Metric geometry of equilibrium thermodynamics. V. Aspects of heterogeneous equilibrium

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The general analysis of phase equilibrium in heterogeneous systems is considered from an abstract geometric point of view. Particular attention is drawn to the thermodynamic "invariants" (or "symmetries"), which arise as null eigenvectors of the thermodynamic metric matrix and can be associated with variations which leave the thermodynamic state unchanged. The analysis of these invariants leads to conditions connecting the thermodynamic field vectors, including Gibbs–Duhem relations, Clausius–Clapeyron equations, Gibbs–Konowalow laws, and systematic generalizations thereof.

I. INTRODUCTION

In foregoing papers,[1-4] a geometric representation of equilibrium thermodynamics has been proposed in which properties of a thermal system are deduced from its geometrical "image" in an abstract Euclidean vector space. While the basic features of this formalism are quite general, attention was often restricted for the sake of simplicity to systems that are completely homogeneous. The thermodynamics of systems consisting of two or more distinct phases introduces certain additional features which it is now our purpose to describe from the geometric vantage point. The vector- and matrix-algebraic techniques of the abstract geometric representation permit one to derive a number of extensions of the classical Gibbsian analysis of heterogeneous equilibrium,[5] particularly in respect to complex multicomponent systems.

II. THERMODYNAMIC INVARIANCE IN HETEROGENEOUS EQUILIBRIUM

A thermodynamic system consisting of c independent chemical components and ν distinct phases will be associated in the usual manner[3] with a metric space $\mathfrak{M}_r$ of dimension $r = c - \nu + 2$, in accordance with Gibbs' phase rule. Reference extensities X_i will be chosen from entropy S, volume V, and mole numbers N_i, $i = 1, 2, \ldots, c$,

$$\{X_i\} = \{S, V, N_1, N_2, \ldots, N_c\}, \tag{2.1}$$

while the associated reference field variables R_i are temperature T, (negative) pressure $-P$, and chemical potentials μ_i, $i = 1, 2, \ldots, c$, respectively,

$$\{R_i\} = \{T, -P, \mu_1, \mu_2, \ldots, \mu_c\}. \tag{2.2}$$

These $c + 2$ fields and extensities are conjugate in the usual sense,

$$R_i = (\partial U / \partial X_i)_{\mathbf{X}}, \qquad i = 1, 2, \ldots, c+2, \tag{2.3}$$

through the thermodynamic potential U, the internal energy. Numerical values attained by X_i for the particular state in question will be labeled ξ_i. In addition, we let $X_i^{(\lambda)}$ denote the extensive variable belonging to the isolated λth phase, with associated numerical value $\xi_i^{(\lambda)}$. We suppose in the usual manner[6] that the phases are so large, and of such a shape, that surface and interfacial effects can be neglected relative to bulk–volume effects, so that

$$X_i = \sum_{\lambda=1}^{\nu} X_i^{(\lambda)}, \qquad \xi_i = \sum_{\lambda=1}^{\nu} \xi_i^{(\lambda)}. \tag{2.4}$$

Each $\xi_i^{(\lambda)}$ ($i = 1, 2, \ldots, c+2$) is in turn proportional to the total extent of phase λ (for example, to its volume) in accordance with the assumed extensive character of these variables.

Because our treatment has heretofore ascribed to the Gibbs phase rule the role of a primary empirical law, the extensive character of the variables X_i (or, rather, a form of generalized homogeneity property of the thermodynamic potential U with respect to these variables) could be deduced as a consequence.[2] However, one could equally well follow the traditional track in taking as empirical laws (i) the bivariant ($r = 2$) character of a simple homogeneous fluid, and (ii) the extensive property of U and of each X_i; from these assumptions the full phase rule, $r = c - \nu + 2$, results as a deduction, as is well known. For present purposes, the distinction between these formal orderings is unimportant, and we proceed on the usual basis that both the phase rule and the extensive character of each X_i represent established empirical facts.

With the $c + 2$ fields R_i of Eq. (2.3) we may associate corresponding vectors $|\mathfrak{R}_i\rangle$ of $\mathfrak{M}_r$,

$$dR_i \leftarrow |\mathfrak{R}_i\rangle, \qquad i = 1, 2, \ldots, c+2 \tag{2.5}$$

and a corresponding Gram (metric) matrix $\mathbf{G}^{(c+2)}$ of order $c + 2$,

$$(\mathbf{G}^{(c+2)})_{ij} = \langle \mathfrak{R}_i | \mathfrak{R}_j \rangle, \qquad i, j = 1, 2, \ldots, c+2, \tag{2.6}$$

where, as usual,

$$\langle \mathfrak{R}_i | \mathfrak{R}_j \rangle = (\partial R_i / \partial X_j)_{\mathbf{X}}. \tag{2.7}$$

The dimensionality r is reflected in the rank (number of nonzero eigenvalues) of the Gram matrix,

$$r = \mathrm{rank}(\mathbf{G}^{(c+2)}) = c - \nu + 2, \tag{2.8}$$

thereby showing that $\mathbf{G}^{(c+2)}$ has exactly ν null eigenvectors which we denote by $\boldsymbol{\eta}^{(\lambda)}$, $\lambda = 1, 2, \ldots, \nu$,

$$\mathbf{G}^{(c+2)} \boldsymbol{\eta}^{(\lambda)} = 0, \qquad \lambda = 1, 2, \ldots, \nu. \tag{2.9}$$

Of course, any linear combination of these ν vectors is still a solution of Eq. (2.9), so that the final choice of ν such linearly independent null eigenvectors is to this extent a matter of convenience.

