A New Integration of the Gibbs-Duhem Equation for Di-gaseous Quaternary Systems

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A novel integration of the Gibbs-Duhem equation has been presented for quaternary solutions containing two volatile components. The new integration formulae relate to calculation of the activities of nonvolatile third and fourth components from the measured activities of volatile first and second components. These formulae are more complex than the conventional ternary or quaternary integrations for solutions consisting of all nonvolatile (or only one volatile) components with constant concentration ratios, in that it contains an additional third term and it also involves integration of a product of two partial derivatives. The present formulae are essential to activity calculations for S-bearing slags or oxygen-containing sulfides, among others. An application of the new formulae has been demonstrated for the S-O-Fe-Cu system mattes by calculating the activities of iron and copper from the observed partial pressures of sulfur and oxygen.

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I. Introduction

Darken(1) was the first to discover that when the chemical potential of one component is known over the entire composition range of a ternary or multi-component solution, the activities of all the other components can be calculated by integrating the Gibbs-Duhem (GD) equation. Followingly, several modified versions were devised to facilitate the integration(2)-(4). All these methods are inapplicable to quaternary solutions where the activities of third and fourth components must be calculated from the measured activities of both first and second components. For the conventional formulae relate to integration of the GD equation with respect to only one known activity, whereas the GD equation has to be integrated simultaneously with respect to two known activities in the present case. Situations of this type arise, for example, in many industrial pyrometallurgical systems such as the dissolution of sulfur in oxidic slags, or that of oxygen in molten sulfides (mattes).

The activities of volatile elements (oxygen and sulfur) in these solutions are often measured simultaneously by equilibrating a molten condensed phase under a controlled gas mixture such as H₂-H₂O-H₂S or CO-CO₂-SO₂. However, the activities of nonvolatile constituents have not been assessed in these melts through lack of integrating formula in the literature. The present note describes the simultaneous integration of the GD equation with respect to two known activities over general quaternary solutions.

II. Mathematical Preparations

Let \( u \) be a continuous function of \( v \) and \( w \) which has the continuous partial derivatives given by

\[
M = \left( \frac{\partial u}{\partial v} \right)_w \quad \text{and} \quad N = \left( \frac{\partial u}{\partial w} \right)_v
\]  

(1)

A variation in \( u \) caused by the increments of \( dv \) and \( dw \) is then given by the following exact differential.
\[ du = M dv + N dw \]  
(2)

Since mixed (cross) derivatives are equal for continuous and differentiable functions, we have

\[ \left(\frac{\partial M}{\partial w}\right)_{v} = \left(\frac{\partial N}{\partial v}\right)_{w} \]  
(3)

When \( M \) is an explicit function of \( v \) and \( w \), it may also be expressed implicitly as

\[ f(M, v, w) = 0 \]  
(4)

Applying the cyclic rule to eq. (4), we find

\[ \left(\frac{\partial M}{\partial w}\right)_{v} \left(\frac{\partial v}{\partial M}\right)_{w} \left(\frac{\partial w}{\partial v}\right)_{M} = -1 \]  
(5)

Substituting eq. (3) in eq. (5), we obtain

\[ \left(\frac{\partial v}{\partial w}\right)_{M} = - \left(\frac{\partial N}{\partial M}\right)_{w} \]  
(6)

III. The GD Equation for Quaternary Solutions

Let us assume a homogeneous quaternary solution in which the atomic (or mole) fractions of the components 1, 2, 3 and 4 are given by \( N_1, N_2, N_3 \) and \( N_4 \), respectively, and

\[ N_1 + N_2 + N_3 + N_4 = 1 \]  
(7)

The GD equation of this solution at constant temperature and total pressure may be expressed as

\[ N_1 d\mu_1 + N_2 d\mu_2 + N_3 d\mu_3 + N_4 d\mu_4 = 0 \]  
(8)

where \( \mu_i \) refers to the chemical potential of component \( i \).

