply. Although of course mathematically correct, the application of Lie's theory is not essential in this case.

In order to eliminate the inconvenient and somewhat disturbing use of absolute values and a rule of signs, the following exposition of the theory of these transformations is presented. The transformations considered are not limited to pure permutations but allow changes in sign, and the octic group is finally obtained out of a larger transformation group as a quotient group without the necessity of using absolute values or a rule of signs. The transformations are represented by matrices whose elements in any single row or column are all null except for one element which equals 1 or -1.

The thermodynamic quantities involved are[3]: the internal energy E, the enthalpy H, Helmholtz' function F, Gibbs' function G, the entropy S, the absolute temperature T (intensive), the absolute pressure P (intensive), and the volume V. All these quantities except T and P are extensive quantities. The quantities H, F, and G are defined relative to E by

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[1] F. O. Koenig, *Families of thermodynamic equations, I,* Journal of Chemical Physics, **3,** 29 (1935).

[2] F. Buckley, *Transformations of the fundamental equations of thermodynamics,* Journal of Research NBS, **33,** 213 (1944).

[3] This notation is perhaps the most common in scientific literature, with the symbol U often used in place of E. The functions F and G, invented by Helmholtz and Gibbs respectively, are generally known as the free energy and the thermodynamic potential, while the American Standards Association has used the term free enthalpy for the function G. The standard usage of American chemists is that of Lewis and Randall, where the functions F and G are denoted by A and F, respectively, and are termed the work function and the free energy.

$$H = E + PV, \tag{1a}$$

$$F = E - ST, \tag{1b}$$

$$G = E + PV - ST. \tag{1c}$$

These definitions, together with the fundamental thermodynamic equation for dE give the equations

$$dE = TdS - PdV, \tag{2a}$$

$$dH = TdS + VdP, \tag{2b}$$

$$dF = -SdT - PdV, \tag{2c}$$

$$dG = -SdT + VdP. \tag{2d}$$

The transformations considered are all transformations which leave Eqs. (1) and (2) invariant, such transformations preserving the validity of any equations derived from Eqs. (1) and (2). The class of equations to which the transformations apply is therefore the class of equations thus derived. If the symbol x is used to denote undetermined matrix elements, the transformations will be of the form

$$\begin{bmatrix} E' \\ H' \\ F' \\ G' \\ S' \\ T' \\ P' \\ V' \end{bmatrix} = \begin{bmatrix} \begin{bmatrix} x & x & x & x \\ x & x & x & x \\ x & x & x & x \\ x & x & x & x \end{bmatrix} & \begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} \\ \begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} & \begin{bmatrix} x & x & x & x \\ x & x & x & x \\ x & x & x & x \\ x & x & x & x \end{bmatrix} \end{bmatrix} \begin{bmatrix} E \\ H \\ F \\ G \\ S \\ T \\ P \\ V \end{bmatrix}. \tag{3}$$

From the invariance of Eqs. (2), the following seven observations on the transformations are made:

I. The off-diagonal 4 by 4 submatrices are necessarily null. This fact allows the transformations to be put in the separated form

$$\begin{bmatrix} E' \\ H' \\ F' \\ G' \end{bmatrix} = \begin{bmatrix} x & x & x & x \\ x & x & x & x \\ x & x & x & x \\ x & x & x & x \end{bmatrix} \begin{bmatrix} E \\ H \\ F \\ G \end{bmatrix}, \tag{4a}$$

$$\begin{bmatrix} S' \\ T' \\ P' \\ V' \end{bmatrix} = \begin{bmatrix} \begin{bmatrix} x & x \\ x & x \end{bmatrix} & \begin{bmatrix} x & x \\ x & x \end{bmatrix} \\ \begin{bmatrix} x & x \\ x & x \end{bmatrix} & \begin{bmatrix} x & x \\ x & x \end{bmatrix} \end{bmatrix} \begin{bmatrix} S \\ T \\ P \\ V \end{bmatrix}. \tag{4b}$$

II. If one of the variables ($EHFG$) is changed in sign, all of them must be thus changed. Such transformations may at this point be excluded as trivial. This exclusion limits the transformation (4a) to pure permutations.

III. The invariance of the equation

$$E - H - F + G = 0 \tag{5}$$

derivable from (1) may be used to limit the transformations (4a) to eight in number, all of which are of the type considered.

IV. Since S is always associated with T in Eqs. (1) and (2), as is P with V, the form of the transformations (4b) must be as shown with two diagonally opposed 2 by 2 submatrices null.

V. The 2 by 2 submatrices of Eqs. (4b) are necessarily of one of five forms, which are abbreviated thus:

$$\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} = e, \tag{6a}$$

$$\begin{bmatrix} -1 & 0 \\ 0 & -1 \end{bmatrix} = -e, \tag{6b}$$

$$\begin{bmatrix} 0 & 1 \\ -1 & 0 \end{bmatrix} = i, \tag{6c}$$

$$\begin{bmatrix} 0 & -1 \\ 1 & 0 \end{bmatrix} = -i, \tag{6d}$$

$$\begin{bmatrix} 0 & 0 \\ 0 & 0 \end{bmatrix} = o. \tag{6e}$$

VI. Transformations of the type in which, for example, both P and V are changed in sign are admittedly trivial but cannot be excluded because they are necessary for closure of the group of transformations (4b).

