Cubic Relation between Thermodynamic Functions and Natural Variables for Chemical Thermodynamic Systems

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Synopsis. The relation between thermodynamic functions and natural variables for chemical thermodynamic systems is represented in terms of the geometry of a cube. Besides being helpful in understanding the abstractive nature of thermodynamic relation, this leads to a useful mnemonic as well.

It is well known that thermodynamic functions are characterized by natural variables and that they are related to one another through the Legendre transformation.[1] What we intend to show in this note is that the relation between thermodynamic functions and natural variables for chemical thermodynamic systems can be represented in terms of the geometry of a cube. Being simple, this does not seem to be trifling. Although it is quite probable that someone has noticed the fact already, no description of it can be seen in thermodynamic and chemical thermodynamic literature, as far as the author knows.[2] Only two kinds of thermodynamic squares,[3–5] which are mnemonic diagrams, have some relation with it, as mentioned later. The author is very afraid that his finding might be really a small rediscovery, but yet he believes that the fact is worth communicating here. It gives both conceptual and practical profits to workers studying and making use of chemical thermodynamics.

In general the thermodynamic function has the Pfaffian form consisting of several constituents, each of which is specified by the conjugate pair of extensive and intensive quantities. Let us denote the extensive and the intensive quantities for the i-th constituent, respectively, by $[1]_i$ and $[-1]_i$, which are rewritten as $[\sigma_i]_i$ with the parameter σ_i taking 1 or -1. We write $-\sigma_i$ as $\bar{\sigma}_i$ and -1 as $\bar{1}$ in the following. Denoting the thermodynamic function of natural variables $[\sigma_1]_1, \cdots, [\sigma_m]_m$ by $[\sigma_1\cdots\sigma_m]$, we can put its Pfaffian form as

$$\mathrm{d}[\sigma_1\cdots\sigma_m] = \sum_{i=1}^{m} \sigma_i[\bar{\sigma}_i]_i\mathrm{d}[\sigma_i]_i, \tag{1}$$

from which it follows immediately that

$$\left(\frac{\partial[\sigma_1\cdots\sigma_m]}{\partial[\sigma_k]_k}\right)_{[\sigma_i]_i(i\neq k)} = \sigma_k[\bar{\sigma}_k]_k. \tag{2}$$

For the Legendre transformation changing one of natural variables from $[\sigma_k]_k$ into $[\bar{\sigma}_k]_k$ it is relevant to define the operator L_k as

$$L_k[\cdots\sigma_k\cdots] = [\cdots\sigma_k\cdots] - \sigma_k[\bar{\sigma}_k]_k[\sigma_k]_k. \tag{3}$$

This definition naturally gives

$$\mathrm{d}L_k[\cdots\sigma_k\cdots] = \mathrm{d}[\cdots\bar{\sigma}_k\cdots], \tag{4}$$

which allows us to put

$$L_k[\cdots\sigma_k\cdots] = [\cdots\bar{\sigma}_k\cdots]. \tag{5}$$

Substituting Eqs. 2 and 5 into Eq. 3, replacing σ_k with $\bar{\sigma}_k$, we have a generalized expression for the Gibbs–Helmholtz type equations

$$[\cdots\sigma_k\cdots] = [\cdots\bar{\sigma}_k\cdots] - [\bar{\sigma}_k]_k\left(\frac{\partial[\cdots\bar{\sigma}_k\cdots]}{\partial[\bar{\sigma}_k]_k}\right)_{[\sigma_i]_i(i\neq k)}. \tag{6}$$

On the other hand, From Eq. 2 the Maxwell relations are summarized in the form

$$\sigma_j\left(\frac{\partial[\bar{\sigma}_j]_j}{\partial[\sigma_k]_k}\right)_{[\sigma_j]_j} = \sigma_k\left(\frac{\partial[\bar{\sigma}_k]_k}{\partial[\sigma_j]_j}\right)_{[\sigma_k]_k} \quad (j\neq k), \tag{7}$$

the fixed variables other than $[\sigma_j]_j$ and $[\sigma_k]_k$ being suppressed for brevity. The abstractive nature of thermodynamic relation is succinctly expressed with the above notation.[6]

Now we confine ourselves to the three-constituent case. Surely this is a restriction, but it yields no serious loss of applicability. Putting $m=3$, we immediately see that our notation is ready to fit the geometry of a cube: Assign $[1]_i$'s and $[\bar{1}]_i$'s to six faces, $[\bar{1}]_i$ being opposite to $[1]_i$, assign $[\sigma_1\sigma_2\sigma_3]$ to the vertex formed by the three faces $[\sigma_1]_1$, $[\sigma_2]_2$, and $[\sigma_3]_3$, and assign L_i to the four edges connecting the vertices around $[1]_i$ with the vertices around $[\bar{1}]_i$. The scheme of the assignment is illustrated in Fig. 1 with a cubist-like manner. It is easy to find the geometrical counterparts of the equations mentioned in the preceding paragraph (vide infra). The cube tells us concisely the cyclic character of thermodynamic relation. Such geometrical emblematization seems to be impossible for general multi-constituent cases within usual "visible" polyhedrons.

