The statistical mechanical theory of concentration fluctuations in mixtures

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A general theory of concentration fluctuations in mixtures is derived. The resulting expressions, which include the Kirkwood–Buff theory as a particular case, relate different partial molar properties to a single combination of molecule number fluctuations within differently defined subsystems. The formalism, therefore, gives rise to a common definition for partial molar energies, volumes, enthalpies, and entropies in terms of molecule number fluctuations exclusively. Likewise, a second function of molecule number fluctuations describes both the mixture’s isobaric specific heat as well as its isothermal compressibility. The partial molar energy and enthalpy definitions, moreover, suggest new methods for the study of mixture properties via computer simulations.

INTRODUCTION

Fluctuations in thermodynamic properties are a consequence of molecular motion. The statistical regularities underlying molecular chaos can be quantified in terms of the equilibrium properties of the system under study: this is the task of the theory of fluctuations, the basis of which is the probabilistic interpretation of entropy.¹

This paper addresses the problem of defining the thermodynamic properties of mixtures in terms of concentration fluctuations exclusively. This restriction gives rise to an interesting simplification whereby the same function of concentration fluctuations defines different partial molar properties. The only distinction between the various partial molar properties lies in the definition of the region of space where molecule number fluctuations are to be studied (the subsystem): thus, the operational definition of a partial molar volume involves the calculation of concentration fluctuations within an open, fixed volume region of space, whereas the corresponding partial molar energy definition involves the same combination of fluctuations, but measured within a constant energy region. Likewise, a single function of concentration fluctuations, but within differently defined subsystems, defines the isobaric specific heat and the isothermal compressibility (\(K_f\)) of a mixture. Throughout this paper, we use the term “concentration fluctuation” generically, to denote a fluctuation in the number of molecules of a given species within an appropriately defined region of space.

Application of the general formalism derived in this paper to the specific case of constant volume (grand canonical) fluctuations gives rise to the Kirkwood–Buff theory of solutions.² The extended fluctuation theory of mixtures presented here allows formally identical descriptions of a wide variety of properties (partial molar volumes, energies, enthalpies, and entropies; isobaric specific heat and isothermal compressibility; chemical potential compositional derivatives) in terms of concentration fluctuations. In addition to this appealing conceptual unity, the new theoretical expressions for partial molar energies and enthalpies can serve as a basis for computer simulation studies of these properties, in analogy with recent partial molar volume³ calculations. Applications of the theory, such as the quantification of the dilute mixture concept from a fluctuation viewpoint, will be addressed in future publications: we focus here exclusively on the derivation of the basic equations.

Because such derivations are essentially an exercise in the transformation of partial derivatives among different sets of independent variables, Legendre transform theory⁴⁻⁷ will be extensively used. The simplicity and methodological unity underlying the manipulations that follow will, it is hoped, contribute towards a more widespread use of transform theory in thermodynamics and statistical mechanics.

In the next section, the general theory of concentration fluctuations in mixtures is derived, starting with the case of subsystems whose size is defined by a single Gibbs-space extensive constraint \((U, S, V)\). There result fluctuation-explicit expressions for partial molar energy, entropy, and volume, and for a mixture’s isobaric specific heat and isothermal compressibility. Mathematically identical expressions for partial molar enthalpies follow when the theory is extended to constant \(H\), constant \(P\) subsystems. Finally, the distinction between mechanical and nonmechanical partial molar properties is addressed in connection with the entropy expressions, which are shown to be mathematically but not operationally identical to their volume, energy, and enthalpy counterparts.

GIBBS-SPACE VARIABLES \((V, S, U)\)

We consider a small part of an equilibrium macroscopic system. Let this subsystem be microcanonical with respect to a single Gibbs-space variable \((V, S, or U)\). This means that the subsystem’s “size” is specified by fixing a single extensive constraint. For example, if \(V\) is fixed, the subsystem is an open control volume. Let \(\delta N_i\) and \(\langle N_i \rangle\) denote, respectively, an instantaneous fluctuation and the average number of species \(i\) molecules within a subsystem. Then, pairwise correlations between species \(i\) and \(j\) molecule number fluctuations are given by⁸⁻⁹ \((\beta = 1/kT)\):

\[
\beta \langle \delta N_i \delta N_j \rangle \left| _V \right. = \left( \frac{\partial N_i}{\partial \mu_j} \right)_{\mu, U, V, r} = - y_i^{(n)} \tag{1},
\]

