THE THERMODORM, A Mnemonic Octahedron of Thermodynamics

A. F. GANGI, N. E. LAMPING, AND P. T. EUBANK
Texas A&M University
College Station, Texas 77843

The development, use, and construction of the THERMODORM[*1], a mnemonic octahedron in terms of the energy functions of thermodynamics and their variables is described. This easily constructed, pocket-sized device provides at a glance the complete set of Maxwell relations and energy function derivatives for k component systems.

THEORETICAL BACKGROUND

For a homogeneous phase of k components in an open system a fundamental equation of thermodynamics[2,3] is given by the expression for the internal energy of the system:

$$U = U(S,V,N_i); \quad i = 1,2, \ldots, k \tag{1}$$

The total differential of the internal energy is:

$$dU = TdS - PdV + \sum_{i=1}^{k} \mu_i dN_i, \tag{2}$$

where the intensive variables (the temperature T, the pressure, P, and the chemical potential, μ_i) are defined by the partial derivatives of the internal energy.[4]

By means of Legendre transformations, the internal energy $U(S,V,N_i)$ can be converted into the other thermodynamic energy functions:[5] the enthalpy $H(S,P,N_i)$, the Helmholtz free energy $A(T,V,N_i)$, the Gibbs free energy $G(T,P,N_i)$, etc. Their differentials are:

$$dH = TdS + VdP + \sum_{i=1}^{k} \mu_i dN_i = dU[P], \tag{3}$$

$$dA = -SdT - PdV + \sum_{i=1}^{k} \mu_i dN_i = dU[T], \tag{4}$$

$$dG = -SdT + VdP + \sum_{i=1}^{k} \mu_i dN_i = dU[T,P] \tag{5}$$

$$d(TS-PV) = TdS - PdV - \sum_{i=1}^{k} N_i d\mu_i = dU[\mu_i] \tag{6}$$

$$d(TS) = TdS + VdP - \sum_{i=1}^{k} N_i d\mu_i = dU[P,\mu_i] \tag{7}$$

[*]"Thermodynamic Octahedral Display Of the Relations of Maxwell"

$$d(-PV) = -SdT - PdV - \sum_{i=1}^{k} N_i d\mu_i = dU[T,\mu_i] \tag{8}$$

and

$$0 = -SdT + VdP - \sum_{i=1}^{k} N_i d\mu_i = dU[T,P,\mu_i], \tag{9}$$

the last relation is also called the Gibbs-Duhem equation. U, H, A, G, TS-PV, TS, and -PV will be termed the energy functions with S, V, P, T, N_i and μ_i as their independent variables. The natural variables of U are S, V, and N_i while those of G are T, P, and N_i, etc.[6]

A total of $7(k + 2)$ Maxwell equations result from cross differentiation of Equations (2-8) of the type

$$\frac{\partial^2 U}{\partial S \partial V} \equiv \frac{\partial^2 U}{\partial V \partial S} \tag{10}$$

to yield, for example,

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

gross differentiation of Equation (9) yields relations of the type

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

since the phrase rule allows but $k + 1$ independent intensive variables from the potentials P, T, and μ_i. Thus,

$$\left(\frac{\partial T}{\partial S}\right)_{P,\mu_i} = \left(\frac{\partial P}{\partial V}\right)_{T,\mu_i} = \left(\frac{\partial \mu_i}{\partial N_i}\right)_{P,T,\mu_j} \equiv 0, \tag{13}$$

since $[dT]_{P,\mu_i} = 0$, etc.

A total of $7(k + 2)$ derivatives may be formed by differentiation of the seven nonzero energy functions with respect to their natural variables. Of the derivatives for TS – PV, TS, –PV, two are
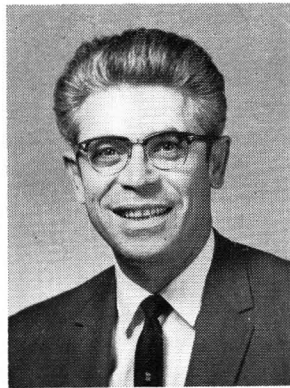
$$\left[\frac{\partial(TS)}{\partial S}\right]_{P,\mu_i} \equiv T \quad \text{and} \quad \left[\frac{\partial(-PV)}{\partial V}\right]_{T,\mu_i} \equiv -P, \tag{14}$$