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Let us examine the effect of a thermodynamic "change" in which each X_i is altered by an amount proportional to the corresponding component of $\eta^{(\lambda)}$,

$$dX_i \propto \eta_i^{(\lambda)}, \qquad i = 1, 2, \ldots, c+2 . \tag{2.10}$$

The usual expression for the associated field changes dR_i,

$$dR_i = \sum_{j=1}^{c+2} \left(\frac{\partial R_i}{\partial X_j} \right)_{\mathbf{X}} dX_j , \tag{2.11}$$

then shows, in conjunction with (2.9), that each $dR_i = 0$, and thus that no change of thermodynamic state occurs in the process described by Eq. (2.10). For this reason it is natural to refer to the vectors $\eta^{(\lambda)}$ as *invariants* (or *symmetries*) of the thermodynamic system, since they correspond to operations (displacements of the X_i) which produce no response in any of the field variables R_i, and thus leave the thermodynamic state unaltered.[7] A familiar example is the uniform scaling of each X_i by an arbitrary positive constant,

$$dX_i = \lambda X_i = \lambda \xi_i , \tag{2.12}$$

which merely leads to a larger or smaller sample of the same thermodynamic state, and is thus without thermodynamic significance. The invariant of Eq. (2.12) was associated in Ref. 2 with the ordinary Gibbs–Duhem equation, but we now wish to consider in a systematic manner those additional invariants $\eta^{(\lambda)}$ which arise in multiphase equilibria. As shown by Eq. (2.9), each such invariant leads to a linear combination of field vectors which vanishes identically in $\mathfrak{M}_r$,

$$\sum_{i=1}^{c+2} \eta_i^{(\lambda)} |R_i\rangle = 0, \qquad \lambda = 1, 2, \ldots, \nu , \tag{2.13}$$

reflecting the linear dependence of the $c+2$ vectors in the r-dimensional space.

In accordance with Eq. (2.8), it will be possible to choose a nonsingular principal submatrix $\mathbf{G} = \mathbf{G}^{(r)}$ of order r from $\mathbf{G}^{(c+2)}$,

$$(\mathbf{G})_{ij} = \langle R_i | R_j \rangle, \qquad i, j = 1, 2, \ldots, r , \tag{2.14a}$$

$$G = \det |\mathbf{G}| \neq 0 . \tag{2.14b}$$

The ν extensities $X_{c-\nu+1}, \ldots, X_{c+2}$ thereby deleted from consideration will be regarded as scale factors having fixed values in all thermodynamic derivatives, thus effectively suppressing the spurious degrees of freedom associated with the invariants $\eta^{(\lambda)}$. The remaining r vectors $|R_i\rangle$ permit the construction of the conjugate basis $|\bar{R}_i\rangle$, satisfying

$$\langle \bar{R}_i | R_j \rangle = \delta_{ij}, \qquad i, j = 1, 2, \ldots, r . \tag{2.15}$$

The conjugate vectors represent the conjugate extensities X_i in the manner of Eq. (2.5),

$$dX_i \rightarrow |\bar{R}_i\rangle = |X_i\rangle, \qquad i = 1, 2, \ldots, r , \tag{2.16}$$

and give rise to the conjugate Gram matrix $\bar{\mathbf{G}}$,

$$(\bar{\mathbf{G}})_{ij} = (\mathbf{G}^{-1})_{ji} = \langle \bar{R}_i | \bar{R}_j \rangle = \left(\frac{\partial X_i}{\partial R_j} \right)_{\mathbf{R}}, \qquad i, j = 1, 2, \ldots, r . \tag{2.17}$$

Of course, the subscript $\mathbf{R}$ in Eq. (2.17) denotes constancy of the $r - 1$ R_k's $(k \neq j)$, *and* of the ν scale factors $X_{c-\nu+1}, \ldots, X_{c+2}$, during the partial differentiation.

III. NATURE OF THE THERMODYNAMIC INVARIANTS

The physical significance of the ν thermodynamic invariants $\eta^{(\lambda)}$, $\lambda = 1, 2, \ldots, \nu$, can be appreciated in a simple manner. As was shown in Ref. 2, the invariant $\eta^{(1)}$ associated with the usual extensive property of each (total) X_i and of (total) U has the elements

$$(\eta^{(1)})_i = \xi_i, \qquad i = 1, 2, \ldots, c+2 . \tag{3.1}$$

This equation shows, as was noted in connection with Eq. (2.12), that multiplication of each X_i by a common proportionality factor merely scales the over-all size of the system, but does not change its thermodynamic state. The spurious "degree of freedom" associated with such scaling can be suppressed by fixing some X_i as a scale factor. The invariant (3.1) may be referred to as a "Gibbs–Duhem invariant" to suggest its close association with this ordinary form of scaling.

