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# DEVELOPMENT OF CONSISTENT LOCAL THERMODYNAMIC RELATIONS FOR NON-EQUILIBRIUM MULTI-COMPONENT FLUID SYSTEMS

L N McCARTNEY & EDMUND J F DICKINSON

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# Development of consistent local thermodynamic relations for non-equilibrium multi-component fluid systems

L N McCartney & Edmund J F Dickinson
Department of Electromagnetic & Electrochemical Technologies

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National Physical Laboratory
Hampton Road, Teddington, Middlesex, TW11 0LW

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# ABSTRACT

This report addresses the issue of formulating thermodynamic equations of state for multi-component chemical systems that can be consistently applied locally (on a volumetric, molar or specific basis) and so can form the thermodynamic basis of a theory for non-equilibrium transport in non-uniform multi-component reacting fluids.

The development of local equations of state, for application in non-uniform multi-component fluid systems, requires the introduction of localised composition variables, such as mole or mass fractions, which are not independent. Robust, unambiguous methods for the mathematical handling of such dependencies are developed, while maintaining close contact with equivalent global thermodynamic relations encountered in uniform systems. While four candidate thermodynamic functions can be the basis of a local equation of state, associated respectively with internal energy, Helmholtz energy, Gibbs energy and enthalpy, the most practically useful is based on the molar Gibbs energy for which the function depends only on intensive state variables (temperature, pressure and composition).

For global thermodynamic systems applicable to multi-component uniform systems having $n$ species in equilibrium, equations of state in the form of Gibbs energy functions (homogeneous of order unity with respect to composition variables) are often known at the outset, enabling the development of corresponding local relations required for simulation purposes. Localisation based on the molar Gibbs energy, using the total number of moles of all species $N$, leads to state variables for composition which are not independent, i.e. the set of $n$ mole fractions $\{x_i\}$. By comparison, localisation with respect to a fixed total number of moles of all species $N^*$, rather than $N$, leads to the concept of pseudo-mole fractions $\{x_i^*\}$. The set of $n$ variables $\{x_i^*\}$ are independent, but tend to the dependent set of mole fractions $\{x_i\}$ when $N^* \to N$. The molar Gibbs energy function resulting from the latter localisation procedure, expressed in terms of pseudo-mole fractions, can be used to generate chemical potentials, and other thermodynamic molar quantities, by using single partial derivatives in a manner analogous to the well-defined approach used for uniform global systems.

Great care is needed when calculating chemical potentials from general molar Gibbs energy functions sourced from literature or experimental data, as it is highly likely that the derived molar Gibbs energy function will lack the homogeneity needed for the use of the single partial derivative formula for chemical potential. A new expression is derived to compute chemical potentials when using a non-homogeneous molar Gibbs energy functions, and a method is presented to construct the homogeneous molar Gibbs energy function of a particular system from any non-homogeneous molar Gibbs energy function. This leads self-consistently to correct general formulae for chemical potentials expressed in terms of intensive state variables, and hence for all partial molar properties for use in local thermodynamic relations.

It is observed that an expression for partial pressure of any species of the system has been proposed that applies to non-ideal multi-component systems, and which reduces to the commonly used expression that has been established only for ideal systems. Alternative thermodynamic formulations based on specific rather than molar quantities, and a molar formulation based on $n – 1$ independent mole fractions, are briefly considered.

## CONTENTS

## 1 INTRODUCTION

The evolution of non-uniform time-dependent multi-component fluid systems can be predicted using non-equilibrium thermodynamic models based on balance equations for mass, momentum (linear and angular), energy and entropy [1-8]. These crucial physical concepts relate the evolution of many variables but do not themselves provide any information on the constitutive properties of the fluid material. Some properties can be defined in terms of thermodynamic variables by making use of an equation of state that relates the various material properties, for uniform systems in equilibrium, whose values must be known in order to predict system evolution. This report addresses the issue of formulating equations of state for a multi-component chemical system that can consistently be applied locally (on a volumetric, molar or specific basis) and so can form the thermodynamic basis of a theory for non-equilibrium transport in multi-component reacting fluids. Such transport theories have widespread application in chemical engineering and electrochemistry; for example, the mass transfer modelling of concentrated mixtures is relevant to the optimisation of fixed bed reactors and fuel cells.

The chemical thermodynamics of multicomponent systems (at equilibrium) is well understood for the case of electrically neutral components [9-11]. Most commonly, an equation of state is defined by expressing the Gibbs energy as a function of temperature, pressure and molar contents of the components. Chemical equilibrium for uniform systems is attained when the global Gibbs energy is at a minimum. It can be proved from the laws of thermodynamics that the condition of chemical equilibrium for any component between two phases can be expressed in terms of equality of the chemical potential of the component across the interface between the two phases, where chemical potential is defined to be the partial derivative of Gibbs energy with respect to the molar content of the component under consideration, all other state variables being held constant. As will be discussed below, the standard framework of chemical thermodynamics enables the definition of further derived properties from the chemical potential, such as partial molar volumes, enthalpies and entropies.

Thermodynamic properties of a uniform system may be classified as extensive or intensive. Extensive properties (e.g. energy, entropy, volume, molar content) are those which scale with the size of the system, such that if any one extensive property is scaled in magnitude by a multiple $\lambda$, holding the values of all intensive, size-independent properties (e.g. pressure, temperature) constant, then all extensive properties of the system will scale in magnitude by $\lambda$. In principle, any extensive property can be used as a metric of the size of a system, although volume, mass and total molar content are the most common choices.

The Gibbs energy is an extensive property and therefore is only meaningfully defined for a uniform system of finite and specified size. To express an equation of state at a specified coordinate within a non-equilibrium continuum fluid, a local equation of state is required, which must be expressed in terms of properties that are expressed as a scalar fields as a function of the coordinates. It is meaningless to speak of the value of an extensive property “at a coordinate” and so the local equation of state must depend only on intensive properties of a corresponding uniform system. As will be discussed below, the transformation of the Gibbs energy to a local form, with a basis exclusively of intensive state variables, inevitably introduces non-uniqueness into its functional form, since for an $n$-component mixture, only $(n-1)$ of the mole or mass fractions are independent. Likewise, if a volumetric formulation is used, all $n$ concentrations may be specified independently, but in this case, the pressure ceases to be an independent variable. As will be discussed in this report, due to the interdependence of state variables in naïve formulations of a local Gibbs energy function, significant care is needed to ensure the validity of the mathematical operations used to derive the chemical potential and other partial molar properties from the local equation of state.

In this report, practical and consistent formulations of the local equation of state are discussed in detail. It will be assumed that the fluid is non-viscous, implying that the thermodynamic pressure involved with equations of state corresponds to the actual pressure at all points in the system and for all times.

## 2 GLOBAL THERMODYNAMIC RELATIONS FOR UNIFORM SYSTEMS

The fundamental thermodynamic relations for uniform multi-component fluid systems involve *global* extensive variables whose values scale proportionally with the size of the system, namely, internal energy $U$, Helmholtz energy $F$, Gibbs energy $G$, enthalpy $H$, entropy $S$, total volume $V$ and the molar contents of the various species $N_k$, $k=1,...,n.$ In contrast to extensive variables, the intensive variables of a uniform multi-component fluid, such as temperature and pressure, do not change in value if the size of the whole system is changed. The internal energy, Helmholtz energy, Gibbs energy and enthalpy are now considered in turn.

The total size of the system can be expressed by either the volume $V$ or its total molar content $N$, defined by

$$N=\sum_{k=1}^{n} N_k\,. \tag{1}$$

### 2.1 INTERNAL ENERGY

The internal energy $U$ of the uniform system is a function of the extensive state variables $S$, $V$ and the set $\{N_i\}$ denoting the state variables $N_k,\ k=1,\ ...,\ n.$ If *any* thermodynamic quantity $\xi$ has its value expressed as a function of the state variables $(S,V,\{N_i\})$, that function will be denoted by $\tilde{\xi}$ implying that $\xi=\tilde{\xi}(S,V,\{N_i\})$ (see Appendix A for further comments on notation used in this report). The internal energy then has the form

$$U=\tilde{U}(S,V,\{N_i\})\,, \tag{2}$$

where the following differential form

$$\mathrm{d}U=T\ \mathrm{d}S-p\ \mathrm{d}V+\sum_{k=1}^{n}\mu_k\ \mathrm{d}N_k\ , \tag{3}$$

leads to the following definitions of intensive quantities, namely, absolute temperature $T$, thermodynamic pressure $p$ and the chemical potentials $\mu_k,\ k=1,\ ...,\ n,$

$$\begin{gathered} T=\frac{\partial\tilde{U}}{\partial S}=\tilde{T}(S,V,\{N_i\}),\qquad p=-\frac{\partial\tilde{U}}{\partial V}=\tilde{p}(S,V,\{N_i\}),\\ \mu_k=\frac{\partial\tilde{U}}{\partial N_k}=\tilde{\mu}_k(S,V,\{N_i\}),\quad k=1,\ ...,\ n. \end{gathered} \tag{4}$$

The relation (2) is a global equation of state for a uniform multi-component system.

The internal energy must be such that, if the size of the uniform system is changed by a numerical factor $\lambda$, then the internal energy $U$ must also change by the same factor so that its value following the change is $\lambda U$. Written mathematically, it follows that the function $\tilde{U}$ has the following property

$$\tilde{U}(\lambda S, \lambda V, \{\lambda N_i\}) \equiv \lambda \tilde{U}(S, V, \{N_i\}) . \tag{5}$$

for any numerical value of the parameter $\lambda$. This relation asserts, therefore, that the function $\tilde{U}$ is homogeneous of order unity in the state variables $S$, $V$ and $N_k$, $k = 1, ..., n$.

The parameter $\lambda$ can also be a variable, rather than a scalar constant. Provided the state variables given in (5) are independent of $\lambda$, it is permissible to differentiate (5) with respect to $\lambda$ and then set $\lambda = 1$, leading to

$$S\frac{\partial \tilde{U}}{\partial S} + V\frac{\partial \tilde{U}}{\partial V} + \sum_{k=1}^{n} N_k \frac{\partial \tilde{U}}{\partial N_k} = \tilde{U}(S, V, \{N_i\}) . \tag{6}$$

On making use of the relations (4), it then follows that

$$ST - Vp + \sum_{k=1}^{n} N_k \mu_k = \tilde{U}(S, V, \{N_i\}) = U, \tag{7}$$

leading to the following well-known thermodynamic relation

$$\sum_{k=1}^{n} N_k \mu_k = U - TS + pV = G, \tag{8}$$

where $G$ is the Gibbs energy of the system.

## 2.2 HELMHOLTZ ENERGY

The equation of state (2) and the associated relations (4) are not usually preferred for the representation of the physical behaviour of multi-component fluids through correlation with experimental data, as the state variable $S$ is not measurable directly. When representing experimental data, it is more convenient to regard the temperature, $T$, as a state variable rather than the entropy $S$. This is achieved on introducing the Helmholtz energy $F$ defined by

$$F = U - TS , \tag{9}$$

so that from (3)

$$\mathrm{d}F = -S\,\mathrm{d}T - p\,\mathrm{d}V + \sum_{k=1}^{n} \mu_k \mathrm{d}N_k . \tag{10}$$

If *any* thermodynamic quantity $\xi$ has its value expressed as a function of the state variables $(T, V, \{N_i\})$, that function will be denoted by $\bar{\xi}$ implying that $\xi = \bar{\xi}(T, V, \{N_i\})$. The relation (10) then implies that a global equation of state for the Helmholtz energy $F$ can be written in the form

$$F = \bar{F}(T, V, \{N_i\}), \tag{11}$$

where the variables $T$, $V$ and $\{N_i\}$ are independent. It follows from (10) that

$$\begin{gathered} S = -\frac{\partial \bar{F}}{\partial T} = \bar{S}(T, V, \{N_i\}), \qquad p = -\frac{\partial \bar{F}}{\partial V} = \bar{p}(T, V, \{N_i\}), \\ \mu_k = \frac{\partial \bar{F}}{\partial N_k} = \bar{\mu}_k(T, V, \{N_i\}) , \quad k = 1, ..., n. \end{gathered} \tag{12}$$

## 2.3 GIBBS ENERGY

When representing experimental data, it is usual to regard the temperature $T$ and pressure $p$ as state variables, rather than $T$ and $V$. This is achieved on introducing the Gibbs energy $G$ defined by (8), which may be written, on using (9),

$$G = F + pV\,, \tag{13}$$

Consider first of all a uniform global system where the Gibbs energy $G$ has the following form

$$G = \hat{G}(T, p, \{N_i\})\,, \tag{14}$$

where the state variables are the absolute temperature $T$, the pressure $p$, and the molar contents $\{N_i\}$ of each of the $i = 1, ..., n,$ species in the system. The relation (14) can be regarded as the keystone for the development of thermodynamic relations associated with uniform multi-component systems, as it uses easily measured state variables, and there are no ambiguities relating to the description of composition. An equation of state of the type (14) is the basis of software applications, such as MTDATA [12] and CALPHAD [13], which are a rich source of data relating to the properties of a large range of multi-component materials which can exist in various phases.

