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Research Article

A New Mnemonic Scheme to Derive Thermodynamics Equations and Maxwell Relations Based on Butterfly Symmetry Approach

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Abstract

In this study, a new mnemonic scheme is proposed for a simple closed system to derive equations in classical thermodynamics potentials that connect the state variables and Maxwell relations based on the butterfly symmetry approach. The proposed method does not have the difficulties in the arrangement and sign of parameters which were found in the geometric diagrams such as square, cub octahedron, concentric multi-circle, Venn diagram, and Natarajan's thermodynamics circles. The suggested method resolves the identical elements and Maxwell's formulas in thermodynamics and energy, enthalpy, Helmholtz and Gibbs equations by creating a matrix through the butterfly symmetry strategy. The most important feature of this method is that the differential and partial derivatives of thermodynamic parameters are formed in matrix arrays. The signs are applied only according to the butterfly symmetry, and unlike the Max Born method, there is no need to pay attention to the direction of arrows.

Keywords: *Mnemonic scheme; thermodynamic relations; Maxwell relations; butterfly symmetry; simple novel method.*

1. Introduction

Thermodynamics is a phenomenological science based on experimental findings and fundamental laws that describe the physicochemical properties of a system as it exchanges matter and energy or reaches equilibrium with its surroundings [1-2]. The principles of thermodynamics allow us to derive and describe the relationships among the state variables (temperature *T*, pressure *P*, volume *V*, and entropy *S*) and thermodynamic potentials (internal energy *U*, enthalpy *H*, Gibbs free energy *G*, and Helmholtz *F*) in an open or closed system. The relationship between the state variables and thermodynamic potentials can be defined by differential and partial differential equations [3]. To recall the position of state variables and the relationship between thermodynamic functions, different mnemonic schemes have been developed in the literature [4-8]. Max Born square is one of the mnemonic schemes, which acts based on the sentence: "Good Physicists Have Studied Under Very Fine Teachers".

The first letters of the mentioned sentence show the arrangement of G-P-H-S-U-V-F-T counterclockwise starting from the six o'clock position, which is shown in Figure 1a.

The four thermodynamic potentials can be positioned between their corresponding state variables. As shown in Figure 1b, the two arrows are drawn towards the potential function, for example *U*, from the two far ends of the inner square diagonally to obtain d*U*. Thus, the differential equation for *U* is obtained by d*U* = (+*T*) d*S*+ (-*P*) d*V*, where the variables (*S* and *V*) are close to the thermodynamic potential parameter (*U*). The variables of states are applied with the two arrows as a memory aid for the positive and negative signs in the differential equation form of the thermodynamic potential. The sign of the state variable becomes positive when the direction of arrows is away from the variables. In contrast, its sign becomes negative when the direction of arrows toward the independent variable. The same arrows are used to obtain other Maxwell relations.

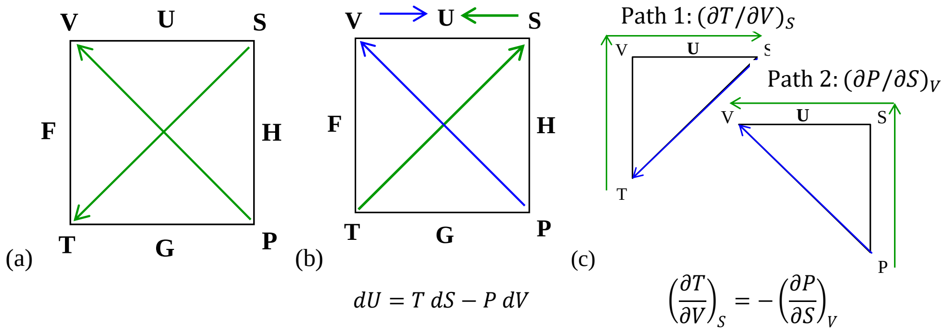

Figure 1. (a) Thermodynamic square presented by Max Born, (b), a scheme to recall the differential form of thermodynamic potentials (c), a scheme to obtain Maxwell relations.