\[
\beta \langle \delta N_i \delta N_j \rangle \left| _S \right. = \left( \frac{\partial N_i}{\partial \mu_j} \right)_{\mu, \Omega, P, S} = - y_i^{(s)} \tag{2},
\]

\[
k^{-1}(\delta N_i, \delta N_j)_{U} = \left( \frac{\partial N_i}{\partial \mu_i / T} \right)_{\mu(i)/T,P/T,U} = y^{(n)}_{ij},
\]
where \(\mu[j]\) denotes constancy of all chemical potentials except for \(\mu_j\), \(\langle \rangle_x\) denotes thermodynamic averaging within an \(X\)-defined subsystem, and \(y^{(n)}_{ij}\) is the second order partial derivative (with respect to variables \(i, j\)) of the \(n\)th Legendre transform \(^4\) of the following basis functions:

\[
y^{(0)} = A \left[ N_1, \ldots, N_n, T, V \right],
\]
\[
y^{(0)} = H \left[ N_1, \ldots, N_n, P, S \right],
\]
\[
y^{(0)} = (S - PV/T) \left[ N_1, \ldots, N_n, P, T, U \right].
\]

The above basis functions are themselves Legendre transforms of the fundamental equation in its energy \(y^{(0)}\) or entropy \(y^{(0)}\) representations; \(y^{(0)}\) can also be obtained from the energy representation as a Massieu–Planck transform. \(^10\)

We recall that the \(k\)th Legendre transform of a basis function \(y^{(0)}(X_1, \ldots, X_m)\) is defined as

\[
y^{(k)}(X_1, \ldots, X_m) = \sum_{i=1}^{k} X_i \xi_i,
\]
where

\[
\xi_i = \left[ \frac{\partial y^{(0)}}{\partial X_i} \right]_{X(l)} = y^{(0)}
\]
and its differential expansion reads

\[
dy^{(k)} = -\sum_{i=1}^{k} X_i d\xi_i + \sum_{i=k+1}^{m} \xi_i dX_i,
\]
where

\[
dy^{(0)} = \sum_{i=1}^{m} \xi_i dX_i
\]
or, in other words,

\[
y^{(k)}(X_1, \ldots, X_k, X_{k+1}, \ldots, X_m).
\]

We now write the \(y^{(n)}\) derivatives [Eqs. (1)–(3)] in terms of their respective \(y^{(0)}\) set of independent variables. Straightforward application of the Legendre transform formalism\(^4,5\) then yields the thermodynamic identities

\[
\beta \langle \delta N_i, \delta N_j \rangle_Y = -y^{(n)}_{ij} = \left[ \frac{B |_{ij}}{B} \right],
\]
\[
\beta \langle \delta N_i, \delta N_j \rangle_S = -y^{(n)}_{ij} = \left[ \frac{C |_{ij}}{C} \right],
\]
\[
k^{-1}(\delta N_i, \delta N_j)_{U} = y^{(n)}_{ij} = \left[ \frac{D |_{ij}}{D} \right],
\]
where \([B |_{ij}, etc.\] denote the cofactors of the \(i, j\) element in the symmetric determinants \([B], etc.\), with elements

\[
B_{ij} = y^{(0)}_{ij} = \left( \frac{\partial \mu_i}{\partial N_j} \right)_{N,U,T,Y},
\]
\[
C_{ij} = y^{(0)}_{ij} = \left( \frac{\partial \mu_i}{\partial N_j} \right)_{N,U,P,S},
\]
\[
D_{ij} = -y^{(0)}_{ij} = \left( \frac{\partial \mu_i / T}{\partial N_j} \right)_{N,U,P,T,U}.
\]

Inversion of the matrix equations (12)–(14) at once leads to

\[
\beta \left( \frac{\partial \mu_i}{\partial N_j} \right)_{N,U,T,V} = \left[ \frac{\Delta^{(p)} |_{ij}}{\Delta^{(p)}} \right], \quad \Delta^{(p)} = \langle \delta N_i, \delta N_j \rangle_Y,
\]
\[
\beta \left( \frac{\partial \mu_i}{\partial N_j} \right)_{N,U,P,S} = \left[ \frac{\Delta^{(S)} |_{ij}}{\Delta^{(S)}} \right], \quad \Delta^{(S)} = \langle \delta N_i, \delta N_j \rangle_S,
\]
\[
k^{-1}(\partial \mu_i / T, \partial N_j)_{N,U,P,T,U} = \left[ \frac{\Delta^{(U)} |_{ij}}{\Delta^{(U)}} \right], \quad \Delta^{(U)} = \langle \delta N_i, \delta N_j \rangle_U,
\]
where, as before, \([\Delta |_{ij}\] is the cofactor of the \(i, j\) element in the symmetric determinant \([\Delta]\), with elements \(\Delta_{ij}\). Next, we write the thermodynamic identities