It follows from (10) and (13) that the corresponding differential relation is

$$\mathrm{d}G = -\,S\,\mathrm{d}T + V\,\mathrm{d}p + \sum_{k=1}^{n} \mu_k \mathrm{d}N_k\,. \tag{15}$$

If *any* thermodynamic variable $\xi$ has its value expressed as a function of the state variables $(T, p, \{N_i\})$, that function will be denoted by $\hat{\xi}$ implying that $\xi = \hat{\xi}(T, p, \{N_i\})$. It follows from (15) that the entropy $S$, the volume $V$ and the chemical potentials $\mu_k,\ k = 1, ..., n,$ are defined by

$$\begin{aligned} S &= -\frac{\partial \hat{G}(T, p, \{N_i\})}{\partial T} = \hat{S}(T, p, \{N_i\}), \\ V &= \frac{\partial \hat{G}(T, p, \{N_i\})}{\partial p} = \hat{V}(T, p, \{N_i\}), \\ \mu_k &= \frac{\partial \hat{G}(T, p, \{N_i\})}{\partial N_k} = \hat{\mu}_k(T, p, \{N_i\})\,, \quad k = 1, ..., n. \end{aligned} \tag{16}$$

The size of a uniform multi-component system can be varied, as above, by using the positive dimensionless variable $\lambda$ so that, in general, the composition of any system is characterised by the variables $\{\lambda N_i\}$.

To be consistent with this approach, the function $\hat{G}$ is required to have the property

$$\hat{G}(T, p, \lambda\{N_i\}) \equiv \lambda \hat{G}(T, p, \{N_i\})\,, \tag{17}$$

for any value of the variable $\lambda$ that must be independent of the state variables $T$, $p$ and $\{N_i\}$. The function $\hat{G}$ is, therefore, homogeneous of order unity in the composition variables $\{N_i\}$. On differentiating (17) with respect to $\lambda$, regarding $T$, $p$ and $\{N_i\}$ as constants, and then setting $\lambda = 1$, it follows on using $(16)_3$ that, consistent with (8)

$$G = \sum_{k=1}^{n} N_k \mu_k\,. \tag{18}$$

The well-known Gibbs-Duhem equation results from eliminating *G* using (15) and (18) leading to

$$S\,\mathrm{d}T - V\,\mathrm{d}p + \sum_{k=1}^{n} N_k\,\mathrm{d}\mu_k = 0. \tag{19}$$

On differentiating (17) with respect to the arguments *T* and *p*, it follows from $(16)_{1,2}$ that

$$\hat{S}(T,p,\lambda\{N_i\}) = -\frac{\partial \hat{G}(T,p,\lambda\{N_i\})}{\partial T} = -\lambda\frac{\partial \hat{G}(T,p,\{N_i\})}{\partial T}, \tag{20}$$

$$\hat{V}(T,p,\lambda\{N_i\}) = \frac{\partial \hat{G}(T,p,\lambda\{N_i\})}{\partial p} = \lambda\frac{\partial \hat{G}(T,p,\{N_i\})}{\partial p}. \tag{21}$$

On using (16), (20) and (21) it is clear that for any value of the dimensionless variable $\lambda$

$$\hat{S}(T,p,\lambda\{N_i\}) \equiv \lambda\hat{S}(T,p,\{N_i\}), \tag{22}$$

$$\hat{V}(T,p,\lambda\{N_i\}) \equiv \lambda\hat{V}(T,p,\{N_i\}), \tag{23}$$

indicating that the functions $\hat{S}$ and $\hat{V}$ are also homogeneous of order unity with respect to the variables $\{N_i\}$, consistent with the requirement that both the entropy *S* and the volume *V* are extensive thermodynamic state variables. It is noted that on differentiating the expression $\hat{\mu}_k(T,p,\{\lambda N_i\})$ with respect to $\lambda$, regarding *T*, *p* and $\{N_i\}$ as constants, and on using $(16)_3$ together with the homogeneity relation (17), it follows that, for all values *k* = 1, …, *n*,

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}\lambda}\hat{\mu}_k(T,p,\{\lambda N_i\}) &= \sum_{j=1}^{n} N_j\frac{\partial\hat{\mu}_k(T,p,\{\lambda N_i\})}{\partial N_j} = \sum_{j=1}^{n} N_j\frac{\partial^2\hat{G}(T,p,\{\lambda N_i\})}{\partial N_j\partial N_k} = \lambda\sum_{j=1}^{n} N_j\frac{\partial^2\hat{G}(T,p,\{N_i\})}{\partial N_j\partial N_k}\\ &= \lambda\sum_{j=1}^{n} N_j\frac{\partial\hat{\mu}_j(T,p,\{N_i\})}{\partial N_k} = \lambda\frac{\partial}{\partial N_k}\left\{\sum_{j=1}^{n} N_j\hat{\mu}_j(T,p,\{N_i\})\right\} - \lambda\hat{\mu}_k(T,p,\{N_i\})\\ &= \lambda\frac{\partial\hat{G}(T,p,\{N_i\})}{\partial N_k} - \lambda\hat{\mu}_k(T,p,\{N_i\}) = 0,\end{aligned} \tag{24}$$

establishing that $\hat{\mu}_k(T,p,\{\lambda N_i\})$ is independent of $\lambda$, which is to be expected as the chemical potentials are intensive quantities.

## 2.4 ENTHALPY

In chemical thermodynamics it can also be useful to consider the enthalpy *H* defined by

$$H = U + pV. \tag{25}$$

On using (3) it then follows that

$$\mathrm{d}H = T\,\mathrm{d}S + V\,\mathrm{d}p + \sum_{k=1}^{n}\mu_k\mathrm{d}N_k \tag{26}$$

If *any* thermodynamic quantity $\xi$ has its value expressed as a function of the state variables $(S,p,\{N_i\})$, that function will be denoted by $\widehat{\xi}$ implying that $\xi = \widehat{\xi}(S,p,\{N_i\})$. It then follows that an equation of state can be specified of the form

$$H = \widehat{H}(S,\ p,\ \{N_i\}), \tag{27}$$

such that

$$T = \frac{\partial \overset{\frown}{H}}{\partial S} = \overset{\frown}{T}(S, p, \{N_i\}), \qquad V = \frac{\partial \overset{\frown}{H}}{\partial p} = \overset{\frown}{V}(S, p, \{N_i\}),$$
$$\mu_k = \frac{\partial \overset{\frown}{H}}{\partial N_k} = \overset{\frown}{\mu}_k(S, p, \{N_i\}) \;, \;\; k = 1, ..., n. \tag{28}$$

## 2.5 SUMMARY AND IDENTIFICATION OF GLOBAL STATE VARIABLES

The global extensive thermodynamic variables *U*, *F*, *G*, *H*, *S*, and *V* considered in this Section are the basis of models describing some of the properties of uniform multi-component systems in equilibrium (assuming body forces such as gravity are ignored). The results, applicable only for uniform multi-component systems, will be used in the next Section to derive, using a direct method, the local thermodynamic relations that are required when modelling non-uniform systems.

Sections 2.1-2.4 have introduced four possible sets of global thermodynamic state variables that can be used to define the state of a thermodynamic system. These are respectively the sets of natural state variables used to define the extensive variables *U*, *F*, *G* and *H*. It is noted that four different over-characters have been used, viz. $\tilde{\xi}$ , $\overline{\xi}$ , $\hat{\xi}$ and $\overset{\frown}{\xi}$ when applied to a function $\xi$ , associated with each set of state variables. This notational approach, which will be particularly useful later when considering molar heat capacities (see Section 2.7), will be used throughout this report. More details are given in Appendix A enabling readers to associate the notation with established approaches often used in thermodynamics.

## 2.6 PARTIAL THERMODYNAMIC QUANTITIES

From (16) it follows that

$$\frac{\partial \hat{\mu}_k}{\partial T} = \frac{\partial^2 \hat{G}}{\partial T \partial N_k} = \frac{\partial}{\partial N_k}\left(\frac{\partial \hat{G}}{\partial T}\right) = -\frac{\partial \hat{S}}{\partial N_k} \equiv -S_k \,, \quad k = 1, ..., n,$$
$$\frac{\partial \hat{\mu}_k}{\partial p} = \frac{\partial^2 \hat{G}}{\partial p \partial N_k} = \frac{\partial}{\partial N_k}\left(\frac{\partial \hat{G}}{\partial p}\right) = \frac{\partial \hat{V}}{\partial N_k} \equiv V_k \,, \quad k = 1, ..., n, \tag{29}$$

leading to the relations

$$S = -\frac{\partial \hat{G}}{\partial T} = -\frac{\partial}{\partial T}\sum_{k=1}^{n} N_k \hat{\mu}_k = -\sum_{k=1}^{n} N_k \frac{\partial \hat{\mu}_k}{\partial T} = \sum_{k=1}^{n} N_k S_k \,, \tag{30}$$

$$V = \frac{\partial \hat{G}}{\partial p} = \frac{\partial}{\partial p}\sum_{k=1}^{n} N_k \hat{\mu}_k = \sum_{k=1}^{n} N_k \frac{\partial \hat{\mu}_k}{\partial p} = \sum_{k=1}^{n} N_k V_k \,. \tag{31}$$

The quantities $S_k$ and $V_k$ defined by (29) are now interpreted as the partial entropy and partial volume for the *k*th species in the uniform system. It follows from (30) and (31) that the partial entropies and partial volumes are intensive thermodynamic variables.

Consider now the quantities defined by the relation

$$U_k = \mu_k + T\,S_k - pV_k \,, \quad k = 1, ..., n. \tag{32}$$

On multiplying (32) by $N_k$ and summing over *k* it is clear, on using (8), (30) and (31), that

$$\sum_{k=1}^{n} N_k U_k = \sum_{k=1}^{n} N_k \mu_k + T \sum_{k=1}^{n} N_k S_k - p \sum_{k=1}^{n} N_k V_k = G + T\,S - pV = U\,, \tag{33}$$

where $U$ is the total internal energy of the uniform system. It is clear from (33) that the quantities $U_k,\ k = 1, ..., n,$ are the partial molar internal energies such that

$$U = \sum_{k=1}^{n} N_k U_k\,, \quad \text{implying also that} \quad F \equiv U - T\,S = \sum_{k=1}^{n} N_k F_k\,, \tag{34}$$

where $F_k$ is the partial Helmholtz energy defined by

$$F_k = U_k - T\,S_k = \mu_k - pV_k\,, \quad k = 1, ..., n\,. \tag{35}$$

On using (8), (33) and (35)

$$pV = \sum_{k=1}^{n} N_k \left(\mu_k - U_k + T\,S_k\right) = \sum_{k=1}^{n} N_k \left(\mu_k - F_k\right), \tag{36}$$

and from (25), $(34)_1$ and (36) that

$$H = \sum_{k=1}^{n} N_k \left(U_k + \mu_k - F_k\right) = \sum_{k=1}^{n} N_k \left(\mu_k + T\,S_k\right) = \sum_{k=1}^{n} N_k H_k\ . \tag{37}$$

The partial enthalpies $H_k$ are defined by the relation

$$H_k = \mu_k + T\,S_k = U_k + \mu_k - F_k = U_k + pV_k\,, \qquad k = 1, \ldots, n, \tag{38}$$

where use has been made of (35).

It is noted that the above definitions of partial thermodynamic quantities are based on the equation of state (14) for the global Gibbs energy depending on the temperature $T$, the pressure $p$ and the composition variables $N_k,\ k = 1, ..., n.$ A consequence of this is that the chemical potentials are also functions of these variables such that, on using (29),

$$\mathrm{d}\mu_i = \frac{\partial \hat{\mu}_i}{\partial T}\,\mathrm{d}T + \frac{\partial \hat{\mu}_i}{\partial p}\,\mathrm{d}p + \sum_{k=1}^{n} \frac{\partial \hat{\mu}_i}{\partial N_k}\mathrm{d}N_k = -S_i\,\mathrm{d}T + V_i\,\mathrm{d}p + \frac{1}{N}\sum_{k=1}^{n} \mu_{ik}\mathrm{d}N_k\,, \tag{39}$$

where $\mu_{ik}$ are intensive thermodynamic quantities defined by

$$\mu_{ik} = N\frac{\partial \hat{\mu}_i}{\partial N_k} = N\frac{\partial^2 \hat{G}}{\partial N_i \partial N_k} = \mu_{ki}\,, \quad i, k = 1, ..., n. \tag{40}$$

It follows from (24) that

$$\sum_{j=1}^{n} N_j \mu_{kj} = \sum_{j=1}^{n} N_j \mu_{jk} = 0\,, \tag{41}$$

implying that no new partial thermodynamic quantities of interpretative value arise from the third term of the R.H.S. of (39). On multiplying (39) by $N_i$ and then summing over all $n$ species, and on using (30) and (31), the Gibbs-Duhem relation (19) is obtained.

The concept of partial pressures is considered below in Section 3.5.

## 2.7 MOLAR HEAT CAPACITIES

When considering heat conduction in a multi-component mixture, it is helpful to introduce the molar heat capacity. It is, therefore, useful to discuss the definition of molar heat capacity in the context of the global thermodynamic treatment described above. The molar heat capacity of a uniform system is the differential quantity of heat required to raise the temperature of one mole of material by one kelvin. The heat added depends on whether the total volume or the pressure is held fixed during the rise in temperature, and these cases need to be distinguished.

