The Diagrammatic Method, the Planck and the Massieu Functions

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A recent series of notes and articles (1–3 but especially ref 3) on the problem of reaction spontaneity and equilibrium constant emphasized the advantage of using the Planck function, \( Y = S - H/T \), instead of the Gibbs function as a criterion for spontaneity. The Planck function belongs to a series of functions known as Massieu functions, after Massieu, who introduced them in 1869, while Gibbs introduced his famous potential in 1875 (4). François-Jacques-Dominique Massieu (Vatterville, 1832—Paris, 1896) was professor of Mineralogy and Geology at the University of Rennes, northern France, and also the general surveyor of the French mines. His interests covered fields from mineralogy to thermodynamics; in fact, it was in this last field that he made his most important scientific contribution with the introduction of the famous entropy-dimensionalized thermodynamic functions that bear his name. These functions, which are rarely cited in chemical thermodynamics textbooks, are useful in the theory of irreversible thermodynamics and in statistical mechanics.

The following are the three most common Massieu functions, although others may be invented and analyzed as particular needs for them arise:

\[
\begin{align*}
M_1 &= -A/T \\
M_2 &= (U - G)/T \\
M_3 &= Y = -G/T
\end{align*}
\]

and the well-known Planck function

\[ M_3 = Y = -G/T \]

Here they are named \( M_1 \), \( M_2 \), and \( M_3 \) for a reason that will be made clear below. Other names have been proposed for the Massieu functions. Callen (4), within the frame of a Legendre transform formalism, calls them \( S(1/T) \), \( S(P/T) \), and \( S(1/T, P/T) \). Callen’s acronym indicates its entropic character, as will also be explained below with the help of the thermodynamic diagram. As is usual in thermodynamics, as soon as a function is proposed it gives rise to a series of multifarious relations. A diagrammatic method to automatically derive and check the wide variety of thermodynamic relations was proposed some years ago (5–7) and subsequently refined (8). It can be applied, with minor variations, to derive a series of interesting relations involving the Massieu functions. Perusal of the short papers cited as refs 6 and (mainly) 7 is fundamental for the understanding of the “geometrical” formalism presented here, and perusal of ref 4 is fundamental for the understanding of the thermodynamic importance of the Massieu functions.

Graphical Illustration of the Massieu Functions

Diagram 1 in Figure 1, to handle the Massieu functions, can be considered the entropy representation of the original thermodynamic diagram for thermodynamic relationships (diagram 2), which in turn can be considered the energy representation of diagram 1. For these two we can use acronyms \( S \)-diagram and \( E \)-diagram.

Together with diagram 1, a series of patterns (F, N, and P) already proposed and used with diagram 2 will be used to simplify the derivation of the different relations entailing the Massieu functions. Notice some nonminor characteristics of the \( S \)-diagram relative to the \( E \)-diagram:

1. Diagram 1 has entropic dimensions, which means that parameters along the two arrows of the diamond, \( U \to 1/T \) and \( V \to P/T \), when used in correspondence with functions \( M_1 \), \( M_2 \), and \( M_3 \), should always be multiplied by each other along the same arrow.
2. The vertical arrowhead no longer points toward the extensive parameter \( V \), a fact that has interesting consequences for the sign of Massieu’s relations.
3. Corner parameters \( S \), \( M_1 \), \( M_2 \), and \( M_3 \) can be considered as functions of the nearby parameters in the diamond:

\[
\begin{align*}
S &= (U, V) \\
M_1 &= M_1(V, 1/T) \\
M_2 &= M_2(U, P/T) \\
M_3 &= M_3(1/T, P/T)
\end{align*}
\]

which explains Callen’s designations for these functions: \( S(1/T), S(P/T) \), and \( S(1/T, P/T) \), for \( M_1, M_2 \) and \( M_3 \), respectively (4).

Utilization of patterns F, N, and P and the rule for the sign, which is based on the arrow’s direction, are explained in a previous paper (7).

Pattern F can be used with \( S \)-diagram 1 to obtain the three relations

\[
\begin{align*}
[\partial M_1 / \partial (1/T)]_V &= -U \quad (1) \\
[\partial M_2 / \partial U]_{P/T} &= 1/T \quad (2) \\
[\partial M_3 / \partial (P/T)]_{1/T} &= -V \quad (3)
\end{align*}
\]

Rotation of this pattern by 90° or 180° around the center of the diamond or around a vertical or horizontal arrow allows

