

The object of this column is to enhance our readers' collections of interesting and novel problems in chemical engineering. Problems of the type that can be used to motivate the student by presenting a particular principle in class, or in a new light, or that can be assigned as a novel home problem, are requested, as well as those that are more traditional in nature and which elucidate difficult concepts. Please submit them to Professor James O. Wilkes (e-mail: wilkes@engin.umich.edu) or Mark A. Burns (e-mail: maburns@engin.umich.edu), Chemical Engineering Department, University of Michigan, Ann Arbor, MI 48109-2136.

# UNUSUAL THREE-PHASE FLASH EQUILIBRIUM PROBLEMS

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A four-credit senior-level course in the Petroleum Engineering Department at Texas A&M University, "Phase Behavior of Hydrocarbon Fluids," covers thermodynamic and transport properties of reservoir fluids and fluids used in oil recovery applications. From the surface to the reservoir, oil and gas pressures vary from atmospheric to over 1000 MPa, and temperatures vary from near zero to about 300°C. An important portion of the course is devoted to the evaluation of various correlations and models, including equations of state (EOS), to solve the phase equilibria at these conditions.

## INTRODUCTION

The evaluation of a two-phase flash problem has become a common exercise in any thermodynamics course in chemical or petroleum engineering. Equilibrium and material-balance relations lead to the common flash function, which can be stated in many different algebraic forms in terms of feed compositions ( $z_i$ ), molar fraction of feed vaporized, ( $f_v$ ), and equilibrium K-values.<sup>[1,2]</sup> But phase equilibria in enhanced oil recovery processes such as steam flooding is complex and usually involves three or more equilibrium phases. In steam-flooding processes, steam is injected into a well to displace oil within the reservoir to a producer well. In this process, heat and mass transfer mechanisms cause multiphase separations. The phases considered are a vapor phase, a hydrocarbon-rich liquid phase (known as the oleic phase), and an aqueous phase. Since chemical species can distribute in all the three phases, there will be three different

partition coefficients or K-values. Only two of them are independent since the third can be evaluated as a linear combination of the other two.

Three-phase flash problems are not commonly taught, although they can become an important tool in teaching fundamental aspects of phase equilibria. We have found interesting examples in three-phase equilibrium problems that are thought-provoking and are very useful for verifying the consistency of common assumptions, screening models for consistency, and analyzing experimental data.

In this paper, we present some of these examples with two- and three-component systems.

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## THE GENERALIZED THREE-PHASE FLASH

A commonly asked question is whether the phase equilibrium compositions depend upon the overall mixture composition. The answer to this problem can be seen in Figure 1, a sketch of a system in three-phase equilibria brought into equilibrium at overall composition  $z_i^1$  with the valve open. The oleic, vapor, and aqueous phase compositions are  $x_i$ ,  $y_i$ , and  $w_i$ , respectively. If the valve is closed at constant pressure and temperature, the system above the valve will have an overall composition  $z_i^2$  different from  $z_i^1$ , but the phase compositions  $x_i$ ,  $y_i$ , and  $w_i$  will not change. Therefore, phase equilibrium compositions are independent of the overall mixture composition. The same principle applies to a two-phase system—this is an important concept that should be stressed.

When a system exhibits three phases, there will be two objective functions (flash functions) to be zeroed simultaneously. As with the two-phase flash problem, there are several algebraic expressions for these objective functions, and Peng and Robinson<sup>[3]</sup> recommended the following:

$$F_1 = \sum_{i=1}^n x_i - \sum_{i=1}^n y_i = 0 \quad (1)$$

$$F_2 = \sum_{i=1}^n w_i - 1 = 0 \quad (2)$$

Phase equilibria in three-phase systems require two sets of equilibrium ratios or K-factors: the vapor-aqueous ( $K_i^{va}$ ) and the vapor-oleic ( $K_i^{vo}$ ) equilibrium ratios, which are defined as

$$K_i^{va} = \frac{y_i}{w_i} \quad \text{and} \quad K_i^{vo} = \frac{y_i}{x_i} \quad (3)$$

The objective functions expressed in terms of these K-values are

$$F_1(f_v, f_o) = \sum_{i=1}^n \frac{z_i K_i^{va} \left( \frac{1}{K_i^{vo}} - 1 \right)}{1 + \left( \frac{K_i^{va}}{K_i^{vo}} - 1 \right) f_o + (K_i^{va} - 1) f_v} = 0 \quad (4)$$

$$F_2(f_v, f_o) = \sum_{i=1}^n \frac{z_i}{1 + \left( \frac{K_i^{va}}{K_i^{vo}} - 1 \right) f_o + (K_i^{va} - 1) f_v} - 1 = 0 \quad (5)$$