Suppose that the components 1 and 2 are volatile, whereas the components 3 and 4 are not, so that the initial ratio of \( N_3 \) to \( N_4 \) remains unchanged in the solution while the vapor pressures (or activities) of the components 1 and 2 are measured simultaneously. When the activity of the component 2 is measured as a function of solution composition under a constant activity of the component 1, or \( d\mu_1 = 0 \), eq. (8) becomes as follows:

\[ [N_2 d\mu_2 + N_3 d\mu_3 + N_4 d\mu_4 = 0]_{\mu_1} \]  
(9)

In order to compare with eq. (2), eq. (9) may be rewritten as

\[ d\mu_4 = \left(\frac{-N_2}{N_4}\right) d\mu_3 + \left(\frac{-N_3}{N_4}\right) d\mu_2 \]  
(10)

IV. Transformation into Integrable Form

Let us equate as follows:

\[ M = \frac{-N_3}{N_4}; \quad N = \frac{-N_2}{N_4}; \quad v = \mu_3; \quad w = \mu_2 \]  
(11)

Substitution of eq. (11) in eq. (6) yields

\[ \left(\frac{\partial \mu_2}{\partial \mu_3}\right)_{N, \mu_1} = - \left(\frac{\partial \mu_3}{\partial N}\right)_{\mu_1, \mu_2} \]  
(12)

A relation similar to eq. (12) was first derived by Gokcen\(^4\). However, the partial derivatives are valid under the restriction of \( \frac{N_1}{N_4} = \text{const} \) in Gokcen's case, as compared to that of \( \mu_1 = \text{const} \) in the present case.

Let us define new functions \( x, y \) and \( z \) as follows.

\[ x = \frac{N_3}{N_4}; \quad y = \frac{N_3}{N_1 + N_4}; \quad z = \frac{N_2}{N_4} \]  
(13)

Noting that \( y = \text{const} \) when \( N_3/N_4 = \text{const} \), eq. (12) may be rewritten as

\[ \left(\frac{\partial \mu_3}{\partial \mu_2}\right)_{y, \mu_1} = - \left(\frac{\partial z}{\partial x}\right)_{\mu_1, \mu_2} \]  
(14)

Substituting eq. (13) in eq. (7) and rearranging yield

\[ N_1 + N_2 + xN_4 + N_4 = 1 \]

or

\[ N_4 = \frac{1 - N_1 - N_2}{1 + x}. \]  
(15)

Using eq. (15), the function \( z \) can be rewritten as

\[ z = \frac{N_2}{N_4} = \frac{(1 + x)N_2}{1 - N_1 - N_2} \]  
(16)

For an explicit function \( z = f(N_1, N_2, x) \), the exact differential is given as
Each of the partial derivatives in eq. (17) can be calculated by differentiating eq. (16) partially. The results are as follows:

\[
\begin{align*}
\frac{\partial z}{\partial N_1/N_{x,y}} &= \frac{(1 + x)N_2}{(1 - N_1 - N_2)N_{x,y}} \\
\frac{\partial z}{\partial N_2/N_{x,y}} &= \frac{(1 + y)(1 - N_1)}{(1 - N_1 - N_2)^2} \\
\frac{\partial z}{\partial x/N_{x,y}} &= \frac{N_2}{1 - N_1 - N_2}
\end{align*}
\]

Substitution of eqs. (18), (19) and (20) in eq. (17), and division of both sides by \(dx\) yield

\[
\frac{dz}{dx} = \frac{(1 + x)N_2}{(1 - N_1 - N_2)^2} \left( \frac{dN_1}{dx} \right)
+ \frac{(1 + y)(1 - N_1)}{(1 - N_1 - N_2)^2} \left( \frac{dN_2}{dx} \right)
+ \frac{N_2}{1 - N_1 - N_2}
\]

Noting that \(x = y/(1 - y)\), we have

\[
\frac{1}{dx} = \frac{(1 - y)^2}{dy}
\]

