

A Mnemonic Scheme for Thermodynamics

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Abstract

A mnemonic scheme is presented to help recall the equations in classical thermodynamics that connect the four state variables (temperature, pressure, volume, and entropy) to the four thermodynamic potentials (internal energy, Helmholtz free energy, enthalpy, and Gibbs free energy). Max Born created a square to help recall the thermodynamic equations. The new scheme here separates the Max Born square into two squares, resulting in easier recalling of several sets of equations, including the Maxwell equations, without complicated rules to remember the positive or negative signs.

Thermodynamics is a phenomenological science based on three fundamental laws, generalized from a broad range of scientific observations, that describes the energy and behavior of an arbitrary system as it reaches equilibrium with its surroundings or exchanges heat, work, or matter with its surroundings. The fundamental laws of thermodynamics govern the universe and subsystems in the universe (excluding nuclear reactions); thus, thermodynamics is a pervasive science fundamental to physics, chemistry, biology, materials science, mechanical engineering, and other disciplines. The principles of thermodynamics allow one to derive relationships among the properties of a system. These relationships dictate the number of properties that have to be determined in order to completely specify all the properties of the system.

The relationships among the four state variables (temperature T , pressure P , volume V , and entropy S) and four thermodynamic potentials (internal energy U , Helmholtz free energy F , enthalpy H , and Gibbs free energy G) are the core of classical thermodynamics (Table I). The chemical potential of species i is μ_i and the number of moles of species i is n_i . The various differential and partial differential equations describing these relationships become difficult to remember. Several mnemonic schemes to help recall the relationships have been developed over the

years;¹⁻⁹ and they are all essentially based on the famous Max Born square¹ shown in Figure 1a, but with different rules to remember the equations and the positive or negative signs in front of the terms.

It is shown here that recalling these equations can be significantly simplified by separating the Born square into two sections, an inner square that contains only the variables T , P , S , and V (thus called the variable square) and an outer square that contains only the potentials G , H , U , and F (thus called the potential square), as shown in Figure 1b. Such a separation retains the advantage of the Born square but makes recalling the equations much more straightforward.

In the new scheme (Figure 1b), the four fundamental thermodynamic potentials, G , H , U , and F , are still on the same sides as the respective natural variables upon which they depend: $G = G(T, P)$, $H = H(S, P)$, $U = U(S, V)$, and $F = F(T, V)$. The various variables and potentials are also flipped upside down with respect to the Born square to make the plus and minus signs consistent with the equations (which will become apparent soon). The conjugate variables (S and T , P and V) are arranged diagonally in the inner square.

The four thermodynamic potentials are related by the Legendre transforms: $H = U + PV$, $F = U - TS$, and $G = H - TS = U + PV - TS = F + PV$. These equations can be recalled by drawing a curved arrow from

one corner of the potential (outer) square to a neighboring corner on the same square, passing through the variable (inner) square diagonally, for example, the curved arrow from U , passing through V and P diagonally, to H (Figure 2a). This reads as $U + VP = H$. The positive sign in front of VP is dictated by the fact that the direction of the arrow passing along the diagonal of the inner square is upward

Table I: List of Several Sets of Fundamental Equations among the Four State Variables and the Four Thermodynamic Potentials in Classical Thermodynamics.

Definitions of Variables and Potentials

T = temperature	P = pressure
V = volume	S = entropy
U = internal energy	H = enthalpy
F = Helmholtz free energy	G = Gibbs free energy

Definitions of F , H , and G from U (Legendre Transforms)

$$F = U - TS$$

$$H = U + PV$$

$$G = H - TS = U + PV - TS = F + PV$$

Differential Equations for U , F , H , and G

$$dU = T dS - P dV \quad dF = -S dT - P dV$$

$$dH = T dS + V dP \quad dG = -S dT + V dP$$

Equations to Compute Variables T , P , V , and S

$$T = \left(\frac{\partial H}{\partial S} \right)_P = \left(\frac{\partial U}{\partial S} \right)_V \quad P = - \left(\frac{\partial U}{\partial V} \right)_S = - \left(\frac{\partial F}{\partial V} \right)_T$$

$$V = \left(\frac{\partial H}{\partial P} \right)_S = \left(\frac{\partial G}{\partial P} \right)_T \quad S = - \left(\frac{\partial G}{\partial T} \right)_P = - \left(\frac{\partial F}{\partial T} \right)_V$$

