A MNEMONIC APPROACH TO THE CLAUSIUS AND MAXWELL DIFFERENTIAL THERMODYNAMIC RELATIONSHIPS

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Abstract. A simple and explicit mnemonic procedure for the derivation of the set of Maxwell's first order partial derivatives and the Clausius relationships, in terms of fundamental thermodynamic parameters (V, T, P and S), is described with illustrative examples. The procedure has been applied, in the first instance, to thermodynamic systems of constant and variable composition and, later, extended to cover cases of constant volume, temperature, pressure and entropy. All this has been taken up with the aid of a computational procedure based on an instructive logic rather than on a mathematical operational logic.

A formal aspect of thermodynamics deals with Clausius and Maxwell differential relationships that are usually discussed in terms of the Legendre transforms for the Helmholtz energy A, Gibbs energy G, enthalpy H and internal energy E. The Clausius relationships are the complete differentials of the thermodynamic potentials just mentioned, while the Maxwell relationships are first order partial derivatives of the type $(\delta x/\delta y)_z$ where x, y and z are any of the four fundamental parameters V, T, P and S.

A great many such relationships exist, and several mathematical methods are available,[1,2] whereby they may be derived. Also, there have appeared in literature some short-hand approaches to this effect,[3] but rather with a limited scope. Consequently, in view of the formal mathematical or conceptual difficulties inherent in these methods, the student of thermodynamics is seldom successful in either deriving or retaining in memory many of the relationships he too often needs as ready reference. To obviate this, the mnemonic approach presented here (Fig. 1) is designed on the basis of an instructive logic. The computational procedure involved is at once rapid and explicit, and as the experience confirms it goes reasonably well even in inexpert hands. We shall show in a while how this figure embraces quite successfully the whole spectrum of the Clausius and Maxwell relationships for systems of constant and variable composition, extended over to cases of constant volume, temperature, pressure and entropy.

Mapping and Featuring the Mnemonic Figure. The figure lends an easy construction. 'A simple guess verifies how the entry pictures various thermodynamic parameters squarely'. Keeping this key-sentence in mind, and the figure in view, a moment's reflection reveals that the figure may be mapped out in seconds. This follows, of course, by starting anticlockwise from parameter A that the whole sequence in the square arrangement sets in at once, leading finally to the terminal parameter S. And that is all.

In the posture shown, the figure may be conceived as if it were assembled of four geometrically identical trapezoids cemented together along their unparallel sides in a way to inscribe an inset square $VTPS$. For the sake of convenience, we shall name these trapezoids after the respective thermodynamic potentials situated at the mid-point of the outer side. A horizontal line bisects the inset square into an upper positive and a lower negative half; this has been done tentatively with a view to facilitate the assignment of proper signs, positive or negative, to a thermodynamic parameter as that of the half in which it is housed. After these general remarks, we now give a brief account of the essential working principles for writing down the complete set of the Clausius and Maxwell relationships by employing the trapezoids and the inset square respectively.

Writing the Clausius Relationships. The most useful thermodynamic systems are those that have a constant composition (fixed number of moles, N) and are subjected to only a hydrostatic pressure, and in which the work done is of PdV type. The whole of the thermodynamics of systems of this character may be developed by varying, in principle, two of the fundamental variables contained in either of the following variable sets: (i) A, T, V; (ii) G, T, P; (iii) H, S, P; (iv) E, S, V. It may then be conceived that a thermodynamic potential in each of these four sets will depend for its value on the remaining two variables—a fact that provides a direct justification to consider a thermodynamic potential, in a given trapezoid, as a natural function of the two contra-positioned (facing) independent parameters. Hence, we have the following functional expressions:

$$A = A(T,V) \qquad \text{(Trapezoid } A\text{)}$$
$$G = G(T,P) \qquad \text{(Trapezoid } G\text{)}$$
$$H = H(S,P) \qquad \text{(Trapezoid } H\text{)}$$
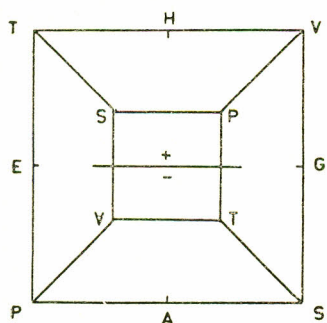$$E = E(S,V) \qquad \text{(Trapezoid } E\text{)}$$

Fig. 1. The mnemonic figure.