\[
\beta \left( \frac{\partial \mu_i}{\partial N_j} \right)_{N,U,T,V} = \beta \left( \frac{\partial \mu_i}{\partial N_j} \right)_{N,U,T,P} + \frac{\beta V}{VT} \bar{V},
\]
\[
\beta \left( \frac{\partial \mu_i}{\partial N_j} \right)_{N,U,P,S} = \beta \left( \frac{\partial \mu_i}{\partial N_j} \right)_{N,U,P,T} + \frac{\Delta S}{K_C},
\]
\[
\frac{1}{k} \left( \frac{\partial \mu_i / T}{\partial N_j} \right)_{N,U,P,T,U} = \frac{\bar{U} \bar{U}_j}{kT^2 \left( \frac{\partial U}{\partial T} \right)_{P/T,N}}.
\]

which can be readily derived via the Legendre transform formalism (see the Appendix). Application of the Gibbs-Duhem equation and the identities

\[
V = \sum_{i=1}^{n} V_i N_i,
\]
\[
S = \sum_{i=1}^{n} S_i N_i,
\]
\[
U = \sum_{i=1}^{n} U_i N_i
\]

leads to Eqs. (18)–(23) results \((u = V \langle N \rangle^{-1}; s = S \langle N \rangle^{-1})\):

\[
\bar{V}_j = u \left[ \sum_{i} X_i |_{ij} \right] \left[ \sum_{i} \sum_{j} X_i x_j |_{ij} \Delta^{(p)} |_{ij} \right]^{-1},
\]
\[
\bar{S}_j = s \left[ \sum_{i} X_i |_{ij} \right] \left[ \sum_{i} \sum_{j} X_i x_j |_{ij} \Delta^{(S)} |_{ij} \right]^{-1},
\]
\[
\bar{U}_j = u \left[ \sum_{i} X_i |_{ij} \right] \left[ \sum_{i} \sum_{j} X_i x_j |_{ij} \Delta^{(U)} |_{ij} \right]^{-1},
\]
\[
kT \langle N \rangle p K_T = \left[ \Delta^{(p)} \left[ \sum_{i} \sum_{j} X_i x_j |_{ij} \right]^{-1} \right],
\]
\[
\langle N \rangle k C_p = \left[ \Delta^{(S)} \left[ \sum_{i} \sum_{j} X_i x_j |_{ij} \right]^{-1} \right],
\]
\[
\frac{\langle N \rangle}{(\beta u)^2} \left( \frac{\partial u}{\partial \mu} \right)_{\beta, p, N} = \left[ \Delta^{(U)} \left[ \sum_{i} \sum_{j} X_i x_j |_{ij} \right]^{-1} \right],
\]
\[
\beta \left( \frac{\partial \mu_i}{\partial N_j} \right)_{\beta, p, N} = \left[ \frac{\Delta |_{ij}}{\Delta \Sigma \Sigma_j x_i x_j |_{ij} - \Sigma \Sigma_j x_i x_j |_{ij} \Delta |_{ij}} \right],
\]

\[
\Delta^{(p)} = \langle \delta N_i, \delta N_j \rangle_Y,
\]

\[
\Delta^{(S)} = \langle \delta N_i, \delta N_j \rangle_S,
\]

\[
\Delta^{(U)} = \langle \delta N_i, \delta N_j \rangle_U,
\]

\[
\Delta = \sum_{i} \sum_{j} X_i x_j |_{ij} \Delta |_{ij}.
\]
where $x_i$ is a mole fraction, Eq. (33) is valid for each of the extensive constraints $(S, U, V)$, summations are over the $n$ mixture components, and all specific quantities are per molecule.

Kirkwood and Buff's derivation, and their resulting expressions [Eqs. (27), (30), and (33)], the latter with volume as constraint, when written in terms of fluctuations instead of pair correlation integrals, are thus seen to be particular cases of the general Gibbs-space formalism presented here. Equations (27)–(29) form a complete set, in that any partial molar property can be obtained therefrom. Partial molar enthalpies are, however, amenable to a fluctuation interpretation mathematically identical to the corresponding $U_i$, $V_i$, and $S_i$ expressions. We address this derivation next.