as a consequence of the phase rule. Other derivatives are consistent with the Maxwell relations. For example,

$$V = \left[\frac{\partial(TS)}{\partial P}\right]_{S,\mu_i} = S\left(\frac{\partial T}{\partial P}\right)_{S,\mu_i} \tag{15}$$

which agrees with the Maxwell relation,

$$\left(\frac{\partial T}{\partial P}\right)_{S,\mu_i} = \left(\frac{\partial V}{\partial S}\right)_{P,\mu_i} \equiv \frac{V}{S} \tag{16}$$

A. F. Gangi received his BS, MS and PhD ('60) in Physics from the University of California at Los Angeles. While at UCLA he was associated with the Institute of Geophysics. His doctoral thesis subject was the diffraction of elastic waves by wedges. He was manager of the Antenna Department at Space-General Corp. in El Monte, California before becoming an Associate Professor of Geophysics at MIT. Presently he is a Professor in the Geophysics Department at Texas A&M University. His research interests are theoretical seismology, properties of the earth's interior and theoretical geophysics.

Of the derivatives for H, A, and G, we find

$$\overline{G}_i \equiv \left(\frac{\partial G}{\partial N_i} \right)_{P,T,N_j} = \mu_i \qquad (17)$$

where $\overline{G}_i$ is the partial molar Gibbs energy.

DEVELOPMENT AND USE

The Maxwell relations and energy function derivatives can be remembered by means of the thermodynamic squares[6,7] with arrows pointing along the diagonals as shown in Figure 1 for the energy functions U, A, G, and H flanked by their natural variables (excluding N_i). The four common Maxwell relations are found using this square. For example, the Maxwell relation

$$\left(\frac{\partial V}{\partial S} \right)_{P,N_i} = \left(\frac{\partial T}{\partial P} \right)_{S,N_i} \qquad (18)$$

is obtained from this square using the following procedure. We take the derivative of the variable in the top *left* corner with respect to the variable in the bottom *left* corner holding constant the variable in the bottom right corner and on the face. We equate this to the derivative of the variable on the top *right* corner with respect to the variable on the bottom *right* corner holding constant the variables in the bottom left corner and on the face. The sign is determined by the arrows; the sign is positive if *both* arrows point either upward or downward. Using this procedure, rotation of the square 90° clockwise yields

$$\left(\frac{\partial S}{\partial P} \right)_{T,N_i} = - \left(\frac{\partial V}{\partial T} \right)_{P,N_i} \qquad (19)$$
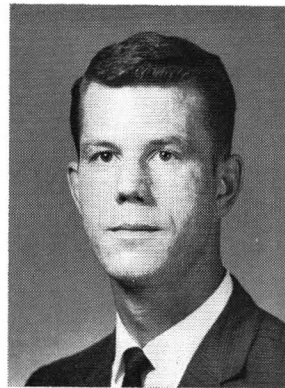
N. E. Lamping received his BS in Geology from the University of Notre Dame, an MS in Geodetic Sciences from Ohio State University and a PhD ('70) in Geophysics from Texas A&M University. His PhD thesis subject was "The Mohorovicic Discontinuity as a Phase Transition." Major Lamping has been awarded the Air Force Commendation Medal twice; once in 1962 for meritorious service and in 1968 for outstanding achievement. He presently is Chief of the Cratering Geophysics Section at the Air Force Weapons Laboratory, Kirtland AFB, New Mexico.