The Pfaffian form of the internal energy U of the ν-component chemical thermodynamic system is written as

$$\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V + \sum_{\kappa=1}^{\nu}\mu_\kappa\mathrm{d}n_\kappa, \tag{8}$$

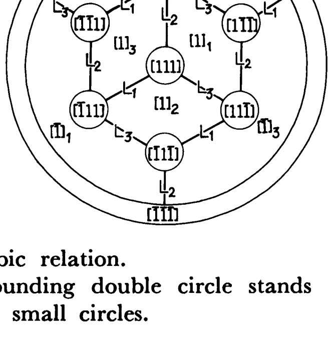

Fig. 1. Cubic relation.
The surrounding double circle stands for a vertex as well as small circles.

where T, S, p, V, μ_κ, and n_κ are the temperature of the system, the entropy, the pressure, the volume, the chemical potential and the amount of substance for the κ-th component, respectively. We have to treat more than three constituents except for the single-component case. It is never unpractical, however, to exclude the thermodynamic function of which natural variables are the chemical potential for some component(s) and the amount of substance for the other component(s). Using μ and n as representatives of μ_κ's and n_κ's, we can work actually within three constituents for chemical thermodynamic systems.[7] Thus the most typical and important choice is: $[1]_1=S$, $[\bar{1}]_1=T$, $[1]_2=-V$, $[\bar{1}]_2=p$, $[1]_3=n$, $[\bar{1}]_3=\mu$, and $[111]=U$. We have $[\bar{1}11]$ as the Helmholtz function A, $[1\bar{1}1]$ as the enthalpy H, and $[\bar{1}\bar{1}1]$ as the Gibbs function G. The grand (canonical) function, well-known in statistical mechanics and often denoted by Ω, corresponds to $[\bar{1}1\bar{1}]$. The others, $[11\bar{1}]$, $[1\bar{1}\bar{1}]$, and $[\bar{1}\bar{1}\bar{1}]$ have neither prevalent symbols nor names. We refer to this cube as U-cube.

Another choice to be mentioned comes from a famous rearrangement in Eq. 8

$$\mathrm{d}S = \frac{1}{T}\mathrm{d}U + \frac{p}{T}\mathrm{d}V - \sum_{\kappa=1}^{\nu}\frac{\mu_\kappa}{T}\mathrm{d}n_\kappa. \tag{9}$$

We set: $[1]_1=U$, $[\bar{1}]_1=1/T$, $[1]_2=V$, $[\bar{1}]_2=p/T$, $[1]_3=n$, $[\bar{1}]_3=-\mu/T$, and $[111]=S$. The three generalized Massieu functions[8] correspond to $[\bar{1}11]$, $[1\bar{1}1]$, and $[\bar{1}\bar{1}1]$; the first one and the third are the Massieu function J and the Planck function Y, respectively. We have $[\bar{1}1\bar{1}]$ as the Kramers function.[9] The others are nameless. This is S-cube. We can obtain various "thermodynamic cubes" likewise.

Next we show that thermodynamic cubes are useful and powerful as a mnemonic tool for thermodynamic relation. For this purpose it is appropriate to exemplify how to have the information from thermodynamic cubes. Let us take U-cube as an example. The view around the vertex G is shown in Fig. 2. We see that G has T, p, and n as natural variables, or reversely, that the thermodynamic function having T, p, and n as natural variables is G. We have the Pfaffian form

$$\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}p + \mu\mathrm{d}n, \tag{10}$$

noting the faces behind and an extra negative sign for an intensive natural variable. A few views around edges are presented in Figs. 3 and 4 with some pliancy. In Fig. 3 we see that G is related to A through the Legendre transformation

$$G = A + pV \tag{11}$$

and that T and n are common natural variables in G and A. Figure 4 illustrates the way of obtaining the Gibbs–Helmholtz equations;

$$U = A - T\left(\frac{\partial A}{\partial T}\right)_{Vn}, \tag{12}$$

$$H = G - T\left(\frac{\partial G}{\partial T}\right)_{pn}. \tag{13}$$

The view around the face n is shown in Fig. 5. This indicates the four thermodynamic functions of which natural variables include n. Their partial derivatives with respect to n are μ (behind). This view is also adaptable for the two-constituent case of no chemical variable. Figure 6 concerns the following two Maxwell relations.

$$\left(\frac{\partial S}{\partial p}\right)_{Tn} = -\left(\frac{\partial V}{\partial T}\right)_{pn}, \tag{14}$$

$$\left(\frac{\partial p}{\partial T}\right)_{Vn} = \left(\frac{\partial S}{\partial V}\right)_{Tn}. \tag{15}$$

Note that an extra negative sign is supposed for every differentiation with respect to an intensive variable. The way of obtaining the Maxwell relations is completely analogous with that of thermodynamic squares. It should be emphasized that thermodynamic cubes have the neat sign convention throughout.

