

Mass variables and chemical potentials in the Gibbs and De Donder formulations of chemical equilibrium

Victor A. Snyder

Soil and Environmental Physics Laboratory, Department of Agronomy and Soils, University of Puerto Rico – Agricultural Experiment Station, 1193 Guayacán St., Botanical Gardens, Río Piedras, Puerto Rico 00926-1118
E-mail: victor.snyder@gmail.com

Received 28 October 2004; revised 4 November 2005; published online 13 April 2006

The classical thermodynamic treatment of chemical equilibria in closed systems is founded on theoretical formulations by J.W. Gibbs and Th. De Donder. These two theories represent mathematically equivalent energy variation problems, related to each other through a mass variable transformation analogous to coordinate transformations in mechanics. Associated with the change in mass variables, chemical potentials of reactive substances are defined differently in the two theories, and are subject to different sets of constraints. Traditionally, the two sets of constraints have been merged into one, by assuming that the chemical potential represents the same variable in both theories, an assumption that is formally inconsistent with the difference in chemical potential definitions. Merging of constraints is still possible if chemical potentials remain invariant in value as a manifestation of symmetry under a Gibbs – De Donder mass transformation, but such symmetry has not been investigated. Here we demonstrate chemical potential invariance by reformulating De Donder's theory using Lagrange multipliers, and combining the resulting constraints on chemical potentials with the classical Gibbs constraints, in a phase equilibration thought experiment. A new form of the Gibbs–Duhem (GD) relation is derived in the De Donder mass system. Comparing this relation to the classical GD equation in Gibbs' component framework, subject to chemical potential invariance, directly yields the linear operator mapping the De Donder mass variables onto the set of Gibbs component masses. Results are illustrated for a simple ion exchange reaction, in the process solving the longstanding problem of determining solid exchanger activities in ion exchanging mixtures. It is pointed out that, even though the Gibbs and De Donder formulations are mathematically equivalent, the formal structure of De Donder's theory allows a more explicit and systematic treatment of constraints, and also defines chemical masses in a form more naturally adapted to typical experimental measurements.

KEY WORDS: chemical equilibrium, chemical potential, chemical affinity, Gibbs–Duhem relation, ion exchange

AMS subject classification: 80A10 (classical thermodynamics) or 80A05 (thermodynamics foundations)

1. Introduction

The classical thermodynamic treatment of chemical equilibrium in closed systems is founded on theoretical formulations by Gibbs [1] and De Donder [2].

In both theories, chemical equilibrium is formally treated as a problem of energy minimization under virtual variation of chemical masses. However, the two theories differ in the number and definition of mass variables [3] and in the way constraints are handled. De Donder's equilibrium formulation appears as a constrained variational problem where masses of all chemical substances are considered as state variables, subject to explicit chemical reaction constraints, and masses are defined as the amounts of respective substances remaining in a phase after chemical reactions and mass exchange with the environment. Gibbs' theory represents the same problem under a mass variable transformation which reduces De Donder's constrained variational problem to one of free variation in "component" masses, with masses now defined simply as the amounts of respective substances exchanged with the environment. The mass transformation relating the two theories closely parallels the well known coordinate transformations of Lagrangian mechanics, by which variational problems in constrained coordinates are transformed to equivalent formulations in freely variable generalized coordinates [4,5]. The only essential difference is that, in chemical systems, the roles of mechanical coordinates and forces are assumed by masses and chemical potentials, respectively, and metric constraints between coordinate frameworks are replaced by stoichiometric relations between sets of mass variables.

As in mechanics, where generalized forces and constraints imposed on them are often altered by coordinate transformation [4,5], chemical potentials and associated constraints are subject to change under a Gibbs – De Donder mass transformation. De Donder's great contribution to equilibrium thermodynamics was discovery of new constraints on chemical potentials, namely the vanishing chemical affinity conditions, which were absent in Gibbs' analysis but occurred naturally in the De Donder transformed mass system.

Apparently unrecognized in de Donder's theory, however, was the fact that not only constraints but also the very definition of the chemical potential changed as a result of mass transformation. In describing the meaning of energy derivatives with respect to mass variables in his theory, De Donder referred to them simply as "the chemical potentials of Gibbs" [2]. Under this interpretation, affinity conditions represented merely additional constraints on the Gibbs chemical potentials, to be added to the set of constraints already obtained by Gibbs. The same interpretation is reflected in other standard treatises on classical chemical thermodynamics [6–8]. Formally, this interpretation is inconsistent with the fact that mass variables, and hence chemical potentials, are defined differently in the Gibbs and De Donder theories.