**ENTHALPY**

The probability of occurrence of a fluctuation within a small, open subsystem in contact with a reservoir is given by

$$p \sim \exp \left\{ \frac{\beta}{2} \left[ \Delta S - \sum \delta x_i \delta N_i \right] \right\},$$

where $T$ is the reservoir's temperature, and $\delta x_i$ denotes a fluctuation in $x_i$ within the subsystem. Expanding the second order variation in terms of $H, P$, and $N_i$ ($i = 1, \ldots, n$) and imposing the constraints

$$\delta H = 0, \quad \delta \beta = 0,$$

we obtain

$$\Delta S - \sum \delta x_i \delta N_i |_{H, P} = -T \sum \delta x_i \frac{T \partial \mu_i}{\partial N_i} |_{H, P},$$

and, therefore,

$$p \sim \exp \left\{ -\frac{1}{2k} \sum \delta x_i \frac{T \partial \mu_i}{\partial N_i} |_{H, P} \right\},$$

which implies

$$\frac{1}{k} \langle \Delta N_i \delta N_j \rangle_{H, P} = \left\langle \frac{E_{ij}}{E} \right\rangle_{E_{ij}} = \left\langle \frac{T \partial \mu_i}{\partial N_j} \right\rangle_{H, P}.$$

Inversion of Eq. (39) leads to

$$k^{-1} \left[ \frac{\partial \mu_i}{\partial N_j} \right]_{H, P} \frac{\langle \Delta (H, P) \rangle_{ij}}{\langle \Delta (H, P) \rangle} = \left[ \frac{\langle \Delta (H, P) \rangle_{ij}}{\langle \Delta (H, P) \rangle} \right],$$

$$\Delta (U, P) = \langle \delta N_i \delta N_j \rangle_{H, P}.$$ (40)

Invoking the thermodynamic identity (see also Appendix)

$$\frac{1}{k} \left[ \frac{\partial \mu_i}{\partial N_j} \right]_{H, P} = \beta \left[ \frac{\partial \mu_i}{\partial N_j} \right]_{T, P, N, U}$$

$$+ \frac{H_i}{k} \frac{\delta \Omega}{\delta T} |_{T, P, N, U},$$

we obtain, as before ($h = H \langle \langle N \rangle \rangle$),

$$\frac{\langle N \rangle}{C_p} \frac{1}{k (\beta \gamma)^2} = \left[ \frac{\Delta (H, P)}{\sum \sum x_i x_j \Delta (H, P)_{ij}} \right]^{-1},$$

$$\langle \Delta (H, P) \rangle = \left[ \frac{\Delta (H, P)}{\sum \sum x_i x_j \Delta (H, P)_{ij}} \right]^{-1},$$

$$\beta \left[ \frac{\partial \mu_i}{\partial N_j} \right]_{T, P, N, U} = \frac{\Delta x_i \Sigma \Sigma x_i x_j \Delta x_j \Sigma x_k \Delta x_k}{\Delta x_i \Sigma x_i x_j \Delta x_j \Sigma x_k \Delta x_k}.$$ (33)

**DISCUSSION**

Partial molar properties represent additive contributions of mixture components to a given extensive property $\lambda$, since

$$\lambda = \sum_{i=1}^{n} N_i \lambda_i.$$

Volume, energy, enthalpy, and entropy are distributed among mixture components according to the same function of pairwise fluctuations, but within differently defined subsystems [Eqs. (27), (28), (29), and (42)]. This conclusion is valid for any thermodynamic system, regardless of molecular shape, size, or symmetry, and is not dependent upon pairwise additivity or any other simplifying assumption.

If we consider, for example, a binary $(i, j)$ mixture, the general relationship between a partial molar quantity $(\lambda_i)$ and the corresponding extensive quantity $(\lambda)$, after rearrangement, reads

$$\overline{\lambda}_i / \langle \lambda \rangle = \frac{1 + x_i \overline{\lambda}_i / \langle \lambda \rangle}{\overline{\lambda}_i / \langle \lambda \rangle}.$$ (44)