*Molar heat capacity at constant volume*

For a given total volume $V$ of a uniform system, use is first made of the internal energy $U = \tilde{U}(S, V, \{N_i\})$ so that the temperature $T$ and pressure $p$ may be calculated using (4) in terms of the state variables $S, V$ and $\{N_i\}$, i.e. $T = \tilde{T}(S,V,\{N_i\})$ and $p = \tilde{p}(S,V,\{N_i\})$. It is possible in principle to manipulate the relation $T = \tilde{T}(S,V,\{N_i\})$ so that the entropy $S$ is expressed as a function of the state variables $T, V$ and $\{N_i\}$, i.e. $S = \bar{S}(T,V,\{N_i\})$. It then follows that

$$U = \bar{U}(T,V,\{N_i\}) \equiv \tilde{U}(\bar{S}(T,V,\{N_i\}),V,\{N_i\}) . \tag{42}$$

Differentiation with respect to the temperature $T$ then leads, on using $(4)_1$ to

$$\frac{\partial \bar{U}}{\partial T} = \frac{\partial \tilde{U}}{\partial S}\frac{\partial \bar{S}}{\partial T} = T\,\frac{\partial \bar{S}}{\partial T} . \tag{43}$$

When using the state variables $T$, $V$ and $\{N_i\}$, this result also follows from (12) as $\bar{U} = \bar{F} + T\bar{S}$. The molar heat capacity at constant volume $C_V$ is defined by

$$C_V = \frac{1}{N}\frac{\partial \bar{U}}{\partial T} = \frac{T}{N}\,\frac{\partial \bar{S}}{\partial T} = -\frac{T}{N}\,\frac{\partial^2 \bar{F}}{\partial T^2} , \tag{44}$$

where $N$ is the total molar content of all species as given by (1), and use has been made of the relation $(12)_1$. It is noted that the pressure $p$ may be expressed in the following form

$$p = \bar{p}\left(T, V, \{N_i\}\right) . \tag{45}$$

In gas dynamics especially, this relation is a commonly expressed alternative form of the equation of state for the system. In principle, (45) contains the same information as the relations defined above as equations of state for the internal, Helmholtz and Gibbs energies (respectively (2), (11) and (14)). The mathematical conversion between (45) and the equations of state defined above follows from $(12)_2$, which defines the relation between the functions $\bar{p}$ and $\bar{F}$.

*Molar heat capacity at constant pressure*

The state variables are now selected to be $T$, $p$ and $\{N_i\}$, and the relation (45) can in principle be manipulated into the form

$$V = \hat{V}\left(T,\, p, \{N_i\}\right) . \tag{46}$$

The molar heat capacity at constant pressure $C_p$ is defined by

$$C_p = \frac{1}{N}\frac{\partial \hat{H}}{\partial T} . \tag{47}$$

From (8) and (25) it follows that $\hat{H} = \hat{G} + T\hat{S}$ so that on using (16)$_1$

$$\frac{\partial \hat{H}}{\partial T} = T\,\frac{\partial \hat{S}}{\partial T} = -T\,\frac{\partial^2 \hat{G}}{\partial T^2}\,. \tag{48}$$

From (47), the molar heat capacity at constant pressure may then be written

$$C_p = \frac{T}{N}\frac{\partial \hat{S}}{\partial T} = -\frac{T}{N}\frac{\partial^2 \hat{G}}{\partial T^2}\,, \tag{49}$$

where from (14) the Gibbs energy is specified by $G = \hat{G}(T, p, \{N_i\})$.

From the relations $U = \tilde{U}(S, V, \{N_i\})$, $S = \hat{S}(T, p, \{N_i\})$, and on using (46), it follows that

$$U = \hat{U}(T, p, \{N_i\}) \equiv \tilde{U}\left(\hat{S}(T, p, \{N_i\}), \hat{V}(T, p, \{N_i\}), \{N_i\}\right). \tag{50}$$

On differentiating with respect to the temperature $T$

$$\frac{\partial \hat{U}}{\partial T} = \frac{\partial \tilde{U}}{\partial S}\frac{\partial \hat{S}}{\partial T} + \frac{\partial \tilde{U}}{\partial V}\frac{\partial \hat{V}}{\partial T}\,. \tag{51}$$

On using (4)$_{1,2}$ it then follows that

$$\frac{\partial \hat{U}}{\partial T} = T\,\frac{\partial \hat{S}}{\partial T} - p\,\frac{\partial \hat{V}}{\partial T}\,, \tag{52}$$

so that from (49) the specific heat at constant pressure may be expressed

$$C_p = \frac{1}{N}\left(\frac{\partial \hat{U}}{\partial T} + p\,\frac{\partial \hat{V}}{\partial T}\right). \tag{53}$$

On using (46) to express the internal energy $U$ in the form

$$U = \hat{U}(T, p, \{N_i\}) \equiv \bar{U}(T, V, \{N_i\}) \equiv \bar{U}(T, \hat{V}\left(T,\ p,\ \{N_i\}\right), \{N_i\})\,, \tag{54}$$

it follows that

$$\frac{\partial \hat{U}}{\partial T} = \frac{\partial \bar{U}}{\partial T} + \frac{\partial \bar{U}}{\partial V}\frac{\partial \hat{V}}{\partial T}\,. \tag{55}$$

The relations (44) and (53) then lead to the following expression for the heat capacity at constant pressure

$$C_p = C_V + \frac{1}{N}\left(\frac{\partial \bar{U}}{\partial V} + p\right)\frac{\partial \hat{V}}{\partial T}\,. \tag{56}$$

The bulk thermal expansion coefficient $\alpha$ is defined as the change in volume per unit volume per unit rise of temperature when the pressure and composition are held fixed so that

$$\alpha = \frac{1}{V}\frac{\partial \hat{V}}{\partial T}\,. \tag{57}$$

It then follows that

$$C_p = C_V + \frac{\alpha V}{N}\left(\frac{\partial \bar{U}}{\partial V} + p\right). \tag{58}$$

It follows from (2) and (3), on setting $S = \bar{S}(T, V, \{N_i\})$, that the internal energy $U$ may be expressed

$$U = \bar{U}(T,V,\{N_i\}) \equiv \tilde{U}(\bar{S}(T,V,\{N_i\},V,\{N_i\}) \,. \tag{59}$$

On using (4)$_{1,2}$, it then follows on differentiation with respect to the volume $V$ that

$$\frac{\partial \bar{U}}{\partial V} = \frac{\partial \tilde{U}}{\partial S}\frac{\partial \bar{S}}{\partial V} + \frac{\partial \tilde{U}}{\partial V} = T\,\frac{\partial \bar{S}}{\partial V} - p. \tag{60}$$

Substitution in (58) leads to

$$C_p = C_V + \frac{\alpha TV}{N}\,\frac{\partial \bar{S}}{\partial V}\,. \tag{61}$$

From (12)$_{1,2}$ it follows that

$$\frac{\partial \bar{S}}{\partial V} = \frac{\partial \bar{p}}{\partial T} = -\frac{\partial^2 \bar{F}}{\partial T \partial V}, \tag{62}$$

so that (61) may be written

$$C_p = C_V + \frac{\alpha TV}{N}\,\frac{\partial \bar{p}}{\partial T}\,. \tag{63}$$

From (45) and (46) it follows that the functions $\bar{p}$ and $\hat{V}$ must have the following property for any values of the variables $T$, $p$ and $\{N_i\}$

$$p \equiv \bar{p}\big(T, \hat{V}(T,\ p, \{N_i\}), \{N_i\}\big). \tag{64}$$

On differentiating (64) with respect to the temperature $T$ keeping $p$ and $\{N_i\}$ fixed, it follows that

$$\frac{\partial \bar{p}}{\partial T} + \frac{\partial \bar{p}}{\partial V}\frac{\partial \hat{V}}{\partial T} \equiv 0\,, \tag{65}$$

enabling (63) to be written

$$C_p = C_V - \frac{\alpha TV}{N}\frac{\partial \bar{p}}{\partial V}\frac{\partial \hat{V}}{\partial T}\,. \tag{66}$$

On differentiating the identity (64) with respect to the pressure $p$ keeping $T$ and $\{N_i\}$ fixed, the following relation is obtained

$$\frac{\partial \bar{p}}{\partial V}\,\frac{\partial \hat{V}}{\partial p} = 1. \tag{67}$$

The isothermal bulk compressibility $K$ is defined as the change in volume per unit volume when a unit pressure is applied while the temperature and composition are held fixed so that

$$K = -\frac{1}{V}\frac{\partial \hat{V}}{\partial p}\,. \tag{68}$$

On using (67), the isothermal bulk modulus $1/K$ is given by

$$\frac{1}{K} = -V\frac{\partial \bar{p}}{\partial V}\,. \tag{69}$$

The relation (66) may then be expressed

$$C_p = C_V + \frac{\alpha}{K}\frac{T}{N}\frac{\partial \hat{V}}{\partial T}\,. \tag{70}$$

On using (57) the molar heat capacity at constant pressure is then written in the following compact form

$$C_p = C_V + \frac{\alpha^2}{K}\frac{TV}{N}. \tag{71}$$

## 3 LOCAL THERMODYNAMIC RELATIONS FOR UNIFORM SYSTEMS

The first step towards the development of thermodynamic relations that can be applied in non-uniform systems is the definition of thermodynamic variables that can be applied at a local rather than global level.

### 3.1 DEFINITION OF MOLAR VARIABLES

When developing models of non-equilibrium thermodynamic processes, such as heat and mass transport, account needs to be taken of the non-uniformities of all the state variables. This can be achieved by first expressing the thermodynamic relations (14)-(23), involving the Gibbs energy for *uniform* systems, in a form applicable to just one mole of all species in the multi-component system (i.e., molar quantities). Two other choices could have been made if unit volumes (volumetric quantities) or unit masses (specific quantities) were selected to normalise the size of the system (see Section 3.6 below).

The relations described in Section 2 apply for a uniform system having volume $V$ when there is a molar content $N$ of all species defined by (1). In such a uniform system, any extensive thermodynamic quantity $\Phi$ may be written $\Phi = N\phi$, where $\phi$ is the value of $\Phi$ normalised with respect to one mole of species of all types, which is referred to as the associated *molar* thermodynamic quantity.

The composition of the multi-component system (but not its size) can be described by the molar concentrations $c_k,\ k = 1, \ldots, n,$ which are measured in moles per unit volume so that

$$c_k = \frac{N_k}{V},\ k = 1, \ldots, n. \tag{72}$$

The total number of moles of all species per unit volume in the system is simply the sum of the concentrations of all the species, and is known as the total concentration, to be denoted here by $c$. Because of the relation (1), it is clear from (72) that

$$\sum_{k=1}^{n} c_k = c = \frac{N}{V} = \frac{1}{v}, \tag{73}$$

where $v$ is the molar volume of the system.

As $c = N/V$ for uniform systems, it follows that any extensive thermodynamic quantity $\Phi$ is such that $\Phi = N\phi = Vc\phi$. The quantities $\phi$ and $c$, which are independent of the global variables $N$ and $V$ characterising the size of the system, are regarded as *local* thermodynamic variables. When considering non-uniform systems for non-equilibrium conditions, both $c$ and $\phi$ must be allowed to depend on position in the system and on time, because each of the species concentrations needs to depend on position and time, and because the value of $\phi$ usually depends on the concentrations of the species present.

The extensive global thermodynamic variables associated with the Gibbs energy are $G$, $S$, $V$ and $N_k,\ k = 1, \ldots, n,$ referring in each case to a total of $N$ moles (i.e. $NN_\mathrm{A}$ molecules in the system where $N_\mathrm{A}$ denotes the Avogadro constant having unit mol$^{-1}$). Composition for uniform systems can, in principle, be referred to any other number of molecules in total, and the analysis given in Section 2 would apply to whatever number is selected. The most convenient approach is to use molar thermodynamic quantities, where system size is normalised with respect to one mole having a fixed number $N_\mathrm{A}$ of elementary constituents (atoms, molecules, etc.) in the uniform system. The molar variables, corresponding to the global counterparts *G*, *S*, *V* and $N_k,\ k=1,\ldots,n,$ are denoted respectively by *g*, *s*, *v* and $x_k,\ k=1,\ldots,n,$ such that

$$g=\frac{G}{N},\qquad s=\frac{S}{N},\qquad v=\frac{V}{N},\qquad x_k=\frac{N_k}{N}=\frac{c_k}{c},\ k=1,\ldots,n, \tag{74}$$

where *N* is defined by (1) and use has been made of (72) and (73). It is clear that the mole fractions $\{x_i\}$ are not independent as they are dimensionless state variables satisfying the relation

$$\sum_{k=1}^{n} x_k=1\,. \tag{75}$$

The molar variables $g,s,v$ and $x_k,\ k=1,\ldots,n,$ are regarded as *local* thermodynamic variables corresponding to the global variables *G*, *S*, *V* and $N_k,\ k=1,\ldots,n.$ It is noted from (19), on dividing by *N*, that the local form of the global Gibbs-Duhem relation has the form

$$s\,\mathrm{d}T-v\,\mathrm{d}p+\sum_{k=1}^{n}x_k\,\mathrm{d}\mu_k=0. \tag{76}$$

## 3.2 DIRECT METHOD OF DERIVING LOCAL THERMODYNAMIC RELATIONS

To avoid having to deal with a set of state variables $\{x_i\}$, which are not independent because of the relation (75), an alternative scaling is first considered where for some given number $N^*$ (measured in moles) the substitution $\lambda=1/N^*$ is made in the homogeneity relation (17) so that

$$\hat{G}(T,p,\{N_i\})\equiv N^*\hat{G}(T,p,\{x_i^*\}), \tag{77}$$

where

$$x_k^*=N_k/N^*,\ k=1,\ldots,n. \tag{78}$$

The independent quantities $\{x_i^*\}$ are regarded as pseudo-mole fractions as on using (1)

$$\sum_{k=1}^{n}x_k^*=\frac{N}{N^*}, \tag{79}$$

so that the set $\{x_i^*\}$ tends to the set of mole fractions $\{x_i\}$ when $N^*\to N$. The mole fractions $\{x_i\}$ have values lying in the range zero to unity that must satisfy the relation (75), whereas the pseudo-mole fractions $\{x_i^*\}$ are non-negative (having values lying in the range zero to infinity) and do not necessarily satisfy (75).

