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Multicomponent Three-Phase Equilibria

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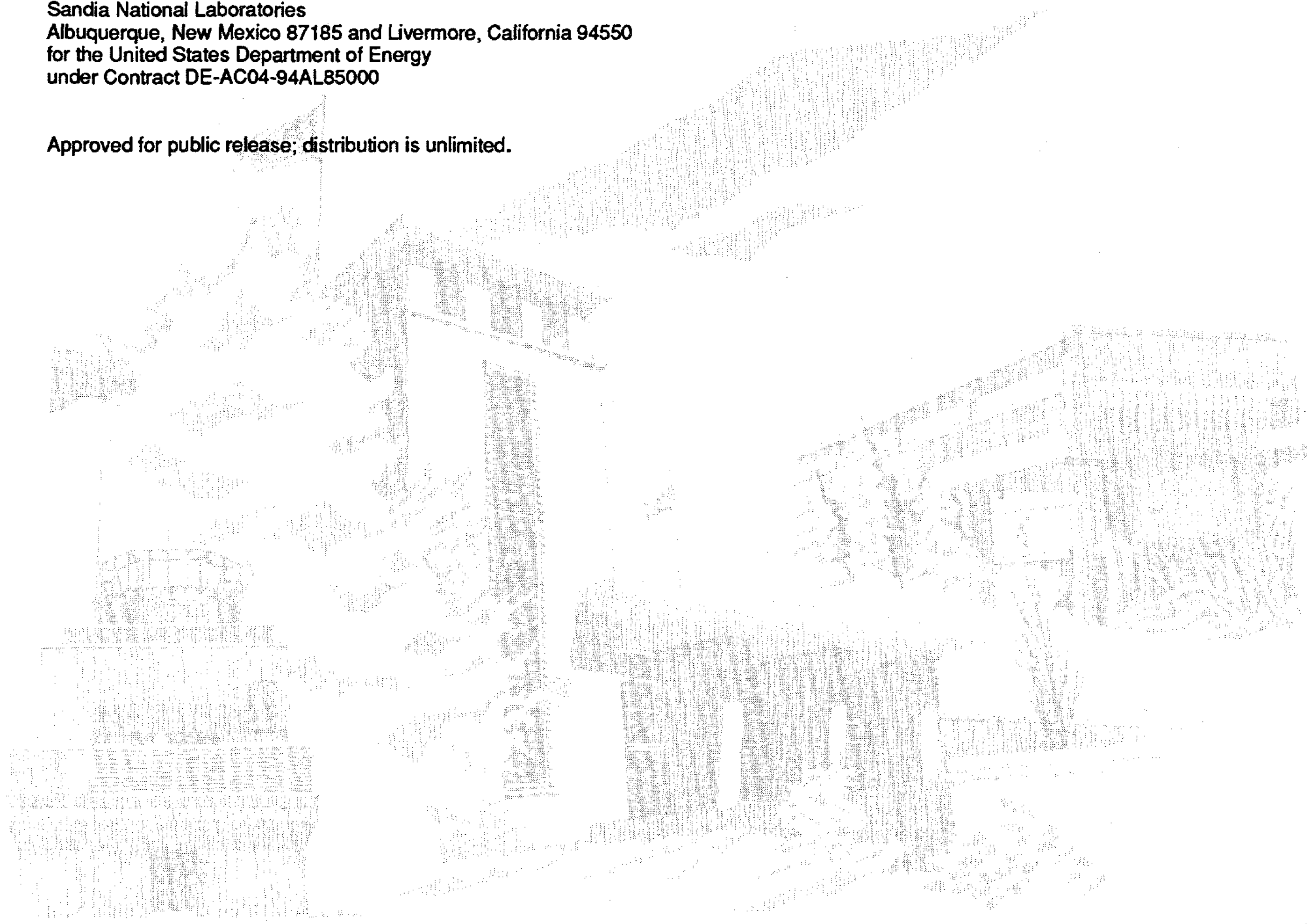

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MULTICOMPONENT THREE-PHASE EQUILIBRIA

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ABSTRACT

This paper presents the relations that describe thermodynamic equilibrium in a three-phase system. Multiple components, including air, water, and oil components, are considered in three phases: 1) aqueous, 2) oil, and 3) gas. Primary variables are specified for each of seven possible phase combinations. These primary variables are then used to determine the necessary secondary variables to completely describe the system. Criteria are also developed to check the stability of each phase configuration and determine possible transitions from one phase configuration to another phase configuration via phase appearances and disappearances.

DLC

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1. INTRODUCTION

In several applications ranging from enhanced oil recovery to subsurface remediation, transport of fluids can occur in three mobile phases—aqueous, oil, and gas. In the case of subsurface remediation, the oil phase is often referred to as a non-aqueous phase liquid, or NAPL, which can be comprised of multiple components such as TCE, benzene, and toluene. These components can be transported through the system in any of the three phases and can partition freely between them. Therefore, in a three-phase system the transport of multiple components can exist in aqueous, oil, and gas phases.

In general, the mass components that comprise a three-phase system include water, air, and the components originating from the NAPL. To simplify the transport formulation, these components are often assumed to exist in local thermodynamic equilibrium. Therefore, if a component exists in one phase, the concentration of that component can be determined in any of the other existing phases based on equilibrium relations for a representative elementary volume. At some sufficiently small volume, the assumption of local thermodynamic equilibrium can be used. However, several factors may act to invalidate this assumption including the application being modeled (such as soil vapor extraction with high flow rates) and the discretization of the model. Therefore, caution and sound judgment should be exercised before applying the simplified equations governing three-phase equilibria for arbitrary processes and domains.

Once local thermodynamic equilibrium is assumed, further assumptions can be made regarding the equilibrium relations to develop closed-form expressions that can be used in numerical simulations of three-phase flow and transport. More rigorous calculations of three-phase equilibria can be developed (Reid et al., 1987), but these often lead to computationally intensive simulations and require chemical data which are not readily available. As a result, this paper will focus on developing simplified equilibrium expressions that are more pragmatic for the end-user. The formulation is similar to the formulation presented by Adenekan (1992) and Adenekan et al.(1993), but this paper will provide more rigorous detail on the equilibrium relations and stability criteria required for each of the seven possible phase combinations that can exist in a three-phase system.

The phase combinations that can exist in a three-phase system are as follows: 1) water only; 2) oil only; 3) gas only; 4) water and oil; 5) water and gas; 6) oil and gas; and 7) water, oil, and gas. In each of these seven possible states, a set of primary variables is chosen to best describe the system. Given these primary variables, a set of secondary variables can then be determined based on equilibrium relations and other thermodynamic relations. Based on these primary and secondary variables, a set of criteria must then be established to determine the stability of the current phase combination. In other words, transitions from one phase combination to another phase combination can occur if one condition is determined to be more stable than the other.

This report will first present the relations that describe thermodynamic equilibrium between any two phases. This will allow the determination of the mole fraction of a particular component in one phase given the mole fraction of that component in another phase. These relations—along with some basic thermodynamic principles—will therefore yield all necessary secondary variables from a given set of primary variables. Finally, this report will provide a detailed description of the steps required to use the equilibrium relations given any of the seven possible phase combinations. For each combination, criterion will be presented to check the stability of each state and determine the possible transition of that state to another phase combination.