P. T. Eubank was a graduate from Rose Polytechnic Institute and received his PhD degree from Northwestern University under Professor J. M. Smith in 1961. He has taught thermodynamics and transport phenomena for the past ten years at Texas A&M University and is on the research staff of the Thermodynamics Research Center there. He is presently pursuing his principal research interest, the physical and thermodynamic properties of polar vapors, under the direction of Professor J. S. Rowlinson at Imperial College, London, England. (right)
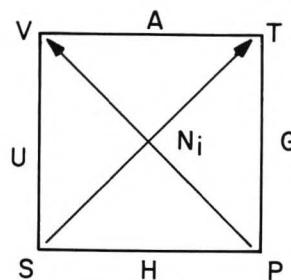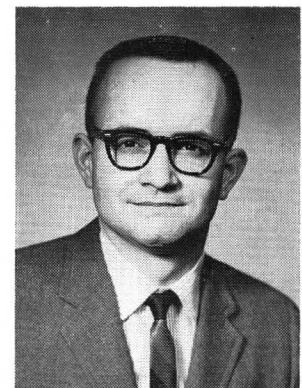
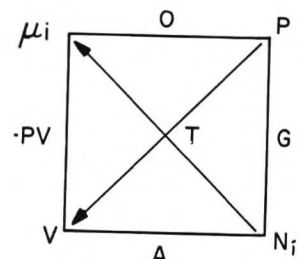Figure 1.—The Common Thermodynamic Square.

Figure 2.—The Constant Temperature Square.

where now the sign is negative because one arrow points upward and the other downward. We have placed N_i at the center of this square since these four Maxwell relations are for the constant N_i.

The square also provides the derivatives of the energy functions such as

$$\left(\frac{\partial U}{\partial S} \right)_{V,N_i} = T, \quad \left(\frac{\partial U}{\partial V} \right)_{S,N_i} = -P, \quad \left(\frac{\partial G}{\partial T} \right)_{P,N_i} = -S$$

The sign is positive if the variable is at the head of the arrow and otherwise negative.

There are six such squares, one for a fixed value of each of the independent variables. Fig-

ure 2, the constant temperature square, yields Maxwell relations such as

$$\left(\frac{\partial \mu_i}{\partial P}\right)_{N_i,T} = \left(\frac{\partial V}{\partial N_i}\right)_{P,T,N_j} = \bar{V}_i \qquad (20)$$

(the partial molar volume) and energy function derivatives such as

We now place the eight energy functions (including the zero Gibbs-Duhem function) on the triangular sides of a regular octahedron with the six independent variables located at the points. The energy functions are placed on the top pyramid of the octahedron so as to reproduce the square of Figure 1 when sighting directly into N_i point. The bottom pyramid of the octahedron reproduces the square of Figure 3 when we look directly into the μ_i point. On the plane bisecting the top and bottom pyramids of the octahedron the U surface intersects the (TS-PV) surface since they share V and S as natural variables — likewise for G and zero which share P, T, and etc. All six mnemonic squares may be seen on the THERMODORM.

CONSTRUCTION

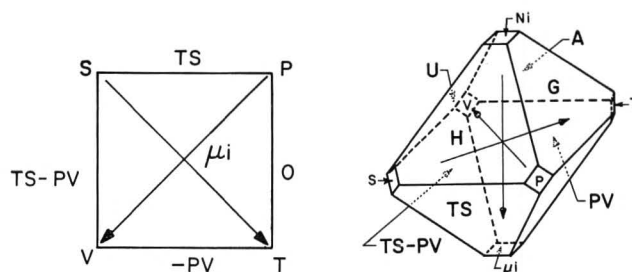Figure 4 is a pictorial representation of a clear plastic model which can be quickly and easily

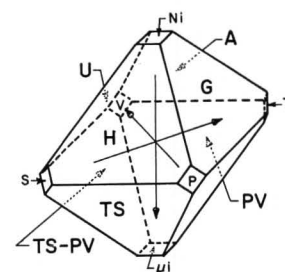**Figure 3.—The Constant Chemical Potential Square.**

Figure 4.—The Energy THERMODORM.

fabricated. The points of the octahedron have been planned normal to the major axes to provide small squares for lettering the independent variables. A common soldering gun with a fine point is adequate for lettering. The arrows, $S \longrightarrow T$, $N_i \longrightarrow \mu_i$ and $P \longrightarrow V$, can be set directly in the mold if the device is cast. Otherwise, a negative sign should be placed before S, N_i, and P. The minus sign is then used when forming Maxwell relations and energy derivatives but is ignored where it appears in the denominator of a partial derivative.

