An Improved Mnemonic Diagram for Thermodynamic Relationships

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While the equations relating the variables P, V, S, T, A, G, H, and U, which represent the variables pressure, volume, entropy, temperature, Helmholtz free energy, Gibbs free energy, enthalpy, and internal energy, respectively, are not complex mathematically, many people have trouble remembering the various relations. This paper discusses a variation of a mnemonic diagram first introduced by Koenig and further developed by Callen. Phillips has recently presented a three-dimensional version of a mnemonic diagram. It is the purpose of the present paper to illustrate that a number of the most important expressions in thermodynamics of simple systems may be developed directly from a mnemonic diagram.

The material that follows is limited to simple systems that are defined to be macroscopically homogeneous, isotropic, uncharged, and chemically inert. The systems are sufficiently large that surface effects can be neglected and are not acted on by electric, magnetic, or gravitational fields. Because of the limitation to simple systems, the variables P and V will be used. Other variables will appear if other work modes are considered.

The Diagram

A thermodynamic diagram of the variables P, V, S, T, A, G, H, and U is formed in the following steps:

2. Arrows from the variables P and S are drawn as shown in Figure 1.

The remaining variables A, G, H, and U are added alphabetically by beginning at the upper right quadrant and proceeding clockwise. Figure 2 is the result.

Several observations concerning the variables in this diagram are immediately apparent:

- Each of the four thermodynamic potentials that form the corners of the diagram is flanked by its natural independent variables. Thus, we see that U is a natural function of S and V, for example.
- This diagram is a rotation of the one presented by Callen. The variables are rotated clockwise by one position. This difference is important as it serves to provide a sign convention to our operations. The various equations relating the variables appearing in the diagram are formed by the following operations:

1. Begin at any corner. Go to the next corner by either a clockwise or a counterclockwise path.
2. The relationship between the first potential, B, and the second potential, C, is given by an equation of the form

\[ B = C \pm DE \] (1)

where the sign will depend upon the direction of travel.

The sign convention is the following: it is positive if we travel toward the arrowhead and negative if we travel away from the arrowhead. This convention will be used in the entire paper.

The following examples will illustrate the method.

Example 1. We desire an expression between U and A. Start at U and travel to A along a row. We then form the expression

\[ U = A + TS \] (2)

Since we are travelling in a row through one natural variable, we obtain the DE term by travelling down the column to the other natural variable, from our starting point, U. The sign is positive because we travel from S to T toward the arrowhead.

Example 2. We desire an expression between A and G. Start at A and travel to G along a column. We then form the expression

\[ A = G - PV \] (3)

The sign on the PV term is minus since we travel from V to P away from the arrowhead. If we repeat the operations from G to H and from H to U, we obtain the following expressions:

\[ G = H - TS \] (4)

and

\[ H = U + PV \] (5)

If we begin at any corner and travel in a counterclockwise direction, we obtain algebraic expressions equivalent to the four equations relating the four thermodynamic potentials shown as eqs 2–5.

While these expressions are not new, it is the first time that they have been developed from a mnemonic diagram.

The Differential Forms of the Potentials

We begin by noting that each of the potentials is flanked by its natural variables. Thus, the differential of U will involve differentials of S and V, for example. The coefficients of these differentials will involve the variables at the other ends of the arrows. The usual sign convention applies. Using these rules, we find

\[ dU = TdS - PdV \] (6)

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\[ dA = -SdT - PdV \]  \hspace{1cm} (7)
\[ dG = -SdT + VdP \]  \hspace{1cm} (8)
\[ dH = TdS + VdP \]  \hspace{1cm} (9)

While it is possible to obtain the relations for the coefficients in the equations just presented from the mnemonic diagram, it is simpler to obtain them by inspection. Thus we can write
\[ \left( \frac{dU}{dV} \right)_S = -P \]  \hspace{1cm} (10)
and
\[ \left( \frac{dU}{dS} \right)_V = T \]  \hspace{1cm} (11)
for example.

