

DIAMONDS ARE A THERMODYNAMICIST'S BEST FRIEND

RALPH D. NELSON, JR.
West Virginia University
Morgantown, WV 26506*

STUDENTS OF THERMODYNAMICS appreciate having some guide through the thicket of definitions and derivations that usually accompany introductory courses. Numerous sayings and designs have been used over the years (Prins, 1948; Guggenheim, 1949; Burgett, 1972; Marino, 1973; Gangi *et al.*, 1972). I believe that a simple geometric construction is best and here-with submit my candidate for "best of show."

The shape of a square within a diamond is easily remembered, and the working relationships are easily derived. The first law, $dE = dq - dw_{out}$, provides a starting point to fill in the terms. Partial derivatives of the various energies are shown to be equal to nonenergy variables. Partial derivatives of the nonenergy variables are related through crossed partial derivatives of the energies. The diamond is useful because it provides a graphic representation of the relations between basic thermodynamic variables.

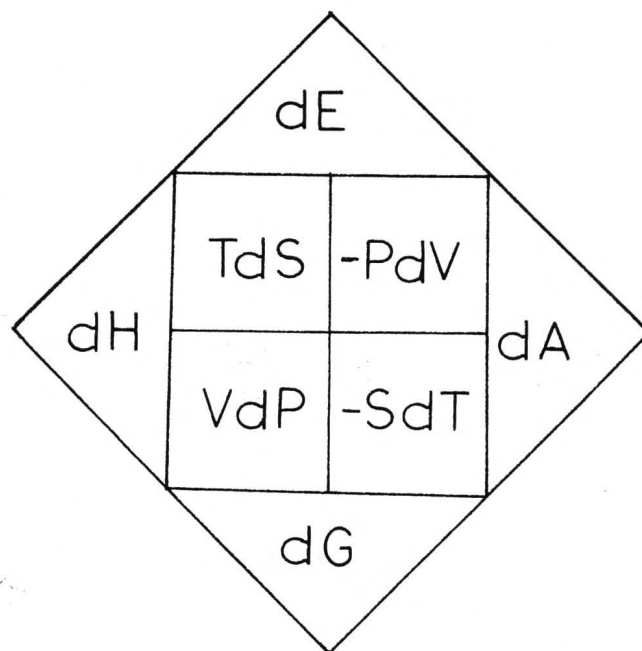
SETTING UP THE DIAMOND

THE FIRST LAW OF thermodynamics states that energy may be converted from one form to another, so that the *total energy flow* into a system is the sum of the various types of energy involved. If the energy flow is due only to heat absorbed, dq , and (piston or shaft) work done by the system, dw_{out} , then $dE = dq - dw_{out}$. A second measure of energy is called enthalpy, H , and is often used when we are dealing with constant pressure systems. The Helmholtz free energy, A , is a measure of maximum work at constant temperature. And the Gibbs free energy, G , is related to chemical reactions and equilibria

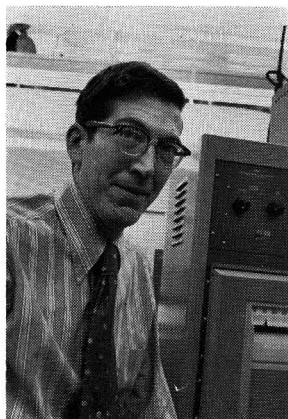
at constant temperature and pressure.

To formalize the relations, draw a diamond with a square inside it, and divide the square into four smaller squares, as shown in the accompanying drawing. In the top three sections, place the definition of total energy flow in terms of heat and work. Place dE in the pointer, TdS (the equivalent of dq here) in the left corner box and $-PdV$ (the equivalent of $-dw_{out}$) in the right corner box. Fill in the remainder of the boxes by "reversing" the terms through the center, so that TdS in the upper left becomes $-SdT$ in the lower right and $-PdV$ in the upper right becomes VdP in the lower left. To fill in the pointers, recall that dH goes next to the heat term TdS (and at constant pressure the other term, VdP would drop out) and that dA goes next to the work term $-PdV$ (and at constant temperature the other term $-SdT$ would drop out). This leaves only one place for dG .

