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Thermodynamic Symmetry and Its Applications - Search for Beauty in Science

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Additional information is available at the end of the chapter

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"A theory is the more impressive the greater the simplicity of its premises are, the more different kinds of things it relates, and the more extended is its area of applicability. Therefore the deep impression that classical thermodynamics made upon me. It is the only physical theory of universal content concerning which I am convinced that, within the framework of applicability of its basic concepts, it will never be overthrown."

(Albert Einstein, 1946)

Abstract

A variety of thermodynamic variables are properly arranged at vertices of an extended concentric multi-polyhedron diagram based on their physical meanings. A symmetric function with "patterned self-similarity" is precisely be defined as the function, which is unchanged not only in function form but also in variable's nature and neighbor relationship under symmetric operations. Thermodynamic symmetry roots in the symmetric reversible Legendre transforms of the potentials. The specific thermodynamic symmetries revealed by the diagram are only one C_3 symmetry about the $U \sim \Phi$ diagonal direction and C_4 and σ symmetries on three U -containing squares. Based on the equivalence principle of symmetry, numerous equations of the 12 families can concisely be depicted by overlapping 12 specifically created rigid, movable graphic patterns on fixed $\{1, 0, 0\}$ diagrams through σ and/or C_4 symmetric operations. Any desired partial derivatives can be derived in terms of several available quantities by a foolproof graphic method. It is the symmetry that made possible to build up the diagram as a model like the Periodic Table of the Elements to exhibit an integration of the entire structure of the thermodynamic variables into a coherent and complete exposition of thermodynamics and to facilitate the subject significantly.

Keywords: thermodynamic symmetry, thermodynamics, symmetry, graphic method, Legendre transforms, polyhedrons, physical chemistry, chemical physics

1. Introduction

An interpretation of thermodynamics being a science of symmetry was proposed by Herbert Callen [1, 2]. While an integration of the entire structure into a coherent and complete exposition of thermodynamics was not undertaken, since it would require repetition of an elaborate formalism with which the reader presumably is familiar. Such an abstract conceptual interpretation has not widely been recognized.

Symmetry generally conveys two primary meanings: beauty and “patterned self-similarity.” A symmetric function with “patterned self-similarity” can precisely be defined as the function, which is unchanged not only in function form but also in variable’s nature and relationship under symmetric operations. Many works, such as an important class of thermodynamic equations being resolved by “standard form” into families [3, 4] and expressed by geometric diagrams (square [5], cub octahedron [6], concentric multi-circle [7], cube [8], and Venn diagram [9]), have revealed symmetry existing in thermodynamics, a keen sense of which is helpful to every one of the subject.

You might wonder about a series of following questions: Why does symmetry exist in thermodynamics? What are specific thermodynamic symmetries? How can we apply the specific symmetries for different purposes? What are significant results of its applications? In this chapter, you will gradually find out answers of all questions above.

2. Configuration of 3D diagram

2.1. Thermodynamic variables

From a mathematical point of view, thermodynamic properties behave like multi-variable functions and can usually be differentiated and integrated. A variety of thermodynamic variables can be classified into natural variables, thermodynamic potentials, and all of the thermodynamic properties of a system, which can be found by taking partial derivatives of a thermodynamic potential of the system with respect to its natural variables if the thermodynamic potential can be determined as a function of its natural variables.

2.1.1. Natural variables and thermodynamic potentials

A thermodynamic potential is a scalar function used to represent the thermodynamic state of a system. One main thermodynamic potential, which has a physical interpretation, is the internal energy, U . The variables that are held constant in this process are termed the natural variables of that potential.

For a single component one phase system, the number of natural variables (independent variables to describe the extensive state) of the system is three. A set of three natural variables for the internal energy are entropy (S), volume (V), and particle number (N), and they are all extensive variables. The integration (Euler's equation) of the fundamental equation for internal energy, $dU = TdS - PdV + \mu dN$, at constant values of the intensive variables [temperature (T), pressure (P), and chemical potential (μ)] yields

$$U(S, V, N) = TS - PV + \mu N \quad (1)$$

Since S and V are often inconvenient natural variables from an experimental point of view, the Legendre transforms are used to define further thermodynamic potentials. Each Legendre transform is a linear change in variables in which one or more products of conjugate variables are subtracted from the internal energy to define a new thermodynamic potential.

2.1.2. Complete set of the thermodynamic potentials

A complete set of Legendre transforms initially from the internal energy $U(S, V, N)$ for the system is shown below [10]. There are no generally accepted symbols for all of the eight thermodynamic potentials, and so a suggestion published in [8] is utilized here.

$$H(S, P, N) = U(S, V, N) - (-P \cdot V) = TS + \mu N \quad (2)$$

$$A(T, V, N) = U(S, V, N) - (T \cdot S) = -PV + \mu N \quad (3)$$

$$\psi(S, V, \mu) = U(S, V, N) - (\mu \cdot N) = TS - PV \quad (4)$$

$$G(T, P, N) = U(S, V, N) - (-P \cdot V) - (T \cdot S) = \mu N \quad (5)$$

$$\Omega(T, V, \mu) = U(S, V, N) - (T \cdot S) - (\mu \cdot N) = -PV \quad (6)$$

$$\chi(S, P, \mu) = U(S, V, N) - (-P \cdot V) - (\mu \cdot N) = TS \quad (7)$$

$$\Phi(T, P, \mu) = U(S, V, N) - (T \cdot S) - (-P \cdot V) - (\mu \cdot N) = 0 \quad (8)$$

2.1.3. Thermodynamic properties

The thermodynamic properties can be expressed in terms of the derivatives of the potentials with respect to their natural variables. These equations are known as equations of state, since they specify the properties of the thermodynamic state.

First-order partial derivative variables:

$$T = \left(\frac{\partial U}{\partial S} \right)_{VN} = \left(\frac{\partial H}{\partial S} \right)_{PN} = \left(\frac{\partial \psi}{\partial S} \right)_{V\mu} = \left(\frac{\partial \chi}{\partial S} \right)_{P\mu} \quad (9)$$

$$-P = \left(\frac{\partial U}{\partial V} \right)_{SN} = \left(\frac{\partial A}{\partial V} \right)_{TN} = \left(\frac{\partial \Omega}{\partial V} \right)_{T\mu} = \left(\frac{\partial \psi}{\partial V} \right)_{S\mu} \quad (10)$$

$$\mu = \left(\frac{\partial U}{\partial N}\right)_{SV} = \left(\frac{\partial H}{\partial N}\right)_{SP} = \left(\frac{\partial A}{\partial N}\right)_{TV} = \left(\frac{\partial G}{\partial N}\right)_{TP} \quad (11)$$

$$-S = \left(\frac{\partial G}{\partial T}\right)_{PN} = \left(\frac{\partial A}{\partial T}\right)_{VN} = \left(\frac{\partial \Omega}{\partial T}\right)_{V\mu} \quad (12)$$

$$V = \left(\frac{\partial G}{\partial P}\right)_{TN} = \left(\frac{\partial H}{\partial P}\right)_{SN} = \left(\frac{\partial \chi}{\partial P}\right)_{S\mu} \quad (13)$$

$$-N = \left(\frac{\partial \Omega}{\partial \mu}\right)_{TV} = \left(\frac{\partial \chi}{\partial \mu}\right)_{SP} = \left(\frac{\partial \psi}{\partial \mu}\right)_{SV} \quad (14)$$

Each first-order partial derivative of a potential is associated (or conjugated) with its corresponding independent (or natural) variable of the potential to comprise a pair of conjugate variables. Above six symbols of the first-order partial derivatives are almost the same as the symbols of the six natural variables, except for three of them ($-S$, $-P$, and $-N$) holding a negative sign ($-$). The negative sign in front of those three variables indicates that they physically seek a maximum, rather than a minimum, during spontaneous changes and equilibriums. The six different symbols of the variables can make three intensive versus extensive conjugate variable pairs ($T \sim S$, $P \sim V$, and $\mu \sim N$), within three products of the conjugate variable pairs ($T \cdot S$, $P \cdot V$, and $\mu \cdot N$) have the same units as the potentials (U , H , A , ψ , G , Ω , χ , and Φ), and they also significantly comprise three opposite sign conjugate variable pairs ($T \sim -S$, $-P \sim V$, and $\mu \sim -N$) if the negative sign ($-$) in front of those three variables ($-S$, $-P$, and $-N$) must be taken into account for an essential necessity explained later.

Second-order partial derivative variables:

C_P (isobaric thermal capacity) and C_V (isochoric thermal capacity)

$$C_{PN} = \left(\frac{\partial H}{\partial T}\right)_{PN} = T \left(\frac{\partial S}{\partial T}\right)_{PN} = -T \left(\frac{\partial^2 G}{\partial T^2}\right)_{PN} = C_P \quad (15)$$

$$C_{VN} = \left(\frac{\partial U}{\partial T}\right)_{VN} = T \left(\frac{\partial S}{\partial T}\right)_{VN} = -T \left(\frac{\partial^2 A}{\partial T^2}\right)_{VN} = C_V \quad (16)$$

Other partial derivative variables:

$$\text{The isobaric expansion coefficient: } \alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P \quad (17)$$

$$\text{The isothermal compressibility: } \kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T \quad (18)$$

etc.

2.1.4. A 3D diagram of the thermodynamic variables

A variety of thermodynamic variables including three conjugate pairs of natural variables, eight thermodynamic potentials, and six first-order partial derivatives can properly be arranged in a concentric multi-polyhedron diagram (**Figure 1**) based on their physical meanings as follows:

1. The natural variables: Three conjugate (intensive $\sim$ extensive) pairs of natural variables, i.e., temperature (T) $\sim$ entropy (S), pressure (P) $\sim$ volume (V), and chemical potential (μ) $\sim$ particle number (N), are arranged at vertices of a small octahedron with the Cartesian coordinates: $T[1,0,0] \sim S[-1,0,0]$, $P[0,-1,0] \sim V[0,1,0]$, and $\mu[0,0,1] \sim N[0,0,-1]$.

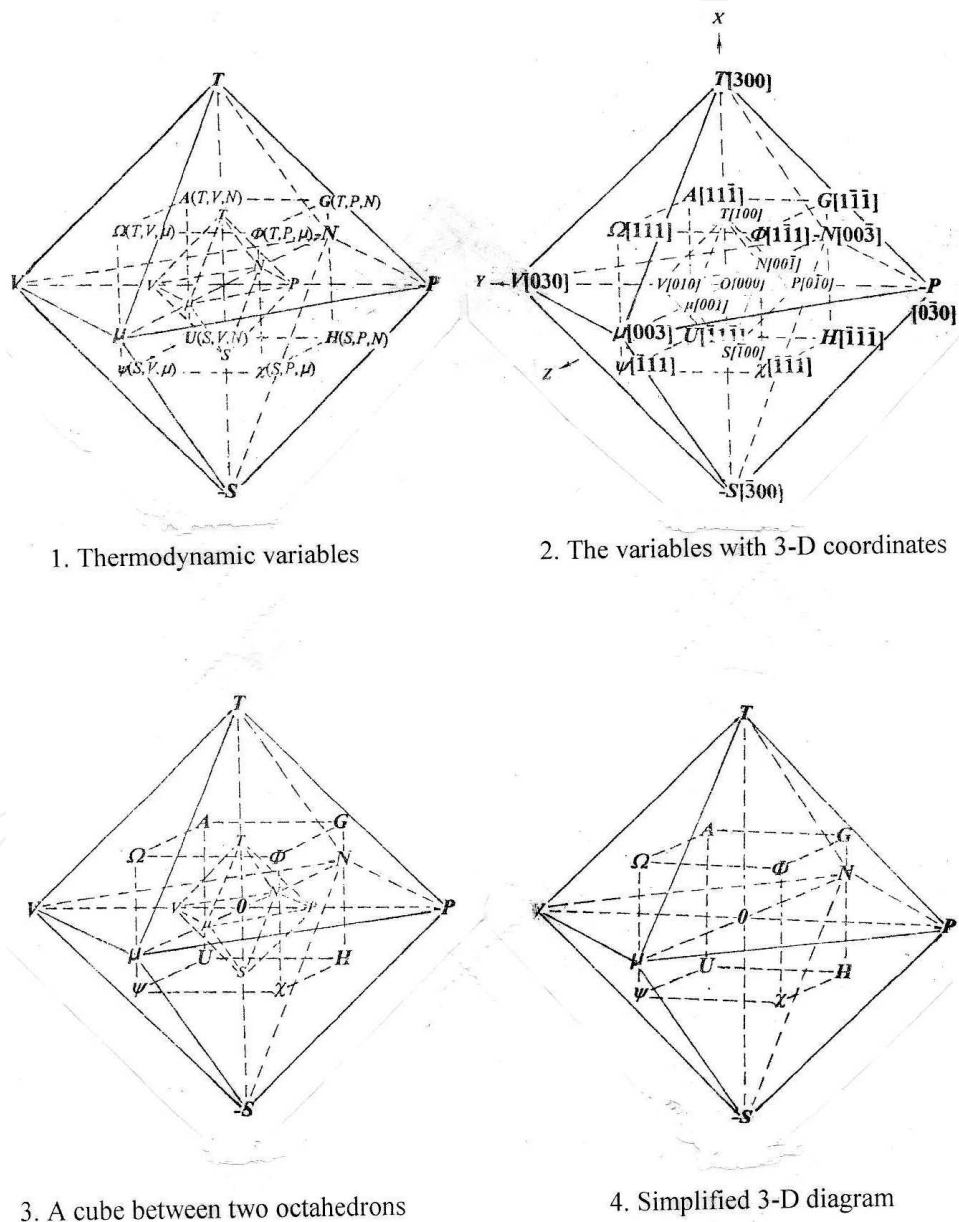


Figure 1. 3D concentric multi-polyhedron diagram.