For simplicity, suppose now that we consider a two-phase system of one chemical component $(c = r = 1, \nu = 2)$, and that the total mass N is chosen as the initial scale factor $X_{r+2} = X_3$ to suppress the Gibbs–Duhem invariant $\eta^{(1)}$. The remaining two extensities $X_1 = S$, $X_2 = V$ must still harbor an additional invariant $\eta^{(2)}$, whose physical origin can be seen in Fig. 1. The figure shows two samples of the same two-phase thermodynamic system which have been arranged to have the same total N, but different S and V. We can write changes in S, V, N in terms of changes in the separate liquid (1) or gaseous (g) phases as

$$\Delta S = \Delta S_1 + \Delta S_g ,$$

$$\Delta V = \Delta V_1 + \Delta V_g , \tag{3.2}$$

$$\Delta N = \Delta N_1 + \Delta N_g .$$

However, the allowed changes that connect these two samples must be such as to maintain constant molar volumes and entropies in each phase, e.g., must be such as to alter the extent, but not the state, of either phase; therefore,
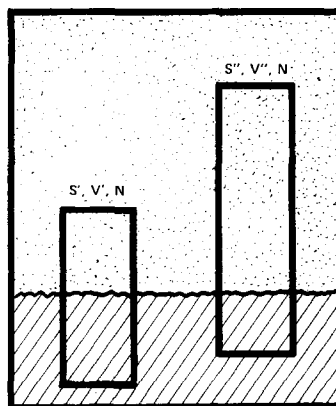

FIG. 1. Two heterogeneous "samples" (of the *same* equilibrium state) having a common value of N, but different values of S and V; interconversion of such samples is not regarded as having thermodynamic significance.

$$\frac{\Delta S_1}{\Delta N_1} = \frac{S_1}{N_1}, \qquad \frac{\Delta S_g}{\Delta N_g} = \frac{S_g}{N_g},$$

$$\frac{\Delta V_1}{\Delta N_1} = \frac{V_1}{N_1}, \qquad \frac{\Delta V_g}{\Delta N_g} = \frac{V_g}{N_g}, \tag{3.3}$$

$$\Delta N = \Delta N_1 + \Delta N_g = 0.$$

With these restrictions, Eqs. (3.2) are

$$\Delta S = \frac{\Delta N_1}{N_1 N_g}(N_g S_1 - N_1 S_g),$$

$$\Delta V = \frac{\Delta N_1}{N_1 N_g}(N_g V_1 - N_1 V_g), \tag{3.4}$$

$$\Delta N = 0.$$

In accordance with Eq. (2.10), the second invariant can therefore be taken as

$$\eta^{(2)} = \begin{pmatrix} N_g S_1 - N_1 S_g \\ N_g V_1 - N_1 V_g \\ 0 \end{pmatrix}, \tag{3.5}$$

whereas the Gibbs–Duhem invariant is, in this same notation,

$$\eta^{(1)} = \begin{pmatrix} S_1 + S_g \\ V_1 + V_g \\ N_1 + N_g \end{pmatrix}. \tag{3.6}$$

Note that the second invariant $\eta^{(2)}$ does not correspond directly to any simple homogeneity or "scaling" property of the thermodynamic potential U (as did $\eta^{(1)}$). Nevertheless, the results of Ref. 2 show that Eqs. (2.9), (2.13) might have been interpreted as arising from some *generalized* homogeneous behavior of the thermodynamic potentials. Such an interpretation, however, tends to obscure the simple physical origin of the symmetry associated with $\eta^{(2)}$.

Since linear combinations of invariants are themselves invariants, we may prefer, instead of (3.5) and (3.6), to work with the combinations $\eta^{(1)}$, $\eta^{(g)}$ defined as

$$\eta^{(1)} = \frac{1}{N_1 + N_g}(N_1 \eta^{(1)} + \eta^{(2)}) = \begin{pmatrix} S_1 \\ V_1 \\ N_1 \end{pmatrix}, \tag{3.7a}$$

$$\eta^{(g)} = \frac{1}{N_1 + N_g}(N_g \eta^{(1)} - \eta^{(2)}) = \begin{pmatrix} S_g \\ V_g \\ N_g \end{pmatrix}. \tag{3.7b}$$

Comparing with (3.1), we recognize that $\eta^{(1)}$ and $\eta^{(g)}$ have the form of Gibbs–Duhem-like invariants for the individual phases 1 and g, but the vector equations (2.13) to which they give rise refer now to field vectors of the *composite* system rather than to those of individual phases.