The above difference in chemical potential definitions does not, of course, preclude the possibility that chemical potentials remain invariant in *value*

during mass transformation, in which case the conventional practice of merging the Gibbs and De Donder constraints on chemical potentials is valid. However, if such invariance does exist, it must be demonstrated not on the basis of assumed identical chemical potential definitions, but rather as symmetry imposed by particular constraints on mass transformations. The author is not aware of any analysis along these lines in the literature.

The objective here is to re-examine the fundamental differences and interrelationships of the Gibbs and De Donder equilibrium theories, with particular attention to mass variables, chemical potentials and associated constraints. The question of symmetry is resolved, and some previously unrecognized thermodynamic relations are derived; specifically, a new form of the Gibbs–Duhem equation and a general method for transforming between the Gibbs and De Donder mass variables. For illustrative purposes, results are applied to simple ion exchange systems, in the process yielding a general solution to the longstanding problem of determining solid exchanger activities.

2. General features of the Gibbs and De Donder equilibrium formulations, with emphasis on mass and chemical potential definitions and associated constraints

2.1. De Donder theory

The fundamental postulate of De Donder's affinity theory [2,6,7] is that the energy of a chemically reactive homogeneous phase, not necessarily at equilibrium, depends generally on the instantaneous or "frozen" masses of all chemical species in that phase. Under this postulate, for the j th phase in a system containing $I = 1, 2, \dots, I$ distinct chemical substances, the variation in Gibbs energy G_j at fixed temperature and pressure is determined by variation in the set $\{M_{ij}\}$ of current masses as

$$dG_j = \sum_{i=1}^I \mu_{ij} dM_{ij}, \quad (1)$$

where μ_{ij} is the chemical potential defined as

$$\mu_{ij} = \frac{\partial G_j}{\partial M_{ij}}. \quad (2)$$

Equilibrium in closed reactive systems is formally treated as a special case of equation (1) where the energy function G_j acquires a stationarity condition, and virtual variations in the M_{ij} become subject to stoichiometric constraints. This renders equation (1) as a classical constrained variational problem.

Two general methods exist for dealing with such problems, which are essentially equivalent except in the way constraints are handled [4,5]. The first is to

directly eliminate non-independent variables or coordinates together with constraint equations, transforming the remaining coordinates in the process, reducing the constrained variational problem to one of freely variable generalized coordinates. Gibbs' equilibrium formulation in terms of independently variable component masses was of this type. The second approach is to formally retain all coordinates as state variables, and explicitly introduce constraint equations together with Lagrange multipliers into the energy stationarity condition, transforming constraints on the coordinates into conditions on the conjugate energy derivatives (chemical potentials in this case) required to maintain those constraints. De Donder's theory was essentially of this nature, although it did not formally involve Lagrange multipliers. In Appendix A, we apply the multiplier method to equation (1) and show that it yields essentially the same results as obtained by De Donder, with an important qualitative distinction to be discussed below.

The first De Donder condition on chemical potentials is the set of $r = 1, 2, \dots, R$ chemical affinity constraints, which for a phase with R independent chemical reactions, are given by:

$$\sum_{i=1}^{I_r} v_{ir} \mu_{ij} = 0 \quad r = 1, 2, \dots, R, \quad (3)$$

where v_{ir} is the stoichiometric coefficient for the i th species in the r th chemical reaction.

A second set of conditions is that chemical potential values for any given substance must be equal in all $j = 1, 2, \dots, J$ phases over which the substance is distributed. This yields the set of I constraint relations:

$$\mu_{i1} = \mu_{i2} = \dots = \mu_{iJ} \quad i = 1, 2, \dots, I. \quad (4)$$

In the derivations using Lagrange multipliers in Appendix A, the two sets of constraints equations (3) and (4) result as independent conditions on the chemical potentials. In contrast, De Donder et al. [2,6] obtained equation (4) as merely a special case of equation (3). This result may be traced to invalid assumptions regarding allowable mass variations in closed systems (see Appendix A for details).

De Donder and Rysselberghe [2] noted, perceptively, that extensivity of equation (1) in the case of macroscopically homogeneous phases implies a Gibbs–Duhem relation in the form:

$$\sum_{i=1}^I M_{ij} d\mu_{ij} = 0. \quad (5)$$

This relation contains a total of I terms, one for each chemical substance, as opposed to only $I-R$ terms as in the usual component-based Gibbs–Duhem

relation. Equation (5) is generally valid under the same conditions as equation (1), including states away from equilibrium. In the non-equilibrium case, equation (5) constitutes the only constraint on chemical potentials. However, in the special case where the $d\mu_{ij}$ correspond to changes between equilibrium states of closed reactive systems, equation (5) becomes subject to the R affinity conditions equation (3), with consequences to be discussed later.