2. The thermodynamic potentials: In order to exhibit a close relationship between each thermodynamic potential and its three correlated natural variables, let four pairs of thermodynamic potentials {internal energy $U(S, V, N) \sim \Phi(T, P, \mu)$, enthalpy $H(S, P, N) \sim \Omega(T, V, \mu)$, Gibbs free energy $G(T, P, N) \sim \psi(S, V, \mu)$, and Helmholtz free energy $A(T, V, N) \sim \chi(S, P, \mu)$ } be located at the opposite ends of four diagonals of a cube with the Cartesian coordinates: $U[-1, 1, -1] \sim \Phi[1, -1, 1]$, $H[-1, -1, -1] \sim \Omega[1, 1, 1]$, $G[1, -1, -1] \sim \psi[-1, 1, 1]$, and $A[1, 1, -1] \sim \chi[-1, -1, 1]$.
3. The first-order partial derivatives: Let the six first-order partial derivatives ($T, -S, -P, V, \mu$, and $-N$) similarly be located at vertices of a large octahedron with the Cartesian coordinates: $T[3, 0, 0]$, $-S[-3, 0, 0]$, $-P[0, -3, 0]$, $V[0, 3, 0]$, $\mu[0, 0, 3]$, and $-N[0, 0, -3]$.

2.2. Variable's neighbor relationship in the diagram

2.2.1. To simplify the diagram

Different categories of the variables are located at different polyhedrons, whereas symbols of the variables at two octahedrons are almost same except for $-S$, $-P$, and $-N$. Therefore, it is possible for us to simplify two octahedrons into the large one (**Figure 1**)(4) if the negative sign ("−") in front of those variables ($-S$, $-P$, and $-N$) could be taken into account by a specific way, which will be described later.

2.2.2. Variable's neighbor relationship

Relations between any two variables can be visually determined by their neighbor relationship in the diagram. Neighbors can be classified as first, second, and third ones based on distances between them. Correlated or conjugate relation between two variables can easily be determined by the neighbor relationship. A pair of conjugate variables are always located at opposite ends of a diagonal of the polyhedron, for example, $T \sim -S$, $-P \sim V$, $\mu \sim -N$, or $U \sim \Phi$. The correlated relation between each potential and its natural variables is always the closest (first) neighbor relationship shown in the diagram.

3. Thermodynamic symmetry

3.1. Symmetry roots in the Legendre transforms

3.1.1. The Legendre transforms

Each Legendre transform (ELT or E) is a leaner conversion between a pair of multiple variable functions [$M = m(x, y, w)$ and $F = f(x, y, z)$], which is associated with a transform from one to another between a pair of conjugate variables (w and z) [11].

The Legendre transform ($E: F \rightarrow M$ and $z \rightarrow w$) is defined as:

$$m(x, y, w) = f(x, y, z) - w \cdot z \quad (19)$$

where the two functions (M and F) and a product term ($w \cdot z$) of the two conjugate variables (w and z) have same units.

Every Legendre transform (E) has its own reverse Legendre transform (RLT or R : $M \rightarrow F$ and $w \rightarrow z$). The reverse Legendre transform (R) is therefore written as:

$$f(x, y, z) = m(x, y, w) + z \cdot w \quad (20)$$

E and R are reversible each other. Reversible Legendre transforms are associated with a pair of the conjugate variables (w and z), a pair of the functions [$M = m(x, y, w)$ and $F = f(x, y, z)$, or $M = m(w)$ and $F = f(z)$, or M and F], and a pair of the reversible conversions (E and R). The reversible Legendre transforms can be written as ($E \leftrightarrow R$), where a double arrow symbol ($\leftrightarrow$) stands for "reversible". There are ($M \leftrightarrow F$) and ($w \leftrightarrow z$) in the reversible ($E \leftrightarrow R$).

3.1.2. Symmetry of the Legendre transforms

3.1.2.1. The Legendre transforms with a pair of same sign conjugate variables

It can be seen by comparing Eq. (19) with Eq. (20) that although they are basically same, but not exactly same since there is a slight difference in an opposite sign (negative or positive) in front of the product term of the two conjugate variables ($w \cdot z$) in the reversible ($E \leftrightarrow R$) under a pair of the same sign conjugate variables (w and z). Therefore, the reversible ($E \leftrightarrow R$), without a general formula, are asymmetric if the two conjugate variables (w and z) have same sign.

3.1.2.2. The Legendre transforms with a pair of opposite sign conjugate variables

Although the reversible ($E \leftrightarrow R$) are asymmetric under a pair of the same sign conjugate variables (w and z), however, if the negative sign ($-$) in front of the product term can be taken into account by a pair of opposite sign conjugate variables (z and $-w$ or $-z$ and w), and if the negative sign ($-$) in front of either negative conjugate variable ($-w$ or $-z$) can be controlled by a pair of opposite conjugate variable treatments (either canceling or keeping the negative sign), which are symbolized as $[]$ and $\{ \}$, respectively, the asymmetric reversible ($E \leftrightarrow R$) is able to become symmetric reversible Legendre transforms ($E^* \leftrightarrow R^*$), where an asterisk symbol ($*$) stands for symmetric. In other words, the asymmetric ($E \leftrightarrow R$) can become symmetric ($E^* \leftrightarrow R^*$) under two required conditions: a pair of the opposite sign conjugate variables (z and $-w$ or $-z$ and w) and a pair of the opposite conjugate variable treatments ($[]$ and $\{ \}$) are involved in the symmetric ($E^* \leftrightarrow R^*$).

3.1.2.3. A general formula for the symmetric reversible Legendre transforms

The general formula for the symmetric ($E^* \leftrightarrow R^*$) must be generalized from the two reversible equations, Eqs. (19) and (20). It can be seen in their common writing order, from left to right, that the two equations commonly consist of two kinds of symbols: one kind of a series of

conventional mathematical symbols, which are an equal sign (=) located between the two functions, an uncertain changeable sign (– or +) located between a pair the functions and the product term, and a product sign (·) located between the two opposite sign conjugate variables, respectively, and another kind of a series of symbols associated with given information, which are a pair of the reversible functions (M and F) and a pair of the involved opposite sign conjugate variables. The given information symbols can be called as first, second, third, and fourth one in the writing order from left to right, respectively.

If we use a pair of square symbols ($\square$ and $\square$) symbolizing a pair of the known functions (M and F), and a pair of different symbols ($[]$ and $\{ \}$) symbolizing a pair of the opposite treatments (canceling and keeping), and put an empty space for the uncertain (or unknown) sign (– or +) located between the functions and the product term, the general formula may be created for the symmetric ($E^* \leftrightarrow R^*$) to be

$$\text{either } \square = \square [] \cdot \{ \} \text{ or } \square = \square \{ \} \cdot [] \quad (21)$$

It can be seen in Eq. (21) that the two different possible orders of the opposite treatments, $[] \cdot \{ \}$ and $\{ \} \cdot []$, would make the general formula uncertain, not unique. The general formula for the symmetric ($E^* \leftrightarrow R^*$) must be unique.

3.1.2.4. The order of the opposite treatments on a pair of the opposite sign conjugate variables

It is found out during my thinking about above problem that only one of two possible opposite signs (either positive or negative) could be bestowed on each conjugate variable to make sense, whereas another opposite sign makes no sense, and similarly that only one of two possible treatment orders (either $[] \cdot \{ \}$ or $\{ \} \cdot []$) can make sense, whereas another opposite order makes no sense. Therefore, a unique opposite treatment order can be determined only by checking against the well-known basic conclusions and formulas in the subject.

After a series of serious checks against some well-known basic conclusions and formulas in thermodynamics, such as the entropy (S) seeks for a maximum, rather than a minimum, during any spontaneous processes and equilibriums, the first-order partial derivative of the potentials (G , A , and Ω) with respect to their natural variable of temperature (T) equals $-S$ in Eq. (12), rather than S (no sign means positive), if the negative sign is bestowed only on those three conjugate natural variables (S , P , and N), respectively, rather than oppositely on T , V , and μ , then a set of the three opposite sign conjugate natural variable pairs ($T \sim -S$, $-P \sim V$, and $\mu \sim -N$) will exactly be same as those six first-order partial derivatives of the potentials in Eqs. (9)–(14) and so on, then it is found out that the right unique order of the two opposite treatments in the general formula must be $[] \cdot \{ \}$, rather than $\{ \} \cdot []$; therefore, the general formula for the symmetric ($E^* \leftrightarrow R^*$) must be symbolized as:

$$\square = \square [] \cdot \{ \} \quad (22)$$

rather than $\square = \square \{ \} \cdot []$, since Eq. (22) makes sense.

3.1.2.5. A general procedure for using the symbolized general formula

If we knew a pair of the two opposite sign conjugate variables (either $-w$ and z or w and $-z$), a pair of the two associated functions (M and F), and a direction of the Legendre transform (either $F \rightarrow M$ or $M \rightarrow F$), thus we would be able to find out the unknown (uncertain) sign of the product term (either $w \cdot z$ or $z \cdot w$) in Eq. (22) for the symmetric ($E^* \leftrightarrow R^*$). The general procedure of a created specific method comprises the following four steps, here take a given Legendre transform ($U \rightarrow H$) as an example.

Step 1: Obtain information about a pair of given potentials $\{U(-S, V, -N)$ and $H(-S, -P, -N)\}$ and a pair of associated opposite sign conjugate natural variables (V and $-P$) as well as the conversion direction ($\rightarrow$) involved in the given conversion ($U \rightarrow H$);

Step 2: Use the first square symbol ($\square$) in Eq. (22) to select the converted (ended) potential $H(-S, -P, -N)$, the second square symbol ($\square$) to select the converting (starting) potential $U(-S, V, -N)$, the third canceling symbol $[]$ to cancel any negative sign of the conjugate variable ($-P$) of the potential $H(-S, -P, -N)$ located in the first place, and the fourth keeping symbol $\{ \}$ to keep any negative sign of the conjugate variable (V) of the potential $U(-S, V, -N)$ located in the second place, respectively;

Step 3: Find out an unknown sign of the product term between the two pairs of the symbols in the general formula, the unknown sign is found out to be positive (+), in this case, since no sign in front of the conjugate variable (V), which is associated with the potential $U(-S, V, -N)$ located in the second place, is kept by the keeping symbol $\{ \}$;

Step 4: Write down a series of results of both the known and the unknown obtained above in the writing order of the general formula from left to right, and double check it for sure as below:

$$H(-S, -P, -N) = U(-S, V, -N) + P \cdot V \quad (23)$$

3.1.3. Symmetry of the thermodynamic potentials

The Legendre transforms are used to define thermodynamic potentials from one to another, thus the exchangeable (reversible) potentials are symmetric when a pair of opposite sign conjugate variables ($T \sim -S$, $V \sim -P$ or $\mu \sim -N$) are treated under a pair of opposite ways (canceling $[]$ or keeping $\{ \}$). Based on the general procedure of the specific method described above, we can write down the reversible Legendre transforms for any pair of the closest neighbor potentials.