The foregoing arguments can evidently be extended to the general case of ν phases, with the result

$$(\eta^{(\lambda)})_i = \xi_i^{(\lambda)}, \qquad \lambda = 1, 2, \ldots, \nu, \qquad i = 1, 2, \ldots, c+2. \tag{3.8}$$

Thus, the ν invariants of the full Gram matrix $\mathbf{G}^{(c+2)}$ arise in a simple manner from ordinary homogeneity properties of the individual phases, and Eq. (2.13) becomes a set of ν vector equations connecting field vectors $|\mathfrak{R}_i\rangle$ of the composite system,

$$\sum_{i=1}^{c+2} \xi_i^{(\lambda)}|\mathfrak{R}_i\rangle = 0, \qquad \lambda = 1, 2, \ldots, \nu, \tag{3.9}$$

which may be compared with geometric Gibbs–Duhem equations for the individual phases,[2]

$$\sum_{i=1}^{c+2} \xi_i^{(\lambda)}|\mathfrak{R}_i^{(\lambda)}\rangle = 0, \qquad \lambda = 1, 2, \ldots, \nu, \tag{3.10}$$

written in terms of the field vectors $|\mathfrak{R}_i^{(\lambda)}\rangle$ of phase λ. Equations (3.9) are the key vector relationships characteristic of heterogeneous equilibrium.

For completeness, we give the form of Eq. (2.13) for the special invariant of Eq. (3.5),

$$\sum_{i=1}^{c+2} (\xi_{c+2}^{(1)}\xi_i^{(2)} - \xi_{c+2}^{(2)}\xi_i^{(1)})|\mathfrak{R}_i\rangle = 0, \tag{3.11}$$

noting that this form applies specifically to a two-phase system with X_{c+2} as scale factor. Of course, Eq. (3.11) is itself a ready consequence of (3.9), as we should expect. Generalizations of Eq. (3.11) for $\nu > 2$ will be derived in a more convenient form in Sec. IV.E.

IV. COEXISTENCE CONDITIONS FOR MULTIPHASE EQUILIBRIA

A. Vector equations among field vectors in composite systems

The general equations (3.9) imply certain connections among the thermodynamic field variables when two or more phases are in coexistence. To derive these relationships, we introduce a special notation for the ν "excess" fields $|\hat{\mathfrak{R}}_\kappa\rangle$,

$$|\hat{\mathfrak{R}}_\kappa\rangle \equiv |\mathfrak{R}_{r+\kappa}\rangle, \qquad \kappa = 1, 2, \ldots, \nu \tag{4.1}$$

and the associated "excess" extensive values $\hat{\xi}_\kappa^{(\lambda)}$,

$$\hat{\xi}_\kappa^{(\lambda)} \equiv \xi_{r+\kappa}^{(\lambda)}, \qquad \kappa = 1, 2, \ldots, \nu \tag{4.2}$$

to distinguish them from the basis fields $|\mathfrak{R}_i\rangle$ and extensive values $\xi_i^{(\lambda)}$, $i = 1, 2, \ldots, r$. The excess extensities $\hat{\xi}_\kappa^{(\lambda)}$ are the "scale factors" of the composite system, and may be exhibited in a $\nu \times \nu$ scale-factor matrix $\hat{\mathbf{L}}$,

$$(\hat{\mathbf{L}})_{\lambda\kappa} = \hat{\xi}_\kappa^{(\lambda)}, \qquad \kappa, \lambda = 1, 2, \ldots, \nu, \tag{4.3}$$

while the basis extensities $\xi_i^{(\lambda)}$ are similarly arranged in a $\nu \times r$ matrix $\mathbf{L}$,

$$(\mathbf{L})_{\lambda i} = \xi_i^{(\lambda)}, \qquad \lambda = 1, 2, \ldots, \nu, \qquad i = 1, 2, \ldots, r. \tag{4.4}$$

Equations (3.9) thereby become

$$\sum_{i=1}^{r} (\mathbf{L})_{\lambda i}|\mathfrak{R}_i\rangle + \sum_{\kappa=1}^{\nu} (\hat{\mathbf{L}})_{\lambda\kappa}|\hat{\mathfrak{R}}_\kappa\rangle = 0 \tag{4.5}$$

for each $\lambda = 1, 2, \ldots, \nu$.