As shown in Figure 1c, the Maxwell’s relation is determined by following the arrows around one of the three corners of the square’s sides, then following around its sides again in a reverse direction ending on the same side of the square. The sign of the Maxwell relation becomes negative when an endpoint has an arrow pointing to it, while the other does not, similar to $(\partial T/\partial V)_S = -(\partial P/\partial S)_V$.

Zhao [9] presented a modified mnemonic double-square scheme based on the Max Born square, in which the Max Born square is separated into two squares, an inner square that includes the state variables, and an outer square that contains the potentials, as shown in Figure 2a. The separation of variables from potential forms retains the advantage of the Max Born square, still it makes easier recalling of several sets of equations, including the Maxwell relations, without complicated rules to distinguish the negative or positive signs. In this method, the differential form of potentials is obtained by drawing two curved arrows toward the potential from the two far ends of the inner square crossing the inner square diagonally. As shown in Figure 2b, these two curved arrows give +*T*d*S* and -*P*d*V* for potential *U* form to obtain the differential form of internal energy, d*U*= *T*d*S* - *P*d*V*. The positive or negative sign of each term is determined by the upward or downward direction of the arrow crossing along the diagonal of the inner square. The Maxwell relations are determined by the inner square (state variables) without considering the outer (thermodynamic potentials) square, as shown in Figure 2c.

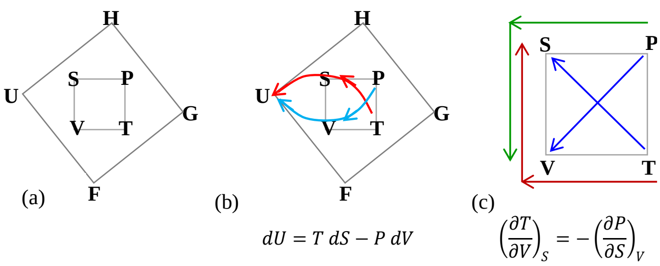

Figure 2. (a) Thermodynamic square presented by Zhao [7], (b) a scheme to recall the differential equations for thermodynamic potentials, and (c) Maxwell relations.

Each of Maxwell's relations is obtained by starting at any corner of the square scheme, going around the square either clockwise or counterclockwise for half a square by considering three variables each time. For example, we can start from *T* to *V* and then to *S*, which results $(\partial T/\partial V)_S$. The positive or negative sign of the term is determined by the upward or downward direction of the arrow connecting the first term letter (*T*) to the third term letter (*S*). As the arrow is upward, thus the term has a positive sign. The same procedure is used to obtain the other part of the Maxwell relationship $[-(\partial P/\partial S)_V]$.

The biggest advantage of this method is that the mode for positive and negative signs is modified compared to the Born square. Kerr and Macosko [10] proposed a “thermodynamic Venn diagram” [11] to derive the relations between the potentials and state variables of a simple system. The internal energy lies at the central point of the diagram, while the other thermodynamic potentials are positioned around the sides of internal energy. The Venn diagram is overlaid with two concentric “shading disks”, and its differential form, which are shown in Figure 3a and 3b, respectively. The method for obtaining the Maxwell relations is the same as described for the thermodynamic square, but the state variables appear at points across a circular arc rather than at the corners of the square. Therefore, there is a “shared arc” instead of the “shared second side”.