Noting further that \(1 + x = 1/(1 - y)\) as well as using eq. (22), eq. (21) can be rewritten as

\[
\frac{dz}{dy} = \frac{(1 - y)^2N_2}{(1 - y)(1 - N_1 - N_2)^2} \left( \frac{dN_1}{dy} \right)
+ \frac{(1 - y)^2(1 - N_1)}{(1 - y)(1 - N_1 - N_2)^2} \left( \frac{dN_2}{dy} \right)
+ \frac{N_2}{1 - N_1 - N_2}
\]

When the derivatives are taken under constant \(\mu_1\) and \(\mu_2\), eq. (23) becomes

\[
\begin{align*}
\left( \frac{\partial z}{\partial x} \right)_{\mu_2,\mu_1} &= \frac{(1 - y)N_2}{(1 - N_1 - N_2)^2} \left( \frac{\partial N_1}{\partial y} \right)_{\mu_2,\mu_1}
+ \frac{(1 - y)(1 - N_1)}{(1 - N_1 - N_2)^2} \left( \frac{\partial N_2}{\partial y} \right)_{\mu_2,\mu_1}
+ \frac{N_2}{1 - N_1 - N_2}
\end{align*}
\]

Substitution of eq. (24) in eq. (14) yields

\[
\left( \frac{\partial \mu_3}{\partial x} \right)_{\mu_2,\mu_1} = \frac{- (1 - y)N_2}{(1 - N_1 - N_2)^2} \left( \frac{\partial N_1}{\partial y} \right)_{\mu_2,\mu_1}
+ \frac{-(1 - y)(1 - N_1)}{(1 - N_1 - N_2)^2} \left( \frac{\partial N_2}{\partial y} \right)_{\mu_2,\mu_1}
+ \frac{-N_2}{1 - N_1 - N_2}
\]

The right-hand side of eq. (25) contains only the activity-composition relations of the components 1 and 2, so that, in principle, the equation can be integrated with respect to \(\mu_2\) to obtain the activity of the component 3 from the known activity values of the components 1 and 2. In reality, however, the integration of eq. (25) with respect to chemical potential \(\mu_2\), or the logarithm of \(a_2\) (activity of the component 2), is often inaccurate due to the fact that \(\mu_2\) becomes minus infinity at \(N_2 = 0\). Preferably, therefore, the integration should be made with respect to \(N_2\) rather than \(\mu_2\). Such conversion can be done by multiplying \((\partial \mu_2/\partial N_2)_{\mu_1,\mu_1}\) on both sides of eq. (25); viz.

\[
\begin{align*}
\frac{\partial \mu_3}{\partial N_2(y,\mu_1)} &= \frac{- (1 - y)N_2}{(1 - N_1 - N_2)^2} \left( \frac{\partial N_1}{\partial y} \right)_{\mu_2,\mu_1}
+ \frac{-(1 - y)(1 - N_1)}{(1 - N_1 - N_2)^2} \left( \frac{\partial N_2}{\partial y} \right)_{\mu_2,\mu_1}
+ \frac{-N_2}{1 - N_1 - N_2}
\end{align*}
\]

There is only one value of \(N_2\) for a given set of \(y\) and \(\mu_2\) under constant \(\mu_1\), or implicitly

\[
[f(N_2, \mu_2, y) = 0]_{\mu_1}
\]

Applying the cyclic rule to eq. (27), we find

\[
\left[ \frac{\partial N_2}{\partial y} \right]_{\mu_1} \left( \frac{\partial \mu_2}{\partial N_2} \right)_{y,\mu_1} = - \left( \frac{\partial \mu_2}{\partial y} \right)_{N_2,\mu_1}
\]