2. MULTICOMPONENT PHASE EQUILIBRIA

This section presents a description of multicomponent phase equilibria using several simplifying assumptions to obtain closed-form equilibrium expressions. In particular, the activity coefficients, which are generally functions of temperature, pressure, and composition, are assumed constant. Justifications for these assumptions will be made in the following sections as the equilibrium relations are developed.

Chemical equilibrium in a multicomponent, multiphase system requires that the chemical potential of each component be equal in all phases (Van Wylen and Sonntag, 1986). This is also equivalent to the requirement that the fugacities of each component be equal in all phases:

$$f_{iw} = f_{io} \qquad f_{iw} = f_{ig} \qquad f_{io} = f_{ig} \tag{1}$$

where f is the fugacity of component i in either the aqueous (w)[†] , oil (o) or gas (g) phases. The fugacity of component i is related to the mole fraction of component i in each phase by the following relations:

$$f_{iw} = x_{iw}\, \gamma_{iw}\, P_{i,sat}\, , \;\; f_{io} = x_{io}\, \gamma_{io}\, P_{i,sat}\, , \;\; f_{ig} = x_{ig}\, \gamma_{ig}\, P \tag{2}$$

[†] The terms aqueous and water are often used interchangeably for the aqueous phase. Rigorously speaking, the water is a mass component in the aqueous phase. However, since the water component comprises the vast majority of the aqueous phase, the subscript *w* (representing water) will be used to denote the aqueous phase throughout this report. This will also avoid confusion with the subscript *a*, which is used to denote the air mass component.

where γ is the fugacity (or activity) coefficient, $P_{i,sat}$ is the vapor pressure of pure liquid i, and P is the total gas pressure. In equation (2), the reference fugacity of pure liquid i has been set equal to the vapor pressure of pure liquid i, $P_{i,sat}$

Two important assumptions will be made regarding the fugacities defined in equation (2). In general, the activity coefficients are dependent on the composition, pressure, and temperature of the system. However, if the gas and the oil phases are assumed to be ideal, the activity coefficients in the oil phase, γ_{io}, and in the gas phase, γ_{ig}, can be set equal to unity. The approximation for the gas phase is generally good for many systems below critical conditions (Reid et al., 1987). The gas phase fugacity, f_{ig} ,in equation (2) then becomes equal to the partial pressure of component i, P_i, where $P_i = x_{ig} P$. The ideality of the oil phase (γ_{io}=1, i $\neq$ air or water) is also applicable to many chemical mixtures of interest in subsurface remediation. However, this assumption is not generally applicable for all chemicals and should be regarded as a limitation within this formulation. Equation (2) can now be used in equation (1) to obtain relations between the mole fractions in all three phases.

Water-Oil Equilibrium

Equations (1) and (2) are used to relate the mole fraction of component i in the aqueous phase to the mole fraction of component i in the oil phase:

$$x_{io}\, \gamma_{io}\, P_{i,sat} = x_{iw}\, \gamma_{iw}\, P_{i,sat} \tag{3}$$

Since the activity coefficient of component i in the water (or aqueous) phase, γ_{iw} , can be interpreted as a measure of the escaping tendency of that component, its value can often be quite large and must be estimated in order to obtain a relation for the mole fractions in equation (3). If we consider a thought experiment in which the mole fraction of pure chemical i in the aqueous phase reaches the solubility limit ($x_{iw} = x_{iw,sol}$), then a separate oil phase will precipitate out with a mole fraction approximately equal to one ($x_{io} \approx 1$). Equation (3) then yields an expression for the activity coefficient of oil component i in the aqueous phase assuming the oil phase is ideal (γ_{io} =1, i $\neq$ a,w):

$$\gamma_{iw} \approx 1/x_{iw,sol} \quad (i \neq a,w) \tag{4}$$

Equation (4) gives the activity coefficient, γ_{iw} , as a function of the solubility limit, $x_{iw,sol}$, which can be assumed constant or a function of temperature, depending on the availability of data. The relation between the mole fraction of an oil component in the oil and aqueous phases can then be expressed as follows:

$$x_{io} = x_{iw} / x_{iw,sol} \quad (i \neq a,w) \tag{5}$$

Although equations (4) and (5) have been derived from a very specific condition—namely, the solubility limit of pure chemical i in the aqueous phase—the solubility limit of many oil components in the aqueous phase is very small. As a result, the dependence of the mole fraction in the oil phase on the mole fraction in the aqueous phase occurs over a very small range ($x_{iw} < x_{iw,sol}$). Therefore, the activity coefficient is assumed to be constant (given by equation (4)) for a given temperature over the range of mole fractions of oil component i in the aqueous phase ($x_{iw} < x_{iw,sol}$). This assumption should also be regarded as a limitation to the formulation presented in this paper.

If component i in equation (3) is water, then the activity coefficient on the right-hand side, γ_{ww}, is one. Performing a thought experiment similar to the previous one in which the water mole fraction in the oil phase reaches its solubility limit, $x_{wo,sol}$, the activity coefficient of water in oil can be approximated as follows:

$$\gamma_{wo} \approx 1/x_{wo,sol} \tag{6}$$

Plugging equation (6) into equation (3) then yields the following equation for the mole fraction of water in the oil phase:

$$x_{wo} = x_{ww}\, x_{wo,sol} \tag{7}$$

Equation (7) states that the mole fraction of the water component in the oil phase is dependent on the solubility limit. This value may need to be estimated based on solubility limits of water in a generic oil mixture. It can also be determined by trial and error, which will be discussed in the concluding section of this paper.

If component i in equation (3) is air, then the activity coefficients and saturated vapor pressures are lumped into a variable called Henry's constant. Equation (3) then yields the following equilibrium expression for air in a water-oil system:

$$x_{ao}\, H_{ao} = x_{aw}\, H_{aw} \tag{8}$$

where H_{ao} and H_{aw} are Henry's constants for air in the oil and aqueous phases, respectively. These values can be found in the literature.

Water-Gas Equilibrium

A relation between the mole fractions of the water and gas phases can be developed by equating the fugacities in the water and gas phases as given in equation (1) and using the definitions of the fugacities in equation (2):

$$x_{iw}\,\gamma_{iw}\;P_{i,sat} = x_{ig}\,P = P_i \tag{9}$$

Using equation (4) for the activity coefficient of oil component *i* in water, equation (9) yields the following expression relating the mole fraction in the aqueous phase to the mole fraction in the gas phase for an oil component:

$$\boxed{x_{iw} = x_{ig}\;x_{iw,sol}\,P\,/\,P_{i,sat} \quad (i \neq a,w)} \tag{10}$$