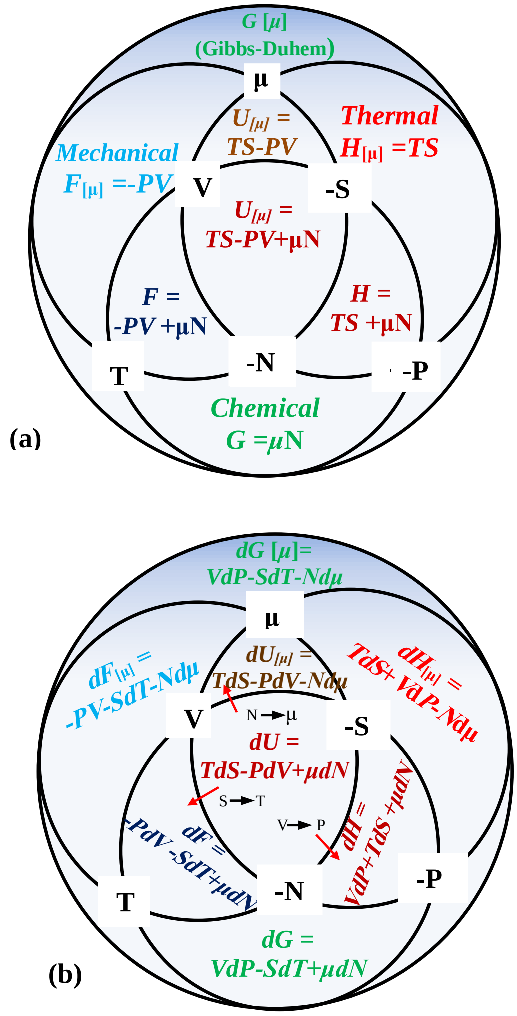

Figure 3. (a) Thermodynamic Venn diagram overlaid with two concentric “shading disks and (b) its differential form.

Although the Venn diagram method can well remember all the thermodynamic quantities, one of the most important problems of this method is that it takes a lot of time to draw, thus the speed of determining each of the thermodynamic quantities is slow. It is also necessary for the user to pay attention to the sign of the quantities and the direction of movement on each of the variables. In fact, if you don’t pay attention to the arrows and the position of the parameters, it leads to choosing the wrong sign or the wrong differential form for each of the thermodynamic quantities**.**

Natarajan [12] proposed two simple mnemonic schemes, named “Natarajan’s Thermodynamics circles”, to present the Maxwell relations geometrically, which are easily used for both closed and open thermodynamic systems. The students’ feedback was that they were able to organize the network of Maxwell thermodynamic relations in their minds carefully. Typically, the procedure for determining Maxwell’s relation to potential *U*: $(\partial T/\partial V)_S = -(\partial P/\partial S)_V$ based on the “Natarajan’s Thermodynamics circle” for a closed thermodynamic system is graphically shown in Figure 4. The start and end of the path that pass along the state variables which are from one of the first partial derivatives of Maxwell’s relation are indicated by the number 1.

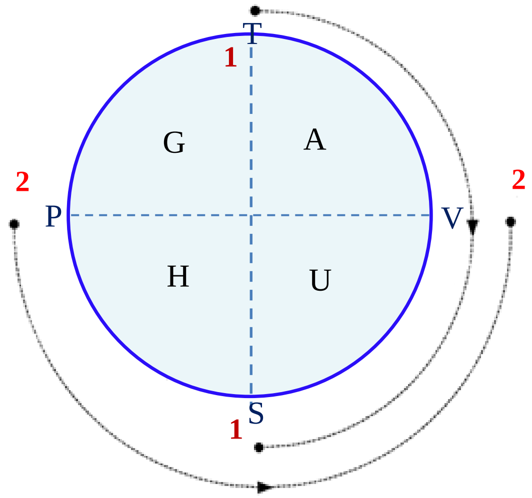

Figure 4. Graphical scheme for determining the Maxwell's relation for potential U: $(\partial T/\partial V)_S = -(\partial P/\partial S)_V$ *based on the "Natarajan's thermodynamics circle" in a closed thermodynamic system [12].*

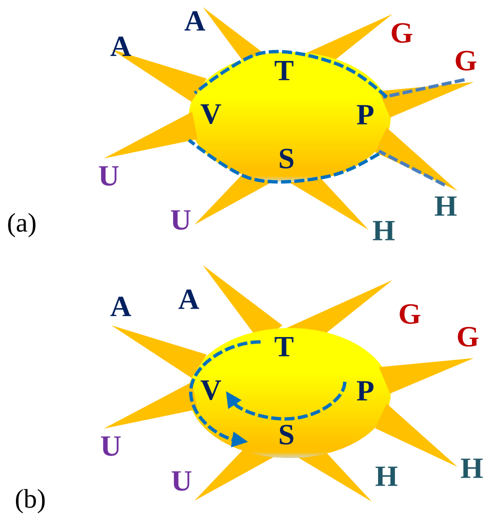

Figure 5. Graphical schemes of (a) the variation of state variables and differential form of thermodynamic potentials by Fishing way, (b) Maxwell relations by swirl way [13].