2.2. Gibbs' framework

Gibbs' formulation of chemical equilibrium was tantamount to eliminating the R non-independent mass variables in equation (1) together with the associated chemical reaction constraints, and transforming the remaining mass variables. This effectively reduced equation (1) to a problem of free variation in $c = I - R$ "component" masses (m_{ij}), where variation of the energy function is given by

$$dG_j = \sum_{i=1}^c \mu'_{ij} dm_{ij} \quad (6)$$

with the chemical potential μ'_{ij} now defined as

$$\mu'_{ij} = \frac{\partial G_j}{\partial m_{ij}}. \quad (7)$$

A prime sign is used to denote formal difference between the Gibbs chemical potential defined by equation (7) and its De Donder analogue in equation (2).

In principle, Gibbs' component masses could have been defined as the amounts of respective substances remaining in a phase after chemical reactions and exchange with the environment, just as for the M_{ij} in De Donder's theory. However, Gibbs chose an alternate definition (in effect a variable transformation on the M_{ij}) wherein component masses m_{ij} represent only the amounts of respective species exchanged with the environment, i.e., substance masses which added to or removed from phase j produce the De Donder equilibrium mass composition $\{M_{ij}\}$.¹ The masses m_{ij} and M_{ij} for a given species are equivalent

¹Gibbs' choice of m_{ij} rather than M_{ij} for defining component masses is evidenced by his constraint imposed on closed multiphase systems, stating that the mass variation for any given component substance must vanish when summed over all phases. For systems with chemically reactive substances, such a constraint is generally valid only if component masses of a phase are defined as the amounts of respective substances exchanged between the phase and its environment [see also equation (A.4) in Appendix A], not as the amounts M_{ij} of substances remaining in the phase at equilibrium. It is precisely inapplicability of Gibbs' constraint to the M_{ij} for reactive substances that allows free virtual variation of extents of reaction in closed multi-phase systems, leading to the chemical affinity constraint (see for example, Ch. VI of Prigogine and Defay [6]).

in the case of chemically inert substances, but are generally different for reactive species.

Because of the generally different values of m_{ij} and M_{ij} for reactive species, there is no simple *a-priori* reason for assuming that the Gibbs chemical potential $\mu'_{ij} = \partial G_j / \partial m_{ij}$ in equation (7) is equivalent to the corresponding De Donder chemical potential $\mu_{ij} = \partial G_j / \partial M_{ij}$ of Eq. (2), the only general requirement on μ'_{ij} and μ_{ij} being that the energy variation dG_j must remain invariant under mass transformation. As noted earlier, if the values of μ'_{ij} and μ_{ij} do remain invariant under the transformation, this must be demonstrated as symmetry imposed by particular constraints of the system.

For the transformed mass system [not the De Donder mass system of equation (1)] Gibbs derived his famous condition that in closed systems the chemical potentials for the i th component must be equivalent in all phases in which that component is distributed:

$$\mu'_{i1} = \mu'_{i2} = \dots = \mu'_{iJ} \quad i = 1, 2, \dots, c. \quad (8)$$

Note that, although equation (8) is formally similar to the condition equation (4) derived earlier for the De Donder chemical potentials, the two relations are not equivalent because the respective mass variables and hence chemical potentials are defined differently. Thus, equations (4) and (8) represent two different sets of conditions which must be simultaneously satisfied.

The Gibbs–Duhem relation in component mass variables is:

$$\sum_{i=1}^c m_{ij} d\mu'_{ij} = 0. \quad (9)$$

Due to the transformed mass system on which it is based, equation (9) contains R fewer terms than its analogue equation (5) in the constrained De Donder system.

Chemical affinity constraints are formally undefined in Gibbs' framework. This is a consequence of the fact that, in Gibbs' implicit transformation of the De Donder mass system, reaction constraint equations (and consequently the affinity constraints) were eliminated along with non-independent mass variables. The effect is analogous to the formal elimination of forces of constraint in mechanics by using coordinate transformations [4,5].

3. Invariance of chemical potential values under a Gibbs – De Donder mass variable transformation

In what follows we first make use of a simple phase-equilibrium thought experiment to show that the constraints equations (4) and (8) imply general invariance of chemical potential values under a Gibbs–De Donder mass transformation. This invariance is then shown to imply, and also to be a consequence of,

independently verifiable stoichiometric constraints among Gibbs and De Donder mass variables.