A pseudo-molar Gibbs energy $g^*$ is now introduced such that

$$g^*=\frac{G}{N^*}=\frac{1}{N^*}\hat{G}(T,p,\{N_i\})\equiv\hat{G}(T,p,\{x_i^*\}), \tag{80}$$

where the independent pseudo-mole fractions $\{x_i^*\}$ satisfy (79). Similarly, on using (22) and (23), the pseudo-molar entropy $s^*$ and pseudo-molar volume $v^*$ are defined by

$$s^* = \frac{S}{N^*} = \frac{1}{N^*}\hat{S}(T, p, \{N_i\}) \equiv \hat{S}(T, p, \{x_i^*\}) , \tag{81}$$

$$v^* = \frac{V}{N^*} = \frac{1}{N^*}\hat{V}(T, p, \{N_i\}) \equiv \hat{V}(T, p, \{x_i^*\}) . \tag{82}$$

The local formulation leading to (80)-(82) follows from applying the substitutions in (83) to both arguments and symbols of partial derivatives in the global analysis given in Section 2.3.

$$\{N_i\} \Rightarrow \{x_i^*\}, \quad G \Rightarrow g^*, \quad S \Rightarrow s^*, \quad V \Rightarrow v^* . \tag{83}$$

These substitutions may be made in the function $\hat{G}(T, p, \{N_i\})$, in the differential form (15) and in the derivatives given by (16). The independence of the set of pseudo-mole fractions $\{x_i^*\}$ means that direct use can be made of the analysis given in Section 2.3, as partial derivatives with respect to each of the $n$ pseudo-mole fractions (holding the remaining ($n$–1) mole fractions constant) can be easily be calculated, although corresponding derivatives with respect to the mole fractions $\{x_i\}$ cannot be calculated in a mathematically meaningful way.

It follows, on making the substitutions $(83)_{1,2}$ in (14), that the resulting local equation of state must have the form consistent with (80)

$$g^* = \hat{G}(T, p, \{x_i^*\}) . \tag{84}$$

It is noted that the same function $\hat{G}$ must be used locally as was used in corresponding global relation. As the global form $\hat{G}(T, p, \{N_i\})$ is homogeneous of order unity in the variables $\{N_i\}$(see (17)), the corresponding local form $\hat{G}(T, p, \{x_i^*\})$ will automatically be homogeneous of order unity in the variables $\{x_i^*\}$. The differential relation corresponding to (84) is

$$\mathrm{d}g^* = -\, s^*\mathrm{d}T + v^*\mathrm{d}p + \sum_{k=1}^{n} \mu_k \mathrm{d}x_k^* , \tag{85}$$

where from (16)

$$\begin{aligned} s^* &= -\frac{\partial \hat{G}(T, p, \{x_i^*\})}{\partial T} = \hat{S}(T, p, \{x_i^*\}), \\ v^* &= \frac{\partial \hat{G}(T, p, \{x_i^*\})}{\partial p} = \hat{V}(T, p, \{x_i^*\}), \\ \mu_k &= \frac{\partial \hat{G}(T, p, \{x_i^*\})}{\partial x_k^*} = \hat{\mu}_k(T, p, \{x_i^*\}) , \quad k = 1, ..., n. \end{aligned} \tag{86}$$

In addition, it follows from (18) and $(74)_1$ that

$$g^* = \sum_{k=1}^{n} x_k^* \mu_k . \tag{87}$$

It is emphasised that the local relations (84)-(87) are based on exactly the same functions $\hat{G}$, $\hat{S}$, $\hat{V}$ and $\hat{\mu}_k,\ k = 1, ..., n,$ having the properties (17), (22) and (23), that were used for the corresponding global relations introduced in Section 2.3, and furthermore that the pseudo-mole fractions $\{x_i^*\}$ describing composition are independent dimensionless quantities. This independence ensures that the partial derivatives in $(86)_3$ are well defined. The same situation arises when using the alternative sets of state variables introduced in Sections 2.1, 2.2 and 2.4.

## 3.3 RESTORING USE OF MOLAR THERMODYNAMIC VARIABLES

Because the pseudo-mole fractions $\{x_i^*\}$ used in Section 3.2 are independent, it follows that they do not, in general, satisfy the relation (75). The final step in the procedure to develop local equations of state, and local thermodynamic relations is to evaluate the local thermodynamic functions derived in Sections 3.2 by taking the limit $N^* \to N.$ From (80)-(82), it is clear that as $\{x_i^*\} \to \{x_i\}$ the pseudo-molar quantities tend to the corresponding molar quantities as follows

$$\begin{aligned} g^* &\to g = \frac{G}{N} = \frac{1}{N}\hat{G}(T,p,\{N_i\}) = \hat{G}(T,p,\{x_i\}), \\ s^* &\to s = \frac{S}{N} = \frac{1}{N}\hat{S}(T,p,\{N_i\}) = \hat{S}(T,p,\{x_i\}), \\ v^* &\to v = \frac{V}{N} = \frac{1}{N}\hat{V}(T,p,\{N_i\}) = \hat{V}(T,p,\{x_i\}), \\ &\hat{\mu}_k(T,p,\{x_i^*\}) \to \hat{\mu}_k(T,p,\{x_i\}),\ k = 1, ..., n. \end{aligned} \tag{88}$$

As expected from (87)

$$g = \sum_{k=1}^{n} x_k \mu_k\,, \tag{89}$$

so that from the local form of the Gibbs-Duhem relation (76) it follows that

$$\mathrm{d}g = -s\,\mathrm{d}T + v\,\mathrm{d}p + \sum_{k=1}^{n} \mu_k \mathrm{d}x_k\,, \tag{90}$$

where from (75)

$$\sum_{k=1}^{n} \mathrm{d}x_k = 0\,. \tag{91}$$

The differential relation (90) should be compared to the corresponding relation (85) where the pseudo-mole fractions are not subject to the condition (91).

It is noted that this direct method of deriving the local equation of state, and the associated local thermodynamic relations, makes use only of one function $\hat{G}$ and its partial derivatives that are used to define the functions $\hat{S}$, $\hat{V}$, $\hat{\mu}_k,\ k = 1, ..., n,$ and the local thermodynamic quantities $s, v$ and $\mu_k,\ k = 1, ..., n.$ It is essential that partial derivatives in (86)$_3$ are taken with respect to the independent pseudo-mole fractions $x_k^*,\ k = 1, ..., n,$ rather than with respect to the mole fractions $x_k,\ k = 1, ..., n.$

## 3.4 LOCAL RELATIONS FOR PARTIAL QUANTITIES AND MOLAR HEAT CAPACITIES

The key relations regarding partial thermodynamic quantities are given by (29) which define the partial entropies and partial volumes denoted respectively by $S_k, V_k,\ k = 1, ..., n.$ By direct substitution using (83), these partial quantities may be calculated using the following local relations

$$\left.\begin{aligned} S_k &= \frac{\partial \hat{S}(T,p,\{x_i^*\})}{\partial x_k^*} = -\frac{\partial^2 \hat{G}(T,p,\{x_i^*\})}{\partial T\,\partial x_k^*}, \\ V_k &= \frac{\partial \hat{V}(T,p,\{x_i^*\})}{\partial x_k^*} = \frac{\partial^2 \hat{G}(T,p,\{x_i^*\})}{\partial p\,\partial x_k^*}, \end{aligned}\right\} \quad k = 1, ..., n, \tag{92}$$

where the functions $\hat{S}$ and $\hat{V}$ are defined by $(86)_{1,2}$. The corresponding partial internal energies $U_k$, partial Helmholtz energies $F_k$ and partial enthalpies $H_k$ may be calculated using the relations (32), (35) and (38) respectively. It should be noted that, because of the relation (18) (or the local form (89)), the chemical potentials can be regarded as partial Gibbs energies. The molar internal energy *u*, molar Helmholtz energy *f*, molar entropy *s*, molar volume *v* and molar enthalpy *h* may then be calculated in terms of partial quantities using the relations (30), (31), (34) and (37) so that

$$u = \frac{U}{N} = \sum_{k=1}^{n} x_k U_k , \quad f = \frac{F}{N} = \sum_{k=1}^{n} x_k F_k , \quad s = \frac{S}{N} = \sum_{k=1}^{n} x_k S_k , \quad v = \frac{V}{N} = \sum_{k=1}^{n} x_k V_k \ , \quad h = \frac{H}{N} = \sum_{k=1}^{n} x_k H_k \ . \quad (93)$$

When considering molar heat capacities, it is more convenient to use the relation (49) to calculate the local form of the expression for molar heat capacity at constant pressure so that

$$C_p = -T \, \frac{\partial^2 \hat{G}(T, p, \{x_i^*\})}{\partial T^2} . \quad (94)$$

The local form of the molar heat capacity at constant volume may then be calculated using the following relation, obtained from (71) using $(74)_3$,

$$C_V = C_p - \frac{\alpha^2}{K} v T \, . \quad (95)$$

## 3.5 CONSIDERATION OF PARTIAL PRESSURES

Since from (72) $c_k = N_k / V$ is the molar concentration of the $k^{\text{th}}$ species, it follows from the global relation (36) that an *intensive* quantity, the pressure *p*, may be written

$$p = \sum_{k=1}^{n} c_k \left( \mu_k - F_k \right) = \sum_{k=1}^{n} c_k \left( \mu_k - U_k + T S_k \right) = \sum_{k=1}^{n} p_k \ , \quad (96)$$

where $p_k$ can be interpreted as the thermodynamic partial pressures that can be defined in general by

$$p_k = c_k \left( \mu_k - F_k \right) = c_k \left( \mu_k - U_k + T S_k \right) = p \, c_k V_k \, , \ \ k = 1, \ldots, n \, , \quad (97)$$

where use has been made of the relation (32). On summing the last form for $p_k$ in (97), it is clear from (96) that the following relation must be satisfied

$$\sum_{k=1}^{n} c_k V_k = 1 , \quad (98)$$

which is consistent with (31). It is noted that when only one species is present so that *n* = 1, it follows that $c_1 V_1 = 1$ so that the partial pressure $p_1 = p$, as to be expected. For a uniform system, and since $c_k = N_k / V,$ it is noted from (31) and (97) that

$$\frac{p_k}{p} = \frac{N_k V_k}{V} = \frac{N_k V_k}{\sum_{i=1}^{n} N_i V_i} \ , \quad (99)$$

so that the ratio of the partial pressure for species *k* to the total pressure is equal to the volume fraction of the $k^{\text{th}}$ species in the multi-component system. For an ideal gas, the molar volume of each species has the same value ($V_k = RT / p$ for all *k*) so that the pressure ratio reduces to the mole fraction of the $k^{\text{th}}$

species, a well-known relationship. The general local relation $p_k = p c_k V_k ,\ k = 1, ..., n,$ indicates one possible new method of characterising the partial pressure for a non-ideal non-viscous fluid mixture.

In the review by Curtiss and Bird [6] it is suggested that the concept of the partial pressure $p_k$ does not follow naturally from the general theory of thermodynamics, but that the gradient of the partial pressure can always be defined as follows

$$\nabla p_k = c_k \nabla \mu_k + c_k S_k \nabla T , \qquad k=1, ..., n . \tag{100}$$

It is useful now to determine the conditions for which this definition of partial pressure gradient is consistent with the relation (97) which leads to

$$\nabla p_k = \left( \mu_k - U_k + TS_k \right) \nabla c_k + c_k \nabla \mu_k - c_k \nabla U_k + T c_k \nabla S_k + c_k S_k \nabla T ,\ k = 1, ..., n. \tag{101}$$

Assume now that each species behaves as though it were the only species present. On using the subscript 'vol' to indicate a thermodynamic variable that is measured per unit volume, and on setting $u_{\text{vol}}^{(k)} \equiv c_k U_k$, $s_{\text{vol}}^{(k)} \equiv c_k S_k$, for $k$ = 1, …, $n$, each species will have an equation of state having the form

$$u_{\text{vol}}^{(k)} = u_{\text{vol}}^{(k)} (s_{\text{vol}}^{(k)}, c_k) \qquad \text{such that} \qquad \mathrm{d}u_{\text{vol}}^{(k)} = T\, \mathrm{d}u_{\text{vol}}^{(k)} + \mu_k \mathrm{d}c_k . \tag{102}$$

It then follows from (97) and $(102)_2$ that

$$c_k \mathrm{d}U_k = T c_k \mathrm{d}S_k + \left( \mu_k + TS_k - U_k \right) \mathrm{d}c_k = T c_k \mathrm{d}S_k + p V_k \mathrm{d}c_k , \tag{103}$$

and that

$$c_k \nabla U_k = T c_k \nabla S_k + p V_k \nabla c_k . \tag{104}$$

Substitution of (104) in (101) using (32) then leads to the relation (100) given by Curtiss and Bird. It follows from the form of the equation of state (102) that the relation (100) defining the gradient of the partial pressure thus appears to be justified only if the various species in a multi-component mixture behave independently, i.e. they do not interact, as would be the case for ideal gas mixtures. In contrast, the relations (97) for partial pressure are defined in this report in a thermodynamically general manner, while still reducing to commonly used constitutive relations when the corresponding simplifications (e.g. ideal gas) are applied to the equation of state.

### 3.6 SPECIFIC THERMODYNAMIC QUANTITIES

When developing local balance equations for multi-component continua, the mass density plays a very important role (see for example [4, 5]). The density of the $k$th species is denoted by $\rho_k$ and is given by

$$\rho_k = M_k c_k ,\ k = 1, ..., n, \tag{105}$$

where $M_k$ denotes the molar mass of the $k$th species. The density of the continuum, denoted by $\rho$, is then given by

$$\rho = \sum_{k=1}^{n} \rho_k . \tag{106}$$

Mass fractions of the various species are then defined such that

$$\omega_k = \frac{\rho_k}{\rho} ,\ k = 1, ..., n, \qquad \text{and} \qquad \sum_{k=1}^{n} \omega_k = 1. \tag{107}$$

Using (73), the relations

$$cu \equiv \rho\varepsilon, \quad cs \equiv \rho\eta, \quad cg \equiv \rho\phi, \tag{108}$$

are now introduced, which define the relationships between the *molar* internal energy $u$, molar entropy $s$, molar Gibbs energy $g$, and the *specific* internal energy $\varepsilon$, specific entropy $\eta$, and specific Gibbs energy $\phi$ respectively.

