Matrix Formalism of the Mnemonic Diagram for Thermodynamic Relationships

Lionello Pogliani

Dipartimento di Chimica, Università della Calabria, 87030 Rende (CS), Italy

Received December 19, 1991

This paper introduces a new computational method to obtain different thermodynamic relationships using ideas from group theory and a matrix formulation of the parameters of the diagram for thermodynamic relationships.

While thermodynamic relations of simple systems are relatively simple mathematically, many people generally remember just one or two thermodynamic expressions and have difficulty deriving the various other expressions. The purpose of this paper is to illustrate a formalism which allows derivation of the most important thermodynamic expressions with the aid of just one starting relationship

$$H = U + PV \tag{1}$$

and also to extract the same starting relation with the help of the starting potential H only. Present formalism, based on some computational notions derived from quantum mechanics and especially from group theory, uses a modified version of the mnemonic diagram for thermodynamic relationships[1,2] (and references therein). The virtue of this formalism is not that it leads to new results, but it does make it possible to extract, in a systematic and mechanical way, the various thermodynamic expressions.

METHOD

Parameters A, G, H, U, P, S, T, and V (which represent Helmholtz free energy, Gibbs free energy, enthalpy, internal energy, pressure, entropy, temperature, and volume) are represented in Figure 1 as two-component (x,y) row matrices.

The matrices representing potentials and remaining variables possess an interesting mathematical property: adjacent potentials or variables are orthogonal to each other. In fact, if one multiplies the matrix representation of one potential or variable into the hermitian adjoint of the matrix representation of another adjacent potential or variable, the result is always zero. This orthogonality rule allows only the following possible combinations (which give rise to an energy-dimensioned term) among variables P, S, T, and V: S and T or P and V.

In order to obtain, by matrix formalism, the thermodynamic relations we are interested in, the following matrices

$$C_4^+ = \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix} \tag{2}$$

$$C_4^- = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \tag{3}$$

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} \tag{4}$$

$$\sigma_y = \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix} \tag{5}$$

which perform a 90° or a –90° rotation about the axis of diagram 1 and a x- or a y-reflection parallel to one of the x and y axes of the same diagram[3] must be used.

The following four matrices are also needed to transform potentials lying over or under the x or y axis into a variable

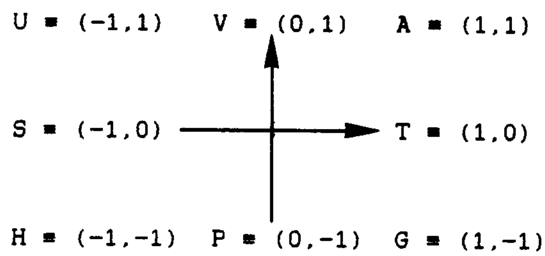

Figure 1. Thermodynamic diagram with the newly defined parameters.

function lying on the axis

$$L_x = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} \tag{6}$$

$$L_{-x} = \begin{pmatrix} -1 & 0 \\ 0 & 0 \end{pmatrix} \tag{7}$$

$$L_y = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \tag{8}$$

$$L_{-y} = \begin{pmatrix} 0 & -1 \\ 0 & 0 \end{pmatrix} \tag{9}$$

Before starting with the different matrix operations, some considerations of signs are necessary. A negative sign for a term in the expression is contributed only by vectors (–1,0) and (0,–1) when (s1) these vectors are not differentiated, excluding the constant parameter, (s2) they are in the 2nd place of a nondifferentiated energy-dimensioned term, and (s3) they are the constant parameter of a wholly differentiated expression; otherwise the sign is always positive.