If $\hat{\mathbf{L}}$ is nonsingular, the ν homogeneous, linear vector equations (4.5) can be solved immediately for the ν excess fields $|\hat{\mathfrak{R}}_\kappa\rangle$ in terms of the chosen independent set $|\mathfrak{R}_i\rangle$ of r basis fields. When each of the vector equations (4.5) is multiplied by $(\hat{\mathbf{L}}^{-1})_{\kappa'\lambda}$ and summed over λ,

there results

$$|\hat{\mathfrak{R}}_\kappa\rangle = - \sum_{i=1}^{r} (\gamma)_{\kappa i} |\mathfrak{R}_i\rangle, \qquad \kappa = 1, 2, \ldots, \nu, \qquad (4.6)$$

where the *coexistence coefficients* $(\gamma)_{\kappa i}$ are given by

$$\gamma = \hat{\mathbf{L}}^{-1}\mathbf{L}. \qquad (4.7)$$

The solution (4.6), (4.7) cannot be used directly if $\hat{\mathbf{L}}$ is singular, but in this case the chosen $|\mathfrak{R}_i\rangle$ represent an improper set of "reference fields" which fail to span the r-dimensional space. Indeed, the requirement

$$\det |\hat{\mathbf{L}}| \neq 0 \qquad (4.8)$$

is a necessary condition for the linear independence of the $|\mathfrak{R}_i\rangle$, as can be seen by multiplying each equation λ of (4.5) by the λth element of any proposed null eigenvector of $\hat{\mathbf{L}}$ and summing over λ. Thus, if condition (4.8) seems to fail, it is only necessary to renumber the fields (that is, make some new division into "reference" and "excess" fields) to make (4.6)–(4.8) valid.

B. General form of the coexistence coefficients

The explicit solution (4.7) can be brought to a useful alternative form after introducing the expression for the inverse scale-factor matrix,

$$(\hat{\mathbf{L}}^{-1})_{\lambda\kappa} = \hat{L}_{\kappa\lambda}^{\text{cof}}/\det |\hat{\mathbf{L}}| \qquad (4.9)$$

($\hat{L}_{\kappa\lambda}^{\text{cof}}$ denoting the cofactor of the $\kappa\lambda$ element of $\hat{\mathbf{L}}$), to obtain

$$(\gamma)_{\lambda i} = \det |\hat{\mathbf{L}}|^{-1} \sum_{\kappa=1}^{\nu} \xi_i^{(\kappa)} \hat{L}_{\lambda\kappa}^{\text{cof}}. \qquad (4.10)$$

The summation on the right-hand side of Eq. (4.10) can then be recognized as the expansion (down the λth column) of a determinant which is like $\det |\hat{\mathbf{L}}|$ except that each $(\hat{\mathbf{L}})_{\kappa\lambda}$ is replaced by $\xi_i^{(\kappa)}$ in column λ. If we now let $\mathbf{1}_i$, $\hat{\mathbf{1}}_\kappa$ denote ν-component column vectors (columns of $\mathbf{L}$ and $\hat{\mathbf{L}}$) whose successive components are labeled by the (superscript) phase numbers,

$$\mathbf{1}_i = \begin{pmatrix} \xi_i^{(1)} \\ \xi_i^{(2)} \\ \vdots \\ \xi_i^{(\nu)} \end{pmatrix} \qquad \hat{\mathbf{1}}_\kappa = \begin{pmatrix} \hat{\xi}_\kappa^{(1)} \\ \hat{\xi}_\kappa^{(2)} \\ \vdots \\ \hat{\xi}_\kappa^{(\nu)} \end{pmatrix}, \qquad (4.11)$$

these two determinants can be written in an obvious notation as

$$\det |\hat{\mathbf{L}}| = \det |\hat{\mathbf{1}}_1 \hat{\mathbf{1}}_2 \cdots \hat{\mathbf{1}}_\nu|,$$

$$\sum_{\kappa=1}^{\nu} \xi_i^{(\kappa)} \hat{L}_{\lambda\kappa}^{\text{cof}} = \det |\hat{\mathbf{1}}_1 \cdots \hat{\mathbf{1}}_{\lambda-1} \mathbf{1}_i \hat{\mathbf{1}}_{\lambda+1} \cdots \hat{\mathbf{1}}_\nu|.$$

Such expressions lead us to represent Eq. (4.10) in a somewhat symbolic form,

$$(\gamma)_{\lambda i} = \frac{\det |\hat{\mathbf{1}}_1 \cdots \hat{\mathbf{1}}_{\lambda-1} \mathbf{1}_i \hat{\mathbf{1}}_{\lambda+1} \cdots \hat{\mathbf{1}}_\nu|}{\det |\hat{\mathbf{1}}_1 \hat{\mathbf{1}}_2 \cdots \hat{\mathbf{1}}_\nu|}, \qquad (4.12)$$

which is the desired solution. According to this expression, the coexistence coefficient $(\gamma)_{\lambda i}$ is found by replacing the λth column of $\hat{\mathbf{L}}$ by the ith column of $\mathbf{L}$ and evaluating a ratio of substituted and unsubstituted determinants. An explicit alternative representation can be

written in terms of the antisymmetrizer operator $\mathfrak{a}$, which works on superscript phase labels according to the prescription

$$\mathfrak{a}\{A^{(1)}B^{(2)} \cdots Z^{(\nu)}\} \equiv \det \begin{vmatrix} A^{(1)} & B^{(1)} \cdots Z^{(1)} \\ A^{(2)} & B^{(2)} \cdots Z^{(2)} \\ \vdots & \vdots & \vdots \\ A^{(\nu)} & B^{(\nu)} \cdots Z^{(\nu)} \end{vmatrix} \qquad (4.13)$$

for a general product $A^{(1)}B^{(2)} \cdots Z^{(\nu)}$; the solution (4.12) is then

$$(\gamma)_{\lambda i} = \frac{\mathfrak{a}\{\xi_i^{(\lambda)} \Pi_{\kappa \neq \lambda}^{\nu} \hat{\xi}_\kappa^{(\kappa)}\}}{\mathfrak{a}\{\Pi_\kappa^{\nu} \hat{\xi}_\kappa^{(\kappa)}\}} \qquad (4.14)$$

valid for each $\lambda = 1, 2, \ldots, \nu$ and each $i = 1, 2, \ldots, r$.