The compressibility-specific heat equation, on the other hand, reads

$$\phi = \frac{\langle \Delta (N, S) \rangle \langle \Delta (S, N) \rangle}{\langle \Delta (N, S) \rangle \langle \Delta (S, N) \rangle} = \phi,$$

where $\phi$ denotes either $\rho k T K_T$, $k C_p / \beta^2$, or $C_v / k (\beta \gamma)^2$. Similarly, for the chemical potential derivative we obtain, after rearrangement,

$$\phi = \frac{\langle \Delta (N, S) \rangle \langle \Delta (S, N) \rangle}{\langle \Delta (N, S) \rangle \langle \Delta (S, N) \rangle} = \phi.$$ (45)
\[
\beta \left( \frac{\partial \mu_j}{\partial x_j} \right)_{T,P} = - \left[ x_j \left( \frac{\langle (N_j)^2 \rangle}{\langle N_j \rangle} \right) + x_i x_j \left( \frac{\langle (N_i N_j)^2 \rangle}{\langle N_i \rangle \langle N_j \rangle} \right)^{-1} \right].
\]

(46)

In Eqs. (44) and (45), the subsystem-defining constraint is simply dictated by the nature of the quantity on the left-hand side. Equation (46) is valid for \( V,S,U \), or \( (H,P) \)-defined subsystems.

Gibbs-space variables \( (V,U,S) \) form a complete set, all other partial molar properties being linear combinations of \( U_l \) with \( PV_l \) and/or \( TS_l \). Accordingly, the “size” of the subsystem within which the appropriate fluctuations are calculated is defined, in each case, by a single extensive constraint.

In the case of enthalpy, the same partial molar generating function can still be used [Eq. (42)], but the subsystem within which fluctuations are computed is now defined by specifying enthalpy and pressure.

Two of the three Gibbs-space partial molar quantities \( \left( \overline{V}_l, \overline{U}_l \right) \) are mechanical, in that they can be defined without invoking the concept of entropy (or temperature). Their fluctuation definitions, accordingly, involve purely mechanical operations. The fluctuation-explicit definition of partial molar entropy, on the other hand, although mathematically identical, cannot be reduced to purely mechanical operations. Entropy, contrary to energy or volume, is a statistical concept, and is undefined instantaneously: a given subsystem configuration has a well-defined energy and volume associated with it, but no entropy (in the case of energy, though, ambiguity exists as to the assignment of interaction energy to different subsystems,\(^1\) but this ambiguity becomes insignificant in the thermodynamic limit). The partial molar generating function, when applied to entropy, calls for the calculation of the appropriate pairwise fluctuations among an ensemble of those subsystems, the logarithms of whose \( \Gamma \)-space volume, when measured in units of \( h^* \) (where \( h \) is now Planck’s constant and \( s \) is the number of degrees of freedom\(^1\)) are equal to within errors small compared with \( k^{-\frac{1}{2}} \left( \langle (N) \rangle^2 \right) \) (i.e., \( \langle (N) \rangle^2 / k \)). Each of these subsystems, observed over an interval short enough so that it can be considered quasistatic\(^1\) (yet longer than its relaxation time) contains, in general, a different number of molecules: This gives rise to the required composition fluctuations at constant entropy.

The generalization of the partial molar concept provided by Eqs. (27)–(29) and (42) is thus mathematical and formal, but not operational. In the case of mechanical properties, the fluctuation expressions can be reduced to the respective fluctuation of molecular properties within boundaries which are instantaneously defined and can be constructed unambiguously by calculating distances, forces, and energies exclusively (this is true even though, in the case of \( U_l \) and \( H_l \), an arbitrary reference must be provided for the assignment of energies to interacting subsystems: results are necessarily insensitive to such a recipe for large enough subsystems).

Equations (29) and (42) are amenable to algorithmic implementation and thus constitute two new techniques for the computer-based study of partial molar properties. Among the various possibilities, we mention \( (N,U,V) \) molecular dynamics for the study of \( \overline{U}_l \), and isothermal–isobaric molecular dynamics\(^2\) for the study of \( \overline{H}_l \). Equation (27), on the other hand, has recently been applied\(^3\) within an \( (N,U,V) \) molecular dynamics algorithm to the study of partial molar volumes. The fluctuation expressions can also be applied to the molecular based study of the properties of dilute mixtures. This topic, which is of relevance in areas such as cluster formation in supercritical systems\(^4\) or ultra-purity attainment\(^1\) will be addressed in future publications.

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APPENDIX: PROOF OF Eqs. (21)–(23) AND (41)

Consider a basis function, \( \psi^{(0)} \), with independent variables \( X_1, \ldots, X_m \). Then

\[
d\psi^{(0)} = \sum_{k=1}^{m} \xi_k \, dX_k,
\]

(A1)

where

\[
\xi_k = \left[ \frac{\partial \psi^{(0)}}{\partial X_k} \right]_{X[k]}.
\]

(A2)

and where \( X[k] \) denotes constancy of all \( X \) except for \( X_k \).