For example, take V and $-P$ as a pair of the opposite sign conjugate natural variables, which are exactly same as a pair of the first-order partial derivatives, and exchange the two conjugate natural variables ($V \leftrightarrow -P$), thus four parallel potential pairs like ($U \leftrightarrow H$), ($A \leftrightarrow G$), ($\Omega \leftrightarrow \Phi$), and ($\psi \leftrightarrow \chi$), shown in **Figure 1**, will mirror-symmetrically be exchanged in each pair, respectively. Some symmetric exchangeable equations in ($U \leftrightarrow H$) and ($A \leftrightarrow G$) can be written down on the spot as follows:

$$U \rightarrow H : H(-S, -P, -N) = U(-S, V, -N) ? [-P] \cdot \{V\} = U(-S, V, -N) + P \cdot V \quad (2)$$

$$H \rightarrow U : U(-S, V, -N) = H(-S, -P, -N) ? [V] \cdot \{-P\} = H(-S, -P, -N) - V \cdot P \quad (1)$$

$$A \rightarrow G : G(T, -P, -N) = A(T, V, -N) ? [-P] \cdot \{V\} = A(T, V, -N) + P \cdot V \quad (5)$$

$$G \rightarrow A : A(T, V, -N) = G(T, -P, -N) ? [V] \cdot \{-P\} = G(T, -P, -N) - V \cdot P \quad (3)$$

Similarly, take $-S$ and T as a pair of the opposite sign conjugate natural variables, which are also exactly same as a pair of the first-order partial derivatives, and exchange the two conjugate natural variables ($-S \leftrightarrow T$), thus four parallel potential pairs like ($U \leftrightarrow A$), ($H \leftrightarrow G$), ($\psi \leftrightarrow \Omega$), and ($\chi \leftrightarrow \Phi$) shown in **Figure 1** will mirror-symmetrically be exchanged in each pair, respectively. Some symmetric exchangeable equations in ($U \leftrightarrow A$) and ($H \leftrightarrow G$) can be written down on the spot as follows:

$$U \rightarrow A : A(T, V, -N) = U(-S, V, -N) ? [T] \cdot \{-S\} = U(-S, V, -N) - T \cdot S \quad (3)$$

$$A \rightarrow U : U(-S, V, -N) = A(T, V, -N) ? [-S] \cdot \{T\} = A(T, V, -N) + S \cdot T \quad (1)$$

$$H \rightarrow G : G(T, -P, -N) = H(-S, -P, -N) ? [T] \cdot \{-S\} = H(-S, P, -N) - T \cdot S \quad (5)$$

$$G \rightarrow H : H(-S, -P, -N) = G(T, -P, -N) ? [-S] \cdot \{T\} = G(T, -P, -N) + S \cdot T \quad (2)$$

It is found out by checking above equations against **Figure 1** that the symbolized general formula [Eq. (22)] works very well and makes sense, that specific symmetries involved in the symmetric reversible conversions of the potentials $\{F^*, (+/-)z\} \leftrightarrow M^*, (-/+)w\}$ are mirror symmetry (σ) with respect to a mirror and fourfold rotating symmetry (C_4) about an axis and that each mirror is always perpendicular to a linking segment of the two opposite sign conjugate variables, and each rotating axis is the linking segments of a pair of opposite sign conjugate variables.

3.1.4. Symmetry of the thermodynamic properties

The thermodynamic properties can be expressed in terms of the derivatives of the potentials with respect to their natural variables. Therefore, many thermodynamic equations (properties) are symmetric too. For example, it can be seen that following four rewritten Maxwell equations

$$\left(\frac{\partial V}{\partial T}\right)_{PN} = -\left(\frac{\partial S}{\partial P}\right)_{TN} \text{ or } \left(\frac{\partial(V)}{\partial T}\right)_{PN} = \left(\frac{\partial(-S)}{\partial P}\right)_{TN} \quad (24)$$

$$\left(\frac{\partial T}{\partial P}\right)_{SN} = \left(\frac{\partial V}{\partial S}\right)_{PN} \text{ or } \left(\frac{\partial(T)}{\partial P}\right)_{SN} = \left(\frac{\partial(V)}{\partial S}\right)_{PN} \quad (25)$$

$$-\left(\frac{\partial P}{\partial S}\right)_{VN} = \left(\frac{\partial T}{\partial V}\right)_{SN} \text{ or } \left(\frac{\partial(-P)}{\partial S}\right)_{VN} = \left(\frac{\partial(T)}{\partial V}\right)_{SN} \quad (26)$$

$$\left(\frac{\partial S}{\partial V}\right)_{TN} = \left(\frac{\partial P}{\partial T}\right)_{VN} \text{ or } \left(\frac{\partial(-S)}{\partial V}\right)_{TN} = \left(\frac{\partial(-P)}{\partial T}\right)_{VN} \quad (27)$$

display mirror symmetry (σ) with respect to both sides of each equation and fourfold rotation symmetry (C_4) about the conjugate pair of μ and $-N$ in **Figure 1**.

3.2. Koenig's results and geometric explanations

There are not generally accepted symbols for all thermodynamic potentials. In Koenig's paper, Callen's transformed symbols [2, 4], which are also recommended by IUPAC [10], were used; whereas, in this chapter, Pate's symbols [8] are used. In order to conveniently discuss Koenig's results, a comparison of these symbols is shown in **Figure 2**, where another kind of symbols

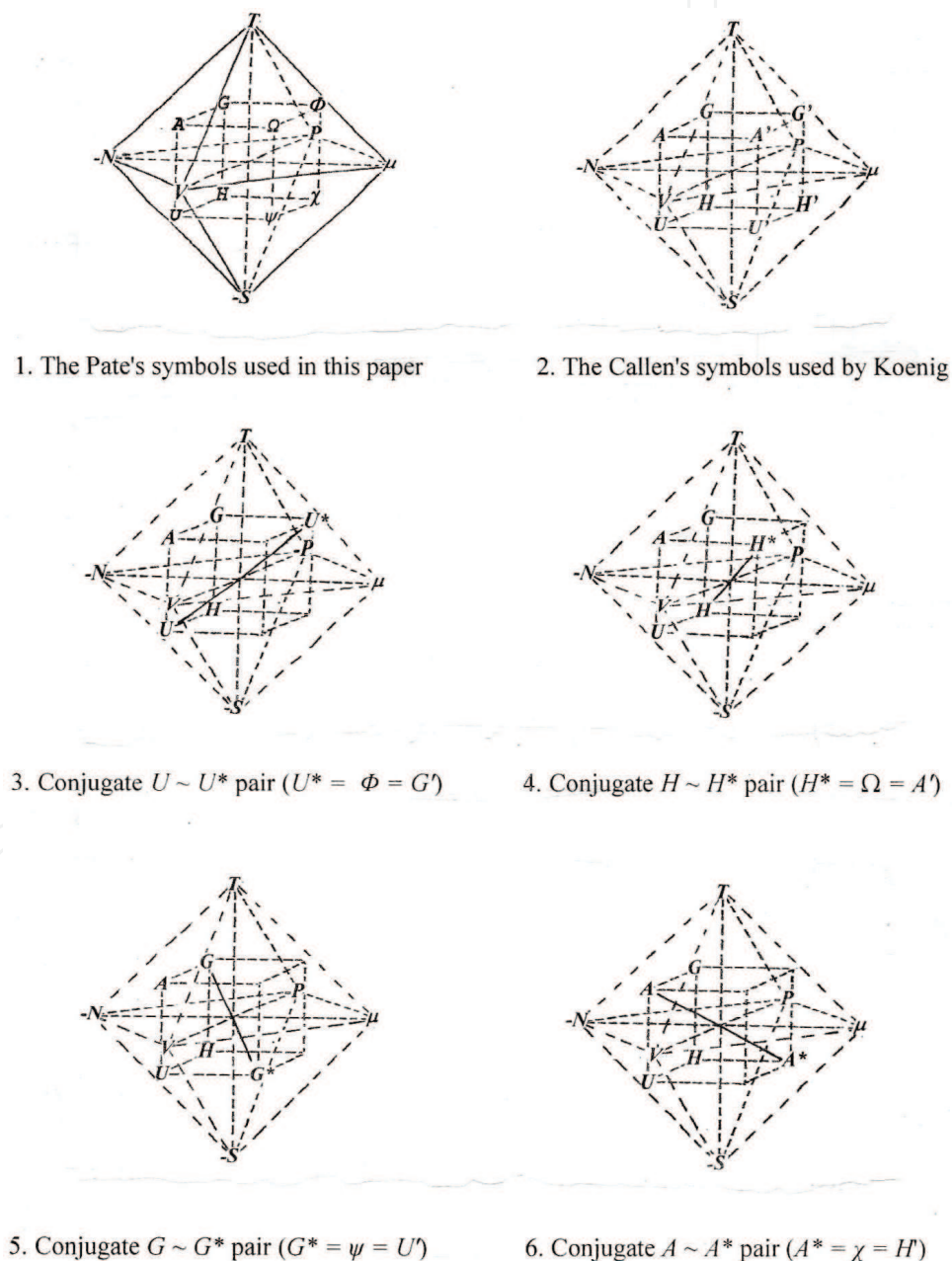


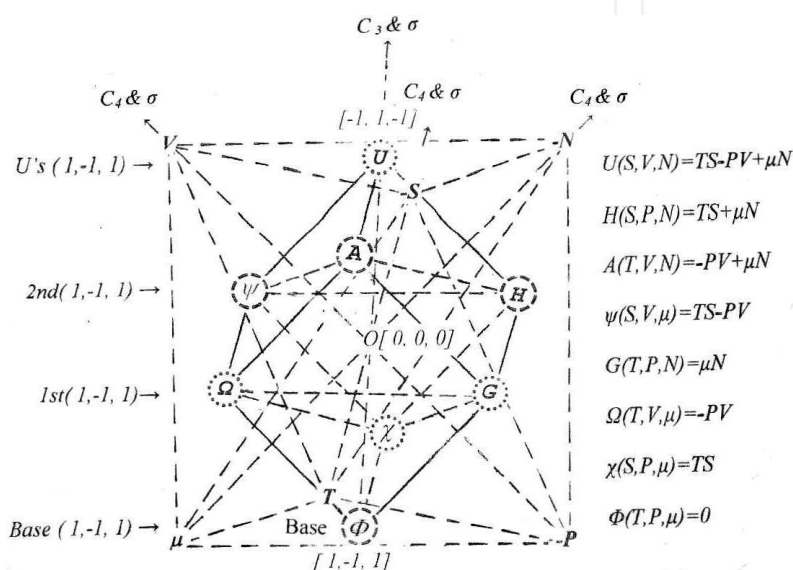
Figure 2. Comparison of the symbols for thermodynamic potentials.

(conjugate ones) is also introduced. The relations among three different kinds of the symbols for four transformed potentials are as follows:

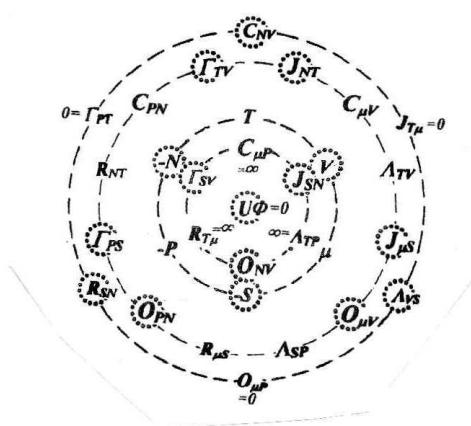
$$U' = \psi = G^*; H' = \chi = A^*; G' = \Phi = U^*; A' = \Omega = H^*.$$

where symbols with a prime (') stand for Callen's transformed ones (**Figure 2(2)**) and symbols with an asterisk (*) stand for conjugate ones (**Figure 2(3–6)**).

Koenig pointed out that an important class of thermodynamic equations being resolved by “standard form” into families [3, 4], and the equations of greatest physical interest belong to



1. The special conjugate $U \sim \Phi$ pair pivoted at $\Phi(T, P, \mu) = 0$



2. The (1, -1, 1) projection diagram

Figure 3. Thermodynamic symmetry: One C_3 symmetry about the $[1, -1, 1]$ ($U \sim \Phi$ diagonal) direction and C_4 and σ symmetries on three U -containing squares.

families having 48, 24, 12, or 8 members. The remaining possibilities for the number of members per family are 6, 4, 3, and 1. Also, he gave one example of each kind:

1. 48 members: $(\partial U/\partial V)_{T,N} = T(\partial P/\partial T)_{V,N} - P$
2. 24 members: $(\partial T/\partial V)_{S,N} = -(\partial P/\partial S)_{V,N}$
3. 12 members: $A = U - TS$
4. 8 members: $dU = TdS - PdV + \mu dN$
5. 6 members: $U - A + G - H = 0$
6. 4 members: $U - G' = TS - PV + \mu N$
7. 3 members: $U + A + G + H - H' - G' - A' - U' = 4\mu N$
8. 1 member: $U - A + G - H + H' - G' + A' - U' = 0$

He evaluated the value of his results being less in the technique, which supplies for generating formulas, than in its revelation of the symmetry of the equations of thermodynamics, a keen sense of which is helpful to every one of the subject.