3.1. Phase equilibration thought experiment

Consider an arbitrary phase (*A*) with heat-conducting but mass-impermeable flexible walls, containing any number of reactive and non-reactive substances at fixed environmental temperature and pressure. A second “test” phase (*B*) contains the same chemically inert species as phase *A* but only one of the reactive substances (*X*). Phase *B* is infinitesimally small relative to phase *A*, and its walls are thermally conducting but rigid. The two phases are first permitted to reach equilibrium individually, and then are allowed to equilibrate with each other by mass exchange through a rigid semi-permeable membrane. The membrane is permeable to reactive substance *X* and to all inert species, but is impermeable to any of the reactive substances different than *X*.

Since phase *B* is infinitesimally small relative to phase *A*, and always remains small due to its rigid walls which prevent volume change, mass transfer between the two phases is negligible relative to the amounts of substances originally present in the infinitely large phase *A*. Thus, equilibration of the two phases has no effect on the mole fraction composition of phase *A*. Also, any osmotic pressure differentials associated with membrane semi-permeability are borne by the rigid walls of phase *B*, so that the pressure of the flexible-walled phase *A* remains equal to the imposed environmental pressure. Under these conditions, the original chemical potential values of all substances in phase *A* remain unaltered by equilibration with *B*.

Because of membrane impermeability to all reactive substances except *X*, no reactive substance other than *X* can ever exist in phase *B*. Consequently *X* never reacts chemically in *B*, so that $m_{XB} = M_{XB}$ and therefore $\mu'_{XB} = \mu_{XB}$. It follows by virtue of constraints equations (4) and (8) that in phase *A* (where *X* does react chemically) we must have $\mu'_{XA} = \mu_{XA}$. The same argument holds for any arbitrary substance designated as *X*, in any reactive phase of arbitrary composition. Thus, in general, the constraints equations (4) and (8) imply invariance of Gibbs and De Donder chemical potential values for any given species under a Gibbs–De Donder mass transformation, i.e.,

$$\mu'_{ij} = \mu_{ij}. \quad (10)$$

3.2. Relation of chemical potential invariance to stoichiometric constraints between Gibbs and De Donder mass variables

The invariance property equation (10) allows direct comparison of Gibbs–Duhem relations equations (5) and (9) in the De Donder and Gibbs frameworks,

respectively, yielding the linear operator mapping the De Donder mass variables onto the set of Gibbs component masses.

To demonstrate this, we first reduce the number of terms in equation (5) to the same number of terms as in equation (9). It was noted earlier that whenever the chemical potential variations $d\mu_{ij}$ in equation (5) correspond to changes in equilibrium states of closed systems, equation (5) becomes subject to the R chemical affinity constraints equation (3). Differentiating these constraints, and substituting them into equation (5), we can eliminate the differentials $d\mu_{ij}$ for R substances such that the remaining $c = I - R$ chemical potential variables represent the same (component) substances as do the $d\mu'_{ij}$ in equation (9). This transforms equation (5) to a modified Gibbs–Duhem relation:

$$\sum_{i=1}^c f_{ij} d\mu_{ij} = 0, \quad (11)$$

where the coefficients f_{ij} are no longer strictly the masses M_{ij} but rather linear combinations of the M_{ij} and stoichiometric coefficients ν_{ir} of the system. A simple example of this type of transformation is given in Appendix B.

By virtue of the chemical potential invariance property equation (10), the $d\mu'_{ij}$ and $d\mu_{ij}$ in corresponding terms of the Gibbs–Duhem relations (9) and (11) are equivalent in value. This imposes that the respective coefficients of the chemical potentials, m_{ij} and f_{ij} , may differ at most by a single scalar λ , i.e.:

$$\frac{f_{ij}}{m_{ij}} = \lambda \quad i = 1, 2, \dots, c, \quad (12)$$

where λ is the same for all c substances. To evaluate λ , we note that for chemically inert substances, $f_{ij} = M_{ij} = m_{ij}$ (see Appendix B for illustration), in which case $\lambda = 1$. Since λ must be same for *all* component substances in a mixture, it follows that even if only one chemically inert species exists in the mixture, even in infinitesimally small amounts, then the set of c equation (12) reduces uniformly to

$$f_{ij} = m_{ij} \quad i = 1, 2, \dots, c. \quad (13)$$

Purely reactive systems (containing no inert substances) may be represented as the limiting case where the amount of inert substances approaches zero. Since equation (13) apply even for infinitesimally small amounts of inert substances, they would therefore seem generally applicable to purely reactive systems as well. In case of doubt, equation (13) can always be verified independently on a case by case basis, by testing consistency with stoichiometric constraints, as illustrated in Appendix B.