If the mass component in equation (9) is water, then equation (9) yields the following expression:

$$\boxed{x_{wg}\,P = x_{ww}\,P_{w,sat} = P_w} \tag{11}$$

If the mass component *i* in equation (9) is air, then a Henry's constant, H_{aw}, is used to give the following relation:

$$\boxed{P_a = x_{ag}\,P = x_{aw}\,H_{aw}} \tag{12}$$

Oil-Gas Equilibrium

Equations (1) and (2) are used to obtain a relationship between the mole fractions in the oil and gas phases:

$$x_{io}\,\gamma_{io}\,P_{i,sat} = x_{ig}\,P = P_i$$

If the mass component is an oil component, the following relationship results:

$$\boxed{x_{io} = x_{ig}\,P\,/\,P_{i,sat} \quad (i \neq a,w)} \tag{13}$$

If the mass component is water, then the activity coefficient of water in oil is approximated as before to yield the following relationship:

$$\boxed{x_{wo} = x_{wg}\,x_{wo,sol}\,P\,/\,P_{w,sat}} \tag{14}$$

If the mass component is air, then Henry's constant for air in oil is used to yield the following relationship:

$$\boxed{x_{ao}\,H_{ao} = x_{ag}\,P = P_a} \tag{15}$$

Other Important Relations

Equations (5)–(15) provide relations that yield the mole fraction of component i in a particular phase given the mole fraction of that component in another existing phase. Therefore, *if the mole fraction of a component is given for one phase, its mole fraction in any other phase can be determined.* In addition to these relations, several additional relations are needed to fully describe the state of a system. The first three are expressions stating that the sum of the mole fractions in each phase is equal to one:

$$\sum_{i=1}^{NK} x_{iw} = \sum_{i=1}^{NK} x_{io} = \sum_{i=1}^{NK} x_{ig} = 1 \tag{16}$$

where NK is the total number of components in the system (including air and water). The next expression states that the sum of all phase saturations equals one:

$$S_w + S_o + S_g = 1 \tag{17}$$

where the phase saturations are defined as the local phase volume divided by the local pore volume. Equations (5)–(15) can be used with a given set of primary variables to determine all remaining secondary variables which include capillary pressure, relative permeability, density, internal energy, enthalpy, and viscosity of each phase. Expressions for these secondary variables will not be presented in this report, but they can be found in Adenekan et al. (1993) and Reid et al. (1987).

3. PHASE COMBINATIONS AND TRANSITIONS

The previous section has established a set of relations to determine secondary variables given a set of primary variables for any phase configuration in a three-phase system. This section will discuss the possible phase combinations that can exist in a three-phase system, the primary variables for each phase combination, and a set of criteria to determine the appearance or disappearance of phases within a given phase configuration. Since the criteria that will be used to determine phase appearances apply to all phase combinations, a discussion of these criteria will be presented first. This will provide the technical basis to analyze the different phase configurations presented later.

3.1 Phase Appearances

Phase appearances in a three-phase system can occur in six different ways as listed in Table 1. The appearance of an aqueous phase can evolve from an oil phase or a gas phase; the appearance of an oil phase can occur from an aqueous phase or a gas phase; and the appearance of a gas phase can evolve from an aqueous phase or an oil phase. If a system exists with two phases present, the criteria used to determine the appearance of a third phase from the two existing phases are considered separately. In some cases, the criteria that determines whether a third phase evolves from two existing phases are identical as a result of the equilibrium relations given in equations (5)–(15). This will become apparent in the development of the criteria for phase appearance.

Table 1. Possible phase appearances.

existing phase:	oil	gas	water	gas	water	oil
evolving phase:	water	water	oil	oil	gas	gas

Criteria for Appearance of an Aqueous Phase

From an oil phase

The appearance of an aqueous phase from an oil phase occurs if the mole fraction of the water in the oil phase exceeds the solubility limit of the water in the oil. The solubility limit of water in an oil is generally dependent on the composition and type of oil present. However, since the solubility limit of water in oil, $x_{wo,sol}$, is generally very small, the value is often approximated as a constant. Therefore, the criterion for the appearance of an aqueous phase from an oil phase can be written as follows:

$$x_{wo} > x_{wo,sol} \tag{18}$$

From a gas phase

The appearance of an aqueous phase from a gas phase occurs if the partial pressure of the water vapor exceeds the saturated vapor pressure of liquid water, $P_{w,sat}$, at the system temperature. Since the partial pressure can be expressed as the product of the mole fraction of the water in the gas phase, x_{wg} , and the total gas pressure, P , this can be written as follows:

$$x_{wg}\,P > P_{w,sat}$$

$$\text{or} \qquad \frac{x_{wg}\,P}{P_{w,sat}} > 1 \tag{19}$$

From a two-phase (oil-gas) system

In a two-phase system with oil and gas phases present, equations (18) and (19) can be used separately to determine the appearance of an aqueous phase from either the oil or gas phases.

Criteria for Appearance of an Oil Phase

From an aqueous phase

The appearance of an oil phase from an aqueous phase will occur if the sum of the mole fractions of the oil components in a hypothetical oil phase exceeds one. A derivation for this criterion has been given in Heidemann (1983), which follows the work of Michelsen (1982). Using equation (5) for the equilibrium relation between the mole fractions in the water and oil phases yields the following expression:

$$\sum_{\substack{i=1 \\ i \neq a,w}}^{NK} \frac{x_{iw}}{x_{iw,sol}} > 1 \qquad (20)$$

where NK is the number of components originating from the oil excluding the air and water components. Note that equation (20) can also be viewed as an expression regarding the partial solubilities of each component in a chemical mixture. If the components in the oil phase are similar, which has already been assumed ($\gamma_{io}=1$), then the pure component solubilities of each component in water should be similar. As a result, the left-hand side of equation (20) is equivalent to the ratio of the mole fraction of a pure chemical to its solubility limit.

From a gas phase

The appearance of an oil phase from an existing gas phase will occur if the sum of the mole fractions of a hypothetical oil phase exceeds one (Heidemann, 1983). Equation (13) is used to relate the mole fractions in a hypothetical oil phase to the mole fractions in a gas phase to yield the following criterion:

$$\sum_{\substack{i=1 \\ i \neq a,w}}^{NK} \frac{x_{ig} P}{P_{i,sat}} > 1 \qquad (21)$$

where NK is the total number of oil components excluding air and water. Note that if equation (10) is used to replace the gas phase mole fraction in equation (21), we obtain the same criterion given in equation (20).

From a two-phase (water-gas) system

Equations (20) and (21) are equivalent as a result of the equilibrium relation given in equation (10). Therefore, the appearance of an oil phase in a water-gas system can be checked using either equation (20) or equation (21).

Criterion for Appearance of a Gas Phase

From an aqueous phase

The appearance of a gas phase from an aqueous phase will occur if the sum of the partial pressures exceeds the total gas pressure of the system. The partial pressures can be expressed in terms of the component mole fractions in the water to yield the following criterion:

$$P_a + P_w + \sum_{\substack{i=1 \\ i \neq a,w}}^{NK} P_i > P \tag{22}$$

where

$$P_a = x_{aw} H_{aw} \tag{23}$$

$$P_w = x_{ww} P_{w,sat}(T) \tag{24}$$

$$P_i = x_{iw} P_{i,sat} / x_{iw,sol} \tag{25}$$

where H_{aw} is the Henry's constant for air in water and equation (9) was used to define the partial pressure of each oil component, P_i.

From an oil phase

The appearance of a gas phase from an oil phase will occur if the sum of the partial pressures exceeds the total gas pressure of the system. Equation (22) can be used, but the definitions for the partial pressures will be based on the mole fractions of the components in an oil phase:

$$P_a = x_{ao} H_{ao} \tag{26}$$

$$P_w = x_{wo} P_{w,sat} / x_{wo,sol} \tag{27}$$

$$P_i = x_{io} P_{i,sat} \tag{28}$$

where H_{ao} is the Henry's constant for air in oil and $x_{wo,sol}$ is the solubility limit of water in oil. Note that the partial pressures defined in equations (23)–(25) are equivalent to those defined in equations (26)–(28) because of the equilibrium relations given in equations (10)–(12).

From a two-phase (water-oil) system

Equation (22) can be used to determine the appearance of a gas phase from a two-phase water-oil system. The definitions for the partial pressures in equations (26)–(28) can be used for equation (22).