A collapsable paper THERMODORM can be easily constructed from the pattern provided by Figure 5. THERMODORMS can be also made for $S(U,V,N_i)$, $V(U,S,N_i)$, and $N_i(U,S,V)$ and the functions obtained by Legendre tranformations
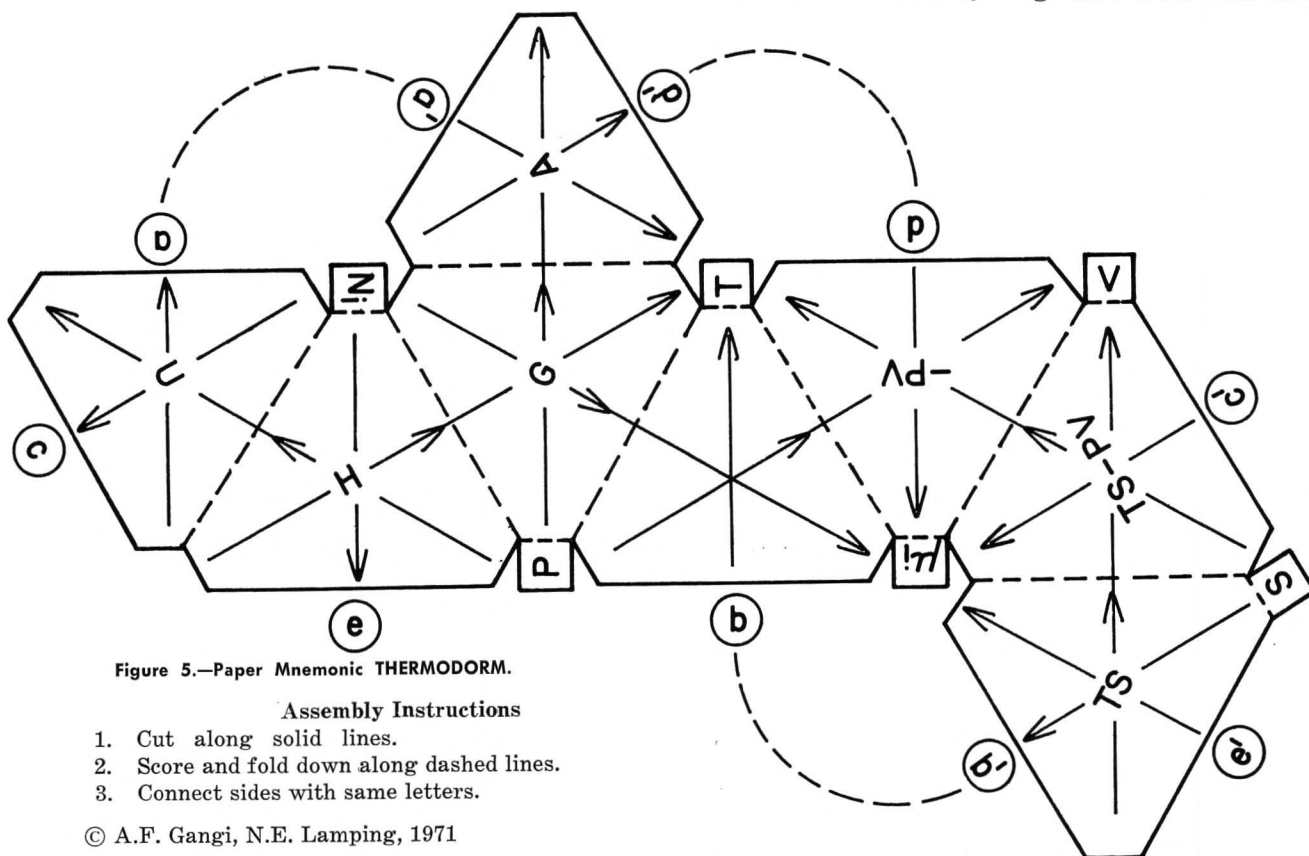

Figure 5.—Paper Mnemonic THERMODORM.

Assembly Instructions
1. Cut along solid lines.
2. Score and fold down along dashed lines.
3. Connect sides with same letters.

© A.F. Gangi, N.E. Lamping, 1971

analogous to that for the energy functions. Transforms of the entropy are termed Massieu functions which yield relations upon cross differentiation analogous to those of Maxwell.