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Figure 1. Top: the thermodynamic \( S \)-diagram for Massieu functions, the normal thermodynamic \( E \)-diagram, and an alternative form of the \( S \)-diagram. Bottom: examples of three uses of patterns, F, N, and P.
us to obtain the associated relations
\[
[\partial M_1/\partial V]_{1/T} = P/T \tag{4}
\]
\[
[\partial M_2/\partial (P/T)]_{U} = -V \tag{5}
\]
\[
[\partial M_3/\partial (1/T)]_{P,T} = -U \tag{6}
\]
as well as the famous relation \([\partial S/\partial U]_V = 1/T\) (see pattern F in Fig. 1) and its rotated companion \([\partial S/\partial V]_U = P/T\), and so on. Use of the N pattern allows us to derive the following relations:
\[
M_1 = S - (1/T)U \tag{7}
\]
\[
M_2 = S - (P/T)V \tag{8}
\]
\[
M_3 = M_2 - (1/T)U \tag{9}
\]
\[
S = M_1 + U(1/T) \tag{10}
\]
Notice, for sign purposes, the right ordering of \(1/T\) and \(U\), \(P/T\) and \(V\), and \(1/T\) and \(U\) along the four N relations of eqs 7–10. Rearranging eq 7 gives the relation \(M_1 = (TS - U)/T\), which because of an N relation of the E-diagram \((A = U - TS)\) [pattern N, Fig. 1)] equals \(-A/\dot{T}\). That is, \(M_1 = -A/\dot{T}\), a result that is used in \(E\)-diagram 3. Equation 9 can be further simplified by incorporating the relation \(M_1 = S - PV/\dot{T}\) into it. We obtain \(M_3 = S - (P/T)V - (1/T)U\), which can be rearranged into \(M_3 = S - (PV + U)/\dot{T}\). The latter, with the aid of another N relation of E-diagram 2 \((H = U + PV)\), yields \(M_3 = S - H/\dot{T} = -G/\dot{T}\). This, in turn, utilizes the N relation \(G = H - TS\) of E-diagram 2. The final result is \(M_3 = -G/\dot{T}\), the well-known Planck function, which has also been inserted into \(S\)-diagram 3.

Massieu function \(M_2\), which has been inserted as-is into \(S\)-diagram 3, can now be "discovered". Pattern N applied to this diagram uncovers the relation
\[
M_2 = -G/\dot{T} + U(1/T) = (U - G)/\dot{T} \tag{11}
\]
which, relative to the intervening potentials, cannot be simplified further.

With the aid of pattern P and \(S\)-diagram 1 it is possible to derive a series of differential forms for the Massieu functions, for example (pattern P, Fig. 1):
\[
dM_2 = dU(1/T) - d(P/T)V = (1/T)dU - Vd(P/T) \tag{12}
\]
Now the introduction of relations 2 and 5 into eq 12 yields the expression for the total differential of \(M_2 = M_2(U, P/T):\)
\[
dM_2 = (\partial M_2/\partial U)_{P,T} dU + (\partial M_2/\partial (P/T))_U d(P/T) \tag{13}
\]
Similarly, all other differential forms for \(S\), \(M_1\), and \(M_3\) can be derived.

Massieu functions \(M_1 = -A/\dot{T}\) and \(M_3 = -G/\dot{T}\) are very important in what is known as the maximum principle for the equilibrium value (4). In fact, \(M_1\) and \(M_3\), being \(A\) and \(G\) minimum, are maximum for constant values of their intensive variables—that is, \(1/T\) for \(M_1\) (constant \(T\), and \(1/T\) and \(P/T\) for \(M_3\) (constant \(T\) and \(P\)). Function \(M_3\) has only a mathematical value with nearly no physical meaning.

The symmetry of \(E\)-diagram 2 allows us to derive the expressions of the chemical potential in a straightforward way:
\[
\mu_i = (\partial U/\partial n_i)_{S,V,N} = \partial (H/\partial n_i)_{S,T,N} = \partial (G/\partial n_i)_{T,P,N}. \tag{19}
\]
In exactly the same way the symmetry of \(S\)-diagram 1 or 3 allows to define the corresponding entropy-dimensional partial molar quantities.

**Conclusion**

The values of the Massieu functions, their relations to other thermodynamic parameters, and the rationale for Callen’s names of the Massieu functions have been derived automatically through the diagrammatic method based on an \(S\) representation of the original diagram for thermodynamic relationships, which can be considered the \(E\) representation of the \(S\) diagram.

I will conclude with a quotation relevant to this paper’s purpose of solving complicated problems by minimum mental effort (9):

“A mathematical theorem is called deep if its proof is difficult. The opposite of difficult is trivial and the word is often used in the sense of a putdown. Now, despite this hierarchical ordering what is deep is in a sense undesirable for there is a constant effort towards simplification, towards the finding of alternative ways of looking at the matter which trivialize what is deep.

**Acknowledgments**

I would like to thank the three referees for their politeness and one of them also for a witty and interesting remark about the use of \(A\) and \(N\) notation for the Helmholtz (free energy) function: “There are still enough of us old folks around that still remember \(F\) representing the Gibbs [free energy] function. The IUPAC ‘green book’ suggests that \(F\) should be used instead of \(A\) only for surface processes where there is a potential confusion problem with surface area.”

**Literature Cited**