Also, the start and end of the path that pass along the state variables, which are from one of the second partial derivatives of Maxwell's relation, are indicated by the number 2. The path directions are shown by the arrows. The sign of relations is considered positive and negative when the direction of the arrows is clockwise and counterclockwise, respectively. The Maxwell relations of other thermodynamic potentials (*H*, *G*, and *A*) can be derived from the "Natarajan's thermodynamic circle".

One of the most common mistakes that may occur in obtaining thermodynamic relationships based on the previous methods is not considering the sign/direction of a formula. Recently, Bhagavanbhai et al. [13] proposed a simple set of rules, named "Fishing with scissors" mnemonic, to cover fundamental thermodynamic equations, Maxwell's relations of thermodynamic potentials with state variables. This method was free from the direction/sign related difficulties that were reported in the previous methods. The graphical schemes for determining (a) the relationship between state variables and partial differential equations of thermodynamic potentials by "Fishing way", and (b) Maxwell's relations by "swirl way" are shown in Figure 5. In the "Fishing way", the relation between thermodynamic potentials and state variables was obtained from tail to mouth of fish as guided by a dashed line (Figure 5a). For example, we can start from *G* to *P* and then to *T* and finally to *V*, which results $(\partial G/\partial P)_T = V$.

In the swirl way, named up-directed and down directed swirls, the Maxwell relations are determined based on the picking up the state terms from sun region in two counter ways (as guided by dashed lines) such that first counter cover vertical half terms of sun, while second counter way horizontal half terms of sun (Figure 5b), which result $(\partial T/\partial V)_S = -(\partial P/\partial S)_V$.

In the present study, we proposed a novel and simple method to derive the classical equations in thermodynamics potentials and Maxwell relations based on the butterfly symmetry method for a closed thermodynamic system. The proposed methodology has solved the problems caused by the arrangement and sign of parameters, which were reported in the other mnemonic procedures such as square, Venn diagrams, and Natarajan's thermodynamics circle.

2. Results of Proposed Methodology

2.1. Relationship between Thermodynamic Potentials and State Variables

According to Figure 6, at first, each of the state variables (*T*, *P*, *S*, and *V*) are placed on the vertical and horizontal axes of the table, respectively. The thermodynamic potentials are placed from the bottom and counter-clockwise in the order of *G*, *U*, *H* and *F*. To help remember the position of the potentials, the first letter from the sentence of: "Good Understand, Highly Favorite" is used in the side of table. Two middle columns have a positive sign and the two side columns have a negative sign (Figure 6b).

According to Figure 6b, we cross the yellow columns diagonally (according to the green arrow) to determine the relationship between *F* and *U*. When passing through each of the columns, we also include the positive or negative sign of that column. For example, to determine the relationship between *F* and *U* with related state variables, we have: *F* = *U* - *TS*. In addition, for *H* and *G* we have: *H* = *G* + *TS*.

To determine the relationship between *H* and *U*, and also *G* and *F*, it is necessary for the sides to make a butterfly form through the vertical dashed lines (according to the red arrow) and consider the parameters in the yellow columns with the related sign. The end of the arrow indicates the desired state variables that must be put in the equation. Therefore, to determine the relationship between *U* and *H*, while passing through the -*PV* column, we will have: *U* = *H* - *PV*. Similarly, the relationship between *G* and *F*, while passing through the +*PV* column, leads to *G* = *F* + *PV* (Figure 6b).