C. Slopes of coexistence curves: Generalized Clausius-Clapeyron equations

The coexistence conditions (4.6), which express the κth excess field $|\hat{\mathfrak{R}}_\kappa\rangle$ in terms of chosen basis fields $|\mathfrak{R}_i\rangle$, can also be written in terms of the conjugate vectors $|\bar{\mathfrak{R}}_i\rangle = |\mathfrak{X}_i\rangle$. With the usual formula [cf. Eq. (3.2) of Ref. 3]

$$|\mathfrak{R}_i\rangle = \sum_{j=1}^{r} (\mathbf{G})_{ij} |\mathfrak{X}_j\rangle, \qquad (4.15)$$

one obtains

$$|\hat{\mathfrak{R}}_\kappa\rangle = - \sum_{i=1}^{r} (\gamma\mathbf{G})_{\kappa i} |\mathfrak{X}_i\rangle, \qquad \kappa = 1, 2, \ldots, \nu. \qquad (4.16)$$

Scalar products of each $|\hat{\mathfrak{R}}_\kappa\rangle$ with the basis fields $|\mathfrak{R}_i\rangle$ and conjugates $|\mathfrak{X}_i\rangle$ can then be evaluated with ease from Eqs. (4.6), (4.16) and the biorthogonality relation (2.15). One obtains immediately

$$\langle \mathfrak{X}_i | \hat{\mathfrak{R}}_\kappa\rangle = \left(\frac{\partial R_{r+\kappa}}{\partial R_i}\right)_\mathbf{R} = - (\gamma)_{\kappa i}, \qquad (4.17)$$

$$\langle \mathfrak{R}_i | \hat{\mathfrak{R}}_\kappa\rangle = \left(\frac{\partial R_{r+\kappa}}{\partial X_i}\right)_\mathbf{X} = - (\gamma\mathbf{G})_{\kappa i}, \qquad (4.18)$$

for all $\kappa = 1, 2, \ldots \nu$, and $i = 1, 2, \ldots, r$. Similarly, the scalar products among the excess fields $|\hat{\mathfrak{R}}_\kappa\rangle$, $|\hat{\mathfrak{R}}_\lambda\rangle$ become (for $\kappa, \lambda = 1, 2, \ldots, \nu$)

$$\langle \hat{\mathfrak{R}}_\kappa | \hat{\mathfrak{R}}_\lambda\rangle = \left(\frac{\partial R_{r+\kappa}}{\partial X_{r+\lambda}}\right)_\mathbf{X} = \left(\frac{\partial R_{r+\lambda}}{\partial X_{r+\kappa}}\right)_\mathbf{X} = (\gamma\mathbf{G}\gamma^t)_{\kappa\lambda}. \qquad (4.19)$$

With the explicit forms (4.12) or (4.14) for the γ coefficients, Eqs. (4.17)–(4.19) become convenient formulas for the slopes of coexistence lines in general phase diagrams, valid for thermodynamic systems of arbitrary numbers of phases and arbitrary chemical complexity. Notice in particular that the derivatives (4.17) among field variables can be evaluated solely in terms of the coexistence coefficients (i.e., in terms of extensive properties $\xi_i^{(\lambda)}$ of the separate phases) without reference to any response functions of the metric matrix $\mathbf{G}$. It would be interesting to examine experimental thermochemical data with the help of such formulas in order to test their compatibility with broad thermodynamic principles.

D. Some special cases

It may be of use to examine the forms assumed by the above equations in a few important special cases:

For the trivial case $\nu = 1$ of a homogeneous system, Eq. (4.14) reduces to

$$(\gamma)_{1i} = \frac{\xi_i}{\xi_{r+1}}, \qquad i = 1, 2, \ldots, r, \tag{4.20}$$

and Eq. (4.6) merely recovers the vector form of the Gibbs–Duhem equation for the single phase, as we should anticipate

For a pure two-phase system ($\nu = 2$, $r = c = 1$), we may choose variables in the usual manner as

$$R_1 = T, \qquad R_2 = -P, \qquad R_3 = \mu,$$
$$X_1 = S, \qquad X_2 = V, \qquad X_3 = N. \tag{4.21}$$