The K-values can be obtained from EOS, from correlations, or from liquid solution models. If the correlations are composition independent, we can demonstrate that the same model cannot be used for both since that will yield a singular Jacobian matrix from the two flash equations.<sup>[4]</sup>

A very common assumption for solving phase equilibria

of hydrocarbons with water is to neglect the solubility of hydrocarbons in the aqueous phase. This is equivalent to having the vapor-aqueous K-values for all hydrocarbon species infinite, and the vapor-aqueous K-value for water equal to its mole fraction in the vapor phase. For the vapor-oleic K-values, one could use EOS or correlations.<sup>[5]</sup>

### Example 1

As an example, we evaluated phase equilibria on the ternary system of heptane/decane/water using Wilson's<sup>[5]</sup> correlation for the K-values, which is widely used in petroleum engineering applications at pressures up to 2 MPa. In the example presented, we evaluated phase equilibria at  $T = 173.63^\circ\text{C}$  and  $P = 0.48 \text{ MPa}$ . Wilson's correlation for the equilibrium ratios is

$$K_i^{vo} = \frac{P_{ci}}{P} \exp \left[ 5.37 (1 - \omega_i) \left( 1 - \frac{T_{ci}}{T} \right) \right] \quad (6)$$

After substituting  $K_i^{vo}$  into Eqs. (4) and (5) and ignoring the solubility of hydrocarbons in water, we solved the flash functions and obtained multiple roots for the three-phase equilibria. This pathological behavior could be attributed to using a wrong model for the water equilibrium ratios, although numerical problems, false solutions, and non-physical answers have been reported in multiphase calculations of systems with water, even using more elaborate models.<sup>[6]</sup>

Table 1 (next page) shows some of the multiple roots obtained for this system. Note that the equilibrium compositions obtained are all different. The student can verify that

all these roots satisfy the material balance constraints. Figure 2 (next page) illustrates the shape of the objective functions defined in Eqs. (4) and (5) versus the sum of the vapor and oleic fractions at the temperature and pressure of study. Only a few curves have been shown for clarity.

### K-FACTORS RELATIONSHIP IN A BINARY THREE-PHASE SYSTEM

If a two-component system coexists in three-phase equilibria, according to the Gibb's phase rule, there is only one degree of freedom. If three phases exist, there will be a unique three-phase pressure for a given temperature.

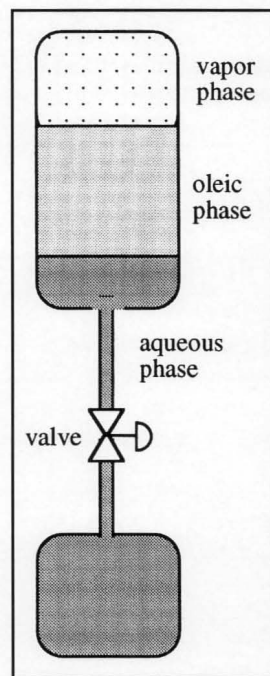


Figure 1. Three-phase equilibrium system.

The set of equations for a bi-

nary, three-phase system is

$$z_1 = f_a w_1 + f_o x_1 + f_v y_1 \quad (7)$$

$$z_2 = f_a w_2 + f_o x_2 + f_v y_2 \quad (8)$$

$$f_a + f_o + f_v = 1 \quad (9)$$

The determinant of the coefficient matrix of the linear equations above is

$$\Delta = \begin{vmatrix} w_1 & x_1 & y_1 \\ w_2 & x_2 & y_2 \\ 1 & 1 & 1 \end{vmatrix} \quad (10)$$

Since

$$\sum_{i=1}^2 x_i = \sum_{i=1}^2 y_i = \sum_{i=1}^2 w_i = 1 \quad (11)$$

substitution of Eq. (11) into Eq. (10) yields a zero determinant. Thus, these equations are linearly dependent, and infinite roots of  $f_a$ ,  $f_o$ , and  $f_v$  can be found. From this determinant, we derived the following relationship among the K-factors of a three-phase binary system

$$\frac{\frac{1}{K_1^{va}} - 1}{\frac{1}{K_2^{va}} - 1} = \frac{\frac{1}{K_1^{vo}} - 1}{\frac{1}{K_2^{vo}} - 1} \quad (12)$$