3.2 Flash Calculations

Equations (18)–(28) represent the criteria for the appearance of a phase in a three-phase system. Once it has been determined that a new phase will evolve, an isothermal flash calculation can be used to reinitialize the mole fractions in all existing phases (Prausnitz et al., 1980; Adenekan et al., 1993). The following sections will describe flash calculations for the six possible phase appearances listed in Table 1.

Flash Calculation—Oil Phase Evolving from Gas Phase

Imagine that equation (21) has been used to determine that an oil phase is evolving from a gas phase. Since the mole fractions in the gas phase following the evolution of the oil phase can change significantly, a flash calculation is performed to determine the mole fractions in the gas and oil phases after the appearance of the oil phase. In the flash calculation, the phase present prior to the evolution (or flash) of the new phase is considered to be the feed stream while the phases present following the evolution (or flash) of the new phase are considered to be the product streams. A mass balance is performed on these streams to yield the following expression for each component, *i*, in the system:

$$F\, z_{ig} = L\, x_{ig} + N\, x_{io} \tag{29}$$

where

F = total moles originally in gas [mol gas]
L = total moles in gas after flash [mol gas]
N = total moles in oil after flash [mol oil]
z_{ig} = initial mole fraction of i in gas [mol i/mol gas]
x_{ig} = mole fraction of i in gas after flash [mol i/mol gas]
x_{io} = mole fraction of i in oil after flash [mol i/mol oil]

Since the total moles before the flash must equal the total moles after the flash (i.e. $F = L + N$), then $L = F - N$. This expression can be substituted in equation (29) along with equations (13)–(15) to yield the following expressions for the mole fractions in the gas, x_{ig}, after the flash:

$$x_{ig} = \frac{z_{ig}}{1 + \alpha\left(\frac{P}{P_{i,sat}} - 1\right)} \qquad (i \neq a,w) \tag{30}$$

$$x_{wg} = \frac{z_{wg}}{1 + \alpha\left(\frac{P\, x_{wo,sol}}{P_{w,sat}} - 1\right)} \tag{31}$$

$$x_{ag} = \frac{z_{ag}}{1 + \alpha\left(\frac{P}{H_{ao}} - 1\right)} \tag{32}$$

where $\alpha = N/F$ [moles in oil after flash/moles in gas before flash]. Since the sum of the gas phase mole fractions equals one as given in equation (16), equations (30)–(32) can be expressed as follows:

$$\sum_{\substack{i=1 \\ i \neq a,w}}^{NK} \left(\frac{z_{ig}}{1 + \alpha\left(\frac{P}{P_{i,sat}} - 1\right)} \right) + \frac{z_{wg}}{1 + \alpha\left(\frac{P\, x_{wo,sol}}{P_{w,sat}} - 1\right)} + \frac{z_{ag}}{1 + \alpha\left(\frac{P}{H_{ao}} - 1\right)} = 1 \tag{33}$$

Equation (33) is used to determine α, which can be then used in equations (30)–(32) to yield values for the mole fractions in the gas phase after the flash. Equations (13)–(15) can then be used to obtain the mole fractions in the oil phase once the gas phase mole fractions are known.

Flash Calculation—Gas Phase Evolving from Oil Phase

If a gas phase is determined to evolve from an oil phase through equation (22), a flash calculation nearly identical to the previous flash calculation can be performed. In this case, F represents the total moles originally in the oil, and z_{io} represents the mole fraction of i in the oil initially. The following equations result from the same procedure used above:

$$x_{ig} = \frac{z_{io}}{1 + \alpha\left(\frac{P}{P_{i,sat}} - 1\right)} \qquad (i \neq a,w) \tag{34}$$

$$x_{wg} = \frac{z_{wo}}{1 + \alpha\left(\frac{P\, x_{wo,sol}}{P_{w,sat}} - 1\right)} \tag{35}$$

$$x_{ag} = \frac{z_{ao}}{1 + \alpha\left(\frac{P}{H_{ao}} - 1\right)} \tag{36}$$

$$\sum_{\substack{i=1\\ i\neq a,w}}^{NK}\left(\frac{z_{io}}{1+\alpha\left(\frac{P}{P_{i,sat}}-1\right)}\right)+\frac{z_{wo}}{1+\alpha\left(\frac{P\,x_{wo,sol}}{P_{w,sat}}-1\right)}+\frac{z_{ao}}{1+\alpha\left(\frac{P}{H_{ao}}-1\right)}=1 \tag{37}$$

Equation (37) is used to determine α [moles in oil after flash/moles in oil before flash], which is then used in equations (34)–(36) to determine the mole fractions in the gas phase after the flash. Equations (13)–(15) can then be used to determine the corresponding mole fractions in the oil phase.

Flash Calculation—Aqueous Phase Evolving from Gas Phase

If equation (19) is used to determine that an aqueous phase is evolving from a gas phase, the following equation can be used to describe the mole fractions in the two phases after the flash:

$$F\,z_{ig} = L\,x_{ig} + N\,x_{iw} \tag{38}$$

where F = total moles in gas before flash
L = total moles in gas after flash
N = total moles in water after flash

Equation (29) can be written in terms of the gas phase mole fractions by using $L = F - N$ and equations (10)–(12) to replace the water mole fractions with gas mole fractions:

$$x_{ig}=\frac{z_{ig}}{1+\alpha\left(\frac{P\,x_{iw,sol}}{P_{i,sat}}-1\right)} \quad (i\neq a,w) \tag{39}$$

$$x_{wg}=\frac{z_{wg}}{1+\alpha\left(\frac{P}{P_{w,sat}}-1\right)} \tag{40}$$

$$x_{ag}=\frac{z_{ag}}{1+\alpha\left(\frac{P}{H_{aw}}-1\right)} \tag{41}$$

where $\alpha = N/F$ and $x_{iw,sol}$ is the solubility limit of component i in water. Summing the gas mole fractions to one yields the following expression:

$$\sum_{\substack{i=1\\ i\neq a,w}}^{NK}\left(\frac{z_{ig}}{1+\alpha\left(\frac{P\,x_{iw,sol}}{P_{i,sat}}-1\right)}\right)+\frac{z_{wg}}{1+\alpha\left(\frac{P}{P_{w,sat}}-1\right)}+\frac{z_{ag}}{1+\alpha\left(\frac{P}{H_{aw}}-1\right)}=1 \tag{42}$$

Equation (42) is used to determine α, which can be used in equations (39)–(41) to determine the gas phase mole fractions after the flash. Equations (10)–(12) can then be used to obtain the aqueous phase mole fractions given the gas phase mole fractions.

Flash Calculation—Gas Phase Evolving from Aqueous Phase

The flash calculation for a gas phase evolving from an aqueous phase is nearly identical to the preceding flash calculation. The only difference is that F now represents the total moles in the aqueous phase and z_{iw} will be used instead of z_{ig} in equation (24). The resulting equations are given as follows:

$$x_{ig} = \frac{z_{iw}}{1 + \alpha\left(\frac{P\,x_{iw,sol}}{P_{i,sat}} - 1\right)} \quad (i \neq a,w) \tag{43}$$

$$x_{wg} = \frac{z_{ww}}{1 + \alpha\left(\frac{P}{P_{w,sat}} - 1\right)} \tag{44}$$

$$x_{ag} = \frac{z_{aw}}{1 + \alpha\left(\frac{P}{H_{aw}} - 1\right)} \tag{45}$$

$$\sum_{\substack{i=1 \\ i \neq a,w}}^{NK} \left(\frac{z_{iw}}{1 + \alpha\left(\frac{P\,x_{iw,sol}}{P_{i,sat}} - 1\right)} \right) + \frac{z_{ww}}{1 + \alpha\left(\frac{P}{P_{w,sat}} - 1\right)} + \frac{z_{aw}}{1 + \alpha\left(\frac{P}{H_{aw}} - 1\right)} = 1 \tag{46}$$

where $\alpha = N/F$ and is determined from equation (46). Equations (43)–(45) are used to determine the gas phase mole fractions and equations (10)–(12) can be used to obtain the aqueous phase mole fractions.