VII. A given transformation (4b) defines at most one transformation (4a). The converse is not true, however, and the correspondence is found to be four to one. Thus the number of transformations (4b) is thirty-two.

The eight transformations (4a), the corresponding thirty-two transformations (4b) expressed using the abbreviations in Eqs. (6), together with eight symbols representing group elements, are listed in Table I.

The transformations (4a) form a group of order eight which is designated as M. The transformations (4b) form a group of order thirty-two which is designated as G. The group G is four to one homomorphic to M, the normal subgroup

$$N = \left(\begin{bmatrix} e & a \\ o & e \end{bmatrix} \begin{bmatrix} e & o \\ o & -e \end{bmatrix} \begin{bmatrix} -e & o \\ o & e \end{bmatrix} \begin{bmatrix} -e & o \\ o & -e \end{bmatrix} \right) \tag{7}$$

of G corresponding to the indentity element of M. From this correspondence is established the isomorphism

$$M \simeq G/N \tag{8a}$$

or the congruence

$$M \equiv G \bmod N. \tag{8b}$$

This group is the octic group, whose multiplication table in terms of the group elements shown in Table I is given in Table II. This multiplication table is consistent with matrix multiplication of the matrices representing either transformations (4a)

TABLE I: The transformations of the thermodynamic variables.

Group Element	Transformations of $\begin{bmatrix} E \\ H \\ F \\ G \end{bmatrix}$	Transformations of $\begin{bmatrix} S \\ T \\ P \\ V \end{bmatrix}$
m_1	$\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}$	$\begin{bmatrix} e & o \\ o & e \end{bmatrix}, \begin{bmatrix} -e & o \\ o & e \end{bmatrix}, \begin{bmatrix} e & o \\ o & -e \end{bmatrix} \begin{bmatrix} -e & o \\ o & -e \end{bmatrix}.$
m_2	$\begin{bmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{bmatrix}$	$\begin{bmatrix} i & o \\ o & i \end{bmatrix}, \begin{bmatrix} -i & o \\ o & i \end{bmatrix}, \begin{bmatrix} i & o \\ o & -i \end{bmatrix}, \begin{bmatrix} -i & o \\ o & -i \end{bmatrix}.$
m_3	$\begin{bmatrix} 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 1 & 0 & 0 & 0 \end{bmatrix}$	$\begin{bmatrix} o & e \\ e & o \end{bmatrix}, \begin{bmatrix} o & e \\ -e & o \end{bmatrix}, \begin{bmatrix} o & -e \\ e & o \end{bmatrix}, \begin{bmatrix} o & -e \\ -e & o \end{bmatrix}.$
m_4	$\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}$	$\begin{bmatrix} o & i \\ i & o \end{bmatrix}, \begin{bmatrix} o & i \\ -i & o \end{bmatrix}, \begin{bmatrix} o & -i \\ i & o \end{bmatrix}, \begin{bmatrix} o & -i \\ -i & o \end{bmatrix}.$
m_5	$\begin{bmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{bmatrix}$	$\begin{bmatrix} e & o \\ o & i \end{bmatrix}, \begin{bmatrix} -e & o \\ o & i \end{bmatrix} \begin{bmatrix} e & o \\ o & -i \end{bmatrix}, \begin{bmatrix} -e & o \\ o & -i \end{bmatrix}.$
m_6	$\begin{bmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{bmatrix}$	$\begin{bmatrix} i & o \\ o & e \end{bmatrix}, \begin{bmatrix} -i & o \\ o & e \end{bmatrix}, \begin{bmatrix} i & o \\ o & -e \end{bmatrix}, \begin{bmatrix} -i & o \\ o & -e \end{bmatrix}.$
m_7	$\begin{bmatrix} 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{bmatrix}$	$\begin{bmatrix} o & e \\ i & o \end{bmatrix}, \begin{bmatrix} o & e \\ -i & o \end{bmatrix}, \begin{bmatrix} o & -e \\ i & o \end{bmatrix}, \begin{bmatrix} o & -e \\ -i & o \end{bmatrix}.$
m_8	$\begin{bmatrix} 0 & 0 & 1 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \end{bmatrix}$	$\begin{bmatrix} o & i \\ e & o \end{bmatrix}, \begin{bmatrix} o & i \\ -e & o \end{bmatrix}, \begin{bmatrix} o & -i \\ e & o \end{bmatrix}, \begin{bmatrix} o & -i \\ -e & o \end{bmatrix}.$

or (4b). The non-identical transformations of the subgroup N are those of the trivial type mentioned in observation VI, and their elimination in the process giving Eqs. (8) is tantamount to disregarding a change in sign of both S and T or of both P and V.