Each of the c identities equation (13) relates one of the Gibbs component masses m_{ij} to a parameter f_{ij} containing some linear combination of stoichiometric coefficients and De Donder masses M_{ij} . The entire set of such relations defines the coordinate transformation mapping the set $\{M_{ij}\}$ of De Donder chemical substance masses onto the set $\{m_{ij}\}$ of c Gibbs component masses. We write this as

$$m_{ij} = F(\{M_{ij}\}), \quad (14)$$

where F is the linear operator uniquely mapping $\{M_{ij}\}$ onto $\{m_{ij}\}$. A corresponding inverse operator F^{-1} , uniquely mapping $\{m_{ij}\}$ onto $\{M_{ij}\}$, does not exist because $\{M_{ij}\}$ contains more variables than $\{m_{ij}\}$. The reader is again referred to Appendix B for a concrete example.

3.3. Invariance of chemical potentials inferred from equation (13)

The procedure used above to infer the mass transformation identities equation (13) parted from the independently demonstrated chemical potential invariance conditions equation (10). We could equally well have proceeded in the opposite direction. That is, given a set of verified stoichiometric constraints equation (13) among Gibbs and De Donder mass variables, chemical potential invariance follows as a consequence. To demonstrate this, we simply note that comparison of the Gibbs–Duhem relations (9) and (11), subject to equation (13), yields a condition on the chemical potentials analogous to equation (12):

$$\frac{\mu_{ij}}{\mu'_{ij}} = \lambda \quad i = 1, 2, \dots, c \quad (15)$$

which for systems with infinitesimal or greater amounts of inert substances yields $\lambda = 1$, reducing equation (15) to the chemical potential invariance condition equation (10). The implication is, of course, that the symmetry-producing constraints on the Gibbs–De Donder mass transformation, which we anticipated earlier, are precisely the stoichiometric relations equation (13).

The reason we did not use equation (13) in the first place to derive chemical potential invariance, and resorted instead to the phase equilibrium thought experiment, was the difficulty in *generally* establishing the identities equation (13) from first principles. That is, even though on a case by case basis one always finds equation (13) to be valid, as in the example of Appendix B, this does not prove that one will never encounter a case where such a condition is invalid, and consequently equation (10) cannot be demonstrated in general. In contrast, by using the phase equilibration thought experiment, we were able to generally demonstrate equation (10), and from there the generality of equation (13).

4. Summary and implications

This paper re-examines the classical Gibbs and De Donder theories of chemical equilibrium, recognizing that the two theories represent the same variational problem under a mass transformation that changes the number and definition of chemical potential variables. It is shown that due to symmetry imposed by stoichiometric constraints, chemical potential values remain invariant under the Gibbs–De Donder mass transformation. It is this invariance which makes possible the traditional merging of constraints on chemical potentials arising in the Gibbs and De Donder theories. For example, even though affinity constraints are formally defined only for the De Donder chemical potentials μ_{ij} , the invariance condition $\mu_{ij} = \mu'_{ij}$ makes it quantitatively indistinguishable to write the constraints in terms of the μ_{ij} or the corresponding Gibbs chemical potentials μ'_{ij} .

A modified form of the Gibbs–Duhem relation [equation (11)] has been derived, and used together with equation (9) to establish the mass transformation operator defined in equation (13). To the author's knowledge, these results have not been published elsewhere. The concepts are applied to ion exchange systems in Appendix B, primarily for illustrative purposes, but also to demonstrate a previously unrecognized general method for treating ion exchange systems. Historically, these systems have resisted rigorous thermodynamic analysis, except under severely restrictive conditions [9,10]. It was precisely the study of ion exchange systems which led the author to recognize the general symmetry relations described here.

Although the Gibbs and De Donder equilibrium formulations represent mathematically equivalent energy variation problems, their different formal structures influence the respective applicabilities. In most experimental situations, the variables of interest and their interrelations are best accommodated within De Donder's theory. For example, in characterizing equilibrium systems, the mass variables usually measured are of the De Donder type, i.e. the current masses of all species, rather than the Gibbs exchanged component masses. Also, by formally considering all chemical substances as state variables and making use of Lagrange multipliers, De Donder framework allows systematic treatment of constraints in ways that are difficult or impossible in Gibbs' theory. Chemical reaction stoichiometries, leading to the affinity conditions, are a classic example of such constraints. Other, more "special" constraints could also in principle be considered within De Donder's framework. A case in point is the electro-neutrality constraint among ionic species in electrolyte solutions. This constraint negates the possibility of treating ionic species as independent variables in Gibbs' theory, leading to the prevalent notion that properties such as ionic masses and chemical potentials are "extra-thermodynamic" in nature. However, there is no reason in principle why, with aid of Lagrange multipliers, the electro-neutrality constraint

and ionic masses cannot be incorporated as rigorously defined thermodynamic entities within the mathematically equivalent De Donder framework.