The global Gibbs energy of a uniform system may be expressed as a function of the masses of each component $m_k = M_k N_k$, $k = 1, \ldots, n$, as follows

$$G = \hat{G}(p, T, \{N_i\}) = \hat{G}(p, T, \{m_i/M_i\}) = \hat{\Phi}(p, T, \{m_i\}) = \hat{\Phi}(p, T, \{M_i N_i\}), \tag{109}$$

so that

$$\mu_k = \frac{\partial \hat{G}}{\partial N_k} = M_k \frac{\partial \hat{\Phi}}{\partial m_k}, \quad k = 1, ..., n. \tag{110}$$

Here, by analogy to the pseudo-mole fractions used above, we denote pseudo-mass fractions $\omega_k^*, k = 1, ..., n,$ as ratios of the mass $m_k$ to a scaling mass $m^*$ such that

$$\omega_k^* = m_k / m^*, \; k = 1, ..., n. \tag{111}$$

The independent quantities $\{\omega_i^*\}$ are regarded as pseudo-mass fractions as

$$\sum_{k=1}^{n} \omega_k^* = \frac{m}{m^*}, \tag{112}$$

where $m$ is the total mass of the system defined by

$$m = \sum_{k=1}^{n} m_k \,. \tag{113}$$

The set $\{\omega_i^*\}$ tends to the set of mass fractions $\{\omega_i\}$ when $m^* \to m$.

It is noted, on using $(74)_4$ and (105)-(107), that

$$\omega_k = \frac{M_k c_k}{\rho} = \frac{M_k x_k}{\sum_{i=1}^{n} M_i x_i}, \; k = 1, ..., n, \quad \text{so that} \quad \omega_k^* = \frac{M_k x_k^*}{\sum_{i=1}^{n} M_i x_i^*}. \tag{114}$$

Using the direct method of scaling substitutions for pseudo-mass fractions (as introduced in Section 3.2 when using mole fractions), the following equation of state and differential expressions result for the specific Gibbs energy

$$\phi \equiv \varepsilon - T\eta + p\Omega = \hat{\Phi}(T, \, p, \{\omega_i^*\}), \tag{115}$$

where $\Omega \equiv 1/\rho$ is the specific volume and

$$\mathrm{d}\phi = -\eta \, \mathrm{d}T + \Omega \mathrm{d}p + \sum_{k=1}^{n} \frac{\mu_k}{M_k} \mathrm{d}\omega_k^*, \quad \eta = -\frac{\partial \hat{\Phi}}{\partial T}, \; \Omega = \frac{\partial \hat{\Phi}}{\partial p}, \quad \mu_k = M_k \frac{\partial \hat{\Phi}}{\partial \omega_k^*}, \; k = 1, ..., n, \tag{116}$$

and where the following relation must be satisfied

$$\phi = \sum_{k=1}^{n} \omega_k^* \frac{\mu_k}{M_k}. \tag{117}$$

When all the required partial derivatives have been calculated, the limit $m^* \to m$ is taken so that the pseudo-mass fractions $\{\omega_i^*\}$ are replaced respectively by the corresponding mass fractions $\{\omega_i\}$, as the relation $(107)_2$ must be satisfied.

# 4 A GENERAL APPROACH TO LOCAL FORMULATIONS

It will become clear that, when formulating local thermodynamic formulations suitable for use in continuum simulations, anomalies can arise, leading to errors that need to be avoided. This Section first gives a simple example of such an anomaly and then describes methods of generalising the discussion in Section 3, while avoiding easily made errors when developing local formulations of thermodynamic relations needed for non-equilibrium simulations.

## 4.1 SIMPLE ILLUSTRATION OF A TYPICAL PROBLEM

Before adding further generality to the local definition of chemical potential, it is first useful to identify an important difficulty that arises on using a naïve definition of chemical potential in conjunction with standard expressions for the chemical potential function. It is clear from Section 3 that all results given have assumed that the Gibbs energy function $\hat{G}$ for a uniform system is known in terms of global state variables. The homogeneity property of the function $\hat{G}$ then leads to an expression for the molar Gibbs energy expressed in terms of local state variables such as mole fractions. As there are many expressions for chemical potentials in the literature expressed in terms of mole fractions, there is a temptation to determine the corresponding molar Gibbs energy function by making use of the relation (89). A simple example will now be considered that will describe the difficulty that will then arise.

For an ideal system, the molar-based chemical potentials are given by (see for example Demeril [7], eq. (1.27) and Guggenheim [9], eq. (4.19.1))[1].

$$\mu_k = \mu_k^0(T, p) + RT \ln x_k, \; k = 1, ..., n. \tag{118}$$

where $R$ denotes the universal gas constant. On using (89), the molar Gibbs energy $g$ is then given by

$$g = \sum_{i=1}^{n} x_i \mu_i = \sum_{i=1}^{n} x_i \mu_i^0(T, p) + RT \sum_{i=1}^{n} x_i \ln x_i . \tag{119}$$

If, by analogy to the local relation (86)$_3$, the chemical potentials are naïvely defined locally by

$$\mu_k = \frac{\partial g}{\partial x_k}, \quad k = 1, ..., n, \tag{120}$$

then, on substituting (119) in (120),

$$\mu_k = \mu_k^0(T, p) + RT \ln x_k + RT, \; k = 1, ..., n, \tag{121}$$

which does not correspond with the expression (118) originally given. This inconsistency implies that the local relation (120) lacks general validity, as will be considered in the next Section. Specifically, the R.H.S. of the relation (119) is not homogeneous of order unity in the variables $\{x_i\}$ and so does not correspond to the function $\hat{G}$ as required by (86)$_3$. Also, with regard to (119), the relation (120)

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[1] It is noted, in passing, that the relation (118) is often written (see for example Demirel [7], eq. (1.29), and Newman & Thomas-Alyea [14], eq. (3.18), (3.19) for electrochemical applications)

$$\mu_k = \mu_k^0(T, p) + RT \ln c_k, \quad k = 1, ..., n,$$

where $c_k$ is the molar concentration of the $k^{\text{th}}$ species. Dimensional considerations indicate that this is incorrect. An acceptable replacement of the mole fraction $x_k$ is the term $c_k / c_k^0$ where $c_k^0$ is a reference concentration for species $k$. Its use requires the modification of the leading term on the R.H.S..

implicitly regards the mole fractions as independent variables, which they are not because of the condition (75).

## 4.2 GENERAL EXPRESSIONS FOR CHEMICAL POTENTIALS

Because of the constraint (75) applied to the mole fraction arguments $\{x_i\}$ appearing in $(88)_1$, the molar Gibbs energy function $\hat{G}(T,p,\{x_i\})$ may be modified by arbitrary combinations of substitutions to the mole fraction variables $\{x_i\}$ obeying (75), to yield an unlimited number of new functions $\vec{g}$ in place of the function $\hat{G}$ such that

$$g = \hat{G}(T,p,\{x_i\}) = \vec{g}(T,p,\{x_i\})\,, \tag{122}$$

for any values of *T*, and *p* even though the functions $\hat{G}(T,p,\{x_i^*\})$ and $\vec{g}(T,p,\{x_i^*\})$ are not identical when expressed in terms of independent variables.

For example, for an ideal binary mixture of the two components A and B,

$$\hat{G}(T,p,N_\mathrm{A},N_\mathrm{B}) = RT\left( (N_\mathrm{A}+N_\mathrm{B})\ln\frac{p}{p_0} + N_\mathrm{A}\ln\frac{N_\mathrm{A}}{N_\mathrm{A}+N_\mathrm{B}} + N_\mathrm{B}\ln\frac{N_\mathrm{B}}{N_\mathrm{A}+N_\mathrm{B}} \right), \tag{123}$$

where $p_0$ is a given reference pressure. According to (83) and $(88)_1$

$$g = \hat{G}(T,p,x_\mathrm{A},x_\mathrm{B}) = RT\left( \left(x_\mathrm{A}+x_\mathrm{B}\right)\ln\frac{p}{p_0} + x_\mathrm{A}\ln\frac{x_\mathrm{A}}{x_\mathrm{A}+x_\mathrm{B}} + x_\mathrm{B}\ln\frac{x_\mathrm{B}}{x_\mathrm{A}+x_\mathrm{B}} \right). \tag{124}$$

If (75) holds, then $x_\mathrm{A} + x_\mathrm{B} = 1$, so that

$$\begin{aligned} g &= \vec{g}_1(p,T,x_\mathrm{A},x_\mathrm{B}) = RT\left( \ln\frac{p}{p_0} + x_\mathrm{A}\ln x_\mathrm{A} + x_\mathrm{B}\ln x_\mathrm{B} \right) \\ &= \vec{g}_2(p,T,x_\mathrm{A},x_\mathrm{B}) = RT\left( \ln\frac{p}{p_0} + x_\mathrm{A}\ln x_\mathrm{A} + (1-x_\mathrm{A})\ln(1-x_\mathrm{A}) \right). \end{aligned} \tag{125}$$

It is clear that the functions $\hat{G}$, $\vec{g}_1$ and $\vec{g}_2$ defined by (124) and (125) are particular instances of an infinite number of possible functions having the same value when $x_\mathrm{A} + x_\mathrm{B} = 1$. Except for the function $\hat{G}$, these functions for molar Gibbs energy *g* are not homogeneous functions of order unity with respect to the variables $\{x_i\}$. Returning to the general case $n > 2$ for dependent mole fractions $\{x_i\}$ satisfying the relation (75), consider the extension of the function $\vec{g}(T,p,\{x_i\})$ to the case where the composition arguments are replaced by the corresponding independent pseudo-mole fractions $\{x_i^*\}$. It will in general be the case that $\vec{g}(T,p,\{x_i^*\})$ and $\hat{G}(T,p,\{x_i^*\})$ are not identical functions, although they always have the same value for the special case where the arguments $\{x_i^*\}$ sum to unity. Here, it is important to recognise that the definition of a partial derivative with respect to a pseudo-mole fraction $x_k^*$, holding all other pseudo-mole fractions constant as in $(86)_3$, applies only in cases for which (75) no longer holds. The derivative relates to a variation of the molar Gibbs energy function away from the physically meaningful subset of mole fraction arguments satisfying (75). This characteristic of the partial derivatives with respect to pseudo-mole fractions (that these derivatives lack intrinsic physicality in isolation) will help to resolve the contradiction noted above, when using a naïve method to evaluate chemical potentials from a Gibbs energy function constructed from given formulae for chemical potentials expressed as functions of mole fractions.

Consistency of local formulations with the global case can be ensured by recognising that the definition of molar Gibbs energy requires that

$$g = \frac{G}{N} = \frac{1}{N}\hat{G}(T,p,\{N_i\}) \equiv \hat{G}(T,p,\{N_i/N\}) \equiv \hat{G}(T,p,\{x_i\}) = \vec{g}(T,p,\{x_i\})\,, \tag{126}$$

where the function $\vec{g}$ could be a simplified form, or some other form, of the function $\hat{G}$ obtained by making use of (75). It is restated that there are an unlimited number of ways in which the function $\vec{g}$ can be constructed involving an unlimited number of substitutions, possibly successive, based on the relation (75). It is shown in Appendix B that the original function $\hat{G}$, first introduced when considering uniform global systems, can be constructed from any of the possible functions $\vec{g}$ using the following relation

$$\hat{G}(T,p,\{x_i^*\}) \;=\; \left(\sum_{k=1}^{n} x_k^*\right)\vec{g}\left(T,p,\left\{x_i^*\Big/\sum_{k=1}^{n} x_k^*\right\}\right). \tag{127}$$

This demonstrates that the homogeneous function $\hat{G}$ of order unity can be generated, if required, from any function $\vec{g}$ for the molar Gibbs energy having the form (122). Naturally, replacing pseudo-mole fractions with mole fractions in (127), thereby enforcing (75), will reduce (127) to (122).

On using (127) and on regarding $\vec{g}$ as a function of the independent variables $(T,p,\{x_i^*\})$ so that partial derivatives can be calculated, the chemical potential of species *i* is obtained using $(86)_3$ and $(88)_4$ so that

$$\begin{aligned}
\mu_i &= \frac{\partial\hat{G}}{\partial x_i^*} \\
&= \vec{g} \;+\; \sum_{j=1}^{n}\frac{\partial\vec{g}}{\partial x_j^*}\left\{\delta_{ij} - x_j^*\Big/\sum_{k=1}^{n} x_k^*\right\} \\
&= \vec{g} \;+\; \sum_{j=1}^{n}\frac{\partial\vec{g}}{\partial x_j^*}(\delta_{ij} - x_j) \\
&= \vec{g} \;+\; \frac{\partial\vec{g}}{\partial x_i^*} - \sum_{j=1}^{n} x_j\,\frac{\partial\vec{g}}{\partial x_j^*}\,,
\end{aligned} \tag{128}$$

i.e. on taking the limit $\{x_i^*\}\rightarrow\{x_i\}$

$$\mu_i \equiv \frac{\partial\hat{G}}{\partial N_i} = \frac{\partial\hat{G}}{\partial x_i^*} = \vec{g} \;+\; \frac{\partial\vec{g}}{\partial x_i^*} - \sum_{j=1}^{n} x_j\,\frac{\partial\vec{g}}{\partial x_j^*}\,. \tag{129}$$

This is the fundamental general expression for the chemical potential of the *i*th species as computed from partial derivatives of any local function $\vec{g}(T,p,\{x_i^*\})$ of independent pseudo-mole fractions before the limit $\{x_i^*\}\rightarrow\{x_i\}$ is taken.