Inserting eq. (28) in eq. (26), we find

\[
\begin{align*}
\left( \frac{\partial \mu_3}{\partial N_2} \right)_{y,\mu_1} &= \frac{- (1 - y)N_2}{(1 - N_1 - N_2)^2} \left( \frac{\partial N_1}{\partial y} \right)_{\mu_2,\mu_1}
+ \frac{(1 - y)(1 - N_1)}{(1 - N_1 - N_2)^2} \left( \frac{\partial \mu_2}{\partial y} \right)_{N_2,\mu_1}
+ \frac{-N_2}{1 - N_1 - N_2}
\end{align*}
\]

The procedures of eqs. (10) through (29)
may be repeated to obtain the following expression for \( \mu_4 \).

\[
\left( \frac{\partial \mu_4}{\partial N_2} \right)_{y, \mu_1} = \frac{y N_2}{(1-N_1-N_2)^2} \left( \frac{\partial N_1}{\partial y} \right)_{N_2, \mu_1} \left( \frac{\partial \mu_2}{\partial N_2} \right)_{y, \mu_1} \]

\[
+ \frac{y(1-N_2)}{(1-N_1-N_2)^3} \left( \frac{\partial \mu_2}{\partial y} \right)_{N_2, \mu_1} \]

\[
+ \frac{-y N_2}{1-N_1-N_2} \left( \frac{\partial \mu_2}{\partial N_2} \right)_{y, \mu_1} \]

(30)

which indicates that the term \((1-y)\) in eq. (29) has been replaced by \((-y)\). In the present note, eqs. (29) and (30) are called the GD equation for di-gaseous quaternary solutions.

It is interesting to note that eqs. (29) and (30) for a quaternary solution containing two volatile components are far more complex than Gokcen's eq. (29) for a quaternary containing no (or only one) volatile component\(^{(4)}\), in that they are composed of three terms (versus two) as well as comprise a product of two partial derivatives (which is absent from Gokcen's). It is also noteworthy that the condition of \( \mu_i = \text{const} \) forms a three-dimensional curved surface, unlike a two-dimensional plane for a constant \( N_i/N_4 \) ratio in Gokcen's case\(^{(4)}\). Consequently, there is no graphical tangent method that can be devised for di-gaseous quaternary GD integrations. As will be shown later in the sample application, the use of Simpson's one-third method on the computer is most convenient for integrating the di-gaseous GD equations.

**V. Integration of the GD Equation for Di-gaseous Quaternaries**

When the chemical potential of the component 2 is known over a wide range of solution composition, all three partial derivatives on the right-hand side of eqs. (29) or (30) can be numerically specified. In order to integrate eq. (29) or (30) with respect to \( N_2 \), we can only choose \( N_2 = 0 \) (i.e. the 1-3-4 ternary) as initial condition. For the activities of all four components must be known for a quaternary composition before it can be chosen as initial condition. Thus, the value of \( \mu_3 \) (or \( \mu_4 \)) has to be known for given values of \( y \) (or \( N_3/N_4 \) ratio) and \( \mu_1 \) in the ternary 1-3-4 solution. If only \( \mu_1 \) has been measured in the ternary 1-3-4, the values of \( \mu_3 \) and \( \mu_4 \) have to be calculated first by integrating the ternary GD equation with the use of the classical Gokcen or other equation.

The chemical potential \( \mu_i \) in eqs. (29) and (30) may be replaced with the partial pressure \( p_i \) of volatile component \( i \) or the Raoultian activity \( a_j \) of non-volatile component \( j \), as follows:

\[
d\mu_i = RT \ln p_i \quad (i = 1, 2) \quad (31)
\]

\[
d\mu_j = RT \ln a_j \quad (j = 3, 4) \quad (32)
\]

where \( R \) refers to gas constant and \( T \) to temperature in Kelvin. Since the terms \( RT \) cancel out from both sides, eq. (29) can be integrated as follows:

\[
\int_{N_2=0}^{N_2} \left( \frac{\partial \ln a_3}{\partial N_2} \right)_{y, \mu_1} \, dN_2 = t_1 + t_2 + t_3 \quad (33)
\]