Appendix A

A.1. Formulation of the multi-phase chemical equilibrium problem in De Donder mass coordinates using Lagrange multipliers

A.1.1. Energy Stationarity condition

We write the overall Gibbs energy variation dG in a multiphase system as the sum of energy variations dG_j in the $j = 1, 2, \dots, J$ individual phases, and set dG to zero consistent with a stationarity condition at equilibrium. With each of the dG_j described by equation (1), the stationarity condition becomes

$$\sum_{j=1}^J \sum_{i=1}^I \mu_{ij} dM_{ij} = 0. \quad (\text{A.1})$$

Since the stationarity condition applies only to systems at equilibrium, the parameter variations in (A.1) are to be interpreted as virtual variations around the respective equilibrium values.

The dM_{ij} in equation (A.1) are subject to various constraints. In order to determine the conditions imposed by these constraints on the chemical potentials μ_{ij} , we first formulate the constraints as vanishing auxiliary conditions with Lagrange multipliers, then introduce them into the stationarity condition equation (A.1), as follows:

A.1.2. Constraints and auxiliary condition due to allowable sources of mass variations

Each of the mass variations dM_{ij} in equation (A.1) is determined by the amount dm_{ij} of substance i exchanged between phase j and its environment, plus any amount produced or consumed within phase j by chemical reactions. We write this as

$$dM_{ij} - dm_{ij} - \sum_{r=1}^{R_i} v_{ir} d\varepsilon_{irj} = 0, \quad (\text{A.2})$$

where R_i is the number of independent chemical reactions involving species i , v_{ir} is the stoichiometric coefficient of species i in the r th reaction, and $d\varepsilon_{irj}$ is the extent of the r th reaction involving species i in phase j . Chemically non-reactive species are included as special cases where $d\varepsilon_{irj} = 0$.

Each of the constraints equation (A.2) can be multiplied times an arbitrary scalar parameter, λ_{ij} , and the resulting constraints added over all I chemical substances and J phases, yielding the auxiliary equation

$$\sum_{i=1}^I \sum_{j=1}^J \lambda_{ij} \left(dM_{ij} - dm_{ij} - \sum_{r=1}^{R_i} v_{ir} d\varepsilon_{irj} \right) = 0, \quad (\text{A.3})$$

where the indices “ ij ” denote that, in general, λ_{ij} has a different value for each species i and phase j .

A.1.3. Constraints and auxiliary condition imposed by system closure

In a closed multi-phase system, the dm_{ij} of equation (A.2) are subject to the constraint that the total amount of a given species i exchanged between the system and its external environment must vanish. Expressing the total exchanged mass as the sum of exchanges in the individual phases, the constraint becomes

$$\sum_{j=1}^J dm_{ij} = 0. \quad (\text{A.4})$$

Multiplying equation (A.4) for each species i by a multiplier λ_i , and summing over all I species yields the auxiliary condition

$$\sum_{i=1}^I \lambda_i \sum_{j=1}^J dm_{ij} = \sum_{j=1}^J \sum_{i=1}^I \lambda_i dm_{ij} = 0. \quad (\text{A.5})$$

The single index “ i ” indicates that the multiplier λ_i is single-valued for the i th species regardless of how it is distributed between phases.

A.1.4. Constraints and auxiliary condition imposed by restrictions on chemical reactions

The $d\varepsilon_{irj}$ in equation (A.2) are subject to the conditions that, for each of the substances $i = 1, 2, \dots, I_r$ participating in the r th reaction in phase j ,

$$\begin{aligned} d\varepsilon_{1rj} &= d\varepsilon_{2rj} = \dots = d\varepsilon_{I_r j} \\ &= d\varepsilon_{rj} \end{aligned} \quad (\text{A.6})$$

This yields a constraint for each substance i and reaction r in the j th phase

$$v_{ir} d\varepsilon_{irj} - v_{ir} d\varepsilon_{rj} = 0. \quad (\text{A.7})$$

Multiplying each constraint times a corresponding scalar λ_{irj} , summing over all substances, reactions and phases, and collecting terms, yields

$$\sum_{j=1}^J \sum_{r=1}^R \sum_{i=1}^{I_r} \lambda_{irj} v_{ir} d\varepsilon_{irj} - \sum_{j=1}^J \sum_{r=1}^R \left(\sum_{i=1}^{I_r} \lambda_{irj} v_{ir} \right) d\varepsilon_{rj} = 0. \quad (\text{A.8})$$