The pointer terms are defined as the sums of the adjacent box terms. The pattern may be



* Current address: Pigments Dept., E. I. DuPont de Nemours Co., Inc., Newport, DE 19804.



Ralph D. Nelson, Jr., earned a B.A. in chemistry at Colby College in 1960 and a Ph.D. in chemistry at Princeton University in 1963. Following research and teaching posts at the National Bureau of Standards, Middlebury College, Brown University, and West Virginia University, he earned an M.S.E. in chemical engineering at West Virginia University in 1974. Research into molecular motions in the liquid state has been supplemented by development of time-shared computer applications. He has recently joined the Pigments Department of Du Pont.

inverted, reflected, or rotated to produce the same relationship between the terms. I find this particular arrangement most suitable. Note that the algebraic signs of the terms are explicit and do not depend on the direction of operation, as is the case with other mnemonics. The various energies are defined as changes, so that absolute values for energies are not implied. Burgett's mnemonic "Good Processes Have Several Energy Variables, All Tied," Marion's "SPorTiVe," and Shih-Ching Su's (C.Y. Wen, private communication) "The Gibbs Potential Has Several Exceptionally Valuable Applications" are all present in the diamond's derivative terms.

USING THE DIAMOND FOR DERIVATIVES

THE MAXWELL RELATIONS equate the first partial derivatives of the various energies to nonenergy variables. Only adjacent pointer energies are involved in the Maxwell relations. The procedure should not be memorized, but understood. The definition of each pointer term involves two box terms. Adjacent pointer terms have one box term in common, *e.g.* $dE = TdS - PdV + dA = -SdT - PdV$. The partial derivative of E with respect to V , holding S constant is $-P$, exactly the same result as taking the partial derivative of the adjacent pointer energy with respect to the common box term's

differential variable, holding the uncommon box term's differential variable constant. For this case we get

$$\left(\frac{dE}{dV}\right)_S = -P = \left(\frac{dA}{dV}\right)_T$$

Try working the three others out yourself, comparing them with expressions in standard thermodynamics texts. Maxwell's relations are handy for replacing a term which is hard to evaluate, such as $(dA/dV)_T$, with one which can be evaluated from available data, such as $-P$.

The *Euler relations* result from the inherent equality of the crossed partial derivatives of the energy variables related as shown in the diagram. The result of two successive partial differentiations of energy with respect to the nonenergy variables used in equilibrium thermodynamics is independent of the order in which the differentiations are carried out, *e.g.*

$$\left\{\frac{d}{dS}\left(\frac{dE}{dV}\right)_S\right\}_V = -\left(\frac{dP}{dS}\right)_V = \left\{\frac{d}{dV}\left(\frac{dE}{dS}\right)_V\right\}_S = \left(\frac{dT}{dV}\right)_S$$

The pattern may be inverted, reflected, or rotated to produce the same relationship between the terms. The algebraic signs of the terms are explicit and do not depend on the direction of operation.

The result on one side is the partial derivative of the nondifferential variable in a box with respect to the differential variable in an adjacent box, holding the original box's differential variable constant. The other side is the same, except that we start in the adjacent box. Derive the other three yourself for practice. Euler relations may be used to evaluate the changes in one nonenergy variable as a second is held constant and a third is changed. Thus we find that $-(dS/dP)_T$ is the same as $(dV/dT)_P$.

FURTHER ELABORATIONS

THE SCHEME ABOVE IS useful for closed systems, surrounded by walls impervious to

(Continued on page 99.)

Mathematical Methods of Chemical Engineering. Vol. 3. Process Modeling Estimation and Identification.

By J. H. Seinfeld and L. Lapidus.
Prentice-Hall, 545 pages.

