The Mnemonic Diagram for Thermodynamic Relationships

Some Remarks

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Recently Rodriguez and Brainard[2] presented an improved mnemonic diagram (Fig. 1) using thermodynamic terms to help the students remember the most important expressions in the thermodynamics of simple systems. The various thermodynamic equations can be generated by applying various rules of connection to the proposed diagram, which is formed by a square of thermodynamic variables and two crossed arrows.

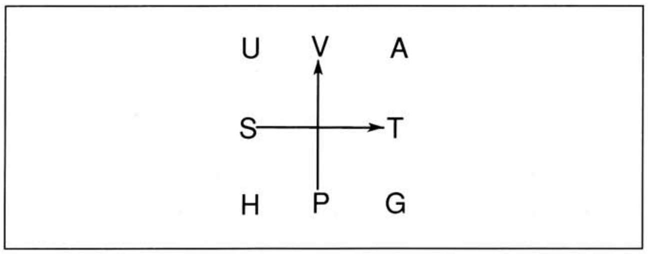


Figure 1. The thermodynamic diagram.

A deeper examination of Rodriguez and Brainard's mnemonic rules shows how to obtain the thermodynamic equations using a simple pattern that overlays their diagram. The patterns themselves are easy to remember because they trace the shape of a letter: N, P, M, F, or μ. This trace indicates the relation among the thermodynamic variables, with the sign of the variable being determined by the flow of the trace against the flow of the arrow. The following rules are used in this pictorial method.

- Letters used to abbreviate energy terms are placed at the corners and sides of the diagram (see Fig. 1).
- To obtain an energy term from the variables in the diamond pattern, multiplication always occurs between the two variables connected by the same arrow.
- To generate the thermodynamic relationships, terms are used in alphabetical order.
- The unprimed term comes before the primed term of the same letter.
- The term with one prime comes before the term with two primes that has the same letter.
- When going from one term on an arrow to the other term on the same arrow, the sign is positive when the flow of tracing the letter approaches the arrowhead.
- The sign is negative when the flow of tracing approaches the arrowtail.
- Otherwise the sign is always positive.

Relations between Neighboring Potentials

The N Pattern

The relationships in this pattern (See Fig. 2) have the following form

$$A = B - CC'$$

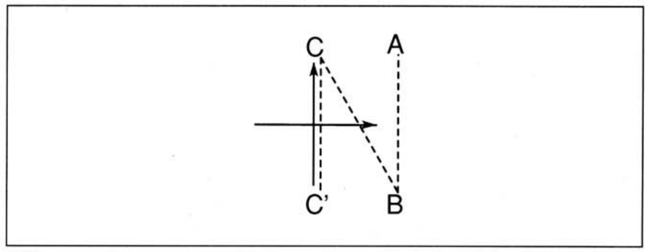


Figure 2. The N pattern.

From C to C' we are travelling towards the arrowtail. Thus, a minus sign appears before the third term of this equation.

By superimposing the dashed lines of the N pattern to Figure 1 and by substituting the alphabetical terms with the corresponding thermodynamic terms we obtain the following equation.

$$A = G - VP \tag{1}$$

With successive 90° rotation of the superimposed N pattern and by substituting (90° substitution) we obtain the following equation.

$$G = H - TS \tag{2}$$

$$H = U + PV \tag{3}$$

$$U = A + ST \tag{4}$$

Rotating the N pattern around its CC' axis by 180° (a 180° substitution, followed by 90° substitutions), we obtain the other four equivalent expressions. For example,

$$U = H - PV$$

Differential Forms of the Potentials

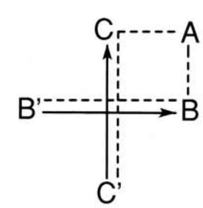
The P Pattern

The relationships for Figure 3 are given by an equation of the following form.

$$dA = -dB(B') - dC(C') \tag{5}$$

For the sign, see the preceding paragraph. With a substitution and by rearranging (for example, $dB(B') = B'\,dB$), we obtain the follwowing equation.

$$dA = -(S\,dT) - (P\,dV) \tag{6}$$



Fiqure 3. The P pattern.

[1]Author to whom correspondence should be addressed.
[2]Rodriguez, J; Brainard, Alan J. *J. Chem. Ed.* **1989**, *66*, 495–496.

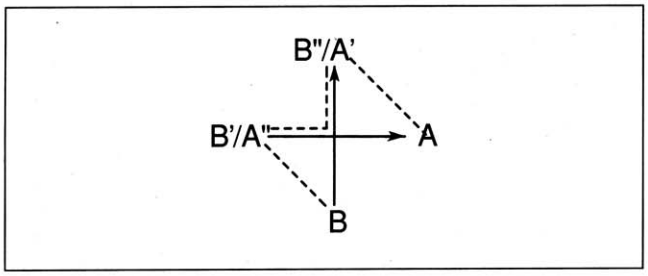


Figure 4. The M pattern.