2.2. Determination of The Differential Form of Thermodynamic Potentials

According to Figure 7, at first, each of the state variables (*T*, *P*, *S*, and *V*) and the differential form of each of the mentioned quantities are placed on the vertical and horizontal axes of the table, respectively. The differential form of the thermodynamic potentials is placed from the bottom and counter-clockwise in the order of *G*, *U*, *H* and *F*.

The formation of the butterfly symmetry mode starts from d*U* and reaches d*H*, and then d*G* and finally d*F*. By moving along the horizontal line that connects *F* to *U* leads to drawing a symmetrical butterfly form.

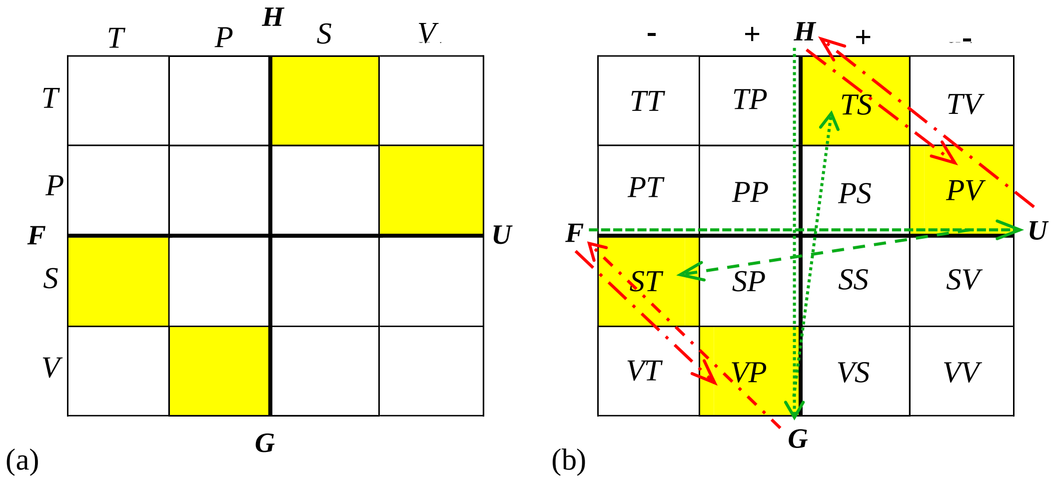

Figure 6. Scheme to obtain the relationship between thermodynamic potentials and the state variables.

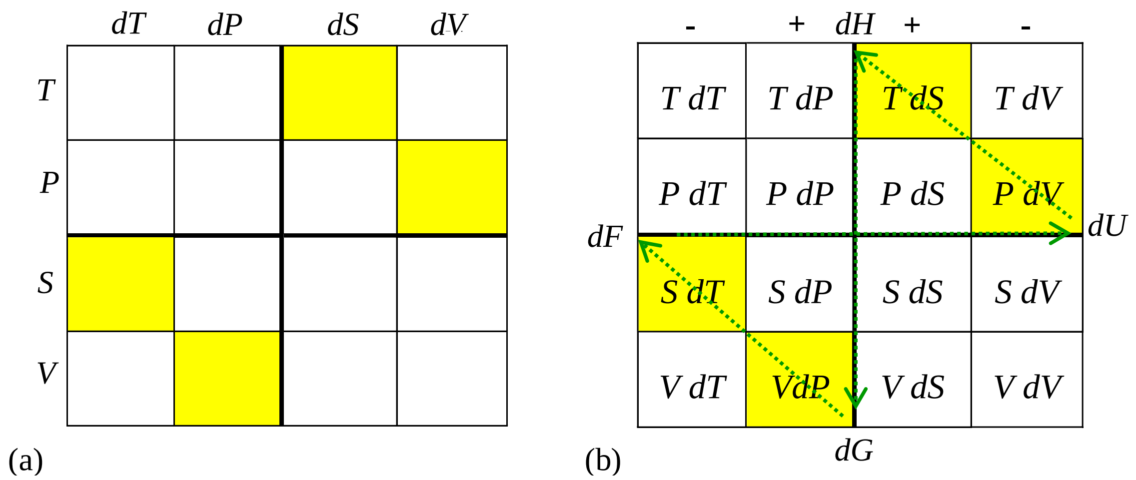

Figure 7. Scheme to obtain the differential form of thermodynamic potentials with state variables.