If we have functional forms of the equilibrium values in terms of pressure and temperature, Eq. (12) could be used as a scheme to find the three-phase equilibrium pressure or

temperature of a binary system. The equilibrium molar compositions, aqueous  $w_i$ , oleic  $x_i$ , and vapor  $y_i$ , are determined from the following expressions:

$$x_1 = \frac{K_1^{va}(K_2^{va} - 1)}{K_1^{vo}(K_2^{va} - K_1^{va})} \quad (13)$$

$$w_1 = \frac{K_2^{va} - 1}{K_2^{va} - K_1^{va}} \quad (14)$$

and the vapor compositions  $y_i$  from the vapor-oleic K-value relation.

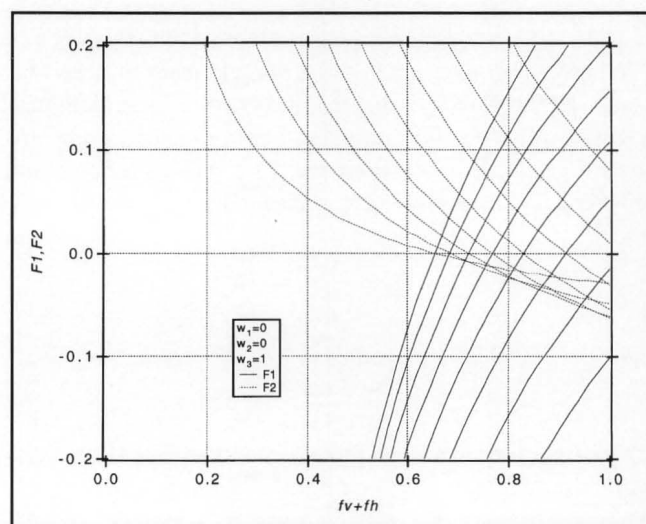


Figure 2. Flash functions at  $T=173.63^\circ\text{C}$  and  $P=0.482$  MPa for the ternary system of Example 1.

**TABLE 1**  
Three-phase flash multiple solutions when the solubility of hydrocarbons in water is neglected and the K-values are composition independent.

$p = 0.482$  MPa     $T = 177$  ( $^\circ\text{C}$ )

Component (i)	(1)	(2)	(3)						
	Heptane	Decane	Water						
Overall Composition - Mole Fraction $z(i)$	0.40	0.20	0.40						
Aqueous Composition - Mole Fraction $x_a(i)$	<b>0.00</b>	<b>0.00</b>	<b>1.00</b>						
Rt#	$f_a$	$f_o$	$f_v$	$x_1$	$x_2$	$x_3$	$y_1$	$y_2$	$y_3$
1	0.367817	0.625861	0.006322	0.630706	0.318852	0.050442	0.832917	0.070085	0.097000
2	0.346768	0.587909	0.065323	0.593317	0.332078	0.074605	0.783541	0.072992	0.143466
3	0.317383	0.546094	0.136523	0.550670	0.347161	0.102169	0.727220	0.076307	0.196473
4	0.280020	0.503986	0.215994	0.506823	0.362672	0.130506	0.669315	0.079717	0.250965
5	0.232139	0.460717	0.307145	0.461715	0.378624	0.159661	0.609746	0.083223	0.307030
6	0.169902	0.415049	0.415049	0.415297	0.395040	0.189663	0.548445	0.086831	0.364724
7	0.011836	0.326094	0.662070	0.333214	0.424071	0.242714	0.440046	0.093212	0.466743



### Example 2

We worked a second example using published experimental data from Heidmann, *et al.*,<sup>[7]</sup> who measured the equilibrium phase compositions of the binary system ethylbenzene (1)/water (2) at 0.11 MPa and 367.6 K. These compositions are

$$x_2 = 0.0186 \quad y_2 = 0.726 \quad w_1 = 0.000086$$

Students can verify Eq. (12) by using the definition of the K-values and the compositions provided.

Figure 3 illustrates all possible solutions for the phase fractions of Example 2 at a fixed overall composition. Figure 4 is a ternary diagram for this system at  $P = 0.11$  MPa and  $T = 367.6$  K, showing all possible combinations of phase fractions (satisfying the material balance and equilibrium constraints) as a function of various overall compositions. For example, the onset and disappearance of the three phases for a mixture with 20% of ethyl benzene occur approximately at  $f_a = 0.3$  and  $f_a = 0.8$ .