Note that from (17), for any numerical value of $\lambda$

$$\hat{G}(T,\;p,\{\lambda x_i^*\}) \equiv \lambda\hat{G}(T,\;p,\{x_i^*\})\,. \tag{130}$$

On differentiating with respect to $\lambda$, assuming that $\lambda$ is independent of the state variables, and then setting $\lambda = 1$, it follows on taking the limit $\{x_i^*\}\rightarrow\{x_i\}$ that

$$\sum_{i=1}^{n} x_i\,\frac{\partial\hat{G}}{\partial x_i^*} = \hat{G}\,, \tag{131}$$

so that when $\vec{g}(T,p,\{x_i^*\}) = \hat{G}(T,p,\{x_i^*\})$ the general expression (129) for the chemical potentials reduces to the simpler form

$$\mu_i = \frac{\partial \hat{G}}{\partial N_i} = \frac{\partial \hat{G}}{\partial x_i^*} \,, \quad i = 1, ..., n. \tag{132}$$

This result is consistent with the relation (86)$_3$ when the relation (75) is satisfied.

## 4.3 ILLUSTRATIVE PROBLEM REVISITED

It can be verified by inspection that the general result (129) yields consistent results when applied to the introductory ‘paradoxical’ example (119), since

$$\vec{g} = \sum_{i=1}^{n} x_i \mu_i^0(T,p) + RT \sum_{i=1}^{n} x_i \ln x_i \,, \tag{133}$$

so that

$$\frac{\partial \vec{g}}{\partial x_k} = \mu_k^0(T,p) + RT(1 + \ln x_k) \,, \tag{134}$$

leading to

$$\begin{aligned} \mu_k &= \vec{g} + \frac{\partial \vec{g}}{\partial x_k} - \sum_{j=1}^{n} x_j \frac{\partial \vec{g}}{\partial x_j} \\ &= \sum_{i=1}^{n} x_i \mu_i^0(T,p) + RT \sum_{i=1}^{n} x_i \ln x_i + \mu_k^0(T,p) + RT(1 + \ln x_k) \\ &\qquad\qquad - \sum_{j=1}^{n} x_j \left[ \mu_j^0(T,p) + RT(1 + \ln x_k) \right] \\ &= \mu_k^0(T,p) + RT \ln x_k \,, \end{aligned} \tag{135}$$

a result that is consistent with (118). Similarly, it can be verified by inspection that all three Gibbs energy functions shown in (124) and (125) yield the same expressions for the chemical potentials for components A and B of a binary mixture.

## 4.4 LOCAL RELATIONS FOR PARTIAL MOLAR QUANTITIES IN THE GENERAL CASE

Having established the general expression (129) for the chemical potential, all other intensive thermodynamic quantities applicable to the local system can be derived using relations already given. That is, following (29)-(31)

$$S_k = -\frac{\partial \hat{\mu}_k}{\partial T} \,, \qquad V_k = \frac{\partial \hat{\mu}_k}{\partial p} \,, \tag{136}$$

$$s = \sum_{k=1}^{n} x_k S_k = -\sum_{k=1}^{n} x_k \frac{\partial \hat{\mu}_k}{\partial T} = -\frac{\partial}{\partial T}\left( \sum_{k=1}^{n} x_k \hat{\mu}_k \right) = -\frac{\partial \vec{g}}{\partial T} \,, \tag{137}$$

$$v = \sum_{k=1}^{n} x_k V_k = \sum_{k=1}^{n} x_k \frac{\partial \hat{\mu}_k}{\partial p} = \frac{\partial}{\partial p}\left( \sum_{k=1}^{n} x_k \hat{\mu}_k \right) = \frac{\partial \vec{g}}{\partial p} \,. \tag{138}$$

The partial molar internal energy, enthalpy, and Helmholtz energy for each component can then be derived using (32), (35), and (38). The heat capacity at constant pressure can be obtained from (49) as follows

$$C_p = -\frac{T}{N}\frac{\partial^2 \hat{G}}{\partial T^2} = -T\,\frac{\partial^2(\hat{G}/N)}{\partial T^2} = -T\,\frac{\partial^2 \vec{g}}{\partial T^2}\,. \tag{139}$$

The expression (94) given previously can be recognised as a special case of (139).

The heat capacities at constant volume and pressure are related by (95), repeated below

$$C_p = C_V + \frac{\alpha^2}{K} vT\,. \tag{140}$$

In this expression, the bulk thermal expansion coefficient and isothermal bulk compressibility given by (57) and (68) may be expressed

$$\alpha = \frac{1}{V}\frac{\partial \hat{V}}{\partial T} = \frac{1}{v}\frac{\partial \hat{v}}{\partial T}\,, \tag{141}$$

$$K = -\frac{1}{V}\frac{\partial \hat{V}}{\partial p} = -\frac{1}{v}\frac{\partial \hat{v}}{\partial p}\,. \tag{142}$$

The combination of the general expression (129) with expressions (136)-(138) constitutes a rubric whereby all intensive thermodynamic quantities of interest for a local formulation are derived from a single Gibbs energy function $\vec{g}$, not necessarily identical to the global function $\hat{G}$. If the function $\hat{G}$ is known and is used, the formulae are simplified. However, if a function $\vec{g}$ is known or can be easily determined that is not identical to $\hat{G}$, as for the illustration in Section 4.3, this function still inherently incorporates all the thermodynamic information about the system. It is essential to recognise that to recover chemical potentials from such a function self-consistently, (129) must be used and not the naïve inappropriate equation (120). Alternatively, any function $\vec{g}$ can be converted to the function $\hat{G}$ using (127); after this conversion, chemical potentials can be obtained using the simpler expression $(86)_3$.

## 4.5 ALTERNATIVE EQUATION OF STATE

An alternative thermodynamic approach will now be described where the equation of state is assumed to involve *n* – 1 independent mole fractions selected from the *n* dependent mole fractions $\{x_i\}$. There is no loss of generality if it is assumed that the mole fraction $x_n$ is eliminated using the relation (75). It then follows on using $(88)_1$ that a molar Gibbs energy function $\vec{g}$ can be defined by

$$g = \vec{g}(T,\ p,\ x_1,\ x_2,\ ...,\ x_{n-1}) \equiv \vec{g}\left(T,\ p,\ x_1,\ ...,x_{n-1},\ 1-\sum_{i=1}^{n-1} x_i\right), \tag{143}$$

This is a special case of a general molar Gibbs energy $\vec{g}(T, p, \{x_i\})$ wherein

$$\frac{\partial \vec{g}}{\partial x_n^*} = 0 \tag{144}$$

On using (75), $(86)_3$ and (143), it is clear that for *k* = 1, …, *n*–1,

$$\xi_k \equiv \frac{\partial \vec{g}}{\partial x_k} \equiv \frac{\partial}{\partial x_k}\left[\vec{g}\left(T,\ p,\ x_1,\ ...,x_{n-1},\ 1-\sum_{i=1}^{n-1} x_i\right)\right] = \frac{\partial \vec{g}}{\partial x_k^*} - \frac{\partial \vec{g}}{\partial x_n^*} = \mu_k - \mu_n\,. \tag{145}$$

To calculate $\mu_n$ in terms of the function $g$ and $\xi_k,\ k = 1,\ ...,\ n-1,$ use is made of the relation (89) so that

$$g = \sum_{k=1}^{n} \left( \mu_k - \mu_n \right) x_k + \mu_n = \sum_{k=1}^{n-1} \xi_k x_k + \mu_n . \tag{146}$$

It then follows that the molar chemical potentials are given by

$$\begin{aligned} \mu_k &= \xi_k + g - \sum_{i=1}^{n-1} \xi_i x_i , \quad k = 1, ..., n-1, \\ \mu_n &= g - \sum_{i=1}^{n-1} \xi_i x_i . \end{aligned} \tag{147}$$

Clearly, (147) is a special case of the general result (129) on using (144).

## 4.6 SPECIFIC GIBBS ENERGY IN THE GENERAL APPROACH

The method used to derive a general expression for molar Gibbs energy shown in (128) can also be applied to the specific Gibbs energy. Consider the specific Gibbs energy to be given by a general function as follows, which unlike the function $\hat{\Phi}$ discussed in Section 3.6 is not necessarily homogeneous in the mass fractions

$$\phi = \vec{\phi} \left( T, p, \{\omega_i\} \right) . \tag{148}$$

Since

$$G = \left( \sum_{k=1}^{n} M_k N_k \right) \vec{\phi} , \tag{149}$$

it follows that

$$\hat{G} \left( T, p, \{N_i\} \right) = \left( \sum_{k=1}^{n} M_k N_k \right) \vec{\phi} \left( T, p, M_1 N_1 \Big/ \sum_{k=1}^{n} M_k N_k , ..., M_n N_n \Big/ \sum_{k=1}^{n} M_k N_k \right) . \tag{150}$$

Thus

$$\begin{aligned} \mu_i \equiv \frac{\partial \hat{G}}{\partial N_i} &= M_i \vec{\phi} + \sum_{j=1}^{n} \frac{\partial \vec{\phi}}{\partial \omega_j^*} \left\{ M_i \delta_{ij} - M_i M_j N_j \Big/ \sum_{k=1}^{n} M_k N_k \right\} \\ &= M_i \vec{\phi} + M_i \sum_{j=1}^{n} \frac{\partial \vec{\phi}}{\partial \omega_j^*} \left( \delta_{ij} - \omega_j \right) = M_i \left( \vec{\phi} + \frac{\partial \vec{\phi}}{\partial \omega_i^*} - \sum_{j=1}^{n} \omega_j \frac{\partial \vec{\phi}}{\partial \omega_j^*} \right) . \end{aligned} \tag{151}$$

i.e.

$$\mu_i \equiv \frac{\partial \hat{G}}{\partial N_i} = M_i \left( \vec{\phi} + \frac{\partial \vec{\phi}}{\partial \omega_i^*} - \sum_{j=1}^{n} \omega_j \frac{\partial \vec{\phi}}{\partial \omega_j^*} \right) . \tag{152}$$

Through an analysis similar to that given in Section 4.4, all local thermodynamic quantities can be determined by specifying the function $\vec{\phi}$. As for the molar Gibbs energy, the simplified formula $(116)_4$ for the chemical potential follows from (152) for the special case $\vec{\phi} = \hat{\Phi}$, due to the property of homogeneity of the function in the mole fractions.

# 5 LOCAL THERMODYNAMIC RELATIONS FOR NON-UNIFORM NON-EQUILIBRIUM SYSTEMS

Having now established a consistent local equation of state, the connection to a continuum will now be established for non-equilibrium conditions.

## 5.1 APPROXIMATION OF NON-UNIFORM NON-EQUILIBRIUM SYSTEMS USING LOCAL THERMODYNAMIC RELATIONS

A simply connected fixed region $\Omega$ is identified which is bounded by a closed surface $\Sigma$. The volume of the region $\Omega$ is denoted by $V$. Clearly

$$V = \int_{\Omega} \mathrm{d}V \,. \tag{153}$$

The region $\Omega$ is now assumed to contain a sample of a multi-component fluid that is not in a state of equilibrium. All physical variables are regarded as being both non-uniform within $\Omega$, and time-dependent. To connect the continuum model to the equations of equilibrium thermodynamics, it is useful to be able to define distributions of global physical quantities for a finite but non-uniform sample of the multi-component system lying in the region $\Omega$ when the system is evolving in time. One way of achieving this objective is first to assume that all intensive thermodynamic variables can be expressed as non-uniform time-dependent scalar fields, which must be defined at all points $\mathbf{r}$ in $\Omega$ for all times $t > 0$. In this way continuum variables can be defined for the distributions of total concentration $c(\mathbf{r},t)$ of all species, molar internal energy $u(\mathbf{r},t)$, molar Helmholtz energy $f(\mathbf{r},t)$, molar Gibbs energy $g(\mathbf{r},t)$, molar entropy $s(\mathbf{r},t)$, and a set of mole fractions $\{x_i(\mathbf{r},t)\}$. The quantities $cu, cf, cg, cs$ and $c_k = cx_k,\ k = 1, ..., n,$ are all measured per unit volume, and as they are considered to be functions of position $\mathbf{r}$ and time $t$, this enables the definition of the following amounts of internal energy $U(t)$, Helmholtz energy $F(t)$, Gibbs energy $G(t)$, entropy $S(t)$ and molar contents $N_k(t),\ k = 1, ..., n,$ found in the non-uniform region $\Omega$ at time $t$.

$$\begin{gathered} U(t) = \int_{\Omega} c(\mathbf{r},t) u(\mathbf{r},t)\,\mathrm{d}V, \quad F(t) = \int_{\Omega} c(\mathbf{r},t) f(\mathbf{r},t)\ \mathrm{d}V, \\ G(t) = \int_{\Omega} c(\mathbf{r},t) g(\mathbf{r},t)\ \mathrm{d}V, \quad S(t) = \int_{\Omega} c(\mathbf{r},t) s(\mathbf{r},t)\ \mathrm{d}V, \\ N_k(t) = \int_{\Omega} c(\mathbf{r},t) x_k(\mathbf{r},t)\ \mathrm{d}V, \quad k = 1, ..., n. \end{gathered} \tag{154}$$

The local equations of state derived for a uniform system (see (84) for example) can also be regarded as local equations of state for the continuum at any single point $\mathbf{r}$ lying within $\Omega$ at any time $t$. This interpretation was assumed when defining thermodynamic quantities using the relations (154) applicable to non-uniform systems.