We define \( \psi^{(1)} \) as

\[
\psi^{(1)} = \psi^{(0)} - \xi_1 \, X_1,
\]

(A3)

or, equivalently,

\[
d\psi^{(1)} = -X_1 \, d\xi_1 + \sum_{k=2}^{m} \xi_k \, dX_k,
\]

(A4)

which implies

\[
\psi^{(1)} = \left[ \xi_1 \, X_2 \ldots X_m \right].
\]

(A5)

Next, we expand \( \xi_i \) \((i \neq 1)\) in terms of the set of independent variables corresponding to \( \psi^{(1)} \),

\[
d\xi_i = \left[ \frac{\partial \xi_i}{\partial X_k} \right]_{X \neq i} \, dX_k,
\]

(A6)

and therefore,

\[
\left[ \frac{\partial \xi_i}{\partial X_k} \right]_{X \neq i} = \left[ \frac{\partial \xi_i}{\partial X_k} \right]_{X \neq i} \, X_k \left[ \frac{\partial \xi_1}{\partial X_k} \right]_{X \neq i} + \left[ \frac{\partial \xi_i}{\partial X_k} \right]_{X \neq i} \, X_1 \left[ \frac{\partial \xi_1}{\partial X_k} \right]_{X \neq i}.
\]

(A7)

or, in Legendre transform notation,

\[
\psi^{(0)} = \left[ \frac{\partial \xi_i}{\partial X_k} \right]_{X \neq i} \, dX_k \left[ \frac{\partial \xi_1}{\partial X_k} \right]_{X \neq i} \, dX_k + \psi^{(1)}.
\]

(A8)

Solving for \( \psi^{(1)} \),

\[
\psi^{(1)} = \psi^{(0)} - \left[ \frac{\partial \xi_i}{\partial X_k} \right]_{X \neq i} \, dX_k \left[ \frac{\partial \xi_1}{\partial X_k} \right]_{X \neq i} \, dX_k + \left[ \frac{\partial \xi_i}{\partial X_k} \right]_{X \neq i} \, dX_k \left[ \frac{\partial \xi_1}{\partial X_k} \right]_{X \neq i} \, dX_k,
\]

(A9)

which implies\(^4\)
\[ y^{(1)}_{ij} = y^{(0)}_i - \frac{y^{(0)}_j y^{(0)}_i}{y^{(0)}_i} \quad (i, j \neq 1). \quad (A10) \]

We now apply Eq. (A10) to the following \( y^{(0)}, y^{(1)} \) pair:

\[ y^{(0)} = G(P, T, N_k); \quad dy^{(0)} = VdP - SdT + \Sigma \mu_k dN_k, \quad (A11) \]

\[ y^{(1)} = A(V, T, N_k); \quad dy^{(1)} = -PdV - SdT + \Sigma \mu_k dN_k, \quad (A12) \]

and obtain Eq. (21). Similarly, application of Eq. (A10) to the following \( [y^{(0)}, y^{(1)}] \) pairs results in Eqs. (22), (23), and (41), respectively.

\[ dy^{(0)} = Sd(-T) + VdP + \Sigma \mu_k dN_k; \quad (A13) \]

\[ dy^{(1)} = TdS + VdP + \Sigma \mu_k dN_k; \quad (A14) \]

\[ y^{(1)} = y^{(1)}(S, P, N_k) = H; \quad y^{(1)} = y^{(1)}(T, P, N_k) = G; \quad (A15) \]

\[ dy^{(0)} = Ud(-1/T) - Vd(P/T) - \Sigma (\mu_k/T)dN_k; \quad (A16) \]

\[ dy^{(1)} = 1/TdU - Vd(P/T) - \Sigma (\mu_k/T)dN_k; \]

\[ y^{(1)} = y^{(1)}(U, P/T, N_k) = S - PV/T; \quad (A17) \]

\[ dy^{(0)} = H(-1/T) - V/TdP - \Sigma (\mu_k/T)dN_k; \]

\[ y^{(0)} = y^{(0)}(-1/T, P, N_k) = -G/T; \]

\[ dy^{(1)} = 1/TdH - V/TdP - \Sigma (\mu_k/T)dN_k; \]

\[ y^{(1)} = y^{(1)}(H, P, N_k) = S. \quad (A18) \]

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1. L. Boltzmann, Wiener Ber. 76, 373 (1877).