Relations between Potentials. Generating Step: the matrix form of the well-known $H = U + PV$ relation, shown in eq 10, can be obtained by operating on potential $H \equiv (-1,-1)$

$$(-1,-1) = (-1,1) + (0,-1)(0,1) \tag{10}$$

with the matrix succession σ_x, L_y, L_{-y} as shown in the right side of eq 11. Operating on potential $(1,-1) \equiv G$ with matrix

$$(-1,-1) = (-1,-1)\sigma_x + (-1,-1)L_y(-1,-1)L_{-y} \tag{11}$$

succession, σ_y, L_x, L_{-x}, as shown in eq 12, we obtain eq 13, i.e., $G = H - TS$ while with the former matrix succession we had obtained $G = A + PV$.

$$(1,-1) = (1,-1)\sigma_y + (1,-1)L_x(1,-1)L_{-x} \tag{12}$$

$$(1,-1) = (-1,-1) - (1,0)(-1,0) \tag{13}$$

The generating step converts the starting vector into a neighboring one and, then, adds to it the product of the projections of these two vectors on the corresponding x or y

0095-2338/92/1632-0386$03.00/0

axis; σ operation, easier to memorize, could be substituted by a C_4 one. As further multiplication between two rows is not possible, matrix operations stop at this level. Operations $\sigma_{x,y}$, $L_{y,x}$, and L_{-y-x} (the generator) could be used to generate the remaining thermodynamic relations, which can also be generated with the aid of the following propagating step.

The propagating step, formally easier than the generating one, operates on the terms of a well-known starting relation with only rotation or reflection matrices, and repeating each time this process with the terms of the newly-obtained relation can generate all other expressions. Operating, for example, on eq 10, with C_4^+ we obtain $U = A + ST$ (eq 14)

$$(10)C_4^+: \quad (-1,-1)C_4^+ = (-1,1)C_4^+ + (0,-1)C_4^+(0,-1)C_4^+ \tag{14}$$

after operations have been performed we have

$$(-1,1) = (1,1) + (-1,0)(1,0) \tag{15}$$

While operating, in the same way, with σ_y we obtain $G = A + PV$

$$(10)\sigma_y: \quad (1,-1) = (1,1) + (0,-1)(0,1) \tag{16}$$

Now, operating on eq 15 with C_4^+, we obtain eq 17 ($A = G - VP$)

$$(15)C_4^+: \quad (1,1) = (1,-1) - (0,1)(0,-1) \tag{17}$$

In this way we can obtain all other relations that hold between potentials. The negative signs in eqs 13 and 17 are supported by the s2 sign convention.

Differential Forms of the Potentials. Propagating Step: starting with the matrix expression of the well-known differential form of potential U, $\mathrm{d}U = T\,\mathrm{d}S - P\,\mathrm{d}V$, shown in eq 18 and operating on the terms of this equation with C_4^+

$$\mathrm{d}(-1,1) = (1,0)\,\mathrm{d}(-1,0) - (0,-1)\,\mathrm{d}(0,1) \tag{18}$$

or σ_y we obtain eqs 19 or 20 ($\mathrm{d}A = -P\,\mathrm{d}V - S\,\mathrm{d}T$ or $\mathrm{d}A = -S\,\mathrm{d}T - P\,\mathrm{d}V$) and operating on eq 19 with C_4^+ we obtain eq 21 ($\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}P$) and so on.

$$(18)C_4^+: \quad \mathrm{d}(1,1) = -(0,-1)\,\mathrm{d}(0,1) - (-1,0)\,\mathrm{d}(1,0) \tag{19}$$

$$(18)\sigma_y: \quad \mathrm{d}(1,1) = -(-1,0)\,\mathrm{d}(1,0) - (0,-1)\,\mathrm{d}(0,1) \tag{20}$$

$$(19)C_4^+: \quad \mathrm{d}(1,-1) = -(-1,0)\,\mathrm{d}(1,0) + (0,1)\,\mathrm{d}(0,-1) \tag{21}$$

Equation 18 could also be obtained with the help of the following generating step performed on vector $(-1,1) \equiv U$

$$\mathrm{d}(-1,1) = (-1,1)L_{-x}\,\mathrm{d}(-1,1)L_x + (-1,1)L_{-y}\,\mathrm{d}(-1,1)L_y \tag{22}$$

Applying generator L_{-x}, L_x, L_{-y}, and L_y to vector $(1,-1) \equiv G$ we obtain eq 24 ($\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}P$)

$$\mathrm{d}(1,-1) = (1,-1)L_{-x}\,\mathrm{d}(1,-1)L_x + (1,-1)L_{-y}\,\mathrm{d}(1,-1)L_y \tag{23}$$

$$\mathrm{d}(1,-1) = -(-1,0)\,\mathrm{d}(1,0) + (0,1)\,\mathrm{d}(0,-1) \tag{24}$$

In the same way, we can generate all the other relations.

