

# Mnemonic Diagrams for Thermodynamic Systems

James M. Phillips

Department of Physics, University of Missouri–Kansas City, Kansas City, MO 64110

In 1929, a compact diagram implying considerable information was used by Max Born in his Göttingen lectures on thermodynamics.<sup>1</sup> It first appears in the literature in 1935 in a paper by F. O. Koenig<sup>2</sup> and has been utilized in a remarkable text by H. B. Callen.<sup>3</sup> Since then, the use of the diagram in thermodynamics has become commonplace for those who find such geometrical representations helpful. The purpose of this note is to present a new mnemonic diagram (Fig. 1) that is a three-dimensional extension of the Born construction.

In the energy formulation of the macroscopic thermodynamics of equilibrium (MTE), the internal energy  $U$  as a function of the extensive independent variables  $X_i$  contains the maximum possible information about a system. The fundamental equation in terms of the generalized extensive parameters is

$$U = U(X_0, X_1, \dots, X_t) \quad (t \geq m + 2) \quad (1)$$

where  $m$  is the number of component species of the system. The conjugate intensive parameters are given by

$$Y_i = (\partial U / \partial X_i)_{X_j} \quad (i \neq j) \quad (2)$$

The differential form of the fundamental equation is written

$$dU = \sum_{i=0}^t Y_i dX_i \quad (3)$$

Equation 3 is the sum of the possible interactions a system of interest may have with a reservoir

$$dU = dQ - dW + dA \quad (4)$$

where  $dQ$  is the heat added to the system,  $dW$  is the work done by the system, and  $dA$  is the diffusive interaction (mass action).

Legendre transformations of the fundamental equation result in the other thermodynamic potential of different "natural" variables

$$f_k = U - \sum_{i=0}^k Y_i X_i \quad (5)$$

The Jacobian

$$J = \frac{\partial(Y_0, Y_1, \dots, Y_k)}{\partial(X_0, X_1, \dots, X_k)} \neq 0 \quad (k \leq t) \quad (6)$$

is the sufficient condition for the existence of a particular transformation.<sup>1,4</sup>

Some of the resulting thermodynamic potentials

$$df_k = - \sum_{i=0}^k X_i dY_i + \sum_{j=k+1}^t Y_j dX_j \quad (7)$$

are more common than others and have been traditionally given names such as Gibbs, Helmholtz, enthalpy, and Grand potentials. Note, in the case  $k = t$ ,  $f_k = 0$ , which gives the Gibbs–Duhem equation

$$\sum_{i=0}^t X_i dY_i = 0 \quad (8)$$

Each transformed potential is a function of its own "natural" independent variables. Term-by-term comparisons of eq

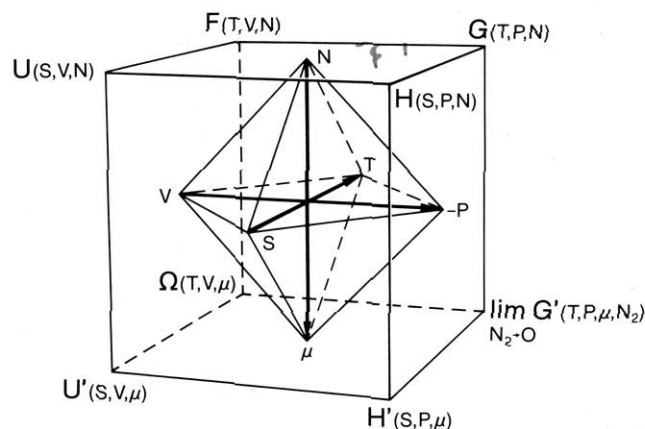


Figure 1. A three-dimensional mnemonic diagram for a simple thermodynamic system. The cube vertices represent the thermodynamic potentials and the adjacent cube faces the corresponding natural variables. Opposing faces are the conjugate pairs of thermodynamic variables. The octahedron edges are guides to the thermodynamic relationships (for details see ref 3). Note the top view is the traditional two-dimensional Born diagram.

7 with the differential  $df_k$  give the thermodynamic derivatives. The partial derivatives of the thermodynamic potential with respect to the extensive variable  $Y_i$  are

$$\partial f_k / \partial Y_i = -X_i \quad (0 \leq i \leq k) \quad (9)$$

and correspondingly

$$\partial f_k / \partial X_j = Y_j \quad (k + 1 \leq j \leq t) \quad (10)$$

The Maxwell relations are determined by changing the order of differentiation with respect to a pair of "natural" variables while holding all others constant. For example,

$$\partial^2 f_k / \partial X_j \partial Y_i = \partial^2 f_k / \partial Y_i \partial X_j \quad (11)$$

Substitution of eqs 9 and 10 into eq 11 gives

$$-(\partial X_i / \partial X_j) = (\partial Y_j / \partial Y_i) \quad i \leq k \text{ and } j > k \quad (12)$$

$$(\partial X_i \partial Y_j) = -(\partial X_j \partial Y_i) \quad i, j \leq k \quad (13)$$

and

$$(\partial Y_i / \partial X_j) = (\partial Y_j / \partial X_i) \quad i, j > k \quad (14)$$

For systems with more than two conjugate pairs of independent thermodynamic variables, not all of the thermodynamic derivatives and Maxwell relations are represented on the same two-dimensional Born diagram. The new three-dimensional mnemonic diagram (Fig. 1) extends the

<sup>1</sup> Tisza, L. *Generalized Thermodynamics*; MIT: Cambridge, MA, 1966.

<sup>2</sup> Koenig, F. O. *J. Chem. Phys.* **1935**, *3*, 29.