A.1.5. Combined stationarity and auxiliary conditions

Subtracting the auxiliary equations (A.3), (A.5) and (A.8) from the energy stationarity condition equation (A.1), and rearranging, yields

$$\begin{aligned} \sum_{j=1}^J \sum_{i=1}^I (\mu_{ij} - \lambda_{ij}) dM_{ij} + \sum_{j=1}^J \sum_{i=1}^I (\lambda_{ij} - \lambda_i) dm_{ij} + \sum_{j=1}^J \sum_{r=1}^R \sum_{i=1}^{I_r} (\lambda_{ij} v_{ir} - \lambda_{irj} v_{ir}) d\varepsilon_{irj} \\ + \sum_{j=1}^J \sum_{r=1}^R \left(\sum_i^{I_r} \lambda_{irj} v_{ir} \right) d\varepsilon_{rj} = 0, \end{aligned} \quad (\text{A.9})$$

where use has been made of the commutation identity:

$$\sum_{j=1}^J \sum_{i=1}^I \sum_{r=1}^{R_i} \lambda_{irj} v_{ir} d\varepsilon_{irj} = \sum_{j=1}^J \sum_{r=1}^R \sum_{i=1}^{I_r} \lambda_{irj} v_{ir} d\varepsilon_{irj}. \quad (\text{A.10})$$

By virtue of the Lagrange multipliers, equation (A.9) can be satisfied by causing all the coefficients of the differentials to vanish. For the first three summation series in equation (A.9), identical vanishing of the coefficients yields that

$$\lambda_{irj} = \lambda_{ij} = \lambda_i = \mu_{ij}. \quad (\text{A.11})$$

As noted earlier, the multiplier λ_i for a given species i has the same value in all phases. Thus, equation (A.11) implies that

$$\mu_{i1} = \mu_{i2} = \dots = \mu_{iJ} = \mu_i, \quad (\text{A.12})$$

which is equation (4) in the main text.

Vanishing of coefficients in the last summation series of equation (A.9), together with identities equations (A.11) and (A.12), yields the chemical affinity constraint for each chemical reaction

$$\sum_{i=1}^I v_{ir} \mu_i = 0 \quad r = 1, 2, \dots, R. \quad (\text{A.13})$$

It should be noted that relations equations (A.12) and (A.13) are mutually independent. In contrast, De Donder and Van Rysselberghe [2] and Prigogine and Defay [6] derived equation (A.12) as a merely special case of equation (A.13),

in which case the two relations cannot be considered independent. The apparent contradiction is resolved noting that the latter derivations implicitly assume arbitrary virtual variations in total mass exchange between phases in a closed system, which is incorrect because these variations vanish as recognized by Gibbs [see also equation (A.4) above].

Appendix B

B.1. Relations between Gibbs–Duhem relations in the Gibbs and De Donder frameworks for a binary ion exchange system

Consider an aqueous suspension of electrically charged colloidal particles, which exchange counter-ions A^{+a} and B^{+b} with surrounding aqueous electrolyte species ACl_a and BCl_b according to the reaction



Here X refers to the amount of negatively charged colloidal surface required to balance a mole of counter-ion A^{+a} or B^{+b} , a and b are respective valencies, and Cl represents a common electrolyte anion such as chloride. The system contains 5 chemical species, i.e. the reactants in equation (B.1) plus liquid water (w), and 4 independently variable components. We choose AX , ACl_a , BCl_b and water as components, leaving BX as the “non-component” substance.

The component-based Gibbs–Duhem relation Eq. (9) for the designated set of component substances is:

$$m_{AX}d\mu'_{AX} + m_{BCl_b}d\mu'_{BCl_b} + m_{ACl_a}d\mu'_{ACl_a} + m_w d\mu'_w = 0. \quad (\text{B.2})$$

The Gibbs–Duhem relation equation (5) for the system in the De Donder framework is

$$M_{AX}d\mu_{AX} + M_{BX}d\mu_{BX} + M_{BCl_b}d\mu_{BCl_b} + M_{ACl_a}d\mu_{ACl_a} + M_w d\mu_w = 0 \quad (\text{B.3})$$

subject to the affinity constraint which we write in differential form as

$$bd\mu_{AX} + ad\mu_{BCl_b} - ad\mu_{BX} - bd\mu_{ACl_a} = 0. \quad (\text{B.4})$$