For example, to determine the differential form of *U* according to Figure 7b, we cross the yellow columns diagonally (according to the green arrow). When passing through each of the columns, we also include the positive or negative sign of that column. For d*U* we have: d*U*= -*P*d*V* + *T*d*S*. Other thermodynamic quantities are determined similarly to this method. To determine the differential form of *H*, it is necessary to move down from the vertical line and consider the parameters in the yellow columns with the mentioned sign. Therefore, to determine d*H* while passing through the +*T*d*S* and +*V*d*P* columns, we will have: d*H* = +*T*d*S* + *V*d*P*. The differential form of *G* is similar to *U*, and to determine *F*, it is similar to *H*.

2.3. Proposed Scheme to Obtain The Maxwell Relations

Figure 8 shows the scheme to recall the differential equations for thermodynamic potentials obtained from the state variables. Each of the state variables is fixed, and the relative derivative form of each of the mentioned quantities is placed on the horizontal axis in the mentioned order. Derivative changes are made with respect to *S*, *V*, *T* and *P*. The slanted green line, shown in Figure 8b, shows the axis of symmetry. In this way, by equalizing each of the relative derivative states placed at the two ends of the line according to the arrows, each of Maxwell's relations with their signs is formed two by two. For example, we have $-(\partial S/\partial V)_T = (\partial P/\partial T)_V$. Other Maxwell relations are determined in the same way.

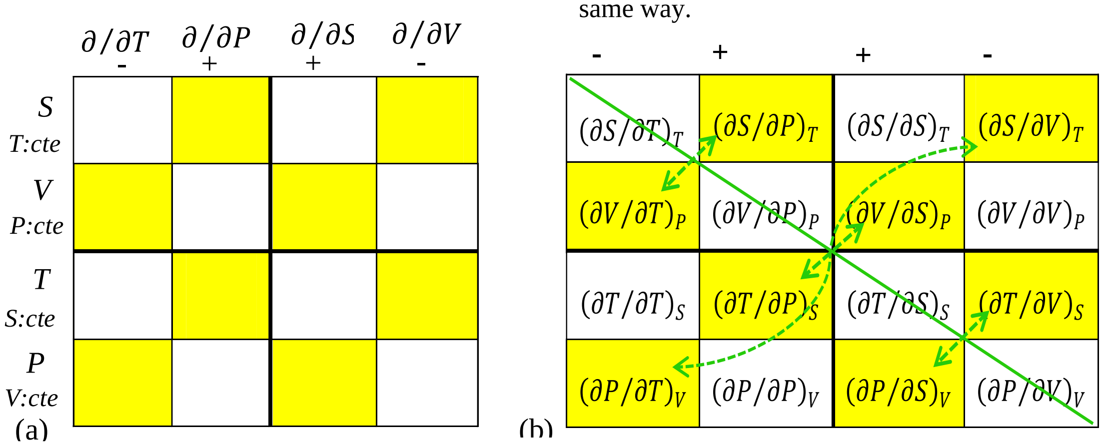

Figure 8. Scheme to obtain the differential equations form of state variables.

3. Conclusions

A mnemonic scheme based on the butterfly symmetry method is suggested to derive classical thermodynamics potentials that connect the state variables and Maxwell's relations in a closed thermodynamic system. This method resolves the identical elements and Maxwell's formulas in the energy, enthalpy, Helmholtz and Gibbs equations by creating a matrix. The most important feature of this method is that the differential and partial derivatives of thermodynamic quantities are formed in matrix arrays. The proposed method does not have the difficulties caused by the arrangement and sign of parameters in the square, cub octahedron, concentric multi-circle, Venn diagrams, and "Natarajan's thermodynamics circles". In addition, the signs are applied only according to the butterfly symmetry, and unlike the Max Born method, there is no need to pay attention to the direction of arrows, which helps to make it easy for students to learn.

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