Maxwell Equations

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

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

Differential Equations for U , F , H , and G with Variable Amounts of Matter

$$dU = T dS - P dV + \sum \mu_i dn_i$$

$$dF = -S dT - P dV + \sum \mu_i dn_i$$

$$dH = T dS + V dP + \sum \mu_i dn_i$$

$$dG = -S dT + V dP + \sum \mu_i dn_i$$

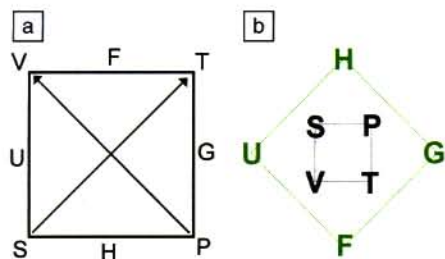


Figure 1. Comparison of the new scheme based on (b) with the Max Born square (a). The Born square (a) was used in several textbooks to help recall thermodynamic equations that relate four thermodynamic variables (temperature T , pressure P , volume V , and entropy S) and four thermodynamic potentials (internal energy U , Helmholtz free energy F , enthalpy H , and Gibbs free energy G). The new double-square scheme (b) significantly simplifies the procedures to recall several sets of thermodynamic equations.

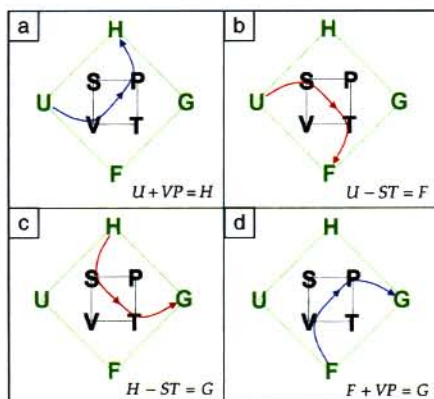


Figure 2. Scheme to recall the Legendre transforms that define the Helmholtz free energy F , enthalpy H , and Gibbs free energy G from the internal energy U .

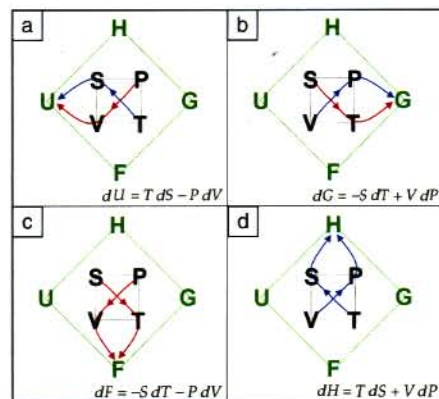


Figure 3. Scheme to obtain the differential equations of the thermodynamic potentials (U , F , H , and G) that are the core of thermodynamic relations.

(Figure 2a). Similarly, the curve in Figure 2b gives $U - ST = F$. The minus sign in front of ST is due to the fact the arrow points downward from S to T . Figures 2c and 2d give $H - ST = G$ and $F + VP = G$. In fact, all of the arrows can be drawn backward, and the equations still work—just remember to use a minus sign when the arrow passing along the diagonal of the inner square is pointing downward.

To obtain the differential of a potential, for example dU , draw two curved arrows toward the potential U from the two far ends of the inner square, that is, P and T , crossing the inner square diagonally, as shown in Figure 3a. These two curved arrows give $+T dS$ and $-P dV$, thus $dU = T dS - P dV$. [The variables (S and V) close to the potential (U) are with differentials.] The positive or negative sign in front of each term is simply determined by the upward or downward direction of the arrow crossing along the diagonal of the inner square. In the same fashion, Figures 3b–3d provide $dG = -S dT + V dP$, $dF = -S dT - P dV$, and $dH = T dS + V dP$.

One can also find the quantity for each of the variables from the partial differential of a potential with respect to the conjugate variable. This is schematically shown in Figure 4. To obtain T , draw a curved arrow from T , and cross the inner square diagonally (thus passing S) toward one of the nearby potentials (e.g., H). The curved arrow gives $T = \partial H / \partial S|_P$. This term has a positive sign because the arrow points upward (Figure 4a). The constant P is shown by the nearby variable with the dotted circle. Note that the T is at the beginning of the curved arrow, not the