Flash Calculation—Oil Phase Evolving from Aqueous Phase

The following equation is used to perform a flash calculation on an oil phase evolving from an aqueous phase as determined by equation (20):

$$F\,z_{iw} = L\,x_{iw} + N\,x_{io} \tag{47}$$

where F = total moles in water before flash
L = total moles in water after flash
N = total moles in oil after flash

Equation (47) is used in conjunction with equations (5), (7), and (8) and $L = F - N$ to yield the following expression for the mole fraction in the aqueous phase after the flash:

$$x_{iw} = \frac{z_{iw}}{1 + \alpha\left(\frac{1}{x_{iw,sol}} - 1\right)} \qquad (i \neq a,w) \tag{48}$$

$$x_{ww} = \frac{z_{ww}}{1 + \alpha\left(x_{wo,sol} - 1\right)} \tag{49}$$

$$x_{aw} = \frac{z_{aw}}{1 + \alpha\left(\frac{H_{aw}}{H_{ao}} - 1\right)} \tag{50}$$

where $\alpha = N/F$. The mole fractions in the aqueous phase are summed to one to yield the following equation:

$$\sum_{\substack{i=1 \\ i \neq a,w}}^{NK} \left(\frac{z_{iw}}{1 + \alpha\left(\frac{1}{x_{iw,sol}} - 1\right)} \right) + \frac{z_{ww}}{1 + \alpha\left(x_{wo,sol} - 1\right)} + \frac{z_{aw}}{1 + \alpha\left(\frac{H_{aw}}{H_{ao}} - 1\right)} = 1 \tag{51}$$

Equation (51) is used to determine α, which is then used to determine the mole fractions in the aqueous phase in equations (48)–(50). Equations (5), (7), and (8) can then be used to determine mole fractions in the oil phase.

Flash Calculation—Aqueous Phase Evolving from Oil Phase

The evolution of an aqueous phase from an oil phase as determine by equation (11) can be handled through a flash calculation nearly identical to the preceding calculation. In this flash calculation, F represents the total moles in the oil phase before the flash, and z_{io} represents the mole fractions in the oil phase before the flash. These parameters are used in equation (29) to yield the following equations:

$$x_{iw} = \frac{z_{io}}{1 + \alpha\left(\frac{1}{x_{iw,sol}} - 1\right)} \qquad (i \neq a,w) \tag{52}$$

$$x_{ww} = \frac{z_{wo}}{1 + \alpha\left(x_{wo,sol} - 1\right)} \tag{53}$$

$$x_{aw} = \frac{z_{ao}}{1 + \alpha\left(\frac{H_{aw}}{H_{ao}} - 1\right)} \tag{54}$$

$$\sum_{\substack{i=1 \\ i \neq a,w}}^{NK} \left(\frac{z_{io}}{1 + \alpha\left(\frac{1}{x_{iw,sol}} - 1\right)} \right) + \frac{z_{wo}}{1 + \alpha\left(x_{wo,sol} - 1\right)} + \frac{z_{ao}}{1 + \alpha\left(\frac{H_{aw}}{H_{ao}} - 1\right)} = 1 \tag{55}$$

where $\alpha = N/F$ and is determined using equation (55). Equations (52)–(54) can then be used to determine the mole fraction in the aqueous phase, and equations (5), (7), and (8) can be used to determine the mole fractions in the oil phase.

Remarks

Of the six flash calculations just presented, only a few may be necessary to obtain reasonable mole fraction distributions after the evolution of a new phase. If the number of moles of the components in the evolved phase is very small compared to the number of moles of those components in the original phase, then the equilibrium relations given in equations (5)–(15) should provide reasonable mole fractions for the evolved phase given the mole fractions in the original phase. For example, if a gas phase evolves from an oil phase, the number of moles of the oil components in the newly evolved gas phase will be significantly less than the number of moles of the oil components in the original oil phase. Therefore, the mole fractions in the oil phase should not change significantly following the evolution of the gas phase, and equation (13) can be used to determine the mole fractions in the new gas phase given the original mole fractions in the oil phase. On the other hand, if an oil phase evolves from a gas phase, the number of moles of the components in the oil phase could be significant compared to the number of moles of those components in the gas phase. As a result, the evolution of the oil phase could significantly change the mole fraction distribution in the original gas phase. Adenekan (1992) apparently supports this view since flash calculations are only performed in the M^{2}NOTS code when a NAPL evolves from a gas phase.

3.3 Phase Combinations

This section will detail the seven different phase combinations that can exist in a three-phase system. In each configuration, possible primary variables and the calculation of necessary secondary variables will be discussed. All of the secondary variables (e.g. capillary pressure, relative permeability, density, internal energy, enthalpy, viscosity) can be determined as a function of pressure, temperature, phase saturation, and mole fractions. The pressure and temperature are always specified as primary variables, so only the phase saturations and mole fractions will be derived for each phase configuration. In addition, the use of equilibrium relations and criteria for phase appearances developed in the preceding sections will be heavily referenced. Finally, criteria for the disappearance of phases will be presented.

Aqueous Phase Only

Possible primary variables in a system containing only the aqueous phase are the pressure, P, the mole fractions of the oil components in the water, x_{iw} $(i \neq a, w)$, the mole fraction of air in the water, x_{aw}, and the temperature, T. Since only one phase is present, the water saturation is obviously one. The mole fraction of the water in the aqueous phase, x_{ww}, can be determined from equation (16) by summing the mole fractions in the aqueous phase to one. These variables are sufficient to determine all other secondary variables.

The stability of the aqueous phase is determined through the relations given in the section on phase appearances. Equation (20) is used to determine the possible appearance of an oil phase, and equation (22) is used to determine the possible appearance of a gas phase. If the evolution of a new phase occurs, the flash calculations described in the previous section are used to determine the new mole fractions in each phase present.

Oil Phase Only

Possible primary variables for a system containing only an oil phase are the pressure, P, the mole fractions of the oil components in the oil phase, x_{io} $(i \neq a, w)$, the mole fraction of air in the oil, x_{ao}, and the temperature, T. The saturation of the oil phase is one, and the mole fraction of water in the oil phase, x_{wo} , can be determined by summing the mole fractions to one (equation (16)). All other secondary variables can be determined from these variables.

The appearance of an aqueous phase can be checked using equation (18), and the appearance of a gas phase can be checked using equation (22). If the evolution of a water or gas phase occurs, the flash calculations described in the previous section can be used to determine the new mole fractions.

Gas Phase Only

Possible primary variables in a phase configuration consisting of only the gas phase are the pressure, P, the mole fractions of the oil components in the gas phase, x_{ig} $(i \neq a, w)$, the mole fraction of air in the gas, x_{ag}, and the temperature, T. The gas saturation is one, and the mole fraction of water in the gas phase, x_{wg}, can be calculated by summing the mole fractions in the gas phase to one.