Negative signs in the right part of eqs 19, 20, 21, and 24 are supported by the s1 sign convention.

Relations for the Coefficients. From eq 18 we can obtain eq 25 (i.e., $(\delta U/\delta V)_S = -P$)

$$[\delta(-1,1)/\delta(0,1)]_{(-1,0)} = -(0,-1) \tag{25}$$

And now, with the aid of the propagating step we can obtain, for example, relations 26 and 27, i.e., $(\delta A/\delta T)_V = -S$ and $(\delta G/\delta T)_P = -S$

$$(25)C_4^+: \quad [\delta(1,1)/\delta(1,0)]_{(0,1)} = -(-1,0) \tag{26}$$

$$(26)\sigma_x: \quad [\delta(1,-1)/\delta(1,0)]_{(0,-1)} = -(-1,0) \tag{27}$$

Negative signs in the right part of these equations are supported by the s1 sign convention.

Ignoring every vector of eq 25, but $(-1,1) \equiv U$, we could have applied to this vector the generating sequence L_y, L_x, and L_{-y} to denominator, constant parameter, and coefficient, respectively.

Maxwell Relations. The generator for the Maxwell relation is the matrix succession C_4^-, σ_y, C_4^+, σ_y, C_4^-, which applied to vector $(1,0) \equiv T$ generates eq 29, i.e., $-(\delta T/\delta V)_S = (\delta P/\delta S)_V$

$$[\delta(1,0)/\delta(1,0)C_4^-]_{(1,0)\sigma_y} = [\delta(1,0)C_4^+/\delta(1,0)\sigma_y]_{(1,0)C_4^-} \tag{28}$$

$$-[\delta(1,0)/\delta(0,1)]_{(-1,0)} = [\delta(0,-1)/\delta(-1,0)]_{(0,1)} \tag{29}$$

while by the aid of the propagating step we obtain the following relations

$$(29)C_4^+: \quad [\delta(0,-1)/\delta(1,0)]_{(0,1)} = [\delta(1,0)/\delta(0,1)]_{(1,0)} \tag{30}$$

$$(30)\sigma_x: \quad [\delta(-1,0)/\delta(0,-1)]_{(1,0)} = -[\delta(0,1)/\delta(1,0)]_{(0,-1)} \tag{31}$$

i.e., $(\delta P/\delta T)_V = (\delta S/\delta V)_T$ and $(\delta S/\delta P)_T = -(\delta V/\delta T)_P$, respectively. The negative sign is given, here, by the s3 sign convention.

The given sign convention, which could be based on x and y directions of diagram 1,[1,2] has the advantage of being more mechanical and avoids continuous reference to any form of diagrams.

CONCLUDING REMARKS

The computational method presented here for thermodynamic relationships based on matrix operations avoids working with figures as much as possible. The entire formalism is unambiguous and, especially, the propagating step is self-explanatory. The construction of the less obvious generating step can be guessed with the help of (i) diagram 1, (ii) the orthogonality rule, and (iii) the fact that only multiplication between two variables results in an energy-dimensioned term. The method presented can be extended to obtain also other, less well-known thermodynamic relationships.

In conclusion, this contribution to the construction of thermodynamic expressions is interesting since as it is a step in deriving a more general computational way to construct any thermodynamic relation with a minimal set of informations, it is not too unwieldy, computationally or conceptually.

REFERENCES AND NOTES

(1) Rodriguez, J.; Brainard, A. A. An Improved Mnemonic Diagram for Thermodynamic Relationships. *J. Chem. Educ.* **1989**, *66*, 495–496.
(2) Pogliani, L.; La Mesa, C. The Mnemonic Diagram for Thermodynamic Relationships. Some Remarks. *J. Chem. Educ.*, in press.
(3) Atkins, P. W. *Physical Chemistry*; Oxford: New York, 1990.