Equation (4.14) then becomes

$$(\gamma)_{11} = \frac{\begin{vmatrix} S^{(1)} & N^{(1)} \\ S^{(2)} & N^{(2)} \end{vmatrix}}{\begin{vmatrix} V^{(1)} & N^{(1)} \\ V^{(2)} & N^{(2)} \end{vmatrix}}, \qquad (\gamma)_{21} = \frac{\begin{vmatrix} V^{(1)} & S^{(1)} \\ V^{(2)} & S^{(2)} \end{vmatrix}}{\begin{vmatrix} V^{(1)} & N^{(1)} \\ V^{(2)} & N^{(2)} \end{vmatrix}}, \tag{4.22}$$

and Eqs. (4.17) are therefore simply

$$\frac{dP}{dT} = \frac{S^{(1)}N^{(2)} - N^{(1)}S^{(2)}}{V^{(1)}N^{(2)} - N^{(1)}V^{(2)}}, \tag{4.23a}$$

$$\frac{d\mu}{dT} = \frac{S^{(1)}V^{(2)} - V^{(1)}S^{(2)}}{V^{(1)}N^{(2)} - N^{(1)}V^{(2)}}. \tag{4.23b}$$

The first of these can be recognized as the ordinary *Clausius–Clapeyron* equation, while the second is an analogous equation determining the slope of the coexistence curve in the μT plane. These equations in turn imply the slope of the coexistence line in the μP plane,

$$\frac{d\mu}{dP} = \frac{S^{(1)}V^{(2)} - V^{(1)}S^{(2)}}{S^{(1)}N^{(2)} - N^{(1)}S^{(2)}}. \tag{4.23c}$$

Another special case arises in univariant systems, $r = 1$, where the number of phases ν is one greater than the number c of components. For this case Gibbs found the explicit determinantal solution,[8]

$$\frac{dP}{dT} = \frac{\begin{vmatrix} S^{(1)} & N_1^{(1)} \cdots N_c^{(1)} \\ S^{(2)} & N_1^{(2)} \cdots N_c^{(2)} \\ \cdot & \cdot \quad\quad \cdot \\ \cdot & \cdot \quad\quad \cdot \\ S^{(\nu)} & N_1^{(\nu)} \cdots N_c^{(\nu)} \end{vmatrix}}{\begin{vmatrix} V^{(1)} & N_1^{(1)} \cdots N_c^{(1)} \\ V^{(2)} & N_1^{(2)} \cdots N_c^{(2)} \\ \cdot & \cdot \quad\quad \cdot \\ \cdot & \cdot \quad\quad \cdot \\ V^{(\nu)} & N_1^{(\nu)} \cdots N_c^{(\nu)} \end{vmatrix}}, \tag{4.24}$$

which is precisely the form given by Eqs. (4.17), (4.12). The Clapeyron Eq. (4.23a) is itself the simplest instance of this result for $c = 1$.

E. Stationary fields and Gibbs–Konowalow laws

The equations (4.6) show how any $r + 1$ of the field vectors are related in the heterogeneous equilibrium of ν

phases. Let us now assume for definiteness that these are labeled

$$|\mathfrak{R}_1\rangle, |\mathfrak{R}_2\rangle, \ldots, |\mathfrak{R}_{r+1}\rangle$$

and write for η_i the $\nu \times \nu$ determinant

$$\eta_i \equiv \det \begin{vmatrix} \xi_i^{(1)} & \xi_{r+2}^{(1)} & \xi_{r+3}^{(1)} \cdots \xi_{c+2}^{(1)} \\ \xi_i^{(2)} & \xi_{r+2}^{(2)} & \xi_{r+3}^{(2)} \cdots \xi_{c+2}^{(2)} \\ \cdot & \cdot & \cdot \quad\quad \cdot \\ \cdot & \cdot & \cdot \quad\quad \cdot \\ \cdot & \cdot & \cdot \quad\quad \cdot \\ \xi_i^{(\nu)} & \xi_{r+2}^{(\nu)} & \xi_{r+3}^{(\nu)} \cdots \xi_{c+2}^{(\nu)} \end{vmatrix}. \tag{4.25}$$

This permits one to write each of Eqs. (4.6) in the more symmetrical form

$$\sum_{i=1}^{r+1} \eta_i |\mathfrak{R}_i\rangle = 0, \tag{4.26}$$

as can be easily verified from the form (4.12) of the coexistence coefficients. Equation (4.26) is obviously related closely to the ordinary Gibbs–Duhem equation, to which it formally reduces when $\nu = 1$, and might be applied to examine the consistency of thermodynamic data in an analogous manner.[9]

By virtue of their additional invariants, multiphase systems can exhibit an interesting variety of behavior which is not possible in homogeneous systems. In particular, the determinantal coefficients η_i can take on either sign or can vanish identically when the phase compositions have certain special values. According to Eq. (4.25), η_i must vanish whenever the determinantal row or column vectors become linearly dependent, e.g., when there exists some linear combination Y of the variables $X_{r+2}, X_{r+3}, \ldots, X_{c+2}$ such that $Y^{(\lambda)} = \xi_i^{(\lambda)}$ for every phase λ. Thus, for example, when $\nu = 2$, η_i will vanish when values of ξ_i and ξ_{c+2} are proportional in the two phases. The vanishing of η_i signals a type of redundancy of the extensive variable X_i, as though the system could be prepared from one fewer chemical component than had been supposed. However, the vanishing of an η_i could arise from such special linear relationships connecting entropies or volumes, as well as the composition variables.