where

\[
t_1 = \int_{N_2=0}^{N_2} \frac{-(1-y)N_2}{(1-N_1-N_2)^2} \left( \frac{\partial N_1}{\partial y} \right)_{N_2, \mu_1} \times \left( \frac{\partial \ln p_2}{\partial N_2} \right)_{y, \mu_1} \, dN_2 \quad (34)
\]

\[
t_2 = \int_{N_2=0}^{N_2} \frac{(1-y)(1-N_1)}{(1-N_1-N_2)^3} \left( \frac{\partial \ln p_2}{\partial y} \right)_{N_2, \mu_1} \, dN_2 \quad (35)
\]

\[
t_3 = \int_{N_2=0}^{N_2} \frac{-N_2}{1-N_1-N_2} \left( \frac{\partial \ln p_2}{\partial N_2} \right)_{y, \mu_1} \, dN_2 \quad (36)
\]

The left-hand side of eq. (33) can be calculated as follows:

\[
\int_{N_2=0}^{N_2} \left( \frac{\partial \ln a_3}{\partial N_2} \right)_{y, \mu_1} \, dN_2 = \int_{N_2=0}^{N_2} (d \ln a_3)_{x, \mu_1} = \ln \frac{a_3(x=\text{const}, \mu_1=\text{const}, N_2=\text{N}_3)}{a_3^*(x=\text{const}, \mu_1=\text{const}, 1-3-4)} \quad (37)
\]

where \( a_3^* \) refers to the activity value of the component 3 in the ternary 1-3-4 solution having the vapor pressure \( p_1 \) at the constant \( N_1/N_4 \) value.

In order to facilitate calculation of the partial derivatives in eqs. (34), (35) and (36), the experimentally measured \( p_2 \) values under constant \( p_1 \) may be expressed as a function of \( y \) and \( N_2 \) namely
Similarly, the measured values of \( N_1 \) may be best expressed as a function of \( y \) and \( p_2 \) under constant \( p_1 \); namely

\[
[N_1 = f(y, p_2)]_{p_1}
\]  

(39)

VI. Integration of the GD Equation for Di-gaseous Ternaries

The GD equation of the ternary 1-2-3 system solutions containing two volatile components 1 and 2 may be expressed as

\[
N_1 \ln p_1 + N_2 \ln p_2 + N_3 \ln a_3 = 0
\]

(40)

Under the conditions of \( p_1 = \text{const} \), or \( d \ln p_1 = 0 \), eq. (40) is simplified to that of a binary system; viz.

\[
[N_2 \ln p_2 + N_3 \ln a_3 = 0]_{p_1}
\]  

(41)

When the activity \( a_3 \) and \( p_1 \) are known as a function of the composition of the binary 1-3 solutions, eq. (41) can be integrated as follows:

\[
\ln \left[ \frac{a_3(N_2 = N_3)}{a_3(1-3)} \right]_{p_1} = -\int_{N_3 = 0}^{N_3} \left[ \frac{N_2}{N_3} \ln p_2 \right]_{p_1} \]  

(42)

On the other hand, for the ternary 1-2-3 solutions, we find

\[
[1-y=0]_{1-2-3}
\]  

(43)

Consequently, the terms \( t_1 \) and \( t_2 \) become zero in eq. (33), and the only term remaining is \( t_3 \), which can readily be seen being identical with eq. (42). In other words, eq. (33) is valid for the quaternary 1-2-3-4 system including its limiting case of the 1-2-3 ternary solutions.