It can be geometrically explained and verified by a well-oriented cub octahedron diagram (**Figure 3**) that his most results are true, however, that the example of the four member family should be sum (plus or addition) of U and G' , rather than difference (minus or subtraction) between them, that the example of the one member family could be difference (minus or subtraction) between U and G' , rather than $U - A + G - H + H' - G' + A' - U' = 0$, and that the revealed symmetry in thermodynamics is not perfect as the geometric symmetry of the cub octahedron is since the zero potential (Φ) damages the cube symmetry.

3.3. Thermodynamic symmetry

The thermodynamic symmetry revealed and verified by above geometric analysis in **Figure 3** exhibits only one C_3 (threefold rotation) symmetry about the $[1, -1, 1]$ ($U \sim \Phi$ diagonal) direction and C_4 (fourfold rotation) and σ (mirror) symmetries on three U -containing squares, where the square including U, H, G , and A is the most important and useful one.

4. Extension

Koenig extended the square [5] to the octahedron [4], developed his results described above, and also raised a question at the end of his paper: Can the octahedron be extended to higher cases? Answer of the question is positive. Based on the equivalence principle of symmetry (reproducibility and predictability) [12], if we knew a sample member of any family, we would be able to know all other members of the family through symmetric operations. So, we can use the verified symmetry to extend the diagram to deal with the second-order partial derivative variables.

4.1. To develop novel C_P type variables and build up an extended 26-face polyhedron

4.1.1. C_P (isobaric thermal capacity) and C_V (isochoric thermal capacity)

Both C_P and C_V are second-order partial derivatives of the Gibbs free energy, $G(T, P, N)$ and the Helmholtz free energy, $A(T, V, N)$, respectively (see Eqs. (15) and (16)), thus they should be arranged at two proper locations outside of the large octahedron, where they close to their correlated variables, i.e., C_{PN} to G, T, P , and N , and C_{VN} to A, T, V , and N , respectively. Their Cartesian coordinates are C_{PN} [3.62, -1.50, -1.50] and C_{VN} [3.62, 1.50, -1.50].

4.1.2. Other members of the C_P 's family

When $N = \text{constant}$, similarly other members of C_P 's family can be defined symmetrically as follows:

$$R_{TN}[h, -k, -h] = \left(\frac{\partial A}{\partial P}\right)_{TN} = -P\left(\frac{\partial V}{\partial P}\right)_{TN} = -P\left(\frac{\partial^2 G}{\partial P^2}\right)_{TN} \quad (28)$$

$$R_{SN}[-h, -k, -h] = \left(\frac{\partial U}{\partial P}\right)_{SN} = -P\left(\frac{\partial V}{\partial P}\right)_{SN} = -P\left(\frac{\partial^2 H}{\partial P^2}\right)_{SN} \quad (29)$$

$$O_{PN}[-k, -h, -h] = \left(\frac{\partial G}{\partial S}\right)_{PN} = -S\left(\frac{\partial T}{\partial S}\right)_{PN} = -S\left(\frac{\partial^2 H}{\partial S^2}\right)_{PN} \quad (30)$$

$$O_{VN}[-k, h, -h] = \left(\frac{\partial A}{\partial S}\right)_{VN} = -S\left(\frac{\partial T}{\partial S}\right)_{VN} = -S\left(\frac{\partial^2 U}{\partial S^2}\right)_{VN} \quad (31)$$

$$J_{SN}[-h, k, -h] = \left(\frac{\partial H}{\partial V}\right)_{SN} = V\left(\frac{\partial P}{\partial V}\right)_{SN} = -V\left(\frac{\partial^2 U}{\partial V^2}\right)_{SN} \quad (32)$$

$$J_{TN}[h, k, -h] = \left(\frac{\partial G}{\partial V}\right)_{TN} = V\left(\frac{\partial P}{\partial V}\right)_{TN} = -V\left(\frac{\partial^2 A}{\partial V^2}\right)_{TN} \quad (33)$$

and others.

4.1.3. An extended polyhedron

Total 24 members of the C_P 's family can be constructed as an extended 26-face polyhedron (rhombicuboctahedron) shown in **Figure 4**. The Cartesian coordinates for 24 vertices of the concentric rhombicuboctahedron are all permutations of $\langle h, h, k \rangle$, where h equals one and half unit ($h = 1.50$), and k is larger than h by $(1 + \sqrt{2})$ times ($k = 3.62$).

Physically, such a scheme shown in **Figure 4** to arrange the four categories of thermodynamic variables at four kinds of the vertices of the extended concentric multi-polyhedron corresponds to Ehrenfest's scheme to classify phase transitions.

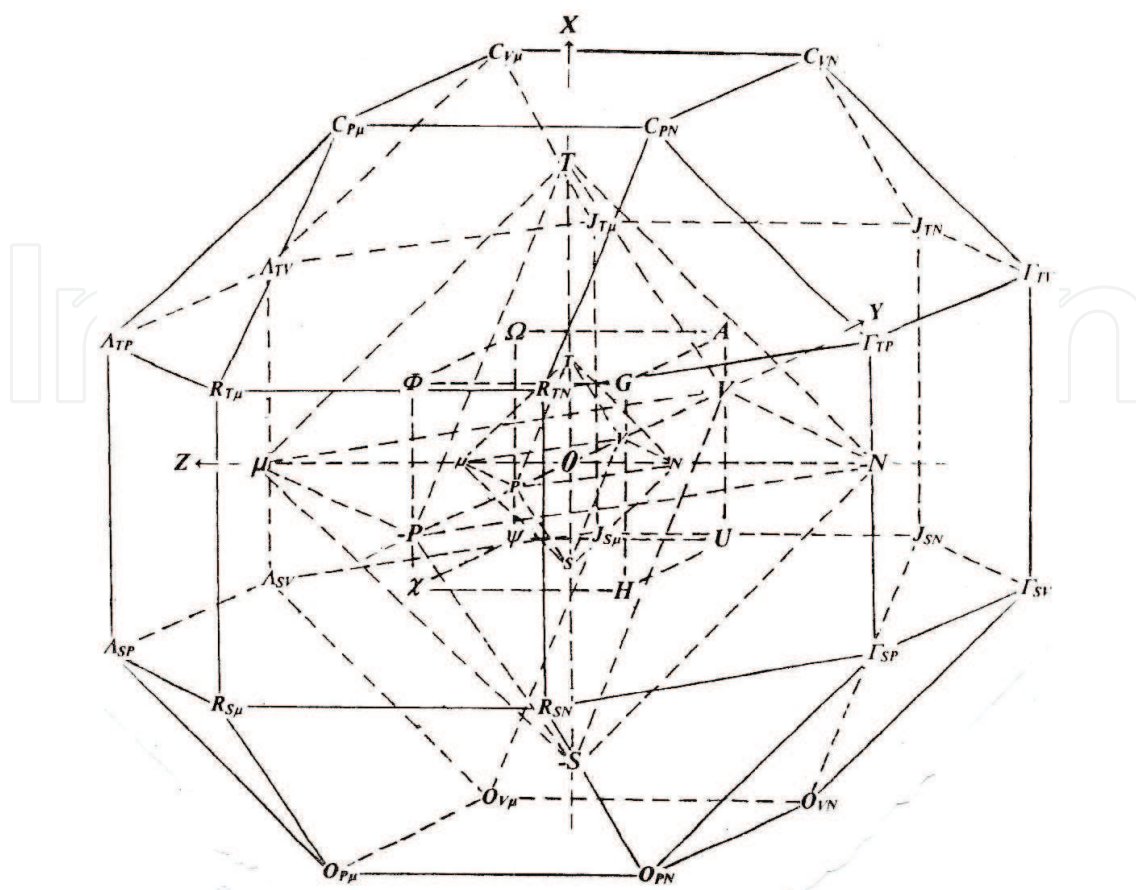


Figure 4. An extended concentric multi-polyhedron diagram in thermodynamics.

4.2. To develop relations for C_P 's family

4.2.1. The closest neighbor relation between C_P and C_V

A closest neighbor relation between C_p and C_V is well known as

$$C_V = C_P - \frac{\alpha^2 VT}{\kappa_T}$$

The relation could also be expressed in terms of the natural variables (T , S , P , V , μ , and N) as

$$C_{PN}(T, -P, -N) \rightarrow C_{VN}(T, V, -N) : C_{VN} = C_{PN} + \left(\frac{\partial V}{\partial T} \right)_{PN} \bullet T \bullet \left(\frac{\partial(-P)}{\partial T} \right)_{VN} \quad (34)$$

$$C_{VN}(T, V, -N) \rightarrow C_{PN}(T, -P, -N) : C_{PN} = C_{VN} + \left(\frac{\partial P}{\partial T} \right)_{VN} \bullet T \bullet \left(\frac{\partial(V)}{\partial T} \right)_{PN} \quad (35)$$

Similarly, the closest neighbor relations for other pairs of the C_p type variables could be

$$R_{SN}(-S, -P, -N) \rightarrow R_{TN}(T, -P, -N) : R_{TN} = R_{SN} + \left(\frac{\partial T}{\partial P}\right)_{SN} \bullet P \bullet \left(\frac{\partial(-S)}{\partial P}\right)_{TN} \quad (36)$$

$$R_{TN}(T, -P, -N) \rightarrow R_{SN}(-S, -P, -N) : R_{SN} = R_{TN} + \left(\frac{\partial S}{\partial P}\right)_{TN} \bullet P \bullet \left(\frac{\partial(T)}{\partial P}\right)_{SN} \quad (37)$$

$$O_{VN}(-S, V, -N) \rightarrow O_{PN}(-S, -P, -N) : O_{PN} = O_{VN} + \left(\frac{\partial P}{\partial S}\right)_{VN} \bullet S \bullet \left(\frac{\partial(V)}{\partial S}\right)_{PN} \quad (38)$$

$$O_{PN}(-S, -P, -N) \rightarrow O_{VN}(-S, V, -N) : O_{VN} = O_{PN} + \left(\frac{\partial V}{\partial S}\right)_{PN} \bullet S \bullet \left(\frac{\partial(-P)}{\partial S}\right)_{VN} \quad (39)$$

$$J_{SN}(-S, V, -N) \rightarrow J_{TN}(T, V, -N) : J_{TN} = J_{SN} + \left(\frac{\partial T}{\partial V}\right)_{SN} \bullet V \bullet \left(\frac{\partial(-S)}{\partial V}\right)_{TN} \quad (40)$$

$$J_{TN}(T, V, -N) \rightarrow J_{SN}(-S, V, -N) : J_{SN} = J_{TN} + \left(\frac{\partial S}{\partial V}\right)_{TN} \bullet V \bullet \left(\frac{\partial(T)}{\partial V}\right)_{SN} \quad (41)$$

These symmetric reversible linear conversions between the two closest C_P type variables are similar to the symmetric reversible Legendre transforms between two closest potentials. Because all of them are resulted from the reversible conversions between a pair of the opposite sign conjugate variables ($T \leftrightarrow -S$ or $-P \leftrightarrow V$).

4.2.2. The parallel relations

It is easily found that following relations are true:

$$C_P \bullet O_P = T \bullet (-S) = -T S \quad (42)$$

$$C_V \bullet O_V = T \bullet (-S) = -T S \quad (43)$$

$$J_T \bullet R_T = V \bullet (-P) = -P V \quad (44)$$

$$J_S \bullet R_S = V \bullet (-P) = -P V \quad (45)$$

They can be called the parallel relations, as shown in the diagram.

4.2.3. The cross relations

It can also be found that following relations are true:

$$C_V \bullet R_T = C_P \bullet R_S \quad (46)$$

$$R_T \bullet O_P = R_S \bullet O_V \quad (47)$$

$$O_P \bullet J_S = O_V \bullet J_T \quad (48)$$

$$C_V \bullet J_S = C_P \bullet J_T \quad (49)$$

They can be called the cross relations, as shown in the diagram.

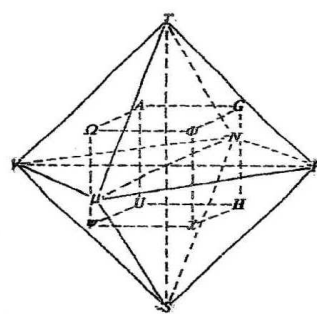
5. Applications

5.1. To distinguish and identify partial derivatives

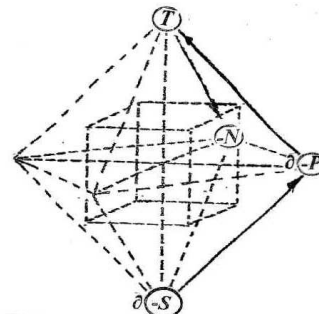
Different partial derivatives can visually be distinguished and identified by variable neighbor relationship in the diagram (Figure 5).