To see the consequences of some vanishing η_i, let us introduce a new set of r fields $|\tilde{\mathfrak{R}}_i\rangle$ which coincides with the old but for a single member $|\mathfrak{z}\rangle$,

$$|\tilde{\mathfrak{R}}_i\rangle = |\mathfrak{R}_i\rangle, \qquad i = 1, 2, \ldots, r-1$$
$$|\tilde{\mathfrak{R}}_r\rangle = |\mathfrak{z}\rangle, \tag{4.27}$$

where $|\mathfrak{z}\rangle$ is arbitrary so long as the resulting set is complete. By "complete" we mean of course that the $|\tilde{\mathfrak{R}}_i\rangle$ should span all r dimensions; whether this is so may in turn be checked by examining the rank of the associated Gram matrix,

$$\text{rank}\{\langle\tilde{\mathfrak{R}}_i|\tilde{\mathfrak{R}}_j\rangle\} = r. \tag{4.28}$$

Thus, the $r - 1$ vectors $|\mathfrak{R}_1\rangle, \ldots, |\mathfrak{R}_{r-1}\rangle$ must themselves span $r - 1$ dimensions. In view of (4.28) we may now introduce the associated conjugate vectors $|\tilde{\mathfrak{x}}_i\rangle$ satisfying

$$\langle\tilde{\mathfrak{R}}_i|\tilde{\mathfrak{x}}_j\rangle = \delta_{ij}. \tag{4.29}$$

Multiplying Eq. (4.26) on the left by some $\langle \tilde{\mathfrak{X}}_j |$, one then obtains

$$0 = \sum_{i=1}^{r-1} \eta_i \delta_{ij} + \eta_r \langle \tilde{\mathfrak{X}}_j | \mathfrak{R}_r \rangle + \eta_{r+1} \langle \tilde{\mathfrak{X}}_j | \mathfrak{R}_{r+1} \rangle, \qquad (4.30)$$

and in particular for $j = r$,

$$0 = \eta_r \langle \overline{\mathfrak{z}} | \mathfrak{R}_r \rangle + \eta_{r+1} \langle \overline{\mathfrak{z}} | \mathfrak{R}_{r+1} \rangle, \qquad (4.31)$$

where $| \overline{\mathfrak{z}} \rangle$ denotes the conjugate of $| \mathfrak{z} \rangle$. Equation (4.31) may also be written in the form

$$0 = \eta_r \left(\frac{\partial R_r}{\partial Z} \right)_{\mathbf{R}} + \eta_{r+1} \left(\frac{\partial R_{r+1}}{\partial Z} \right)_{\mathbf{R}}, \qquad (4.32)$$

where the vector subscripts denote constancy of $R_1, \ldots, R_{r-1}$ in the usual manner.

With the help of Eq. (4.32) it is now possible to establish some simple theorems concerning the possibility of *stationary points* (e.g., maxima, minima, or horizontal inflections) in thermodynamic phase diagrams. In each case we suppose that R_i, R_j are chosen from any set of $r+1$ field variables (spanning at least $r-1$ dimensions), and that η_i, η_j are defined as in Eq. (4.25) for a system of ν coexisting phases.

Theorem 1. If $\eta_i = 0$, then any R_j for which $\eta_j \neq 0$ is necessarily stationary with respect to any thermodynamic change in which the remaining $r-1$ fields (e.g., all but R_i and R_j) are held constant.

Theorem 2. If R_j is stationary with respect to any change which alters R_i while holding constant the remaining $r-1$ fields (e.g., all but R_i and R_j), then $\eta_i = 0$.

The proof of these theorems follows quite directly from Eq. (4.32) and need not be detailed here. Note that the thermodynamic variable Z could be chosen quite arbitrarily (for example, as a composition variable for one of the phases) so long as it is independent of $R_1, \ldots, R_{r-1}$. Various special cases of these theorems were first deduced theoretically by Gibbs,[10] then rediscovered empirically by Konowalow,[11] and are often now referred to as Gibbs–Konowalow laws.[12] Such rules relate maxima or minima in the boiling points of binary and higher mixtures to the compositions of their phases (which enter through the determinantal coefficients η_i), and as such provide the framework for analyzing distillation processes, azeotropy, and so forth. Vector-algebraic expressions such as (4.25), (4.26) should make it feasible to pursue interesting features of phase diagrams even in quite complex chemical systems.

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[6]See, e.g., J. G. Kirkwood and I. Oppenheim, *Chemical Thermodynamics* (McGraw-Hill, New York, 1961), p. 55.
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