VII. Sample Application to the S-O-Fe-Cu Mattes

The S-O-Fe-Cu system mattes were equilibrated at 1473 K for 20 hours with the CO-CO2-SO2 system gas of known composition. Since carbon does not dissolve in the mattes, the gas mixture merely controls the partial pressures of oxygen and sulfur, which can readily be calculated from the free energy data for various gaseous compounds. The Cu/Fe ratio in the initial charge does not change, while sulfur and oxygen contents of the matte vary till they reach equilibrium with the gas. The oxygen contents in quenched samples were determined gravimetrically by hydrogen reduction method. On the other hand, the sulfur...
## Table 1 Partial pressure of oxygen and atomic fraction of sulfur of the S-O-Fe-Cu system mattes at 1473 K and $P_O=0.09$. \(N_O\), \(N_{Fe}\)=atomic fraction of sulfur and oxygen in mattes; \(y=\frac{N_{Fe}}{N_{Fe}+N_{Cu}}\)

| \(x\) | \(P_S\) | \(P_O\) | \(N_O\) | \(N_{Fe}\) | \(N_{Cu}\) | \(a_{Cu}\) | \(a_{Fe}\) | \(a_{CuO}\) | \(a_{FeO}\) | \(a_{FeO_3}\) |
|---|---|---|---|---|---|---|---|---|---|---|
| 1.000 | 0.090 | 0.0 | 0.0000 | 0.5027 | 0.4973 | 0.0000 | 0.0000 | 0.0371 | 1.000 | 0.000 |
| 1.000 | 0.090 | 1.0 | 0.0075 | 0.4796 | 0.5279 | 0.0000 | 0.0000 | 0.0329 | 0.000 | 0.886 |
| 1.000 | 0.090 | 3.0 | 0.0978 | 0.4368 | 0.5634 | 0.0000 | 0.0000 | 0.0279 | 0.000 | 0.752 |
| 1.000 | 0.090 | 7.0 | 0.1623 | 0.3645 | 0.6372 | 0.0000 | 0.0000 | 0.0221 | 0.000 | 0.589 |
| 1.000 | 0.090 | 13.0 | 0.2303 | 0.2847 | 0.4850 | 0.0000 | 0.0000 | 0.0172 | 0.000 | 0.463 |
| 1.000 | 0.090 | 20.0 | 0.2916 | 0.2281 | 0.4823 | 0.0000 | 0.0000 | 0.0137 | 0.000 | 0.369 |

## Table 2 Activity-composition relations for the S-O-Fe-Cu mattes at 1473 K and $P_O=0.09$. \(N_O\), \(N_{Fe}\)=atomic fraction of sulfur and oxygen in mattes; \(y=\frac{N_{Fe}}{N_{Fe}+N_{Cu}}\)

| \(x\) | \(P_S\) | \(P_O\) | \(N_O\) | \(N_{Fe}\) | \(N_{Cu}\) | \(a_{Cu}\) | \(a_{Fe}\) | \(a_{CuO}\) | \(a_{FeO}\) | \(a_{FeO_3}\) |
|---|---|---|---|---|---|---|---|---|---|---|
| 0.0 | 0.090 | 0.0 | 0.0000 | 0.4721 | 0.5279 | 0.0000 | 0.0000 | 0.0371 | 1.000 | 0.000 |
| 1.0 | 0.0405 | 0.4596 | 0.5336 | 0.3336 | 0.6664 | 0.0000 | 0.0000 | 0.0366 | 0.000 | 0.886 |
| 2.0 | 0.0683 | 0.4370 | 0.3298 | 0.1640 | 0.3297 | 0.0000 | 0.0000 | 0.0279 | 0.000 | 0.463 |
| 4.0 | 0.0958 | 0.4008 | 0.3356 | 0.1678 | 0.3300 | 0.0000 | 0.0000 | 0.0221 | 0.000 | 0.369 |
| 10.0 | 0.1198 | 0.3651 | 0.3434 | 0.1717 | 0.3300 | 0.0000 | 0.0000 | 0.0172 | 0.000 | 0.222 |
| 20.0 | 0.1390 | 0.3436 | 0.34491 | 0.1725 | 0.3300 | 0.0000 | 0.0000 | 0.0137 | 0.000 | 0.115 |
| 50.0 | 0.090 | 0.0 | 0.0000 | 0.4840 | 0.5160 | 0.0000 | 0.0000 | 0.0371 | 1.000 | 0.000 |
| 100.0 | 0.0405 | 0.4596 | 0.5336 | 0.3336 | 0.6664 | 0.0000 | 0.0000 | 0.0366 | 0.000 | 0.886 |
| 200.0 | 0.0683 | 0.4370 | 0.3298 | 0.1640 | 0.3297 | 0.0000 | 0.0000 | 0.0279 | 0.000 | 0.463 |
| 400.0 | 0.0958 | 0.4008 | 0.3356 | 0.1678 | 0.3300 | 0.0000 | 0.0000 | 0.0221 | 0.000 | 0.369 |
| 800.0 | 0.1198 | 0.3651 | 0.3434 | 0.1717 | 0.3300 | 0.0000 | 0.0000 | 0.0172 | 0.000 | 0.222 |
| 1600.0 | 0.1390 | 0.3436 | 0.3441 | 0.1725 | 0.3300 | 0.0000 | 0.0000 | 0.0137 | 0.000 | 0.115 |