5.1.1. "Maxwell equations"-like partial derivatives

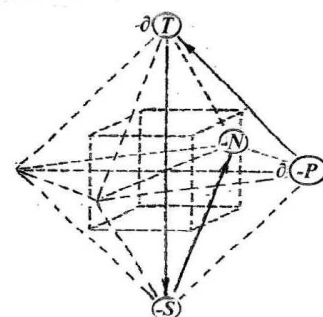
Any partial derivative, $(\partial X/\partial Y)_Z$, can be expressed by a ratio of other two partial derivatives, $(\partial X/\partial Y)_Z = \{-(\partial Z/\partial Y)_X/(\partial Z/\partial X)_Y\}$, based on Euler's chain relation $(\partial X/\partial Y)_Z \cdot (\partial Y/\partial Z)_X \cdot (\partial Z/\partial X)_Y = -1$.



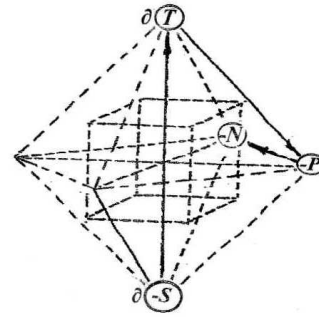
1. The simplified 3-D diagram



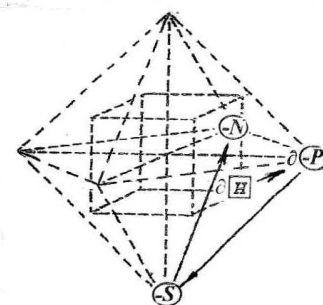
2. $(\partial S/\partial P)_{TN}$ (Maxwell-I)



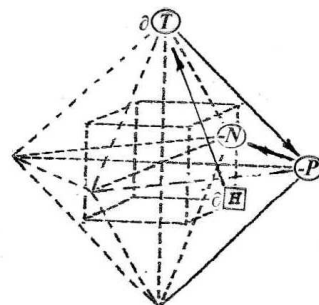
3. $(\partial P/\partial T)_{SN}$ (Maxwell-II)



4. $(\partial S/\partial T)_{PN}$ (Maxwell-III)



5. $(\partial H/\partial P)_{SN} = V$



6. $(\partial H/\partial T)_{PN} = C_{PN}$

Figure 5. Different variable neighbor relationships.

$(\partial Z/\partial X)_Y = -1$, where three partial derivatives look like same in their forms and variable's categories, but different each other from their variable neighbor relationship in thermodynamics (**Figure 5-2-4**). For an example, $(\partial P/\partial T)_{SN} = \{-(\partial S/\partial T)_{PN}/(\partial S/\partial P)_{TN}\}$, all of them look as same as the Maxwell partial derivatives, but they are different. It is quite difficult to determine, which one is a real Maxwell partial derivative or not by their forms and variables only.

The partial derivative $(\partial S/\partial P)_{TN}$, which is involved in one of the Maxwell equations $(\partial(S)/\partial P)_{TN} = -(\partial V/\partial T)_{PN}$ [Eq. (24)], can be called a Maxwell-I partial derivative. It stands for a partial derivative of the function S , $S = S(P, T, N)$, with respect to one of S 's first neighbor variables, P , while holding S 's two order-mixed (second and first) neighbor variables, T and N , constant (**Figure 5-2**). The partial derivative $(\partial P/\partial T)_{SN}$ can be called Maxwell-II or inverted Maxwell-I partial derivative. It stands for a partial derivative of the function P , $P = P(T, S, N)$, with respect to one of P 's first neighbor variables, T , while holding P 's other two first neighbor variables, S and N , constant (**Figure 5-3**). The partial derivative $(\partial S/\partial T)_{PN}$, which can be called Maxwell-III partial derivative, stands for a partial derivative of the function S , $S = S(T, P, N)$, with respect to S 's second neighbor (or conjugate) variable, T , while holding S 's two first neighbor variables, P and N , constant (**Figure 5-4**). Therefore, Maxwell like partial derivatives can be visually distinguished by the variable neighbor relationship in the diagram and identified (or classified) into three different families: Maxwell-I, -II, and -III partial derivatives.

5.1.2. $(\partial H/\partial P)_{SN}$ and $(\partial H/\partial T)_{PN}$

Two partial derivatives $(\partial H/\partial P)_{SN}$ and $(\partial H/\partial T)_{PN}$ look like same in their forms and variable's categories but totally different each other from their physical meanings: $(\partial H/\partial P)_{SN} = V$ (volume) and $(\partial H/\partial T)_{PN} = C_P$ (isobaric heat capacity). Such a difference between them can also visually be distinguished by their different variable neighbor relations shown in **Figure 5-5** and **6**. The partial derivative $(\partial H/\partial P)_{SN}$ stands for a partial derivative of the enthalpy H , $H = H(P, S, N)$, with respect to one of H 's first neighbor (or natural) variables, P , while holding H 's other two first neighbor variables, S and N , constant, whereas another partial derivative, $(\partial H/\partial T)_{PN}$, stands for a partial derivative of the enthalpy H , $H = H(T, P, N)$ with respect to one of H 's second neighbor variables, T , while holding H 's two first neighbor variables, P and N , constant.

It should be emphasized here after the above analysis that the general formula of a family regarding to a group of similar partial derivatives must be unchanged not only in form but also in variable's nature and neighbor relationship under symmetric operations, conversely, that those similar partial derivatives, which display same form and variable's category without same variable's neighbor relationship, are not classified into a same family since they do not have a general formula, and that any difference in the variable's neighbor relationship can certainly be distinguished by the diagram.

5.2. Predict novel members of families

5.2.1. The Gibbs-Helmholtz equation's family

When we discuss temperature dependence of the Gibbs free energy, the famous Gibbs-Helmholtz equation is satisfied as:

$$\left(\frac{\partial(G/T)}{\partial T}\right)_{PN} = -\frac{H}{T^2} \quad \text{or} \quad \left(\frac{\partial(\frac{G}{T})}{\partial(\frac{1}{T})}\right)_{PN} = H \quad (50)$$

It can be predicted by the σ and C_4 symmetries, then justified by conventional derivation that following other members of the family are true:

$$\left(\frac{\partial(\frac{G}{T})}{\partial(\frac{1}{T})}\right)_{PN} = H = \left(\frac{\partial(\frac{U}{V})}{\partial(\frac{1}{V})}\right)_{SN} \quad (51)$$

and

$$\left(\frac{\partial(\frac{A}{T})}{\partial(\frac{1}{T})}\right)_{VN} = U = \left(\frac{\partial(\frac{H}{P})}{\partial(\frac{1}{P})}\right)_{SN} \quad (52)$$

5.2.2. The Jacobian equations

The Jacobian method is useful and entirely foolproof [13, 14]. If we could combine it with this method, it would be more helpful for anyone of the subject.

The Jacobian of two functions (f and g) with respect to two independent variables (x and y) is defined by

$$J(f, g) = \frac{\partial(f, g)}{\partial(x, y)} = \begin{pmatrix} (\partial f / \partial x)_y & (\partial g / \partial x)_y \\ (\partial f / \partial y)_x & (\partial g / \partial y)_x \end{pmatrix} \quad (53)$$

If the functions (f and g) or the variables (x and y) are interchanged, then sign is changed, and if one function and one variable are identical, the Jacobian reduces to a single partial derivative. For example, if $g = y$, then

$$J(f, y) = \frac{\partial(f, y)}{\partial(x, y)} = -\frac{\partial(y, f)}{\partial(x, y)} = \frac{\partial(y, f)}{\partial(y, x)} = \left(\frac{\partial f}{\partial x}\right)_y \quad (54)$$

If the functions (f and g) and the variables (x and y) are functions of a new set of variables (w and z), then

$$J(f, g) = \frac{\partial(f, g)}{\partial(x, y)} = \frac{\partial(f, g) / \partial(w, z)}{\partial(x, y) / \partial(w, z)} = \frac{\partial(f, g)}{\partial(w, z)} \cdot \frac{\partial(w, z)}{\partial(x, y)} \quad (55)$$

In practice, it is convenient to take T and P as the independent variables since they are readily controlled experimentally. Based on Eq. (55), that is equivalent to $J(T, P) = 1$, since $J(T, P) = \frac{\partial(T, P)}{\partial(T, P)} = 1$. Conversely, if $J(T, P) = 1$ that means to take T and P as the independent variables.

One of the Jacobian equations for the internal energy $U(S, V, N)$ could be derived from dividing the fundamental equation ($dU = TdS - PdV + \mu dN$) by dx at constant y , where x and y are any suitable variables

$$\left(\frac{\partial U}{\partial x}\right)_y = (T) \cdot \left(\frac{\partial S}{\partial x}\right)_y + (-P) \cdot \left(\frac{\partial V}{\partial x}\right)_y + (\mu) \cdot \left(\frac{\partial N}{\partial x}\right)_y$$

Using Eq. (54), the Jacobian equation for the internal energy is obtained as:

$$J(U, y) = (T) \cdot J(S, y) + (-P) \cdot J(V, y) + (\mu) \cdot J(N, y) \quad (56)$$

Eq. (56) is similar to the fundamental equation for the internal energy. Each potential has

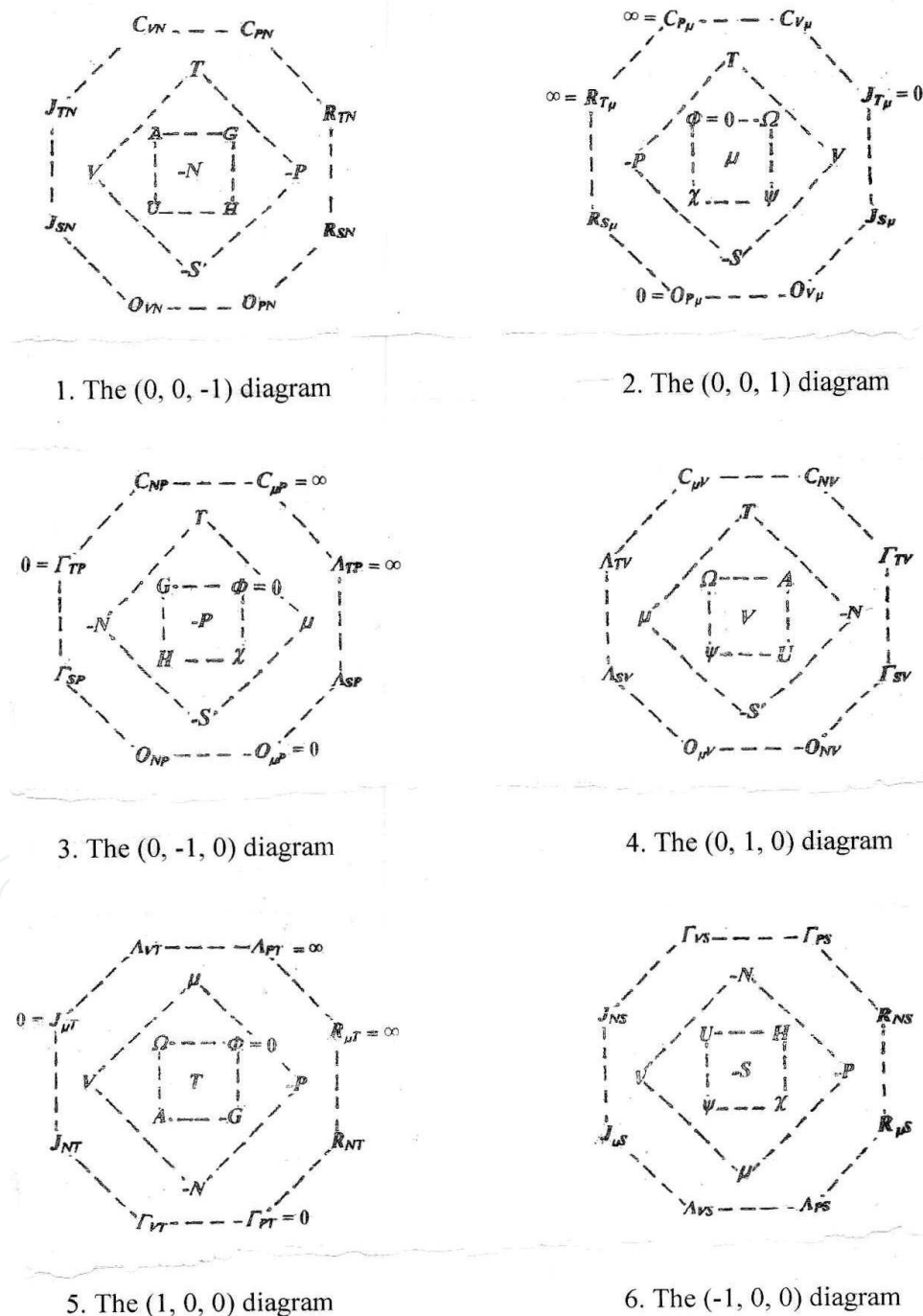


Figure 6. Six {1, 0, 0} projection diagrams.

its own total differential and its corresponding Jacobian equation. Thus, total number of the Jacobian equations is same as the total number of the potentials, it is eight.