To obtain a unique solution, we need to find an independent equation involving these phase fractions. One of these relationships is the apparent total molar volume of the system, which can be measured or fixed:

$$V_{Mt} = f_v V_{Mv} + f_o V_{Mo} + f_a V_{Ma} \quad (15)$$

where  $V_{Mv}$ ,  $V_{Mo}$ , and  $V_{Ma}$  are the vapor, liquid-hydrocarbon, and aqueous molar volumes that can be evaluated from an EOS at the pressure, temperature, and composition of the phase. For consistency, the same EOS should have been used in evaluating the K-values that determined the three-phase equilibrium state. Phase compositions and phase volumes could also be available experimentally.

The phase fractions will then be uniquely determined from the following expressions:

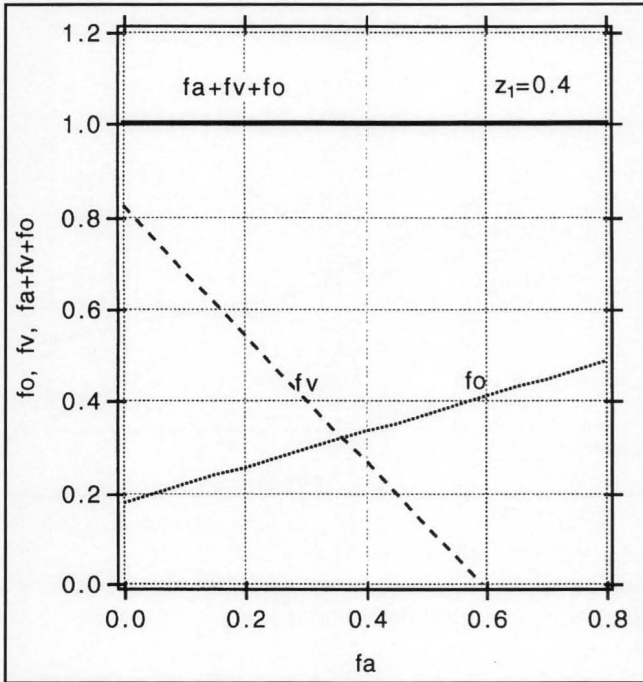
$$f_a = \frac{(x_2 - y_2)V_{Mt} - (z_2 - x_2)V_{Mv} - (y_2 - z_2)V_{Mo}}{(x_2 - y_2)V_{Ma} - (w_2 - x_2)V_{Mv} - (y_2 - w_2)V_{Mo}} \quad (16)$$

$$f_o = \frac{z_2 - y_2 - (w_2 - y_2)f_a}{x_2 - y_2} \quad (17)$$

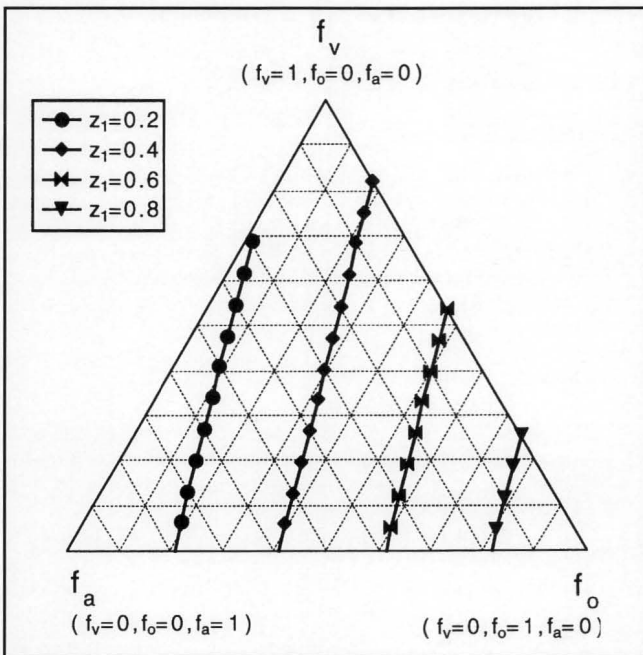
and the vapor phase fraction  $f_v$  is obtained by subtracting  $(f_a + f_o)$  from one.