\[ P_O = 12N_O + (A_2y + A_1y^2)N_O^2 + \exp(B_1y + B_2y^2 + B_3y^3) \frac{N_O}{N_O^2} + \exp(C_1y + C_2y^2) \]

\[ \frac{\partial P_O}{\partial N_O} = 12 + 2(A_2y + A_1y^2)N_O + 3\exp(B_1y + B_2y^2 + B_3y^3)N_O^2 + 4\exp(C_1y + C_2y^2) \]

\[ \frac{\partial P_O}{\partial N_O} = (A_2 + 2A_1y)N_O^2 + \exp(B_1 + B_2y + B_3y^3)N_O^3 \]

\[ \frac{\partial P_O}{\partial y} = \frac{1}{P_O} \left( \frac{\partial \ln P_O}{\partial y} \right) \]

\[ \frac{\partial \ln P_O}{\partial y} = \frac{1}{N_O} \left( \frac{\partial P_O}{\partial y} \right) \]
contents have been estimated based on the literature data\textsuperscript{(5)-(7)}.

Let 1 = sulfur, 2 = oxygen, 3 = iron and 4 = copper, and also

\begin{align*}
  P_S &= p_S^{1/2}, \quad \text{(atm)}^{1/2} \\
  P_O &= 10^6 p_O^{1/2}, \quad \text{(atm)}^{1/2}
\end{align*}

\text{(44)} \quad \text{(45)}

The experimental results of \( P_O \) and \( N_S \) obtained under the constant condition of \( P_S = 0.09 \) can be approximated by eqs. (1.1) and (1.2), Table 1. Henry’s law is observed in eq. (1.1), as the ratio \( P_O / N_O \) becomes a constant value with \( N_O \) approaching zero. The values calculated by eqs. (1.1) and (1.2) are compared with the observed ones in Figs. 1 and 2.

The partial derivatives required for eqs. (29) to (30) can readily be calculated from eqs. (1.1) and (1.2). The results are summarized in Table 1. The known activity-composition relations in the ternary S–Fe–Cu system mattrses\textsuperscript{(7)} serve as the initial conditions for the quaternary GD integrations. The Raoultian activities of Fe(s) and Cu(l) in the S–O–Fe–Cu quaternary mattrses can then be calculated by integrating eqs. (29) and (30) with respect to \( N_O \). The numerical computations have been made by use of Simpson’s one-third rule with a step of \( N_O = 0.0001 \). These Fe(s) and Cu(l) activities can be combined with the partial pressures of oxygen and sulfur as well as the known free energy data (or equilibrium constants) for the formation of the compounds FeS(l), CuS\textsubscript{0.5}(l), FeO(l) and FeO\textsubscript{1.33}(s) to calculate their Raoultian activities in the mattrses. The computed results are summarized in Table 2.

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