The possible appearance of an aqueous phase from the gas phase can be determined by equation (19), and the possible appearance of an oil phase can be determined by equation (21). If the evolution of a water or oil phase occurs, the flash calculations given in the preceding section can be used to determine the new mole fractions.

Two-phase—Aqueous and Oil

Possible primary variables in a two-phase system consisting of both aqueous and oil phases are the pressure, P, the mole fractions of the oil components in the oil phase, x_{io} $(i \neq a, w)$, the aqueous phase saturation, S_w, and the temperature, T. The oil phase saturation can be determined by summing the phase saturations to one and setting the gas saturation to zero (equation (17)). The mole fraction of the water in the oil phase has been assumed earlier to be some fixed constant—the solubility limit of water in a generic oil mixture. This was used in the criterion for the appearance of an aqueous phase from an oil phase. Although the assumed solubility limit of water in a generic oil mixture can be used to determine the mole fraction of water in the oil phase (as in M^2NOTS), a more rigorous approach can also be taken.

The mole fractions of water and air in the oil phase can be determined simultaneously by implementing the equilibrium relations. Given the mole fractions of the oil components in the oil phase as primary variables, equation (5) can be used to determine the mole fractions in the aqueous phase. In addition, equations (7) and (8) can be used to relate the water and air mole fractions in the aqueous and oil phases. The result is two unknowns, x_{ao} and x_{wo}, and two additional equations given by equation (16) which can be used to solve the two unknowns. The equations that need to be solved are given as follows:

$$x_{ao} + x_{wo} = 1 - \sum_{\substack{i=1 \\ i \neq a,w}}^{NK} x_{io} \tag{56}$$

$$\frac{H_{ao}}{H_{aw}} x_{ao} + \frac{1}{x_{wo,sol}} x_{wo} = 1 - \sum_{\substack{i=1 \\ i \neq a,w}}^{NK} x_{iw,sol}\, x_{io} \tag{57}$$

Cramer's rule gives the following solution to equations (56) and (57):

$$x_{ao} = \frac{\dfrac{1 - \sum\limits_{\substack{i=1 \\ i \neq a,w}}^{NK} x_{io}}{x_{wo,sol}} + \sum\limits_{\substack{i=1 \\ i \neq a,w}}^{NK} \left(x_{iw,sol}\, x_{io}\right) - 1}{\dfrac{1}{x_{wo,sol}} - \dfrac{H_{ao}}{H_{aw}}} \tag{58}$$

$$x_{wo} = \frac{1 - \sum\limits_{\substack{i=1 \\ i \neq a,w}}^{NK} \left(x_{iw,sol}\, x_{io}\right) - \dfrac{H_{ao}}{H_{aw}} \left(1 - \sum\limits_{\substack{i=1 \\ i \neq a,w}}^{NK} x_{io}\right)}{\dfrac{1}{x_{wo,sol}} - \dfrac{H_{ao}}{H_{aw}}} \tag{59}$$

Now that all of the mole fractions in the oil phase have been determined, equations (5), (7), and (8) can be used to obtain the mole fractions in the aqueous phase. The stability of this two-phase system can be checked using equation (22) to determine if a gas phase can appear. In addition, the possible disappearance of either the water or oil phases can be determined by the phase saturations. If the aqueous phase saturation exceeds one, then the oil phase disappears. On the other hand, if the aqueous phase saturation is less than zero, then the aqueous phase disappears.

Two-Phase—Aqueous and Gas

Possible primary variables for a two-phase system consisting of aqueous and gas phases are the pressure, *P*, the mole fractions of the oil components in the gas phase, x_{ig} $(i \neq a,w)$, the aqueous phase saturation, S_w, and the temperature, *T*. Equation (17) can be used to determine the gas phase saturation by simply summing the phase saturation to one and setting the oil phase saturation to zero. The air and water mole fractions in the gas phase still need to be determined in order to completely describe the system.

Equation (11) can be used to relate the water mole fraction in the aqueous and gas phases. A good approximation is to set the mole fraction of the water in the aqueous phase to one, yielding an expression for the mole fraction of water in the gas phase as a function of the gas pressure and the saturated vapor pressure of water at the system temperature. The mole fraction of air in the gas phase can then be determined by summing the mole fractions in the gas phase to one (equation (16)). This approximation has been used by Adenekan (1992), but a more rigorous formulation to determine the water and air mole fractions in the gas phase is presented here.

First, the mole fractions of the oil components in the aqueous phase can be expressed as functions of the mole fractions in the gas phase using equation (10). Equations (11) and (12) are also used to express the air and water mole fractions in the aqueous phase as functions of the mole fractions in the gas phase. Equation (16) is then used to sum the mole fractions in both the aqueous and gas phases to one. This results in two equations for two unknowns, x_{wg} and x_{ag}, which are given below:

$$x_{ag} + x_{wg} = 1 - \sum_{\substack{i=1 \\ i \neq a,w}}^{NK} x_{ig} \tag{60}$$

$$\frac{P}{H_{aw}} x_{ag} + \frac{P}{P_{w,sat}} x_{wg} = 1 - \sum_{\substack{i=1 \\ i \neq a,w}}^{NK} \left(\frac{x_{iw,sol} P}{P_{i,sat}} x_{ig} \right) \tag{61}$$

Cramer's rule is used to solve for the two unknowns in equations (60) and (61). The resulting expressions for x_{wg} and x_{ag} are given as follows:

$$x_{ag} = \frac{\dfrac{P}{P_{w,sat}} \left(1 - \displaystyle\sum_{\substack{i=1 \\ i \neq a,w}}^{NK} x_{ig} \right) + \displaystyle\sum_{\substack{i=1 \\ i \neq a,w}}^{NK} \left(\frac{x_{iw,sol} P}{P_{i,sat}} x_{ig} \right) - 1}{P \left(\dfrac{1}{P_{w,sat}} - \dfrac{1}{H_{aw}} \right)} \tag{62}$$

$$x_{wg} = \frac{1 - \displaystyle\sum_{\substack{i=1 \\ i \neq a,w}}^{NK} \left(\frac{x_{iw,sol} P}{P_{i,sat}} x_{ig} \right) - \dfrac{P}{H_{aw}} \left(1 - \displaystyle\sum_{\substack{i=1 \\ i \neq a,w}}^{NK} x_{ig} \right)}{P \left(\dfrac{1}{P_{w,sat}} - \dfrac{1}{H_{aw}} \right)} \tag{63}$$

Equations (11) and (12) can then be used to express the air and water mole fractions in the aqueous phase as functions of the mole fractions in the gas phase as given by equations (62) and (63). Now that all the mole fractions in each phase and all of the phase saturations have been determined, equations (20) or (21) can be used to determine the possible appearance of an oil phase.

The disappearance of the aqueous phase can be checked by the aqueous phase saturation. If S_w is less than zero, then the aqueous phase disappears. However, if S_w is greater than one, than the gas phase disappears.

Two-Phase—Oil and Gas

Possible primary variables in a two-phase system consisting of oil and gas phases are the pressure, P, the mole fractions of the oil components in the gas phase, x_{ig} $(i \neq a, w)$, the oil phase saturation, S_o, and the temperature, T. As in the previous configurations, the air and water mole fractions in the gas phase must be determined in order to completely describe the system. The gas phase saturation can easily be determined by equation (17).