### EVALUATION OF PHASE FRACTIONS

To estimate the phase fractions for this example system, we arbitrarily selected an overall composition of ethylbenzene ( $z_1 = 0.4$ ) and evaluated the phase molar volumes using the Peng-Robinson equation of state at the experimental pressure, temperature, and phase compositions. Since the pressure and the temperature of this system remain constant, each phase must keep its intensive properties (*e.g.*, equilib-



**Figure 3.** Oleic and vapor phase fractions as a function of aqueous phase fraction and overall compositions in the three-phase binary system of Example 2.



**Figure 4.** Phase fractions as a function of overall mixture composition for the system of Example 2.

rium composition, density), regardless of its relative amount in the system. Figure 5 shows the determination of the phase fractions from Eqs. (16) and (17). As a suggested exercise, the student should find the values of the molar volumes.

For a three-phase ternary system, the equilibrium compositions ( $x_i$ ,  $y_i$ ,  $w_i$ ) and phase fractions ( $f_a$ ,  $f_v$ ,  $f_h$ ) can be determined explicitly and uniquely given  $K_i^{va}$  and  $K_i^{vo}$ .

### EXERCISE

As an exercise the student may solve the three-phase equilibria on the following three-phase ternary artificial data:

Species "i"	1	2	3
$K_i^{va}$	34449.2	13509.0	0.2703
$K_i^{vo}$	1.16668	0.44607	892.19
$z_i$	0.3	0.3	0.4

The following solution should be obtained:

i	1	2	3
$x_i$	0.3938	0.6059	0.0003
$y_i$	0.4594	0.2703	0.2703
$w_i$	0.000013	0.00002	0.999967
$f_a = 0.29991$	$f_o = 0.33010$	$f_v = 0.36999$	

### CONCLUSIONS

We have presented simple three-phase equilibria problems when water is included. This paper contains exercises that are thought-provoking in the classroom. In particular, when there is negligible solubility of hydrocarbons in the aqueous phase, these problems lend themselves to further analysis and evaluation of other equilibrium-ratio models. For a binary system in three-phase equilibria, we have presented a constraining procedure to obtain a unique solution for the phase splitting.

### ACKNOWLEDGMENTS

The authors acknowledge the donors of The Petroleum Research Fund, administered by the ACS, for supporting this research.

### NOMENCLATURE

$f_a, f_o, f_v$	aqueous, oleic, and vapor phase fraction, respectively
$K_i$	K-factors in a two-phase system
$K_i^{va}$	vapor/aqueous equilibrium ratio for species "i"
$K_i^{vo}$	vapor/oleic equilibrium ratio for species "i"
$P_{ci}$	critical pressure of species "i" (MPa)
$T_{ci}$	critical temperature of species "i" (°C)
$V_{Ma}$	molar volume in aqueous phase ( $L^3/\text{mole}$ )

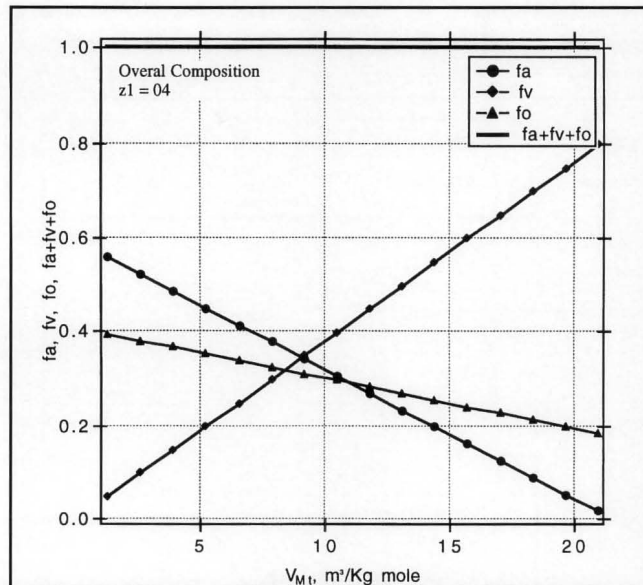


Figure 5. Phase fractions as a function of total molar volume for the system of Example 2.

$V_{Mo}$  molar volume in oleic phase ( $L^3/\text{mole}$ )

$V_{Mt}$  total molar volume in three phases ( $L^3/\text{mole}$ )

$V_{Mv}$  molar volume in vapor phase ( $L^3/\text{mole}$ )

$\omega_i$  acentric factor of species "i"

$w_i$  mole fraction of species "i" in aqueous phase

$x_i$  mole fraction of species "i" in oleic phase

$y_i$  mole fraction of species "i" in vapor phase

$z_i$  mole fraction of species "i" in overall mixture

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