5.3. To depict thermodynamic equations by an invented graphic method

Based on the equivalence principle of symmetry (reproducibility and predictability) [12], if we knew a sample member of any family we would be able to know all members of the family through symmetric operations [15].

5.3.1. Resolve the 3D diagram into 2D diagrams

Carrying out symmetric operations on the 3D diagram is complicated and quite difficult, whereas doing so on 2D diagrams will be much easier instead. The simplified concentric multi-polyhedron diagram could be resolved into six 2D $\{1, 0, 0\}$ projection diagrams, which are shown in **Figure 6-1–6**, and each 2D diagram consists of two squares and an octagon and exhibits the fourfold rotation (C_4) and the mirror (σ) symmetries. The “ $-N$ ”-centered $(0, 0, -1)$ diagram (**Figure 6-1**) contains the most common thermodynamic variables ($U, H, G, A, T, -S, -P, V, C_{PN}, C_{VN}, O_{PN}, O_{VN}, J_{TN}, J_{SN}, R_{TN}$, and R_{SN}), and it is chosen as first fixed diagram to depict the most familiar basic thermodynamic equations.

5.3.2. Specific notations

5.3.2.1. Graphic patterns for thermodynamic equations

It was mentioned that thermodynamic equations can be grouped into families with “standard forms.” Each family with a standard form, or a general formula, can be expressed by a specifically created graphic pattern, which consists of a series of mixed special symbols arranged in a writing order (path) of the formula. Different families are distinguished by different patterns, which display differences in their forms, symbols, and writing orders (paths) graphically.

5.3.2.2. Graphic notations for partial derivatives

A first-order partial derivative of a multi-variable function, $f = f(x, y, z)$, is expressed by $(\partial f / \partial x)_{yz}$. It consists of two parts in the form: a series of mathematical symbols (∂ and ∂) and a series of variables (f, x, y , and z). Thus, it can be expressed by a specifically created graphic pattern, $\partial O \rightarrow \partial O \rightarrow O \rightarrow O$ or $\partial \square \rightarrow \partial O \rightarrow O \rightarrow O$, where a series of mathematical symbols (∂ and ∂) and a series of variable’s selecting symbols (O and/or $\square$) are alternately mixed together and arranged in a writing order of the partial derivative.

5.3.2.3. Arrows show directions

Arrows show directions of the writing order in a given general formula. For example, arrows ($\rightarrow$) in the graphic pattern, $\partial O \rightarrow \partial O \rightarrow O \rightarrow O$, show directions of the writing order for the partial derivative, $(\partial f / \partial x)_{yz}$.

5.3.2.4. Different symbols for selecting different categories of the variables

A square symbol “□” is used for selecting the potential variables located at four corners of the small square. Both large circle symbol “○” and small circle symbol “○” are used for selecting the opposite sign conjugate variables located at four corners of the large square. The difference between the large and the small circles is only significant for those three variables ($-S$, $-P$, and $-N$). The large circle symbol (“○”) keeps negative sign in front of those variables, whereas the small circle symbol (“○”) cancels the negative sign instead. They are equivalent to a pair of the opposite treatment symbols, { } and [], mentioned before. A special symbol “⊗” is used for selecting the C_P type variables located at eight corners of the octagon.

5.3.2.5. Symbols for some common mathematical operations

A line segment linking two selected variables, “○ --- ○” or “⊗ --- ⊗”, represents a product “●” of the two selected variables. A slash between two symbols, “⊗/○”, stands for a ratio of the variable selected by the special symbol (“⊗”) to the variable selected by the large circle symbol (“○”). Symbols including =, d , ∂ , ∂^2 , and J stand for equal, differential, first-order partial derivative, second-order partial derivative, and Jacobian, respectively, as usual. Sometimes the equal symbol (“=”) is omitted. Symbol for addition (positive sign, “+”, or plus) is always omitted. Symbol for subtraction (negative sign, “−”, or minus) is never shown in the graphic patterns, but it is kept from those selected conjugate variables with the negative sign ($-S$, $-P$, and $-N$) in the fixed diagram by the large circle (“○”).

5.4. General procedure of the invented graphic method

A general procedure to depict all members of 12 thermodynamic families comprises four steps as follows.

Step 1: To employ the (0, 0, −1) diagram (**Figure 6-1**) as a fixed foundation, where four categories of common used thermodynamic variables being arranged at four kinds of locations including unchangeable natural variable (N) at center, four thermodynamic potentials (U , H , G , and A) at four corners of a small square, four first-order partial derivatives of the thermodynamic potentials, or two pairs of the opposite sign intensive versus extensive conjugate variables, i.e., temperature versus entropy and pressure versus volume (T versus $-S$ and $-P$ versus V) at two ends of two diagonals of a large square, and eight C_P type second-order partial derivatives of the thermodynamic potentials (the isobaric thermal capacity, C_{PN} , the isochoric thermal capacity, C_{VN} , and six other C_P type variables (O_{PN} , O_{VN} , J_{TN} , J_{SN} , R_{TN} , and R_{SN}) at eight vertices of an octagon.

Step 2: To create a graphic pattern (or a general formula) for depicting each family on the fixed diagram. It includes choosing a familiar equation in the family as a sample equation of the family, identifying categories of all involved variables in the sample equation, determining a writing order of the sample equation, and resolving the sample equation into two parts: a series of symbols of mathematical expressions and a series of involved variables in the sample equation in the writing order, using a set of specific symbols correctly and individually for each mathematical expression and each category of the involved variables in the sample equation individually, alternately, and gradually, and combining a series of

mathematical symbols with a series of variable selecting symbols together in the writing order of the sample equation.

Step 3: To overlap each family's specific, rigid, movable graphic pattern (Patterns 1–12) on! the fixed diagram for depicting other members of the family. It includes picking up a series of involved variables on the diagram by a series of variable selecting symbols in the graphic pattern, and combining a series of the mathematical symbols with a series of selected variables together in the writing order correspondingly and alternately to depict other member of the family through σ and/or C_4 symmetric operation individually and gradually.

Step 4: To substitute the fixed foundation diagram from one to another gradually (from **Figure 6-1–6**), and continuously to depict more members of each family in a same way above until having all members of the 12 families done.

5.5. Graphic patterns for 12 families

5.5.1. The Legendre transforms

$$-P \rightarrow V; H(-S, -P, -N) \rightarrow U(-S, V, -N) : U = H + V \bullet (-P) \quad (57)$$

Pattern 1: $\square = \square \quad \bigcirc \text{---} \bigcirc$ parallel

where an uncertain sign (positive or negative) of the product term depends on sign of the converting (starting) conjugate variable without or with a negative sign ("−"), which is selected by a large circle symbol ("○") located at end. In terms of the order of writing right equations on the spot, it is always true to select the converted (ended) potential first for any equations of this family and to select the converted (ended) conjugate variable using a small circle symbol ("○") first for the product term.

5.5.2. The first-order partial derivative variables

$$\left(\frac{\partial A}{\partial T}\right)_V = (-S) \quad (58)$$

Pattern 2: $\partial \square \rightarrow \partial \bigcirc \rightarrow \bigcirc = \bigcirc$

5.5.3. The Maxwell equations

$$\left(\frac{\partial(V)}{\partial T}\right)_P = \left(\frac{\partial(-S)}{\partial P}\right)_T \quad (59)$$

Pattern 3: Two " $\partial \bigcirc \rightarrow \partial \bigcirc \rightarrow \bigcirc$ " equal each other

Both paths go around the large square reversely.

5.5.4. The Maxwell-II equations (or the inverted Maxwell equations)

$$\left(\frac{\partial(-S)}{\partial P}\right)_V = \left(\frac{\partial(V)}{\partial T}\right)_S \quad (60)$$

Pattern 4: Two “ $\partial \bigcirc \rightarrow \partial \bigcirc \rightarrow \bigcirc$ ” equal each other

Both paths pass through the center like a shape of “8” or “ ∞ .”

5.5.5. The fundamental thermodynamic equations

$$dU = (T) \cdot dS + (-P) \cdot dV \quad (61)$$

Pattern 5: $d\Box = \bigcirc \text{---} d\bigcirc \quad \bigcirc \text{---} d\bigcirc$

5.5.6. The Gibbs-Helmholtz equation's family

$$\left(\frac{\partial(G/T)}{\partial(1/T)}\right)_P = H \quad (62)$$

Pattern 6: $\partial(\Box/\bigcirc) \rightarrow \partial(1/\bigcirc) \rightarrow \bigcirc = \Box$

5.5.7. The C_P type variables

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P \quad (63)$$

Pattern 7: $\text{\textcircled{X}} = \partial \Box \rightarrow \partial \bigcirc \rightarrow \bigcirc$

5.5.8. The relations between Maxwell-III and C_P type variables

$$\left(\frac{\partial V}{\partial P}\right)_S = \frac{R_S}{(-P)} \quad (64)$$

Pattern 8: $\partial \bigcirc \rightarrow \partial \bigcirc \rightarrow \bigcirc = \text{\textcircled{X}}/\bigcirc$

5.5.9. The closest neighbor relations like C_V and C_P

$$C_{PN}(T, -P, -N) \rightarrow C_{VN}(T, V, -N) : C_V = C_P + \left(\frac{\partial V}{\partial T}\right)_P \cdot T \cdot \left(\frac{\partial(-P)}{\partial T}\right)_V \quad (65)$$

Pattern 9: $\text{\textcircled{X}} = \text{\textcircled{X}} \left(\frac{\partial \bigcirc}{\partial \bigcirc}\right)_\bigcirc \cdot \bigcirc \cdot \left(\frac{\partial(\bigcirc)}{\partial \bigcirc}\right)_\bigcirc$

where a product term consists of three parts (two Maxwell-I partial derivatives and a mid variable, T in this case), the two Maxwell-I partial derivatives are symmetric each other with

respect to a mirror, which is perpendicular to a line segment of a pair of the opposite sign conjugate variables ($-P \rightarrow V$) and passes through the mid variable (T), an uncertain sign (positive or negative) of the product term in the Pattern 9 depends on sign of the converting (starting), rather than the converted (ended), conjugate variable without or with a negative sign (" $-$ "), and the converting (starting) conjugate variable ($-P$) is selected by a large circle symbol (" $\bigcirc$ "), which is located at numerator of the second Maxwell-I partial derivative. In terms of the order of writing right equations on the spot, it is always true to select the converted (ended) C_P type variable first for any equations of this family and to select the converted (ended) conjugate variable using a small circle symbol (" $\bigcirc$ ") first for the product term.

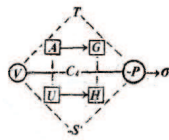
SUMMARY-I

The general procedure:

1. The $(0, 0, -1)$ diagram;
2. The graphic patterns (1 ~ 12);
3. The σ and C_P symmetries;
4. The other $\{1, 0, 0\}$ diagrams.