## 5.2 USE OF MOLAR GIBBS ENERGY AND CHEMICAL POTENTIALS IN NON-UNIFORM NON-EQUILIBRIUM SYSTEMS

For non-uniform time-dependent systems, the local equation of state requires from (84), on taking the limit $\{x_i^*\} \to \{x_i\}$ as described in Section 3.3, that for all points $\mathbf{r}$ in $\Omega$ and for all times $t$

$$g(\mathbf{r},t) = \hat{G}(T(\mathbf{r},t),\ p(\mathbf{r},t),\ \{x_i(\mathbf{r},t)\}),\ i = 1, ..., n. \tag{155}$$

The relations (86) then assert that the molar entropy, molar volume and chemical potentials can be defined for each point $\mathbf{r}$ in $\Omega$ and for all times $t$, so that

$$\begin{aligned} s &= \hat{S}(T(\mathbf{r},t),\ p(\mathbf{r},t),\ \{x_i(\mathbf{r},t)\}) = s(\mathbf{r},t), \\ v &= \hat{V}(T(\mathbf{r},t),\ p(\mathbf{r},t),\ \{x_i(\mathbf{r},t)\}) = v(\mathbf{r},t), \\ \mu_k &= \hat{\mu}_k(T(\mathbf{r},t),\ p(\mathbf{r},t),\ \{x_i(\mathbf{r},t)\}) = \mu_k(\mathbf{r},t),\ k = 1, ..., n. \end{aligned} \tag{156}$$

wherein the symbols $s$, $v$, $\mu_k, k = 1, ..., n,$ are now being used to represent the time-dependent distributions of the molar entropy, molar volume and chemical potentials at given points **r** in $\Omega$ at any time *t*. These are the symbols that will be used when developing the field equations governing the evolution of the system. The symbols $\hat{S}, \hat{V}$ and $\hat{\mu}_k, k = 1, ..., n,$ first introduced when considering a global system, are used here to denote functions of the independent local state variables *T*, *p* and $x_k^*, k = 1, ..., n,$ derived from the equation of state (84) and (86). It is emphasised that the symbols define exactly the same functions for both global and local formulations.

On using any molar Gibbs energy function in the general form (122), expressed in terms of mole fractions rather than independent pseudo-mole fractions, the relation (155) is replaced by

$$g(\mathbf{r},t) = \vec{g}(T(\mathbf{r},t),\ p(\mathbf{r},t),\ \{x_i(\mathbf{r},t)\}). \tag{157}$$

If the homogeneous expression (155) is used, the chemical potentials $\mu_k(\mathbf{r},t)$ can be computed at each point in the continuum from the local equation of state using (132). If the general expression (157) is used, the chemical potentials $\mu_k(\mathbf{r},t)$ must be computed at each point in the continuum using the more involved expression (129). Once the chemical potentials are computed, all partial molar quantities (as continuum properties) can be derived directly from the chemical potentials, as above using the relations given in Section 4.4.

## 5.3 EXPLICIT EXPRESSIONS FOR DIFFUSIONAL DRIVING FORCES

Diffusional driving forces per unit volume characteristically involve the gradients of chemical potentials. It is useful to provide the expressions for $\nabla\mu_i$ resulting from the relations (129) and (132). From (129)

$$\nabla\mu_i = \nabla\vec{g} + \nabla\left(\frac{\partial\vec{g}}{\partial x_i^*}\right) - \sum_{j=1}^{n} x_j \nabla\left(\frac{\partial\vec{g}}{\partial x_j^*}\right) - \sum_{j=1}^{n} \frac{\partial\vec{g}}{\partial x_j^*}\nabla x_j\,, \quad i = 1, ..., n. \tag{158}$$

As $\vec{g}$ is a function of *T*, *p* and $\{x_i\}$, it follows that

$$\nabla\vec{g} = \frac{\partial\vec{g}}{\partial T}\nabla T + \frac{\partial\vec{g}}{\partial p}\nabla p + \sum_{k=1}^{n}\frac{\partial\vec{g}}{\partial x_k^*}\nabla x_k\,, \tag{159}$$

and that

$$\nabla\left(\frac{\partial\vec{g}}{\partial x_k^*}\right) = \frac{\partial^2\vec{g}}{\partial T\,\partial x_i^*}\nabla T + \frac{\partial^2\vec{g}}{\partial p\,\partial x_i^*}\nabla p + \sum_{k=1}^{n}\frac{\partial^2\vec{g}}{\partial x_i^*\partial x_k^*}\nabla x_k\,. \tag{160}$$

Substitution of (159) and (160) in (158) leads to

$$\begin{aligned}\nabla\mu_i = &\left(\frac{\partial\vec{g}}{\partial T} + \frac{\partial^2\vec{g}}{\partial T\,\partial x_i^*} - \sum_{j=1}^{n} x_j\frac{\partial^2\vec{g}}{\partial T\,\partial x_j^*}\right)\nabla T + \left(\frac{\partial\vec{g}}{\partial p} + \frac{\partial^2\vec{g}}{\partial p\,\partial x_i^*} - \sum_{j=1}^{n} x_j\frac{\partial^2\vec{g}}{\partial p\,\partial x_i^*}\right)\nabla p \\ &+ \sum_{k=1}^{n}\left(\frac{\partial^2\vec{g}}{\partial x_k^*\partial x_i^*} - \sum_{j=1}^{n} x_j\frac{\partial^2\vec{g}}{\partial x_k^*\partial x_j^*}\right)\nabla x_k\,, \quad i = 1, ..., n.\end{aligned} \tag{161}$$

By incorporating the partial molar entropy and volume, this can be written more succinctly as

$$\nabla\mu_i = -S_i\nabla T + V_i\nabla p + \sum_{k=1}^{n}\left(\frac{\partial^2\vec{g}}{\partial x_k^*\partial x_i^*} - \sum_{j=1}^{n} x_j\frac{\partial^2\vec{g}}{\partial x_k^*\partial x_j^*}\right)\nabla x_k, i = 1, ..., n, \tag{162}$$

where on using (129) and (136)

$$S_i = -\left( \frac{\partial \vec{g}}{\partial T} + \frac{\partial^2 \vec{g}}{\partial T \, \partial x_i^*} - \sum_{j=1}^{n} x_j \frac{\partial^2 \vec{g}}{\partial T \, \partial x_j^*} \right), \quad V_i = \frac{\partial \vec{g}}{\partial p} + \frac{\partial^2 \vec{g}}{\partial p \, \partial x_i^*} - \sum_{j=1}^{n} x_j \frac{\partial^2 \vec{g}}{\partial p \, \partial x_i^*} \, . \tag{163}$$

When the chemical potentials are obtained using (132), it follows on using (92) that the following simpler expression results

$$\nabla \mu_i = - S_i \nabla T + V_i \nabla p + \sum_{k=1}^{n} \frac{\partial^2 \hat{G}}{\partial x_k^* \partial x_i^*} \nabla x_k , \quad i = 1, ..., n. \tag{164}$$

It is noted on using (40), (41) and (83) that in the limit $\{x_i^*\} \to \{x_i\}$ this result may be expressed

$$\nabla \mu_i = - S_i \nabla T + V_i \nabla p + \sum_{k=1}^{n} \mu_{ik} \nabla x_k , \quad i = 1, ..., n, \tag{165}$$

where

$$\sum_{j=1}^{n} x_j \mu_{kj} = \sum_{j=1}^{n} x_j \mu_{jk} = 0, \quad k = 1, ..., n \, . \tag{166}$$

## 6 DISCUSSION

While the emphasis of this report is focused on a local equation of state involving molar thermodynamic variables, it is emphasised that such an approach is not the only possibility. Indeed, as was described in Section 3.6 and Section 4.6 a mass-based formulation is also possible leading to a local set of specific thermodynamic variables. A closer examination of Section 5 reveals that it is possible to define a local set of thermodynamic variables measured per unit volume, rather than per mole or unit mass. It is clear from Section 5 that thermodynamic variables per unit volume relate more simply to their corresponding global quantities by integration across fixed spatial coordinates than do molar and specific quantities. For this case the local state variables are the temperature $T$ and the concentrations of species, $c_k$, $k = 1, ..., n$, and it is noted that they are independent. It has been shown previously that the use of this approach avoids all the problems of dependent state variables discussed in this report, but at the expense of having the pressure $p$ as a dependent state variable. This disadvantage is very significant as the use of a volumetric approach would mean that the vast amount of experimentally measured thermodynamic property data (at constant pressure) could not be used. For this reason, there has been no attempt in this report to consider the volumetric approach in detail. Also, consideration of electrochemical systems, where charged species need to be considered in the presence of a local electrical field, has been excluded, although the framework presented in this report is intended to underpin future work in this direction.

On a broader scale, this report focuses a great deal on the concept of an equation of state which can be used to define various material properties. This concept may then be used to develop the field equations required by continuum models of multi-component fluids through the application of fundamental physical principles involving balance equations of mass, momentum, energy and entropy. Approaches have been made in the literature (see for example [4]) for which equations of state merge into the background information, with the derivation of thermodynamic relations from the equation of state being replaced by an axiomatic approach involving principles described as (see [2] for example) equipresence, objectivity, and material invariance. The 'Axiom of equipresence' states that 'at the outset, all functionals should be expressed in terms of the same list of independent constitutive variables until the contrary is deduced.' The 'Axiom of objectivity' states that 'the constitutive equations must be form-invariant with respect to rigid motions of the spatial frame of reference' while the 'Axiom of material invariance' states that 'constitutive equations must be form-invariant with respect to a group of orthogonal transformations and translations of the material coordinates.' While the principles of objectivity and material invariance are universally accepted, it is observed here that the principle of equipresence, as applied in the literature, does lead to the expected relationships that are commonly accepted, as in references [1, 5, 7 ,8].

Some formulations in the literature (see for example [3]) regard a continuum mixture of *n* species as *n* interpenetrating continua each having its own temperature. Equations of state then need to be imposed for each of the *n* continua involved. A consideration of this approach is beyond the scope of this report, although in this case, each continuum is its own phase which could be treated according to the methods presented in this report. Mathematically, homogenisation of porous materials also takes a similar approach, requiring overlay of multiple phases in the same region of space; this is not forbidden by our treatment.

This report has considered only the equations of state relevant to non-viscous multi-component fluids. The concepts introduced can be extended so that suitable equations of state can be developed for multi-component solids where concepts of stress and strain tensors need to be introduced. For crystallographic systems, the concepts of lattice strains together with lattice defects such as vacancies and interstitials need to be introduced as additional state variables. If there is a need for additional state variables, it is always possible to construct a free energy function analogous to the Gibbs energy which depends on only intensive state variables and molar contents (perhaps in the solid-state also considering molar contents of conventionally fictitious species such as vacancy defects) [15]. Such a free energy would have an equation of state with the same or similar properties to those we discuss – our insights apply particularly to the conversion of molar contents to mole fractions, in transforming from a global to a local equation of state. Other partial molar quantities arising from the extensive variables paired to any new intensive variables in an equation of state could be developed in the same manner as indicated here for entropy and volume.

## 7 CONCLUSIONS

The following conclusions can be drawn from the analysis presented in this report:

1. The development of local equations of state for application in non-uniform multi-component fluid systems requires the introduction of localised composition variables, such as mole and mass fractions, which are not independent. Robust, unambiguous methods for the mathematical handling of such dependencies can be developed, while maintaining close contact with equivalent global thermodynamic relations encountered in uniform systems.

2. While there are four candidate thermodynamic functions that can be the basis of a local equation of state, associated respectively with internal energy, Helmholtz energy, Gibbs energy and enthalpy, the most practically useful approach is based on the molar Gibbs energy in which the function depends only on intensive state variables (temperature, pressure and composition).

3. An alternative expression for the partial pressure of any species has been proposed that applies to non-ideal multi-component systems, and which equates to the commonly used expression (product of mole fraction and total pressure) in the case of an ideal mixture.

4. If an expression for the global Gibbs energy of a multi-component system is available, then it is possible to use this function to define a local molar Gibbs energy function, provided that an

independent set of pseudo-mole fractions is introduced to enable partial derivatives with respect to these variables to be computed in a mathematically meaningful way. Having computed all required partial derivatives, the pseudo-mole fractions are then replaced as arguments by the corresponding dependent set of mole fractions.

5. Great care is needed when calculating chemical potentials from general molar Gibbs energy functions (sourced from literature or experimental data), as it is highly likely that the derived molar Gibbs energy function will not possess the required homogeneity. A method is presented that derives a new expression for chemical potentials that applies also to non-homogeneous molar Gibbs energy functions, as well as being able to construct from these a molar Gibbs energy function having the required homogeneity. This leads self-consistently to correct formulae for chemical potentials expressed in terms of intensive state variables. Using the chemical potentials, all partial molar properties for use in local thermodynamic relations can be derived from general molar Gibbs energy functions.