To illustrate the general application of these transformations the equations obtained by transforming two given thermodynamic equations are shown in Table III. The two given equations are those shown in the table opposite the symbol m_1, which

TABLE II: Multiplication table for the octic group.

	m_1	m_2	m_3	m_4	m_5	m_6	m_7	m_8
m_1	m_1	m_2	m_3	m_4	m_5	m_6	m_7	m_8
m_2	m_2	m_1	m_4	m_3	m_6	m_5	m_8	m_7
m_3	m_3	m_4	m_1	m_2	m_8	m_7	m_6	m_5
m_4	m_4	m_3	m_2	m_1	m_7	m_8	m_5	m_6
m_5	m_5	m_6	m_7	m_8	m_1	m_2	m_3	m_4
m_6	m_6	m_5	m_8	m_7	m_2	m_1	m_4	m_3
m_7	m_7	m_8	m_5	m_6	m_4	m_3	m_2	m_1
m_8	m_8	m_7	m_6	m_5	m_3	m_4	m_1	m_2

TABLE III: Examples of equations obtained from the transformations.

Transformation	First Example	Second Example
m_1	$\left(\frac{\partial S}{\partial T}\right)_V = \frac{1}{T}\left(\frac{\partial E}{\partial T}\right)_V$	$\left(\frac{\partial P}{\partial T}\right)_V = \frac{P}{T} + \frac{1}{T}\left(\frac{\partial E}{\partial V}\right)_T$
m_2	$\left(\frac{\partial T}{\partial S}\right)_P = -\frac{1}{S}\left(\frac{\partial G}{\partial S}\right)_P$	$\left(\frac{\partial V}{\partial S}\right)_P = \frac{V}{S} - \frac{1}{S}\left(\frac{\partial G}{\partial P}\right)_S$
m_3	$\left(\frac{\partial P}{\partial V}\right)_T = \frac{1}{V}\left(\frac{\partial G}{\partial V}\right)_T$	$\left(\frac{\partial S}{\partial V}\right)_T = \frac{S}{V} + \frac{1}{V}\left(\frac{\partial G}{\partial T}\right)_V$
m_4	$\left(\frac{\partial V}{\partial P}\right)_S = -\frac{1}{P}\left(\frac{\partial E}{\partial P}\right)_S$	$\left(\frac{\partial T}{\partial P}\right)_S = \frac{T}{P} - \frac{1}{P}\left(\frac{\partial E}{\partial S}\right)_P$
m_5	$\left(\frac{\partial S}{\partial T}\right)_P = \frac{1}{T}\left(\frac{\partial H}{\partial T}\right)_P$	$\left(\frac{\partial V}{\partial T}\right)_P = \frac{V}{T} - \frac{1}{T}\left(\frac{\partial H}{\partial P}\right)_P$
m_6	$\left(\frac{\partial T}{\partial S}\right)_V = -\frac{1}{S}\left(\frac{\partial F}{\partial S}\right)_V$	$\left(\frac{\partial P}{\partial S}\right)_V = \frac{P}{S} + \frac{1}{S}\left(\frac{\partial F}{\partial V}\right)_S$
m_7	$\left(\frac{\partial P}{\partial V}\right)_S = \frac{1}{V}\left(\frac{\partial H}{\partial V}\right)_S$	$\left(\frac{\partial T}{\partial V}\right)_S = \frac{T}{V} - \frac{1}{V}\left(\frac{\partial H}{\partial S}\right)_V$
m_8	$\left(\frac{\partial V}{\partial P}\right)_T = -\frac{1}{P}\left(\frac{\partial F}{\partial P}\right)_T$	$\left(\frac{\partial S}{\partial P}\right)_T = \frac{S}{P} + \frac{1}{P}\left(\frac{\partial F}{\partial T}\right)_P$

represents the identity transformation. As an example of the carrying out of one of these transformations, the m_7 transformation of the second equation of Table III is here given in detail. The transformed value of E is shown by

$$\begin{bmatrix} 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{bmatrix} \begin{bmatrix} E \\ H \\ F \\ G \end{bmatrix} = \begin{bmatrix} H \\ G \\ E \\ F \end{bmatrix} \tag{9a}$$

to be H. For the $(STPV)$ transformation any one of the four matrices given may be used, as

$$\begin{bmatrix} o & e \\ -i & o \end{bmatrix}\begin{bmatrix} S \\ T \\ P \\ V \end{bmatrix} = \begin{bmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & -1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{bmatrix}\begin{bmatrix} S \\ T \\ P \\ V \end{bmatrix} = \begin{bmatrix} P \\ V \\ -T \\ S \end{bmatrix}. \tag{9b}$$

Hence the equation

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{P}{T} + \frac{1}{T}\left(\frac{\partial E}{\partial V}\right)_T \tag{10a}$$

is transformed into

$$\left(\frac{\partial T}{\partial V}\right)_S = \frac{T}{V} - \frac{1}{V}\left(\frac{\partial H}{\partial S}\right)_V. \tag{10b}$$

Since $m_7 = m_5 m_3$ from Table II, Eq. (10b) can also be obtained by applying m_3 to the equation obtained by the m_5 transformation of Eq. (10a).