For mnemonics in thermodynamics,[10] we already have two kinds of thermodynamic squares, the Born

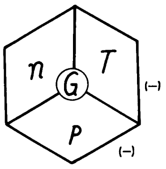

Fig. 2. Natural variables.

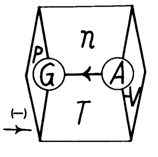

Fig. 3. The Legendre transformation.

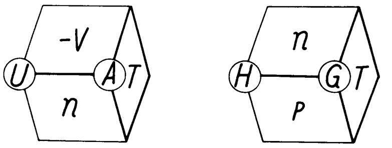

Fig. 4. The Gibbs–Helmholtz equations.

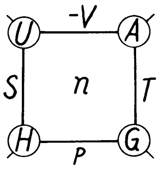

Fig. 5. Thermodynamic functions of a common natural variable.

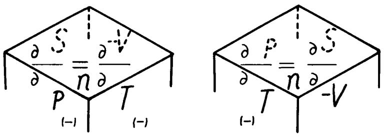

Fig. 6. The Maxwell relations.

diagram[3,4,11] and the Christie diagram,[5,12] which are suited to the Maxwell relations. Sign convention aside, a square in a thermodynamic cube gives the Christie diagram, which corresponds essentially to the Born diagram. The latter has thermodynamic functions and natural variables at sides and vertices, respectively, contrarily to the former. They work equivalently, as far as one square is concerned. Anyhow, no mnemonic is seriously necessary in the case of the two constituents (S,T) and (p,V). It is other cases that need a mnemonic tool.[13] It is undoubtful that a thermodynamic cube is far more excellent and general, even as a mnemonic, than a set of several thermodynamic squares with individual assignment of thermodynamic functions and natural variables.[3]

References

1) For example, H. B. Callen, "Thermodynamics," John Wiley & Sons, New York (1960), Chap. 5.

2) The author has checked a lot of descriptions related to the subject. There exist, however, so many books and articles on thermodynamics and chemical thermodynamics that he remains far away from the exhaustive inquiry.

3) H. B. Callen, "Thermodynamics," John Wiley & Sons, New York (1960), Section 7.2.

4) E. O. Koenig, *J. Chem. Phys.*, **3**, 29 (1935).

5) D. E. Christie, *Am. J. Phys.*, **25**, 486 (1957).

6) Thermodynamics itself is abstractive in the sense that it concerns no concrete form of thermodynamic functions.

7) As the case may be, we have additional terms $Xdx+\cdots$, say, due to an external field in Eq. 8. Even in such cases, if we choose three constituents relevantly with the rest of the Pfaffian form fixed, the cubic relation is valid within a defined family of thermodynamic functions. The relevant choice will be almost exclusively the original three.

8) H. B. Callen, "Thermodynamics," John Wiley & Sons, New York (1960), Section 5.4.

9) No symbol seems to prevail for this function.

10) As tabulation of its own value, we should cite Shaw's Jacobian table as well as Bridgman's table, which are more than mnemonics: A. N. Shaw, *Phil. Trans. Roy. Soc. London A*, **234**, 299 (1935); P. W. Bridgman, "Condensed Collection of Thermodynamic Formulas," Harvard University Press, Cambridge, Massachusetts (1926); J. C. Slater, "Introduction to Chemical Physics," McGraw-Hill, New York (1939), p. 27.

11) Not a few books contain description of such a thermodynamic square as quoted in Callen's book (Ref. 3). This kind of thermodynamic squares was initiated by M. Born in his lecture in 1929 according to L. Tisza, who named it the Born diagram: L. Tisza, "Generalized Thermodynamics," MIT Press, Cambridge, Massachusetts (1966), p. 64.

12) The Christie diagram originates from a mnemonic of natural variables for the $(S,T)-(p,V)$ case; see the references cited in Christie's note (Ref. 5). U-cube may be regarded as an improved generalization of the Christie diagram.

13) As a "real" mnemonic tool we recommend a truncated cube with symbols of thermodynamic functions on triangular faces, the edges around which are, of course, spurious.