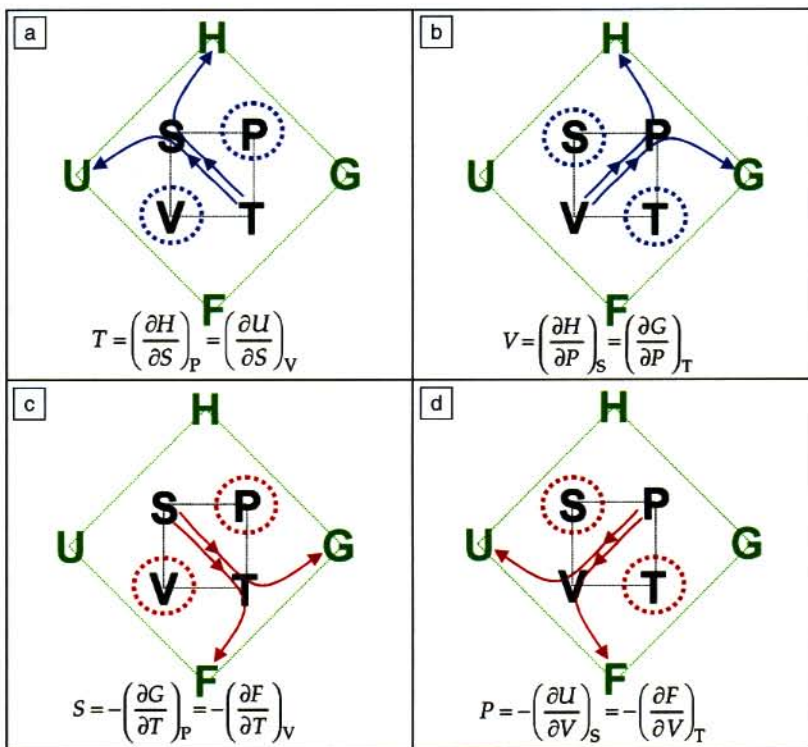


Figure 4. Scheme to obtain the quantity of one variable from the partial differential of a thermodynamic potential with respect to the conjugate variable.

end of it (somewhat backward). However, this curved arrow still points toward a thermodynamic potential term (a corner of the outer square) as do all of the other arrows in Figures 2 and 3. In this regard, the scheme is consistent. Similarly, the arrow can go toward U , thus giving $T = \partial U / \partial S|_V$. Similar equations can be obtained for V , S , and P , as shown in Figures 4b–4d.

The Maxwell relations involve only the variables, not the thermodynamic potentials; thus, they can be obtained using the inner (variable) square only without bothering with the outer (potential) square, as shown in Figure 5. In this case, one can start at any corner of the square, going around the square either clockwise or counterclockwise for half a square (including three variables each time). For

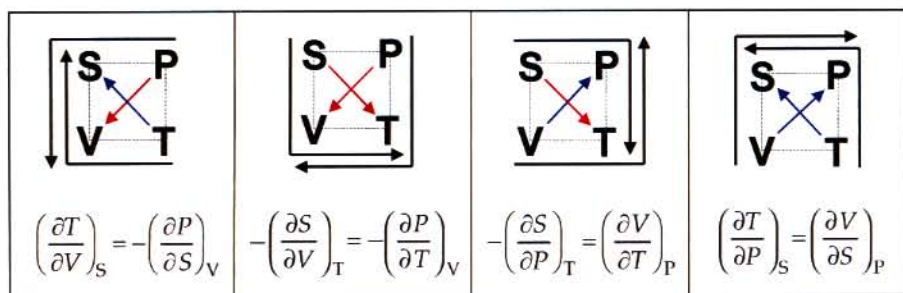


Figure 5. Scheme to obtain the Maxwell equations.

instance, from T to V to S , it yields the partial derivative of T with respect to V at constant S (left-hand side of Figure 5). The positive or negative sign of the term is again dictated by the upward or downward direction of the arrow connecting the first letter (T) to the third letter (S) (thus crossing the square diagonally). For the case of T to V to S , the arrow is upward, so the term has a positive sign. To find the other part of the Maxwell pair, perform the same procedure starting with the fourth variable (the only one that is not included before) and going in the opposite direction with respect to the first term; which would give the partial derivative of P with respect to S at constant V (or simply read as partial P , partial S at constant V). This term has a negative sign because the arrow from P to V points downward. The other three Maxwell equations can be obtained in the same way as shown in Figure 5. This scheme is basically the same as the Born square.^{8,9} The only differences are that the locations of the variables are flipped upside down and the way to remember the positive and negative signs is slightly modified.

To help remember the arrangements/positions of the variables and potentials in Figure 1b, one can invoke Gilverry's sentence:³ "Good Professors Have Studied Under Very Fine Teachers." (I took the liberty to switch the original word "Physicists" to "Professors" to "glorify" my own profession and to reflect the fact that thermodynamics is fundamental not only to physics, but to chemistry, biology, materials science, mechanical engineering, and other disciplines.) The first letters

from this sentence reflect the arrangements of G - P - H - S - U - V - F - T counter-clockwise starting from the three o'clock position.

All of the above equations are among the hardest to remember in classical thermodynamics without a mnemonic scheme. When the composition or amount of a chemical species changes, one can simply add a term $\sum \mu_i dn_i$ to each of the four differential equations (dU , dH , dG , and dF in Figure 3 and Table I) and derive the rest of the equations using Maxwell relations. The μ_i and n_i are the chemical potential and the number of moles of the species i , respectively. Fortunately, the term $\sum \mu_i dn_i$ remains the same, and the sign in front of it is always positive for the four differential equations, for example, $dG = -S dT + V dP + \sum \mu_i dn_i$. Alternatively, one can use a "thermodynamic cube" or a "thermodynamic cuboctahedron" to help remember the relationships;⁵⁻⁹ but this capability is lost when the three-dimensional devices are not readily available.

Acknowledgments

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