<sup>3</sup> Callen, H. B. *Thermodynamics: An Introduction to the Physical Theories of Equilibrium Thermodynamics and Irreversible Thermodynamics*; Wiley: New York, 1960.

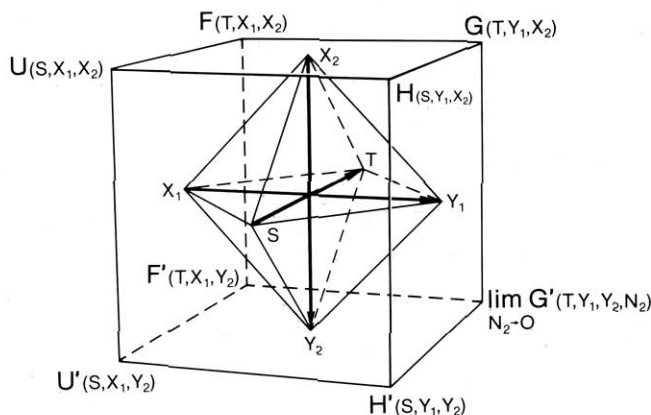


Figure 2. The generalized version of the mnemonic diagram given in Figure 1.

representation to three conjugate pairs. This could be all three possible types of system-reservoir interactions shown in eq 4. Systems with a diffusive interaction but two conjugate pairs of work variables also fit the symmetry of Figure 1.

Figure 1 depicts an octahedron whose vertices are on the face centers of an enclosing cube. The diagonals of the octahedron are arrows connecting conjugate pairs and indicating the signs given in eq 7. The cube vertices are the possible thermodynamic potentials whose "natural" variables are the adjacent cube faces. Legendre transformations move the representation from the internal energy corner  $U(S, V, N)$  to the other named potentials [ $F(T, V, N)$ , Helmholtz;  $G(T, P, N)$ , Gibbs;  $H(S, P, N)$ , enthalpy; and  $\Omega(T, V, \mu)$ , grand]. The  $G'$  vertex is, by Legendre transformation, the Gibbs-Duhem zero (eq 8). For purposes of justifying the related edges of Figure 1, the thermodynamic derivatives and Maxwell relations related to  $G'$  may be considered results from a two-component system  $(\mu_2, N_2)$  in the dilute limit of the second component ( $N_2 \rightarrow 0$ ).<sup>4</sup> The Jacobian for the transformation is in general non-zero. The subsequent Maxwell relations may be demonstrated from the ideal gas formulas for equation of state, entropy, and chemical potential. However, caution should be used. In the dilute limit of the second component, even though the relationships can be derived, they are often not very useful. For example, from the Gibbs-Duhem equation for the simple system the pressure may be

written as a function of  $\mu$  and  $T$ . The corresponding Maxwell relation reduces to zero equals zero. One of the "natural" variables, in this case pressure, has become dependent.

The rules for using the three-dimensional diagram are the same as the two-dimensional one. These rules are outlined clearly by Callen.<sup>3</sup> Notice that the top view of Figure 1 is the Born diagram. Figure 2 is the generalized version of the new diagram with  $X_1 Y_1$  and  $X_2 Y_2$  as the conjugate pairs of thermodynamic variables. The entropic formulation of thermodynamics can be represented in the fashion of Figure 1 by using the  $U$  vertex as the entropy  $S(U, V, N)$  and the  $S$  face center as  $U$ . The conjugate pairs are then  $U \rightarrow 1/T$ ,  $V \rightarrow P/T$ , and  $N \rightarrow \mu/T$ . The  $F$  vertex becomes the Massieu function  $\Psi(1/T, V, N)$  and then  $\Omega$  vertex the Kramers function  $q(1/T, V, \mu/T)$ . The Planck formulation can also be formed by the  $G$  vertex of Figure 1 becoming  $\Phi(1/T, P, N)$  and the conjugate pairs  $V/T \rightarrow P$ ,  $H \rightarrow 1/T$ , and  $N \rightarrow -\mu/T$ .

To illustrate the Maxwell relations with Figure 1, consider the simple system

$$dU = T dS - P dV + \mu dN$$

Each opposing pairs of edges of the octahedron indicate one of the several Maxwell relations, for example the  $T$ -to- $V$  edge and the  $-P$ -to- $S$  edge for the familiar

$$(\partial T / \partial V)_{S, N} = -(\partial P / \partial S)_{V, N}$$

For another example, consider a one-dimensional piezoelectric fiber with length  $L$  and tension  $J$  with the electric polarization  $P$  and internal electric field  $E$ . The change in the internal energy is

$$dU = T dS + J dL + E dP$$

In terms of the variables  $T, P, E$  the notation in Figure 2 is  $X_1, Y_1 \rightarrow L, J$  and  $X_2, Y_2 \rightarrow P, E$ . The  $X_2$ -to- $Y_1$  edge and the opposing  $X_1$ -to- $Y_2$  edge indicate

$$(\partial P / \partial J)_{T, E} = (\partial L / \partial E)_{T, J}$$

The figures give at a glance the "eight" possible thermodynamic potentials, the three accompanying thermodynamic derivatives, and the three Maxwell relations for each. For those who find mnemonic devices helpful, the above figures illustrate in a very compact form a number of thermodynamic relationships.

#### Acknowledgment

I wish to thank L. W. Bruch for very informative discussions. Acknowledgment is made to the Donors of The Petroleum Research Fund, administered by the American Chemical Society, for the support for this study.

<sup>4</sup> Courant, R.; Hilbert, D. *Methods of Mathematical Physics*; Interscience-Wiley: New York, 1962; Vol. 2, p 34.