Eliminating the “non-component” differential $d\mu_{BX}$ from equation (B.3) using equation (B.4), gives the modified Gibbs–Duhem relation equation (11) in the form

$$\begin{aligned} & \left(M_{AX} + \frac{b}{a}M_{BX} \right) d\mu_{AX} + \left(M_{BCl_b} + M_{BX} \right) d\mu_{BCl_b} \\ & + \left(M_{ACl_a} - \frac{b}{a}M_{BX} \right) d\mu_{ACl_a} + M_w d\mu_w = 0. \end{aligned} \quad (\text{B.5})$$

The coefficients of the $d\mu_i$ in equation (B.5) may be recognized as the functions f_{ij} of equation (11), so that identities equation (13) assume the specific form:

$$f_{AX} = M_{AX} + \frac{b}{a}M_{BX} = m_{AX}, \quad (\text{B.6a})$$

$$f_{BCl_b} = M_{BCl_b} + M_{BX} = m_{BCl_b}, \quad (\text{B.6b})$$

$$f_{ACl_a} = M_{ACl_a} - \frac{b}{a}M_{BX} = m_{ACl_a}, \quad (\text{B.6c})$$

$$f_w = M_w = m_w. \quad (\text{B.6d})$$

These relations, inferred solely from equations (10) and (13), can be verified independently by checking their consistency with stoichiometric mass balance constraints under the designated choice of components. For instance, equation (B.6a) reflects the fact that the M_{AX} moles of component species AX remaining at equilibrium are equal to the m_{AX} moles of AX added originally to the mixture, minus the moles of AX consumed in the ion exchange reaction with electrolyte species BCL . The number of moles of AX consumed in this reaction is given by the term $b/a M_{BX}$, where the M_{BX} moles of non-component species BX appearing in the system provide a measure of the extent of reaction. Inspection of the remaining identities equations (B.6b–d) shows similar consistency with stoichiometric constraints.

The set of linearly independent relations equations (B.6a–d) defines the coordinate transformation equation (14) mapping the De Donder mass vector $\{M_{ij}\}$ onto the Gibbs component mass vector $\{m_{ij}\}$. Note the non-invertible nature of this transformation; i.e., specifying only the set $\{M_{ij}\}$ is sufficient to define $\{m_{ij}\}$, but specifying $\{m_{ij}\}$ does not allow determining $\{M_{ij}\}$ without additional information such as equilibrium constants and the set of state functions $\mu_{ij}(\{M_{ij}\})$.

It should be noted that, in the case of reactive substances, the above transformation often yields negative values for the component masses m_{ij} . Such quantities may at first glance seem physically absurd, but in fact are easily achieved experimentally as shown in [9].

Equation (B.5) represents a general solution to the longstanding problem of determining solid exchanger activities in ion exchanging mixtures. Existing thermodynamic methods, based on a formulation of Gaines and Thomas [10], are severely restrictive in that exchanger activities can only be measured under conditions of constant water potential and negligible electrolyte adsorption on the solid phase. None of these restrictions apply to equation (B.5). Note that the only parameter in this equation which cannot be measured experimentally in aqueous ion exchange systems is the exchanger chemical potential μ_{AX} . This allows direct determination of μ_{AX} by integrating equation (B.5) in terms of the measurable parameters. [An equivalent result was obtained earlier by the author in (9), but using a much more cumbersome derivation]. Even though here

equation (B.5) is applied only to binary ion exchange systems, it can readily be generalized to include any number of electrolytes and exchanger species.

References

- [1] J.W. Gibbs, *The Scientific Papers of J. Willard Gibbs*, Vol. 1, *Thermodynamics* (Dover, New York, 1961).
- [2] Th. De Donder and P. Van Rysselberghe, *Thermodynamic Theory of Affinity* (Stanford, 1936).
- [3] M. Hillert, *Phase Equilibria, Phase Diagrams and Phase Transformations* (Cambridge, U.K., 1998).
- [4] H. Goldstein, *Classical Mechanics* (Addison-Wesley, Reading, 1980).
- [5] C. Lanczos, *The Variational Principles of Mechanics* (Dover, New York, 1986).
- [6] I. Prigogine and R. Defay, *Chemical Thermodynamics* (Longman, London, 1954).
- [7] J.G. Kirkwood and I. Oppenheim, *Chemical Thermodynamics* (McGraw-Hill, New York, 1961).
- [8] E.A. Guggenheim, *Thermodynamics* (John Wiley and Sons, New York, 1967).
- [9] V.A. Snyder and N. Cavallaro, *Soil Sci. Soc. Am. J.* 61 (1997) 36.
- [10] G.L. Gaines and H.C. Thomas, *J. Chem. Phys.* 21 (1953) 714.