**The Maxwell Relations**

These are formed by starting at any point in the diamond formed by the variables \(S, V, T,\) and \(P.\) We merely write the letters of three variables as we travel in a clockwise or a counterclockwise rotation in the diamond. We then go to the remaining variable and travel in the counter direction.

The following equations result:
\[ \left( \frac{dT}{dV} \right)_S = -\left( \frac{dP}{dS} \right)_V \]  \hspace{1cm} (12)
\[ \left( \frac{dS}{dV} \right)_T = \left( \frac{dP}{dT} \right)_V \]  \hspace{1cm} (13)
\[ \left( \frac{dS}{dP} \right)_T = -\left( \frac{dV}{dT} \right)_P \]  \hspace{1cm} (14)
\[ \left( \frac{dT}{dS} \right)_P = \left( \frac{dV}{dS} \right)_P \]  \hspace{1cm} (15)

Now these equations could have been obtained by inspection of eqs 6 through 9. Using the mnemonic diagram, we have been able to obtain them without recourse to the differential forms, however.

**Other Relations**

It is possible to develop additional relations among the various partial derivatives by use of the diagram. These relations result by application of the following steps.

1. Begin at any corner, say \(B.\) Travel to the next variable, \(C.\) (The path may be either clockwise or counterclockwise.) Then travel to the next variable, say \(D,\) on the diamond path. This step forms the partial of \(B\) with respect to \(C\) at constant \(D.\)
2. Continue to travel in the same direction on the diamond path. The variable located, say \(E,\) is the first term in the right-hand side of the desired equation.

3. The remaining term is formed by retracing the diamond. The coefficient is the variable that is in the denominator of the partial derivative. This step forms the partial of \(E\) with respect to \(D\) at constant \(C.\) The sign follows the usual convention.

The following serves as an example of the method.

The \( (\partial U/\partial V)_T \) is desired. We begin at \(U\) and travel to \(V.\) We then go to \(T\) and next to \(P.\) From \(P\) we retrace our steps to \(T\) and then \(V.\) Utilizing the sign convention we can write immediately
\[ \left( \frac{dU}{dV} \right)_T = -P + T\left( \frac{dP}{dT} \right)_V \]  \hspace{1cm} (16)

When generating some expressions it is necessary to introduce a Maxwell expression to obtain a relation that can be utilized more directly. As there are four corners and two directions of travel, eight relations may be obtained using this method. These relations have been developed from a mnemonic diagram for the first time.

Eight additional relations may also be obtained from the diagram. We generate them by performing the following operations:

1. Start at any corner, say \(B.\) Travel to the next variable, say \(C.\) Next travel to the variable at the other end of the arrow, \(E.\) This operation forms the partial of \(B\) with respect to \(C\) at constant \(E.\)
2. The first term on the right-hand side of the equation is the variable at the other end of the arrow, \(E.\)
3. We next form the partial of \(F,\) the other natural variable for \(B,\) with respect to \(C\) at constant \(E.\) The coefficient of this term is the variable at the other end of the arrow connecting the variable \(F.\)

The following serves as an example of the method:

As before, there are four corners, and, since we can travel either in a clockwise or a counterclockwise direction, this method enables us to generate eight relations.

If partial derivatives of the form \( (\partial H/\partial V)_T \) are desired, there is no simple method of obtaining them from the diagram. It is easier to obtain \( (\partial H/\partial P)_T \) using the operations just described and multiplying it by \( (\partial P/\partial V)_T \) and then applying the chain rule.

The various relations for the energy capacity terms can also be obtained from the diagram, but they are more easily obtained from their definitions.

Thus we see that the mnemonic diagram allows us to write the essential equations relating the eight thermodynamic properties in a straightforward method. While no new expressions have been developed, some equations have been developed from a mnemonic diagram for the first time. It is believed that the present diagram can help the student learn the relationships more readily.

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