Let us start with an obvious example. Suppose we want to write a relationship for the change in internal energy dE in terms of changes in volume dV and entropy dS. In doing so, we would certainly select V and S as the two independent variables in trapezoid E—the flanking parameters P and T, however, are to be appended as coefficients to dV and dS respectively. Recalling that V is negative and S is positive by virtue of our sign convention (*loc. cit*), the trapezoid at once suggests:

$$dE = TdS - PdV \qquad (1)$$

which is the desired Clausius relationship. From these premises now emerges the formal skeleton of the remaining three Clausius relationships applicable to thermodynamic systems of constant composition, namely,

$$dA = -SdT - PdV \qquad (2)$$
$$dG = -SdT + VdP \qquad (3)$$
$$dH = +TdS + VdP \qquad (4)$$

Writing the Maxwell Relationships. The process simply consists in expressing a first order partial derivative of the Maxwellian type in terms of a connective notation manifesting a directional dependence. Accordingly, using an arrow as a connective between any two parameters, the mnemonic version of the partial derivative $(\delta x/\delta y)z$, for instance, would look like $x \rightarrow y$, which represents a directional conjunction between x and y. However, in this mnemonic notation, the parameter z (to be kept constant) has been omitted because of the fact that any such parameter is always placed diagonally, in the mnemonic square, to x and thus can be labelled to the derivative rightaway.

Now, for the purpose of writing the Maxwell relationships, we shall be confining ourselves to equating those conjunctional pairs only that are directionally equivalent, i.e. which connect two unlike parameters in the same parallel direction. Based on this guiding rule—the rule of directional equivalence—the formal structure of the Maxwell relationships can be built up. To exemplify, we consider the thermal expansion of a body at constant pressure; that is to say, we aim at having a Maxwell relation involving $(\delta V/\delta T)_P$. In our mnemonic notation, this partial derivative would look like $V \rightarrow T$, which when equated with its permissible conjunctional equivalent $S \rightarrow P$ will yield the desired result. Thus, within the domain of the rule of directional equivalence, $(\delta V/\delta T)_P = -(\delta S/\delta P)_T$, (constant N), where P and T, held constant, are the diagonal parameters to V and S respectively and the positive and negative signs on the right and left-hand sides of the expression are to be inferred from those of P and T. Likewise, we may have $(\delta V/\delta S)_P = (\delta T/\delta P)_S$; $(\delta S/\delta P)_T = -(\delta V/\delta T)_P$; $(\delta P/\delta T)_V = (\delta S/\delta V)_T$.

As is implied directly, the inset square may as well be utilized alternatively for systems of constant chemical potential, μ. In this context we could have: $T \rightarrow V = P \rightarrow S$; $S \rightarrow V = P \rightarrow T$; $T \rightarrow P = V \rightarrow S$.

Extending to other Systems. The Clausius relationships for systems of constant composition may be
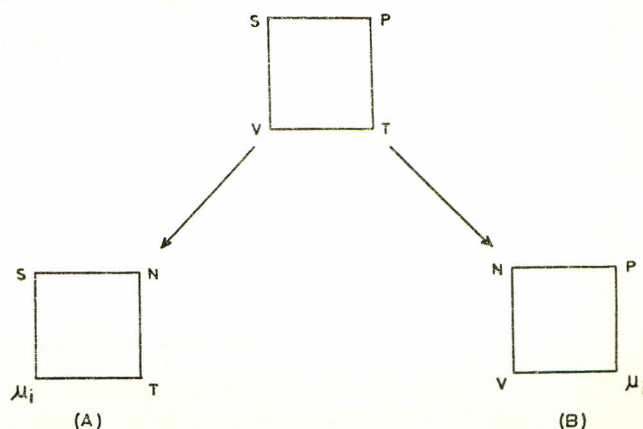

Fig. 2. The transformed squares: (A) for systems at constant 'P' and or V; (B) for system at constant S or T.

adapted easily for those of variable composition by simply adding to them the summation term $\Sigma \mu_i dN_i$. For example, $dE, = TdS - PdV + \Sigma \mu_i dN_i$, and so on for the remaining relations of the Clausius set. For the Maxwell relations, the inset square may be effectively transformed, in the first instance, through the diagonal displacement of the parameters P and V and, later, through that of S and T, into two postures as shown explicitly in Fig. 2.

Now, referring to these transformed squares (A) and (B), and keeping track of the procedure laid down before, we may summarize the Maxwell relations under constraint of constant pressure, volume, temperature or entropy as specified against each:

Square (A)

Constant P	Constant V
$T \rightarrow N = \mu_i \rightarrow S$	$T \rightarrow N = \mu_i \rightarrow S$
$S \rightarrow N = \mu_i \rightarrow T$	$S \rightarrow N = \mu_i \rightarrow T$
$T \rightarrow \mu_i = N \rightarrow S$	$T \rightarrow \mu_i = N \rightarrow S$
	$S \rightarrow \mu_i = N \rightarrow T$

Square (B)

Constant S	Constant T
$P \rightarrow N = \mu_i \rightarrow V$	$P \rightarrow N = \mu_i \rightarrow V$
$V \rightarrow N = \mu_i \rightarrow P$	$V \rightarrow N = \mu_i \rightarrow P$
$P \rightarrow \mu_i = N \rightarrow V$	$P \rightarrow \mu_i = N \rightarrow V$
$V \rightarrow \mu_i = N \rightarrow P$	

References

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3. F.O. Koening, J. Chem. Phy., **3**, 29 (1935).