The remaining mole fractions are determined by summing all the mole fractions in the oil and gas phases to one as shown in equation (16). Equations (13)–(15) can be used to relate the mole fractions in the oil phase to the mole fractions in the gas phase so that the following two equations can be used to solve the two unknowns, x_{ag} and x_{wg}:

$$x_{ag} + x_{wg} = 1 - \sum_{\substack{i=1 \\ i \neq a,w}}^{NK} x_{ig} \tag{64}$$

$$\frac{P}{H_{ao}} x_{ag} + \frac{x_{wo,sol} P}{P_{w,sat}} x_{wg} = 1 - \sum_{\substack{i=1 \\ i \neq a,w}}^{NK} \left(\frac{P}{P_{i,sat}} x_{ig} \right) \tag{65}$$

Cramer's rule is used to solve equations (64) and (65) for x_{ag} and x_{wg}:

$$x_{ag} = \frac{\dfrac{x_{wo,sol} P}{P_{w,sat}} \left(1 - \displaystyle\sum_{\substack{i=1 \\ i \neq a,w}}^{NK} x_{ig} \right) + \displaystyle\sum_{\substack{i=1 \\ i \neq a,w}}^{NK} \left(\frac{P}{P_{i,sat}} x_{ig} \right) - 1}{P \left(\dfrac{x_{wo,sol}}{P_{w,sat}} - \dfrac{1}{H_{ao}} \right)} \tag{66}$$

$$x_{wg} = \frac{1 - \displaystyle\sum_{\substack{i=1 \\ i \neq a,w}}^{NK} \left(\frac{P}{P_{i,sat}} x_{ig} \right) - \dfrac{P}{H_{ao}} \left(1 - \displaystyle\sum_{\substack{i=1 \\ i \neq a,w}}^{NK} x_{ig} \right)}{P \left(\dfrac{x_{wo,sol}}{P_{w,sat}} - \dfrac{1}{H_{ao}} \right)} \tag{67}$$

All of the mole fractions in the gas phase have been defined, either through equations (66) and (67) or through the specified primary variables. All of the remaining mole fractions in the oil phase can be determined through equations (13)–(15). Also, the possible appearance of an aqueous phase from the oil phase can be determined with equation (18), and the possible appearance of an aqueous phase from a gas phase can be determined with equation (19). The disappearance of the oil phase will occur if the oil saturation, S_o, becomes less than zero. The disappearance of the gas phase occurs if the oil saturation becomes greater than one.

Three-Phase—Aqueous, Oil, and Gas

Possible primary variables in a three-phase system are the pressure, P, the gas phase saturation, S_g, the mole fractions of the oil components in the gas phase, x_{ig} *($i \neq a,w$, one oil component)*, the water phase saturation, S_w, and the temperature, T. Unlike the previous phase configurations, two phase saturations are specified here so that the third phase saturation, S_o, can be determined from equation (17). The remaining mole fractions that need to be determined to completely describe the system are the mole fractions of the air and water components in the gas phase and the mole fraction of one oil component, say x_{1g}, in the gas phase. These three unknowns can be determined through equation (16), which states that the sum of all the mole fractions in each of the three phases sums to one. Equations (10)–(15) are used to relate the mole fractions in the aqueous and oil phases to the mole fractions in the gas phase. The resulting three equations are shown below in matrix form:

$$[\mathrm{A}]\,\{\mathbf{x}\} = \{\mathbf{b}\}$$

$$\begin{bmatrix} 1 & 1 & 1 \\ \dfrac{P}{H_{ao}} & \dfrac{x_{wo,sol}P}{P_{w,sat}} & \dfrac{P}{P_{1,sat}} \\ \dfrac{P}{H_{ao}} & \dfrac{P}{P_{w,sat}} & \dfrac{x_{1w,sol}P}{P_{1,sat}} \end{bmatrix} \begin{Bmatrix} x_{ag} \\ x_{wg} \\ x_{1g} \end{Bmatrix} = \begin{Bmatrix} 1 - \sum\limits_{\substack{i=2 \\ i \neq a,w}}^{NK} x_{ig} \\ 1 - \sum\limits_{\substack{i=2 \\ i \neq a,w}}^{NK} \left(\dfrac{P}{P_{i,sat}} x_{ig} \right) \\ 1 - \sum\limits_{\substack{i=2 \\ i \neq a,w}}^{NK} \left(\dfrac{x_{iw,sol}P}{P_{i,sat}} x_{ig} \right) \end{Bmatrix} \tag{68}$$

Cramer's rule can be applied to equation (68) to solve for the three unknowns:

$$x_{ag} = \frac{\det\left[A(1)\right]}{\det\left[A\right]}, \quad x_{wg} = \frac{\det\left[A(2)\right]}{\det\left[A\right]}, \quad x_{1g} = \frac{\det\left[A(3)\right]}{\det\left[A\right]} \tag{69}$$

where

$$\det\left[A\right] = P^2 \left(\frac{x_{wo,sol}\, x_{1w,sol}}{P_{w,sat}\, P_{1,sat}} + \frac{1}{H_{aw}\, P_{1,sat}} + \frac{1}{H_{ao}\, P_{w,sat}} + \right.$$

$$+\frac{x_{1w,sol}}{H_{ao}P_{1,sat}}-\frac{1}{P_{w,sat}P_{1,sat}}-\frac{x_{wo,sol}}{H_{aw}P_{w,sat}}\Bigg) \tag{70}$$

$$\det\left[A(1)\right]=\left(1-\sum_{\substack{i=2\\ i\neq a,w}}^{NK}x_{ig}\right)\frac{P^2\,x_{wo,sol}\,x_{1w,sol}}{P_{w,sat}P_{1,sat}}+\left(1-\sum_{\substack{i=2\\ i\neq a,w}}^{NK}\left(\frac{x_{iw,sol}P}{P_{i,sat}}x_{ig}\right)\right)\frac{P}{P_{1,sat}}+$$

$$+\left(1-\sum_{\substack{i=2\\ i\neq a,w}}^{NK}\left(\frac{P}{P_{i,sat}}x_{ig}\right)\right)\frac{P}{P_{w,sat}}-\left(1-\sum_{\substack{i=2\\ i\neq a,w}}^{NK}\left(\frac{x_{iw,sol}P}{P_{i,sat}}x_{ig}\right)\right)\frac{x_{wo,sol}P}{P_{w,sat}}-$$

$$\left(1-\sum_{\substack{i=2\\ i\neq a,w}}^{NK}x_{ig}\right)\frac{P^2}{P_{w,sat}P_{1,sat}}-\left(1-\sum_{\substack{i=2\\ i\neq a,w}}^{NK}\left(\frac{P}{P_{i,sat}}x_{ig}\right)\right)\frac{x_{1w,sol}P}{P_{1,sat}} \tag{71}$$

$$\det\left[A(2)\right]=\left(1-\sum_{\substack{i=2\\ i\neq a,w}}^{NK}x_{ig}\right)\frac{P^2}{H_{aw}P_{1,sat}}+\left(1-\sum_{\substack{i=2\\ i\neq a,w}}^{NK}\left(\frac{x_{iw,sol}P}{P_{i,sat}}x_{ig}\right)\right)\frac{P}{H_{ao}}+$$