Reviewed by R. Aris, University of Minnesota

Any topic in applied mathematics which has attained reasonable maturity will have acquired a considerable primary and secondary literature into which the engineer must dig in his efforts to master its methods. But, if his first steps may seem simple, like those of the descent to Avernus, the task of really penetrating the subject and winning his way back again to the daylight is, as Virgil says, another story—'hoc opus, hic labor est'. Hence the peculiar value of reliable guides to that nether world of mathematical ideas that lies at the foundation of our profession and provides the basis for understanding of chemical processes. Lest it seem ambiguous to commend one's friends as guides to the underworld, I hasten to add that they are no flunkeys of the tourist industry but

members of that select company of erudite guides of which Virgil himself is the best known. For this book will not yield much to the casual reader who thinks he can breeze through it with half his attention, but will be found invaluable by the serious student who wants to understand the modern theory of estimation and identification.

In stressing these, the second and third divisions of the book, I am not overlooking the early discussion of modeling and Laplace transform. A brief introductory chapter leads to a discussion of the types of equation that are of value in modeling chemical processes. The emphasis here is not on illustrating the details of actual derivations, but on the rationale of model building and the types of system that arise and their inter-relations. This is followed by an excellent survey of the Laplace transform which includes both the discrete z-transform and a treatment of the numerical inversion.

There are of course many books available on the Laplace transform and several on modeling, though the treatment here is admirably clear, but what makes this book uniquely valuable is the subsequent discussion of stochastic models, estimation theory and process identification. This covers

(Continued on page 100.)

THERMO DIAMOND: Nelson

Continued from page 67.

the passage of matter. If open systems are considered, the energy flow associated with the flow of matter must be added to each energy definition, *i.e.* $dE = TdS - PdV + \sum \mu_i dn_i$, where μ_i is the chemical potential of species *i* and dn_i is the change in the number of moles of species *i* in the system. Note that *E* is related to extensive measures of the system. We can speak of molar entropy, molar volume, and number of moles in the extensive measures. The enthalpy change has one less extensive change in its definition, replacing the $-PdV$ used in dE with VdP . Similarly, dA has one intensive change in its definition, while dG has two intensive changes, VdP and $-SdT$.

The intensive counterpart of $\sum \mu_i dn_i$ is $-\sum n_i d\mu_i$, and if we draw a second diamond for energy relations in which the intensive term $-\sum n_i d\mu_i$ is used, we replace the pointer terms, dE , dH , dA , dG , with new energy variables $d(TS-PV)$, $d(TS)$, $d(-PV)$, and O (the last not being a definition). Gangi, Lamping, and Eu-

bank elaborate on the relations involving this side of the diamond and have a copyrighted design, called a THERMODORM, to illustrate them. The definition of $d(TS - PV)$ involves one intensive term; those of $d(TS)$ and $d(-PV)$ involve two.

Additional relations may be developed if heat capacities are related to entropy, if electromotive force is related to Gibbs free energy, or if equilibrium constants are related to Gibbs free energy. The reader is encouraged to elaborate these as an exercise. The frequent use of $\Delta H - T\Delta S$ in place of ΔG for processes occurring at constant temperature and pressure may be understood in terms of the diamond. At constant *T* and *P* we have simply $dG = \sum \mu_i dn_i$, which is what dH would be at constant pressure if we subtracted out the TdS term.

REFERENCES

- C. Burgett, CHEMTECH, March, 1972, p. 189.
- A. F. Gangi, N. E. Lamping, and P. T. Eubank, Chem. Eng. Educ., Winter, 1972, pp. 30-35.
- E. A. Guggenheim, "Thermodynamics—an Advanced Treatise" Interscience, New York, 1949, p. 21.
- P. A. Marino, AIChE Student Members Bulletin, Spring, 1973, p. 9.
- J. A. Prins, J. Chem. Phys. 16, 65 (1948).