With successive 90° substitutions we obtain the following equations.

$$dG = (V\,dP) - (S\,dT) \tag{7}$$

$$dH = (T\,dS) + (V\,dP) \tag{8}$$

$$dU = -(P\,dV) + (T\,dS) \tag{9}$$

The Maxwell Relations

The M Pattern

The relationships of Figure 4 are given by an equation of the following form.

$$-\left(\frac{\partial A}{\partial A'}\right)_{A''} = \left(\frac{\partial B}{\partial B'}\right)_{B''} \tag{10}$$

Tracing from A to A'', we approach an arrowtail. From B to B'' the tracing approaches an arrowhead. With a substitution we obtain the following equation.

$$-\left(\frac{\partial T}{\partial V}\right)_{S} = \left(\frac{\partial P}{\partial S}\right)_{V} \tag{11}$$

With successive 90° substitutions we obtain the following equations.

$$\left(\frac{\partial P}{\partial T}\right)_{V} = \left(\frac{\partial S}{\partial V}\right)_{T} \tag{12}$$

$$\left(\frac{\partial S}{\partial P}\right)_{T} = -\left(\frac{\partial V}{\partial T}\right)_{P} \tag{13}$$

$$-\left(\frac{\partial V}{\partial S}\right)_{P} = -\left(\frac{\partial T}{\partial P}\right)_{S} \tag{14}$$

Other Relations

The F Pattern

The form of the relationships of Figure 5 is given below.

$$\left(\frac{\partial A}{\partial A'}\right)_{A''} = -B \tag{15}$$

Tracing from A' to B, we approach the arrowtail. Thus, one of the two terms (A' or B) should be negative. With a substitution we obtain the following equation.

$$\left(\frac{\partial A}{\partial T}\right)_{V} = -S \tag{16}$$

With successive 90° substitutions we obtain the following equations.

$$\left(\frac{\partial G}{\partial P}\right)_{T} = V \quad \text{(F upside down)} \tag{17}$$

$$\left(\frac{\partial H}{\partial S}\right)_{P} = T \tag{18}$$

$$\left(\frac{\partial U}{\partial V}\right)_{S} = -P \tag{19}$$

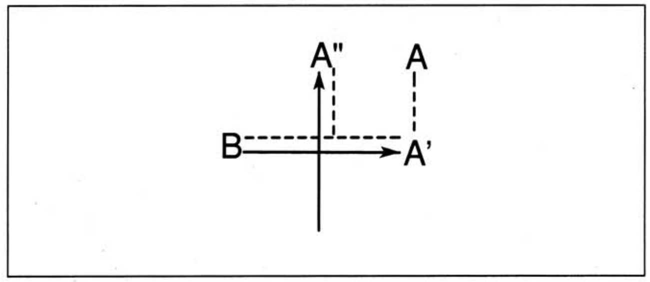


Figure 5. The F pattern.

With a 180° substitution around the A'' axis, followed by 90° substitutions we obtain the other four relationships. The following is an example.

$$\left(\frac{\partial A}{\partial V}\right)_{T} = -P \quad \text{(F right side up)}$$

Other Relations

The μ Pattern

The relationships of Figure 6 have the following form.

$$\left(\frac{\partial A}{\partial A'}\right)_{A''_1} = \left(\frac{\partial A}{\partial A'}\right)_{A''_2} - \left(\frac{\partial A''_2}{\partial A'}\right)_{A''_1}\left(\frac{A''_1}{1}\right) \tag{20}$$

The following should be noted.

- A' appears only as a denominator
- Constant terms are the two primed terms in the following order: 1, 2, 1.
- A''_1 and A''_2 constant terms behave also as multiplicative and numerator terms, respectively, in the third member of eq 20.

Tracing from A''_2 to A''_1 (third member of eq 20), we approach the arrowtail. With a substitution (and rearranging the third member of eq 20), we obtain the following equation.

$$\left(\frac{\partial A}{\partial T}\right)_{P} = \left(\frac{\partial A}{\partial T}\right)_{V} - P\left(\frac{\partial V}{\partial T}\right)_{P} \tag{21}$$

With successive 90° substitutions we obtain the following equations.

$$\left(\frac{\partial G}{\partial P}\right)_{S} = \left(\frac{\partial G}{\partial P}\right)_{T} - S\left(\frac{\partial T}{\partial P}\right)_{S} \tag{22}$$

$$\left(\frac{\partial H}{\partial S}\right)_{V} = \left(\frac{\partial H}{\partial S}\right)_{P} + V\left(\frac{\partial P}{\partial S}\right)_{V} \tag{23}$$

$$\left(\frac{\partial U}{\partial V}\right)_{T} = \left(\frac{\partial U}{\partial V}\right)_{S} + T\left(\frac{\partial S}{\partial V}\right)_{T} \tag{24}$$

By substituting eqs 16 and 13 into eq 21, we obtain eq 16 of Rodriguez and Brainard. With a 180° substitution around the A''_1–A''_2 axis, followed by successive 90° substitutions, four more μ-pattern relationships can be obtained.

By changing the subscript of eq 23 from V to T, and using eq 18, we obtain eq 17 of the cited paper. The corresponding pattern would be a mixing of the F and μ patterns.

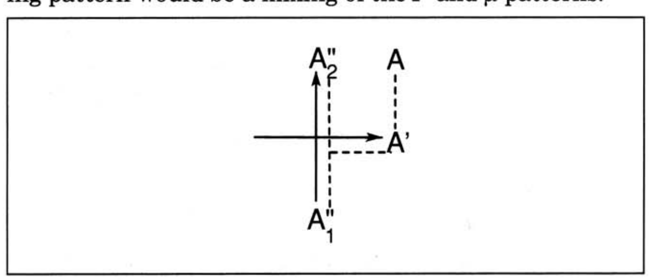


Figure 6. The μ pattern.