$$+\left(1-\sum_{\substack{i=2\\ i\neq a,w}}^{NK}\left(\frac{P}{P_{i,sat}}x_{ig}\right)\right)\frac{x_{1w,sol}P}{P_{1,sat}}-\left(1-\sum_{\substack{i=2\\ i\neq a,w}}^{NK}\left(\frac{x_{iw,sol}P}{P_{i,sat}}x_{ig}\right)\right)\frac{P}{P_{1,sat}}-$$

$$\left(1-\sum_{\substack{i=2\\ i\neq a,w}}^{NK}x_{ig}\right)\frac{P^2\,x_{1w,sol}}{H_{ao}P_{1,sat}}-\left(1-\sum_{\substack{i=2\\ i\neq a,w}}^{NK}\left(\frac{P}{P_{i,sat}}x_{ig}\right)\right)\frac{P}{H_{aw}} \tag{72}$$

$$\det\left[A(3)\right]=\left(1-\sum_{\substack{i=2\\ i\neq a,w}}^{NK}x_{ig}\right)\frac{P^2}{H_{aw}P_{w,sat}}+\left(1-\sum_{\substack{i=2\\ i\neq a,w}}^{NK}\left(\frac{x_{iw,sol}P}{P_{i,sat}}x_{ig}\right)\right)\frac{x_{wo,sol}P}{P_{w,sat}}+$$

$$+\left(1-\sum_{\substack{i=2\\ i\neq a,w}}^{NK}\left(\frac{P}{P_{i,sat}}x_{ig}\right)\right)\frac{P}{H_{a,w}}-\left(1-\sum_{\substack{i=2\\ i\neq a,w}}^{NK}\left(\frac{x_{iw,sol}P}{P_{i,sat}}x_{ig}\right)\right)\frac{P}{H_{ao}}-$$

$$\left(1-\sum_{\substack{i=2\\ i\neq a,w}}^{NK}x_{ig}\right)\frac{P^2\,x_{wo,sol}}{H_{aw}P_{w,sat}}-\left(1-\sum_{\substack{i=2\\ i\neq a,w}}^{NK}\left(\frac{P}{P_{i,sat}}x_{ig}\right)\right)\frac{P}{P_{w,sat}} \tag{73}$$

Equations (69)–(73) along with the specified primary variables completely determine the mole fractions in the gas phase. Equations (10)–(15) can then be used to determine the mole fractions in the aqueous and oil phases.

The disappearance of a phase(s) can occur in one of six possible combinations: 1) aqueous phase disappears; 2) oil phase disappears; 3) gas phase disappears; 4) aqueous and gas phases disappear; 5) aqueous and oil phases disappear; and 6) oil and gas phases disappears. The criteria for the disappearance of any of these phase combinations are given in Table 2.

Table 2. Phase disappearance criteria in a three-phase system.

Phase Disappearance	Criteria
aqueous	$S_w \leq 0$ and $S_g > 0$ and $S_o > 0$
oil	$S_o \leq 0$ and $S_w > 0$ and $S_g > 0$
gas	$S_g \leq 0$ and $S_w > 0$ and $S_o > 0$
aqueous and gas	$S_w \leq 0$ and $S_g \leq 0$
aqueous and oil	$S_w \leq 0$ and $S_o \leq 0$
oil and gas	$S_o \leq 0$ and $S_g \leq 0$

4. CONCLUDING REMARKS

This paper has presented thermodynamic equilibrium relations that can be used to describe a three-phase system. Table 3 summarizes the seven possible phase configurations that can exist in a three-phase system, along with the possible primary variables that can be specified for each configuration. This report has detailed the methodology for determining all necessary secondary variables from the primary variables and the equilibrium relations. Criteria have also been established to determine the appearance or disappearance of phases in each of the seven possible phase configurations.

This work is based on the premise of local thermodynamic equilibrium. This assumption allows the determination of the mole fraction of a component in an existing phase given the mole fraction of that component in another phase in any local region. For many applications in subsurface transport, such as soil remediation with low flow rates, this approximation appears to be valid as long as the spatial discretization is finer than the size of the heterogeneities in the system (Ho et al., 1994).

Table 3. Phase combinations and primary variables in a three-phase system.

Phase Combination	Primary Variables
1) Aqueous (or water) only	P, x_{iw} $(i \neq a,w)$, x_{aw}, T
2) Oil (or NAPL) only	P, x_{io} $(i \neq a,w)$, x_{ao}, T
3) Gas only	P, x_{ig} $(i \neq a,w)$, x_{ag}, T
4) Aqueous and Oil	P, x_{io} $(i \neq a,w)$, S_w, T
5) Aqueous and Gas	P, x_{ig} $(i \neq a,w)$, S_w, T
6) Oil and Gas	P, x_{ig} $(i \neq a,w)$, S_o, T
7) Aqueous, Oil, and Gas	P, S_g, x_{ig} $(i \neq a,w$, *one oil component*$)$, S_w, T

Another important assumption in this paper is in regards to the determination of the activity and fugacity coefficients in the equilibrium relations given in equations (3)–(15). The gas phase was assumed ideal based on Reid et al. (1987), and the oil phase was assumed ideal based on many chemical mixtures found at remediation sites. In addition, the activity coefficients for the oil and water components in the water and oil phases were assumed constant and were based on the solubility limits of each component. The motivation for this assumption was, in part, due to the limited available data necessary to calculate the activity coefficients for an arbitrary chemical mixture and water. Also, since the solubility of most oil components in water (and vice versa) is very small, the range over which these activity coefficients depend on the mole fractions is expected to be small. Thus, a constant value was assumed for the activity coefficients that describe the interaction between the aqueous and oil phases.

Finally, most of the chemical parameters that are needed to perform the equilibrium calculations can be found in Reid et al. (1987). Other thermodynamic parameters pertaining to air and water can be found in most thermodynamic literature. Some parameters, such as Henry's constant for air in oil and the solubility limit of water in oil, are more ambiguous. Since the oil phase can be a mixture of many different chemicals, these parameters will vary depending on the chemical mixture. However, a constant value can often be assigned to these parameters because of the low solubilities of water and air in an oil mixture. If these parameters cannot be found in the literature, then the equations in section 3.3 can be used to pre-determine values in a trial-and-error method that will yield physically reasonable mole fractions for the system of interest. Ho (1995) calculated the solubility of water in oil for an oil-gas system using equations (66) and (67) in a trial-and-error fashion. The results of those simulations were found to be insensitive to variations in that value to within an order of magnitude. Table 4 provides some estimates for these “hard to find” parameters.

Table 4. Estimated values for “hard to find” parameters.

Parameters	Value	Reference
H_{aw}	1×10^{10}	Pruess (1991)
H_{ao}	2×10^{8}	Adenekan (1992)
$x_{wo,sol}$	0.02	Ho (1995)—trial and error using equations (66) and (67) with an arbitrary chemical mixture at 20°C

NOMENCLATURE

f	fugacity (Pa)
F	total moles in a phase before the evolution of a new phase (mol)
H	Henry's constant (Pa)
L	total moles in a phase after the evolution of a new phase (mol)
N	total moles in a phase after the evolution of a new phase (mol)
NK	total number of mass components in each phase
P	pressure (Pa)
S	phase saturation
T	temperature (°C)
x	mole fraction
z	mole fraction of a component in a phase before the evolution of a new phase
α	N/F
γ	activity or fugacity coefficient

<u>subscripts</u>

a	air mass component
g	gas phase
i	mass component
o	oil phase
w	aqueous phase or water mass component
sat	denotes saturated vapor pressure (Pa)
sol	denotes solubility limit (mol/mol)

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