SUMMARY

The theoretical basis, use, and construction of a mnemonic octahedron for the representation of the energy functions and their derivatives together with the Maxwell equations, has been presented. The device, which is easily constructed to any size—desk top or pocket version, should be valuable to both students and teachers. Although classic thermodynamics requires a minimum of memorization, we hope the THERMODORM will aid the student in understanding and unifying the energy functions together with their variables and prove to be more than an optimal crib-sheet for closedbook exams. □

REFERENCES

1. Gangi, A. F., and N. E. Lamping, Thermodynamic Functions and Potentials with their Corresponding Maxwell Relations Derived and Displayed on THERMODORMS, Patent Disclosure, Texas A&M University, College Station, Texas (January, 1970).
2. Denbigh, K., The Principles of Chemical Equilibrium, pp. 74-80, Cambridge Univ. Press, Cambridge, England (1961).
3. Buckingham, A. D., The Laws and Applications of Thermodynamics, pp. 56-59, Pergamon Press, Oxford, England (1964).
4. Callen, H. B., Thermodynamics, p. 31, John Wiley and Sons, Inc., New York (1960).
5. Ibid. 98.
6. Ibid, 117-121.
7. Koenig, F. O., J. Chem. Phys. 3, 29 (1935).

ChE book reviews

Processes and Systems in Industrial Chemistry, H. P. Meissner, Prentice-Hall, Englewood Cliffs, N.J. (1971), 386pp., $14.95.

This book is primarily an introductory discussion of reaction kinetics and associated thermodynamics from an industrial chemical point of view. The author, however, includes chapters on liquid-solid equilibria, material balances and energy balances. There is also a chapter on the frequently neglected topic of electrochemical operations. Roughly one-third of the book is devoted to problems. The book is noteworthy in relating the discussion and the problems to specific chemical processes.

R. S. Kirk
University of Massachusetts

Ed. Note. The author has classified processes "by (1) types of equilibria, (2) types of energy management problems, (3) types of rate problems (including catalysis), and (4) types of flow sheet patterns and materials handling problems." The book contains eleven chapters titled: Equilibrium in homogeneous systems; Heterogeneous reaction equilibria; Liquid-solid equilibria involving ions; Management of materials; Management of heat energy; Homogeneous reaction rates; Catalytic reactions and reactors; Reactions between gases and solids; Chemical reactors; Reactions having an unfavoragle ΔF; and Industrial electrochemical operations. There are 125 realistic case-type problems for effective illustration of the material.

SANDALL—

Nomenclature

A_n, B_n	Eigenvalues
C	Molar concentration
d	Drop diameter
D	Diffusion coefficient
k	Individual phase mass transfer coefficient
K	Overall mass transfer coefficient
m	Slope of equilibrium curve
$\overline{N}_A$	Average mass transfer rate
Re	Reynolds number
Sc	Schmidt number
v	Drop velocity
$\overline{x}$	Average mole fraction benzoic acid in water phase
x^*	Mole fraction benzoic acid that would be in equilibrium with the bulk toluene phase concentration
θ	Contact time
μ	Absolute viscosity

Subscripts:

T	Toulene phase
w	Water phase

REFERENCES

1. Handlos, A. E. and T. Baron, "Mass and Heat Transfer from Drops in Liquid-liquid Extraction", AIChE Journal, 3, 127 (1957).
2. Higbie, R., "The Rate of Absorption of a Pure Gas into a Still Liquid During Short Periods of Exposure," Trans. Am. Inst. Chem. Engrs, 31, 365 (1935).
3. Klee, A. J. and R. E. Treybal, "Rate of Rise or Fall of Droplets," AIChE Journal, 2, 444 (1956).
4. Kronig, R. and J. C. Brink, "On the Theory of Extraction from Falling Droplets," Appl. Sci. Research, A2, 142 (1950).
5. Ranz, W. E. and W. R. Marshall, "Evaporation from Drops," Chem. Eng. Prog., 48, 173 (1952).
6. Treybal, R. E., Liquid Extraction, 2nd ed., McGraw-Hill Book Co., Inc., New York, 188 (1963).