## REFERENCES

1. J. O. Hirschfelder, C. F. Curtiss and R. B. Bird, ‘Molecular theory of gases and liquids’, John Wiley & Sons Inc., New York; Chapman & Hall, London (1954).
2. A. C. Eringen, ‘Mechanics of continua’, John Wiley & Sons Inc., New York – London –Sydney (1967).
3. I. Muller, ‘A thermodynamic theory of mixtures of fluids’, Arch. Rational Mech. Anal. **28**, 1-39, (1968).
4. C. Truesdell, ‘Rational thermodynamics’, McGraw-Hill series in modern applied mathematics, New York – London – Sydney – Toronto (1969).
5. S. R. de Groot and P. Mazur, 1984, ‘Non-equilibrium thermodynamics’, Dover Publcns. Inc., New York (1984).
6. C. F. Curtiss and R. B. Bird, ‘Multi-component diffusion’, Ind. Eng. Chem. Res., **38**, 2515-2522, (1999).
7. Y. Demirel, ‘Nonequilibrium thermodynamics: transport and rate processes in physical, chemical and biological systems’, Elsevier, Amsterdam-London-New York, 2nd edition. (2007).
8. R. B. Bird, W. E. Stewart and E. N. Lightfoot, ‘Transport phenomena’, 2nd Edition, John Wiley and Sons Inc., New York – London – Sydney (2007).
9. E. A. Guggenheim (1967) *Thermodynamics: An Advanced Treatment for Chemists and Physicists*, 5th revised edition, North-Holland Publishing Company, Amsterdam.
10. B. Ott, J. Boerio-Goates (2000) *Chemical Thermodynamics: Principles and Applications*, Elsevier Academic Press, San Diego, CA.
11. P. Atkins, J. de Paula, J. Keeler (2017) *Atkins' Physical Chemistry*, 11th Edition, Oxford University Press, Oxford.
12. MTDATA, Hampton Thermodynamics Ltd. https://www.sciencedirect.com/science/article/abs/pii/S0364591602000366
13. CALPHAD, https://thermocalc.com/about-us/methodology/the-calphad-methodology/
14. J. Newman and K. E. Thomas-Alyea, ‘Electrochemical systems’, 3rd Edition, (2004), John Wiley & Sons Inc., Hoboken, New Jersey, USA.
15. L. N. McCartney, ‘Vacancy diffusion in a crystal’, Acta Metall., **23**, 769-777, (1975).

## APPENDIX A: NOTATION TO IDENTIFY STATE VARIABLES

This Appendix summarises the notation used to specify the state variables defined for all thermodynamic functions in the above text, providing some 'translations' of key relations into conventional notation.

Throughout, the notation $\partial / \partial x_i^*$ indicates partial differentiation of a function of mole fractions, in which the mole fractions are treated as independent for the purpose of partial differentiation.

**Table A1. State variable notation.**

| Notation | State Variables | Natural Equation of State |
|---|---|---|
| $\tilde{\xi}$ | $S, V, \{N_i\}$ | Internal energy, $U = \tilde{U}$ |
| $\widehat{\xi}$ | $S, p, \{N_i\}$ | Enthalpy, $H = \widehat{H}$ |
| $\bar{\xi}$ | $T, V, \{N_i\}$ | Helmholtz energy, $F = \bar{F}$ |
| $\hat{\xi}$ | $T, p, \{N_i\}$ | Gibbs energy, $G = \hat{G}$ |
| $\vec{\xi}$ | $T, p, \{x_i\}$ | Molar Gibbs energy, $g = \vec{g}$ |

The differential relations for each thermodynamic variable given through an equation of state are

$$\begin{aligned}
\mathrm{d}U &= T\,\mathrm{d}S - p\,\mathrm{d}V + \sum_{k=1}^{n} \mu_k\,\mathrm{d}N_k\,, \\
\mathrm{d}H &= T\,\mathrm{d}S + V\,\mathrm{d}p + \sum_{k=1}^{n} \mu_k \mathrm{d}N_k\,, \\
\mathrm{d}F &= -S\,\mathrm{d}T - p\,\mathrm{d}V + \sum_{k=1}^{n} \mu_k\,\mathrm{d}N_k\,, \\
\mathrm{d}G &= -S\,\mathrm{d}T + V\,\mathrm{d}p + \sum_{k=1}^{n} \mu_k \mathrm{d}N_k\,, \\
\mathrm{d}g &= -s\,\mathrm{d}T + v\,\mathrm{d}p + \sum_{k=1}^{n} \mu_k \mathrm{d}x_k\,.
\end{aligned} \tag{A1}$$

Entropy $S$, temperature $T$, volume $V$, and pressure $p$, are defined in equations of state as follows

$$\begin{aligned}
S &= -\frac{\partial \bar{F}}{\partial T} \equiv -\left(\frac{\partial F}{\partial T}\right)_{V,\{N_i\}} \\
&= -\frac{\partial \hat{G}}{\partial T} \equiv -\left(\frac{\partial G}{\partial T}\right)_{p,\{N_i\}}\,,
\end{aligned} \tag{A2}$$

$$\begin{aligned}
T &= \frac{\partial \tilde{U}}{\partial S} \equiv \left(\frac{\partial U}{\partial S}\right)_{V,\{N_i\}} \\
&= \frac{\partial \widehat{H}}{\partial S} \equiv \left(\frac{\partial H}{\partial S}\right)_{p,\{N_i\}}\,,
\end{aligned} \tag{A3}$$

$$\begin{aligned} V &= \frac{\partial \widehat{H}}{\partial p} \equiv \left(\frac{\partial H}{\partial p}\right)_{S,\{N_i\}} \\ &= \frac{\partial \hat{G}}{\partial p} \equiv \left(\frac{\partial G}{\partial p}\right)_{T,\{N_i\}} , \end{aligned} \tag{A4}$$

$$\begin{aligned} p &= -\frac{\partial \tilde{U}}{\partial V} \equiv -\left(\frac{\partial U}{\partial V}\right)_{S,\{N_i\}} \\ &= -\frac{\partial \bar{F}}{\partial V} \equiv -\left(\frac{\partial F}{\partial V}\right)_{T,\{N_i\}} . \end{aligned} \tag{A5}$$

The chemical potential of component *k* is given in terms of extensive thermodynamic variables as

$$\left.\begin{aligned} \mu_k &= \frac{\partial \tilde{U}}{\partial N_k} \equiv \left(\frac{\partial U}{\partial N_k}\right)_{S,V,\{N_{j\neq k}\}} \\ &= \frac{\partial \widehat{H}}{\partial N_k} \equiv \left(\frac{\partial H}{\partial N_k}\right)_{S,p,\{N_{j\neq k}\}} \\ &= \frac{\partial \bar{F}}{\partial N_k} \equiv \left(\frac{\partial F}{\partial N_k}\right)_{T,V,\{N_{j\neq k}\}} \\ &= \frac{\partial \hat{G}}{\partial N_k} \equiv \left(\frac{\partial G}{\partial N_k}\right)_{T,p,\{N_{j\neq k}\}} , \end{aligned}\right\} \quad k = 1, \ldots, n, \tag{A6}$$

where $\{N_{i\neq j}\}$ refers to the set of values $\{N_i\}$ apart from the variable $N_j$. With respect to the molar Gibbs energy, the chemical potential of component *k* is given by

$$\begin{aligned} \mu_k &= \vec{g} + \frac{\partial \vec{g}}{\partial x_k^*} - \sum_{i=1}^{n} x_i \frac{\partial \vec{g}}{\partial x_i^*} \\ &= g + \left(\frac{\partial g}{\partial x_k^*}\right)_{T,p,\{x_{j\neq k}^*\}} - \sum_{i=1}^{n} x_i \left(\frac{\partial g}{\partial x_i^*}\right)_{T,p,\{x_{j\neq i}^*\}} . \end{aligned} \tag{A7}$$

Molar entropy is given by

$$\begin{aligned} s &= \frac{S}{N} \\ &= -\frac{1}{N}\frac{\partial \hat{G}}{\partial T} \equiv -\frac{1}{N}\left(\frac{\partial G}{\partial T}\right)_{p,\{N_i\}} \\ &= -\frac{\partial \vec{g}}{\partial T} \equiv -\left(\frac{\partial g}{\partial T}\right)_{p,\{x_i\}} . \end{aligned} \tag{A8}$$

Molar volume is given by

$$\begin{aligned} v &= \frac{V}{N} \\ &= \frac{1}{N}\frac{\partial \hat{G}}{\partial p} \equiv \left(\frac{\partial G}{\partial p}\right)_{T,\{N_i\}} \\ &= \frac{\partial \vec{g}}{\partial p} \equiv \left(\frac{\partial g}{\partial p}\right)_{T,\{x_i\}} . \end{aligned} \tag{A9}$$

Partial molar entropy and volume of component *k* are given by

$$\begin{aligned} S_k &= -\frac{\partial \hat{\mu}_k}{\partial T} \equiv -\left(\frac{\partial \mu_k}{\partial T}\right)_{p,\{N_i\}} \\ &= -\frac{\partial \vec{\mu}_k}{\partial T} \equiv -\left(\frac{\partial \mu_k}{\partial T}\right)_{p,\{x_i\}} , \end{aligned} \tag{A10}$$

$$\begin{aligned} V_k &= \frac{\partial \hat{\mu}_k}{\partial p} \equiv \left(\frac{\partial \mu_k}{\partial p}\right)_{T,\{N_i\}} \\ &= \frac{\partial \vec{\mu}_k}{\partial p} \equiv \left(\frac{\partial \mu_k}{\partial p}\right)_{p,\{x_i\}} . \end{aligned} \tag{A11}$$

Molar heat capacities at constant volume and pressure are given by

$$C_V = -\frac{T}{N}\frac{\partial^2 \bar{F}}{\partial T^2} \equiv -\frac{T}{N}\left(\frac{\partial^2 F}{\partial T^2}\right)_{V,\{N_i\}} , \tag{A12}$$

$$\begin{aligned} C_p &= -\frac{T}{N}\frac{\partial^2 \hat{G}}{\partial T^2} \equiv -\frac{T}{N}\left(\frac{\partial^2 G}{\partial T^2}\right)_{p,\{N_i\}} \\ &= -T\frac{\partial^2 \vec{g}}{\partial T^2} \equiv -T\left(\frac{\partial^2 g}{\partial T^2}\right)_{p,\{x_i\}} . \end{aligned} \tag{A13}$$

The bulk thermal expansion coefficient is given by

$$\alpha = \frac{1}{V}\frac{\partial \hat{V}}{\partial T} \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{p,\{N_i\}} \equiv \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_{p,\{x_i\}} . \tag{A14}$$

The isothermal bulk compressibility is given by

$$K = -\frac{1}{V}\frac{\partial \hat{V}}{\partial p} \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_{T,\{N_i\}} \equiv -\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_{T,\{x_i\}} . \tag{A15}$$

These four quantities are related by

$$C_p = C_V + \frac{\alpha^2}{K} vT . \tag{A16}$$

## APPENDIX B: CONSTRUCTION OF THE GLOBAL GIBBS ENERGY FUNCTION

In Section 4.2, it was pointed out that expressions for the molar Gibbs energy of the form (122), namely

$$g = \vec{g}(T, p, \{x_i\}) \,, \tag{B1}$$

lead to an infinite number of possible functions $\vec{g}$ because of their dependence on mole fractions which are not independent, but must satisfy the relation (75), namely

$$\sum_{k=1}^{n} x_k = 1 \,. \tag{B2}$$

Molar Gibbs energies, obtained by applying the relation (89) to literature expressions for the chemical potentials, and molar Gibbs energies obtained by empirical fitting to experimental data, are generically expressed in the form (B1), but are not necessarily homogeneous of order unity in the mole fractions, unless particular care is taken to ensure this. In order to apply the molar Gibbs energy function to the local relations introduced in Section 3, it is useful to be able to reconstruct the original function $\hat{G}$ from any of the possible functions $\vec{g}$ .

The composition variables $\{x_i\}$ in (B1) are defined in terms of molar contents by

$$x_i = N_i \Big/ \sum_{k=1}^{n} N_k \,, \quad i = 1, 2, ..., n \,. \tag{B3}$$

It then follows from (B1) that the corresponding global Gibbs energy for a uniform system is

$$G = \left( \sum_{k=1}^{n} N_k \right) g = \left( \sum_{k=1}^{n} N_k \right) \vec{g}(T, p, \{x_i\}) = \left( \sum_{k=1}^{n} N_k \right) \vec{g} \left( T, p, \left\{ N_i \Big/ \sum_{k=1}^{n} N_k \right\} \right) = \bar{G}(T, p, \{N_i\}) \,. \tag{B4}$$

By inspection, it is clear that the function $\bar{G}$ introduced in (B4) is homogeneous of order unity. As the original function $\hat{G}(T, p, \{N_i\})$ is also homogeneous of order unity, it follows that

$$\hat{G}(T, p, \{N_i\}) = \left( \sum_{k=1}^{n} N_k \right) \hat{G} \left( T, p, \left\{ N_i \Big/ \sum_{k=1}^{n} N_k \right\} \right) . \tag{B5}$$

On subtracting (B5) from (B4)

$$\bar{G}(T, p, \{N_i\}) - \hat{G}(T, p, \{N_i\}) = \left( \sum_{k=1}^{n} N_k \right) \left[ \vec{g} \left( T, p, \left\{ N_i \Big/ \sum_{k=1}^{n} N_k \right\} \right) - \hat{G} \left( T, p, \left\{ N_i \Big/ \sum_{k=1}^{n} N_k \right\} \right) \right] . \tag{B6}$$

Because of the way in which multiple functions $\vec{g}$ have been defined, the R.H.S. is zero for all values of the independent variables $\{N_i\}$ so that

$$\bar{G}(T, p, \{N_i\}) \equiv \hat{G}(T, p, \{N_i\}) \,. \tag{B7}$$

It then follows from (B4) that it is established that the required function $\hat{G}$ can be constructed from the functions represented by $\vec{g}$ using the relation

$$G = \left( \sum_{k=1}^{n} N_k \right) g = \left( \sum_{k=1}^{n} N_k \right) \vec{g} \left( T, p, \left\{ N_i \Big/ \sum_{k=1}^{n} N_k \right\} \right) = \hat{G}(T, p, \{N_i\}) \,. \tag{B8}$$

With respect to the independent pseudo-mole fractions $\{x_i^*\}$ introduced in the main text, on applying the substitution $(83)_1$ to (B8) it also follows that

$$\hat{G}(T, p, \{x_i^*\}) = \left( \sum_{k=1}^{n} x_k^* \right) \vec{g}\left( T, p, \left\{ x_i^* \middle/ \sum_{k=1}^{n} x_k^* \right\} \right). \tag{B9}$$