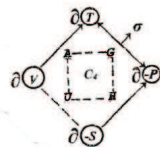
The $(0, 0, -1)$ diagram



The Pattern 1

$$\square = \square \quad \bigcirc \text{---} \bigcirc \text{ parallel}$$

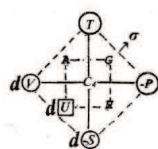
$$U = H + V \cdot (-P) = H - P \cdot V$$



The Pattern 3

Two $\partial \bigcirc \rightarrow \partial \bigcirc \rightarrow \bigcirc$ equal and go reversely

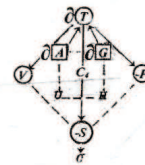
$$(\partial(V)/\partial T)_P = (\partial(-S)/\partial P)_T$$



The Pattern 5

$$d\square = \bigcirc \text{---} d\bigcirc \quad \bigcirc \text{---} d\bigcirc$$

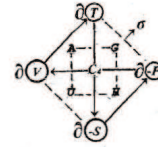
$$dU = (T) \cdot dS + (-P) \cdot dV$$



The Pattern 2

$$\partial \square \rightarrow \partial \bigcirc \rightarrow \bigcirc = \bigcirc$$

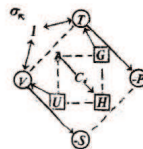
$$(\partial A/\partial T)_V = (-S)$$



The Pattern 4

Two $\partial \bigcirc \rightarrow \partial \bigcirc \rightarrow \bigcirc$ equal and look like ∞

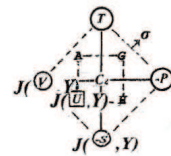
$$(\partial(-S)/\partial P)_V = (\partial(V)/\partial T)_S$$



The Pattern 6

$$\partial(\square/\bigcirc) \rightarrow \partial(I/\bigcirc) \rightarrow \bigcirc = \square$$

$$(\partial(G/T)/\partial(I/T))_P = H$$



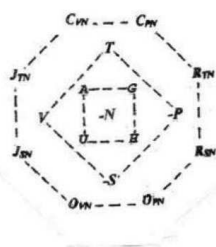
The Pattern 12

$$J(\square, Y) = \bigcirc \text{---} J(\bigcirc, Y) \quad \bigcirc \text{---} J(\bigcirc, Y)$$

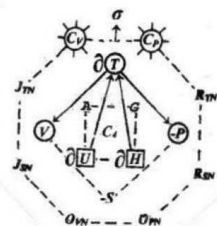
$$J(U, Y) = (T) \cdot J(S, Y) + (-P) \cdot J(V, Y)$$

Figure 7. Summary-I of the Patterns (1–6 and 12) on the $(0, 0, -1)$ diagram.

SUMMARY-II



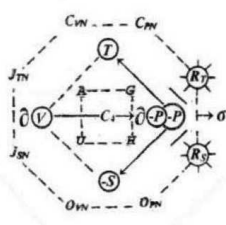
The (0, 0, -1) diagram



The Pattern 7

$$\odot = \partial \square \rightarrow \partial O \rightarrow O$$

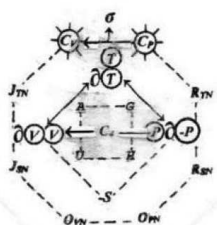
$$C_P = (\partial H / \partial T)_P$$



The Pattern 8

$$\partial O \rightarrow \partial O \rightarrow O = \odot / \bigcirc$$

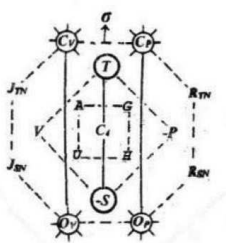
$$(\partial V / \partial P)_T = R_T / (-P)$$



The Pattern 9

$$\odot = \odot (\partial O / \partial O)_O \cdot O \cdot (\partial O / \partial O)_O$$

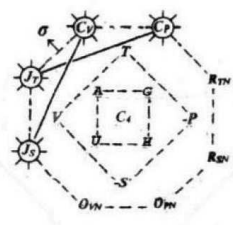
$$C_V = C_P + (\partial V / \partial T)_P \cdot T \cdot (\partial (-P) / \partial T)_V$$



The Pattern 10

$$\odot \text{ --- } \odot = \bigcirc \text{ --- } \bigcirc \text{ parallel}$$

$$C_P \cdot O_P = (T) \cdot (-S)$$



The Pattern 11

$$\odot \text{ --- } \odot = \odot \text{ --- } \odot \text{ cross}$$

$$J_T \cdot C_P = J_S \cdot C_V$$

Figure 8. Summary-II of the Patterns (7-11) on the (0, 0, -1) diagram.

5.5.10. The parallel relations

$$C_P \cdot O_P = (T) \cdot (-S) = -T S \quad (66)$$

Pattern 10: $\odot \text{ --- } \odot = \bigcirc \text{ --- } \bigcirc$

5.5.11. The cross relations

$$J_T \bullet C_P = J_S \bullet C_V \quad (67)$$

Pattern 11: ☼ --- ☼ = ☼ --- ☼

5.5.12. The Jacobian equations

$$J(U, Y) = (T) \bullet J(S, Y) + (-P) \bullet J(V, Y) \quad (68)$$

Pattern 12: $J(\square, Y) = \bigcirc \text{---} J(\bigcirc, Y) \quad \bigcirc \text{---} J(\bigcirc, Y)$

This Pattern 12 is similar to Pattern 5: $d\square = \bigcirc \text{---} d\bigcirc \quad \bigcirc \text{---} d\bigcirc$.

All the above 12 graphic patterns are summarized in **Figures 7** and **8**.

5.6. To derive any desired partial derivatives in terms of $T, S, P, V, \mu, N, C_P, \alpha, \kappa_T$ and ω

If we want to know the total differential of a multi-variable function, we need to know what its partial derivatives are. Often, there is no convenient experimental method to evaluate the partial derivatives needed for the numerical solution of a problem. In this case, we must calculate the partial derivatives and relate them to other quantities that are readily available, such as $T, S, P, V, \mu, N, C_P, \alpha, \kappa_T$ and ω (the molar grand canonical potential of the system, $\omega = (\partial\Omega/\partial N)_{VT}$).

5.6.1. Results of C_P type variables

Results of the 24 C_P -type variables are derived and given as follows:

$$C_{PN} = C_P \quad (69)$$

$$C_{VN} = C_{PN} + \left(\frac{\partial V}{\partial T}\right)_{P,N} \bullet T \bullet \left(\frac{\partial(-P)}{\partial T}\right)_{V,N} = C_P - \frac{\alpha^2 VT}{\kappa_T} \quad (70)$$

$$J_{TN} = \left(\frac{\partial G}{\partial V}\right)_{TN} = V \left(\frac{\partial P}{\partial V}\right)_{TN} = \frac{-1}{\kappa_T} \quad (71)$$

$$J_{SN} = \frac{J_{TN} \bullet C_{PN}}{C_{VN}} = \frac{-C_{PN}}{\kappa_T C_{VN}} = \frac{C_{PN}}{\alpha^2 VT - \kappa_T C_{PN}} \quad (72)$$

$$O_{PN} = \frac{T \bullet (-S)}{C_{PN}} = \frac{-TS}{C_{PN}} \quad (73)$$

$$O_{VN} = \frac{T \bullet (-S)}{C_{VN}} = \frac{\kappa_T ST}{\alpha^2 VT - \kappa_T C_{PN}} \quad (74)$$

$$R_{TN} = \frac{V \bullet (-P)}{J_{TN}} = \kappa_T PV \quad (75)$$

$$R_{SN} = \frac{V \bullet (-P)}{J_{SN}} = \kappa_T PV - \frac{\alpha^2 V^2 PT}{C_{PN}} \quad (76)$$

$$O_{P\mu} = \left(\frac{\partial \Phi}{\partial S} \right)_{P\mu} = -S \left(\frac{\partial T}{\partial S} \right)_{P\mu} = -S \left(\frac{\partial^2 \chi}{\partial S^2} \right)_{P\mu} = 0 \quad (77)$$

$$J_{T\mu} = \left(\frac{\partial \Phi}{\partial V} \right)_{T\mu} = V \left(\frac{\partial P}{\partial V} \right)_{T\mu} = -V \left(\frac{\partial^2 \Omega}{\partial V^2} \right)_{T\mu} = 0 \quad (78)$$

$$\Gamma_{PT} = \left(\frac{\partial \Phi}{\partial N} \right)_{PT} = N \left(\frac{\partial \mu}{\partial N} \right)_{PT} = -N \left(\frac{\partial^2 G}{\partial N^2} \right)_{PT} = 0 \quad (79)$$

$$C_{P\mu} = \left(\frac{\partial \chi}{\partial T} \right)_{P\mu} = T \left(\frac{\partial S}{\partial T} \right)_{P\mu} = -T \left(\frac{\partial^2 \Phi}{\partial T^2} \right)_{P\mu} = \infty \quad (80)$$

$$R_{T\mu} = \left(\frac{\partial \Omega}{\partial P} \right)_{T\mu} = -P \left(\frac{\partial V}{\partial P} \right)_{T\mu} = -P \left(\frac{\partial^2 \Phi}{\partial P^2} \right)_{T\mu} = \infty \quad (81)$$

$$\Lambda_{PT} = \left(\frac{\partial G}{\partial \mu} \right)_{PT} = \mu \left(\frac{\partial N}{\partial \mu} \right)_{PT} = -\mu \left(\frac{\partial^2 \Phi}{\partial \mu^2} \right)_{PT} = \infty \quad (82)$$

$$\begin{aligned} C_{V\mu} &= \left(\frac{\partial \Psi}{\partial T} \right)_{V\mu} = T \left(\frac{\partial S}{\partial T} \right)_{V\mu} = -T \left(\frac{\partial^2 \Omega}{\partial T^2} \right)_{V\mu} \\ &= C_{VN} + \left(\frac{\partial \mu}{\partial T} \right)_{NV} \bullet T \bullet \left(\frac{\partial(-N)}{\partial T} \right)_{\mu V} \\ &= C_{PN} - \frac{\alpha^2 VT}{\kappa_T} + \left(\frac{\partial \mu}{\partial T} \right)_{NV} \bullet T \bullet \left(\frac{\partial(-N)}{\partial T} \right)_{\mu V} \end{aligned} \quad (83)$$

$$\begin{aligned} J_{S\mu} &= \left(\frac{\partial \chi}{\partial V} \right)_{S\mu} = V \left(\frac{\partial P}{\partial V} \right)_{S\mu} = -V \left(\frac{\partial^2 \Psi}{\partial V^2} \right)_{S\mu} \\ &= J_{SN} + \left(\frac{\partial \mu}{\partial V} \right)_{NS} \bullet V \bullet \left(\frac{\partial(-N)}{\partial V} \right)_{\mu S} \\ &= \frac{C_{PN}}{\alpha^2 VT - \kappa_T C_{PN}} + \left(\frac{\partial \mu}{\partial V} \right)_{NS} \bullet V \bullet \left(\frac{\partial(-N)}{\partial V} \right)_{\mu S} \end{aligned} \quad (84)$$

$$\begin{aligned} O_{V\mu} &= \left(\frac{\partial \Omega}{\partial S} \right)_{V\mu} = -S \left(\frac{\partial T}{\partial S} \right)_{V\mu} = -S \left(\frac{\partial^2 \Psi}{\partial S^2} \right)_{V\mu} \\ &= O_{VN} + \left(\frac{\partial \mu}{\partial S} \right)_{NV} \bullet S \bullet \left(\frac{\partial(-N)}{\partial S} \right)_{\mu V} \\ &= \frac{\kappa_T ST}{\alpha^2 VT - \kappa_T C_{PN}} + \left(\frac{\partial \mu}{\partial S} \right)_{NV} \bullet S \bullet \left(\frac{\partial(-N)}{\partial S} \right)_{\mu V} \end{aligned} \quad (85)$$

$$\begin{aligned} R_{S\mu} &= \left(\frac{\partial \Psi}{\partial P}\right)_{S\mu} = -P \left(\frac{\partial S}{\partial P}\right)_{S\mu} = -P \left(\frac{\partial^2 \chi}{\partial P^2}\right)_{S\mu} \\ &= R_{SN} + \left(\frac{\partial \mu}{\partial P}\right)_{NS} \bullet P \bullet \left(\frac{\partial(-N)}{\partial P}\right)_{\mu S} \end{aligned} \quad (86)$$

$$= \kappa_T PV - \frac{\alpha^2 V^2 PT}{C_{PN}} + \left(\frac{\partial \mu}{\partial P}\right)_{NS} \bullet P \bullet \left(\frac{\partial(-N)}{\partial P}\right)_{\mu S}$$

$$\begin{aligned} \Gamma_{VT} &= \left(\frac{\partial \Omega}{\partial N}\right)_{VT} = N \left(\frac{\partial \mu}{\partial N}\right)_{VT} = -N \left(\frac{\partial^2 A}{\partial N^2}\right)_{VT} = \omega \\ \Lambda_{VT} &= \left(\frac{\partial A}{\partial \mu}\right)_{VT} = \mu \left(\frac{\partial N}{\partial \mu}\right)_{VT} = -\mu \left(\frac{\partial^2 \Omega}{\partial \mu^2}\right)_{VT} \end{aligned} \quad (87)$$

$$= \frac{\mu \bullet (-N)}{\Gamma_{VT}} = \frac{-\mu N}{\omega} \quad (88)$$

$$\begin{aligned} \Gamma_{VS} &= \left(\frac{\partial \Psi}{\partial N}\right)_{VS} = N \left(\frac{\partial \mu}{\partial N}\right)_{VS} = -N \left(\frac{\partial^2 U}{\partial N^2}\right)_{VS} \\ &= \Gamma_{VT} + \left(\frac{\partial S}{\partial N}\right)_{TV} \bullet N \bullet \left(\frac{\partial T}{\partial N}\right)_{SV} \\ &= \omega + \left(\frac{\partial S}{\partial N}\right)_{TV} \bullet N \bullet \left(\frac{\partial T}{\partial N}\right)_{SV} \end{aligned} \quad (89)$$

$$\begin{aligned} \Gamma_{PS} &= \left(\frac{\partial \chi}{\partial N}\right)_{PS} = N \left(\frac{\partial \mu}{\partial N}\right)_{PS} = -N \left(\frac{\partial^2 H}{\partial N^2}\right)_{PS} \\ &= \Gamma_{VS} + \left(\frac{\partial P}{\partial N}\right)_{VS} \bullet N \bullet \left(\frac{\partial V}{\partial N}\right)_{PS} \\ &= \omega + \left(\frac{\partial S}{\partial N}\right)_{TV} \bullet N \bullet \left(\frac{\partial T}{\partial N}\right)_{SV} + \left(\frac{\partial P}{\partial N}\right)_{VS} \bullet N \bullet \left(\frac{\partial V}{\partial N}\right)_{PS} \end{aligned} \quad (90)$$

$$\begin{aligned} \Lambda_{VS} &= \left(\frac{\partial U}{\partial \mu}\right)_{VS} = \mu \left(\frac{\partial N}{\partial \mu}\right)_{VS} = -\mu \left(\frac{\partial^2 \Psi}{\partial \mu^2}\right)_{VS} \\ &= \frac{\mu \bullet (-N)}{\Gamma_{VS}} = \frac{-\mu N}{\omega + \left(\frac{\partial S}{\partial N}\right)_{TV} \bullet N \bullet \left(\frac{\partial T}{\partial N}\right)_{SV}} \end{aligned} \quad (91)$$

$$\begin{aligned} \Lambda_{PS} &= \left(\frac{\partial H}{\partial \mu}\right)_{PS} = \mu \left(\frac{\partial N}{\partial \mu}\right)_{PS} = -\mu \left(\frac{\partial^2 \chi}{\partial \mu^2}\right)_{PS} = \frac{\mu \bullet (-N)}{\Gamma_{PS}} \\ &= \frac{-\mu N}{\omega + \left(\frac{\partial S}{\partial N}\right)_{TV} \bullet N \bullet \left(\frac{\partial T}{\partial N}\right)_{SV} + \left(\frac{\partial P}{\partial N}\right)_{VS} \bullet N \bullet \left(\frac{\partial V}{\partial N}\right)_{PS}} \end{aligned} \quad (92)$$

The above 24 results of the C_P type variables are useful for deriving other partial derivatives. It can also be seen on (1, -1, 1) projection diagram (**Figure 3-2**) that locations of three zero-value ($O_{P\mu}$, $J_{T\mu}$, Γ_{PT}) and three infinite-value ($C_{P\mu}$, $R_{T\mu}$, Λ_{PT}) C_P type variables display the C_3 (three-fold rotation) symmetry about the $U \sim \Phi$ pair at the center of the diagram.

5.6.2. To derive any desired partial derivatives

Any desired partial derivatives, $\left(\frac{\partial X}{\partial Y}\right)_{ZW}$, can be derived in terms of $T, S, P, V, \mu, N, C_P, \alpha, \kappa_T$ and ω by using the graphic patterns (Patterns 1–12) and the results of C_P type variables. Two examples are shown below:

Example 1 $(\partial G / \partial S)_V = ?$

$$\begin{aligned}
\left(\frac{\partial G}{\partial S}\right)_V &= \left(\frac{\partial(A + P \bullet (V))}{\partial S}\right)_V \quad (\text{Pattern 1}) \\
&= \left(\frac{\partial(U + T \bullet (-S) + P \bullet (V))}{\partial S}\right)_V \quad (\text{Pattern 1}) \\
&= \left(\frac{\partial U}{\partial S}\right)_V - T - S \left(\frac{\partial T}{\partial S}\right)_V + V \left(\frac{\partial P}{\partial S}\right)_V \\
&= T - T - S \left(\frac{O_V}{(-S)}\right) - V \left(\frac{\partial T}{\partial V}\right)_S \quad (\text{Patterns 2, 8 \& 3}) \\
&= O_V - V \left(\frac{-(\partial S/\partial V)_T}{(\partial S/\partial T)_V}\right) \quad (\text{chain eq.}) \\
&= \frac{T \bullet (-S)}{C_V} - V \left\{ \frac{-(\partial P/\partial T)_V}{C_V/T} \right\} \quad (\text{Patterns 10, 3 \& 8}) \\
&= \frac{T \bullet (-S)}{C_V} + V \left\{ \frac{-\frac{(\partial V/\partial T)_P}{(\partial V/\partial P)_T}}{C_V/T} \right\} \quad (\text{chain eq.}) \\
&= \frac{T \bullet (-S)}{C_V} + \frac{V(\alpha/\kappa_T)}{C_V/T} \quad (\alpha \text{ \& } \kappa_T \text{'s def.}) \\
&= \frac{-TS}{C_V} + \frac{\alpha VT}{\kappa_T C_V} = \frac{\alpha VT - \kappa_T TS}{\kappa_T C_V} \\
&= \frac{\alpha VT - \kappa_T TS}{\kappa_T (C_P - \alpha^2 VT/\kappa_T)} = \frac{\alpha VT - \kappa_T TS}{\kappa_T C_P - \alpha^2 VT} \quad (C_V \text{'s result})
\end{aligned}$$

Example 2 $(\partial A)_H = ?$

This is a question chosen from Bridgman's thermodynamic equations [16], where the symbol of the question stands for the Jacobian of two functions (A and H) with respect to two independent variables (T and P), i.e. $J(T, P) = 1$.

$$\begin{aligned}
(\partial A)_H &= \partial(A, H) = J(A, H) \\
&= (-S) \bullet J(T, H) + (-P) \bullet J(V, H) \quad (\text{Pattern 12}) \\
&= (S) \bullet J(H, T) + (P) \bullet J(H, V) \quad (\text{Eq. (54)})
\end{aligned}$$

where, $J(H, T) = (V) \bullet J(P, T) + (T) \bullet J(S, T)$ (Pattern 12)

$$\begin{aligned}
&= (V) \bullet \frac{J(P, T)}{J(T, P)} + (T) \bullet \frac{J(S, T)}{J(T, P)} \quad (J(T, P) = 1) \\
&= -(V) - (T) \bullet \frac{\partial(S, T)}{\partial(P, T)} \quad (\text{Eq. (54)})
\end{aligned}$$

$$\begin{aligned}
 &= -(V) - (T) \bullet \left(\frac{\partial S}{\partial P} \right)_T = -V + T \bullet \left(\frac{\partial V}{\partial T} \right)_P \text{ (Eq. (54) \& Pattern 3)} \\
 &= -V + T \bullet (\alpha V) = \alpha VT - V = (\alpha T - 1)V \text{ (\alpha's definition)}
 \end{aligned}$$

and

$$\begin{aligned}
 J(H, V) &= (V) \bullet J(P, V) + (T) \bullet J(S, V) \text{ (Pattern 12)} \\
 &= (V) \bullet \frac{J(P, V)}{J(T, P)} + (T) \bullet \frac{J(S, V) J(T, V)}{J(T, V) J(T, P)} \text{ (} J(T, P) = 1 \text{ \& Eq. (55))} \\
 &= -(V) \bullet \left(\frac{\partial V}{\partial T} \right)_P + (T) \bullet \left(\frac{\partial S}{\partial T} \right)_V \left(\frac{\partial V}{\partial P} \right)_T \text{ (Eq. (54))} \\
 &= -(V) \bullet (\alpha V) + (T) \bullet \left(\frac{C_V}{T} \right) (-\kappa_T V) \text{ (\alpha, } \kappa_T \text{'s def. \& Pattern 8)} \\
 &= -\alpha V^2 + \left(C_P - \frac{\alpha^2 VT}{\kappa_T} \right) (-\kappa_T V) \text{ (} C_V \text{'s result)} \\
 &= -\alpha V^2 - C_P \kappa_T V + \alpha^2 V^2 T = \alpha V^2 (\alpha T - 1) - C_P \kappa_T V
 \end{aligned}$$

Finally, substitute the results of $J(H, T)$ and $J(H, V)$ into the above equation and yield

$$\begin{aligned}
 (\partial A)_H &= J(A, H) = S \bullet J(H, T) + P \bullet J(H, V) \\
 &= S \bullet \{(\alpha T - 1)V\} + P \bullet \{\alpha V^2 (\alpha T - 1) - C_P \kappa_T V\} \\
 &= V \{(\alpha T - 1) \bullet (S + \alpha PV) - C_P \kappa_T P\}
 \end{aligned}$$

6. Discussion

There are not generally accepted symbols and names for all thermodynamic potentials; however, based on the fact that sum of any pair of the diagonal potentials in the cube is same and equals the internal energy of the system, i.e., $\square + \square^* = TS - PV + \mu N = U(S, V, N)$, it is suggested that three unnamed thermodynamic potentials $\Phi(T, P, \mu)$, $\psi(S, V, \mu)$, and $\chi(S, P, \mu)$ may be meaningfully named to be conjugate internal energy, conjugate Gibbs free energy, and conjugate Helmholtz free energy, respectively, with respect to $U(S, V, N)$, $G(T, P, N)$, and $A(T, V, N)$.

There are not generally accepted symbols and names for all 24 C_P type variables; however, it is clearly found out that an integration of the entire structure of a variety of thermodynamic variables is complete and highly coherent with symmetry. For example, a complete set of the 24 C_P type variables (C_{PN} , C_{VN} , O_{PN} , O_{VN} , J_{TN} , J_{SN} , R_{TN} , R_{SN} , $C_{P\mu}$, $C_{V\mu}$, $O_{P\mu}$, $O_{V\mu}$, $J_{T\mu}$, $J_{S\mu}$, $R_{T\mu}$, $R_{S\mu}$, Λ_{PT} , Λ_{VT} , Γ_{PT} , Γ_{VT} , Λ_{PS} , Λ_{VS} , Γ_{PS} , and Γ_{VS}) were initially defined for a completion based on the equivalence principle of symmetry, and they are finally proven to relate each other with three concise (closest neighbor, parallel, and cross) relations symmetrically and consistently.

Based on the fact that the scheme to build up the extended concentric multi-polyhedron corresponds to Ehrenfest's scheme to classify phase transitions, it is reasonable for us to predict that the coherent and complete structure of thermodynamics may further be extended along with novel research results about higher order phase transitions in future.

Based on the fact that symmetry plays an important role to integrate the entire structure of the thermodynamic variables into a coherent and complete exposition of thermodynamics, it is reasonable for us to consider the symmetry as one of foundations (or axioms) of the subject and therefore to believe thermodynamics being a science of symmetry.

7. Conclusions

1. A variety of four categories of total 44 thermodynamic variables are properly arranged at the vertices of the extended concentric multi-polyhedron diagram based on their physical meanings.
2. A symmetric function with "patterned self-similarity" is precisely be defined as the function of a general formula for each family in thermodynamics, which is unchanged not only in function form but also in variable's nature and neighbor relationship under symmetric operations.
3. Although the reversible Legendre transforms ($E \leftrightarrow R$) are asymmetric under a pair of the same sign conjugate variables (w and z), however, the asymmetric ($E \leftrightarrow R$) can become symmetric ($E^* \leftrightarrow R^*$) under two required conditions: a pair of the opposite sign conjugate variables (z and $-w$ or $-z$ and w) and a pair of the opposite conjugate variable treatments (canceling and keeping the negative sign) are involved in the symmetric ($E^* \leftrightarrow R^*$).
4. Thermodynamic symmetry roots in the symmetric reversible Legendre transforms of the potentials under the opposite sign conjugate natural variable pairs ($T \sim -S$, $-P \sim V$, and $\mu \sim -N$). The specific thermodynamic symmetries revealed by the extended concentric multi-polyhedron diagram are only one C_3 (threefold rotation) symmetry about the $U \sim \Phi$ diagonal direction and C_4 (fourfold rotation) and σ (mirror) symmetries on three U -containing squares, where the square including U , H , G , and A is the most important and useful one.
5. Based on the equivalence principle of symmetry (reproducibility and predictability), numerous (more than 300) equations of 12 families can concisely be depicted by overlapping 12 specifically created rigid, movable graphic patterns on the fixed $\{1, 0, 0\}$ diagrams through σ and/or C_4 symmetric operations. Any desired partial derivatives can be derived in terms of several available quantities by the foolproof graphic method.
6. It is the symmetry that made possible to build up the diagram as an elegant model to exhibit an integration of the entire structure of the thermodynamic variables into a coherent and complete exposition of thermodynamics. The model has much common with the Periodic Table of the Elements in chemistry.

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