**Pergamon**

**0098-1354(93)E0017-4**

# CALCULATION OF MULTIPHASE EQUILIBRIUM

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**Abstract**—A method for calculation of the phase distribution in multiphase equilibrium assuming composition independent fugacity- or activity-coefficients is described. The phase distribution calculation is formulated as a minimization problem and permits automatic and efficient handling of an arbitary number of pure phases. An extension to reacting mixtures is given, the result being a minimization problem with a number of independent variables equal to the sum of the number of independent reactions and the number of nonpure phases.

## INTRODUCTION

Successive substitution procedures have found widespread application in phase equilibrium calculation due to their robustness and simplicity. Successive substitution for calculating the isothermal flash alternates between evaluation of thermodynamics properties (fugacity or activity coefficients) at the current estimate of the phase distribution, and a recalculation of phase amounts and compositions, assuming composition independent thermodynamic properties.

In the classical successive substitution procedure (Henley and Rosen, 1969; Prausnitz *et al.*, 1980) this process is repeated until convergence is obtained, whereas more recent modifications apply quasi-Newton methods (Boston and Britt, 1978) or other acceleration methods (Mehra *et al.*, 1980; Michelsen, 1982a, b) to improve performance.

The recalculation of the phase distribution is trivial for two-phase mixtures. Application of the Rachford–Rice method reduces the computational problem to that of determining the zero of a monotonic function. Although the computational effort is still modest for multiphase problems the calculation of the phase distribution is more complex (Henley and Rosen, 1969; Michelsen, 1982a, b; Nelson, 1987) since phases may vanish or emerge during the iterative calculation.

The aim of this paper is to describe a simple and reliable procedure for handling the multiphase distribution calculation. In addition is presented an extension of the procedure to simultaneous calculation of chemical equilibrium.

## MULTIPHASE PHYSICAL EQUILIBRIUM

We assume that the overall composition of a $C$ component mixture is specified by the component molar amounts $(N_1, N_2, \ldots, N_C)$. It is further assumed that the mixture is capable of splitting into $F$ phases (which may not all be present at equilibrium) and that the fugacity coefficients are known and assumed to be composition independent within each phase. Our objective is to determine the amount and the composition of each phase.

The following conditions apply at equilibrium:

*Component material balances:*

$$\sum_{j=1}^{F} \beta_j y_{ij} = N_i, \quad i = 1, 2, \ldots, C, \tag{1}$$

where $\beta_j$ is the total molar amount of phase $j$, and $y_{ij}$ is the mole fraction of component $i$ in phase $j$.

*Equilibrium relations:*

$$y_{11}\varphi_{i1} = y_{i2}\varphi_{i2} = \cdots = y_{iF}\varphi_{iF},$$
$$i = 1, 2, \ldots, C. \tag{2}$$

where $\varphi_{ij}$ is the fugacity coefficient of component $i$ in phase $j$.

*Summation of mole fractions:*

$$\sum_{i=1}^{C} y_{ij} = 1, \quad j = 1, 2, \ldots, F. \tag{3}$$

In addition, the $\beta_j$ must be nonnegative.

If the set of equations (1–3) can be satisfied with $\beta_j > 0$, $j = 1, 2, \ldots, F$ all phases are present at equilibrium (under the assumption of composition independent fugacity coefficients). This is not always possible as one or more of the assumed phases can be absent from the equilibrium mixture. Stability analysis (Michelsen, 1982b) yields the condition that a phase $m$, which is absent at equilibrium ($\beta_m = 0$) must satisfy $\Sigma_i y_{im} < 1$, rather than equation (3).

The set of equations (1–3) can be reduced as follows:

We define the objective function:

$$Q(\beta) = \sum_{j=1}^{F} \beta_j - \sum_{i=1}^{C} N_i \ln E_i. \tag{4}$$

where

$$E_i = \sum_{k=1}^{F} \frac{\beta_k}{\varphi_{ik}}. \tag{5}$$

The phase molar amounts at equilibrium are given by the vector $\beta$ that minimizes $Q$, subject to the constraints:

$$\beta_j \geq 0, \quad j = 1, 2, \ldots, F. \tag{6}$$

As the solution, the mole fractions in the individual phases are given by:

$$y_{ij} = \frac{N_i}{\varphi_{ij} E_i}. \tag{7}$$

We immediately observe that the mole fractions defined by equation (7) satisfy the material balances:

$$\sum_{j=1}^{F} \beta_j y_{ij} = \frac{N_i}{E_i} \sum_{j=1}^{F} \frac{\beta_j}{\varphi_{ij}} = N_i \tag{8}$$

and the equilibrium relations:

$$y_{i1}\varphi_{i1} = y_{i2}\varphi_{i2} = \cdots = y_{iF}\varphi_{iF} = \frac{N_i}{E_i}. \tag{9}$$

At a minimum of $Q$, where the constraint on the $\beta_j$ is inactive:

$$\frac{\partial Q}{\partial \beta_j} = 0$$

or

$$1 - \sum_{i=1}^{C} \frac{N_i}{E_i \varphi_{ij}} = 0. \tag{10}$$

i.e. $\sum_{i=1}^{C} y_{ij} = 1$, and the summation of mole fractions condition is satisfied.

A minimum with phase $m$ absent at equilibrium requires

$$\beta_m = 0, \quad \frac{\partial Q}{\partial \beta_m} > 0$$

or

$$\sum_{i=1}^{C} y_{im} < 1, \tag{11}$$

corresponding to the stability criterion mentioned earlier for phase $m$ being absent.

The objective function $Q$ is a convex function defined on the convex set $\beta$. The convexity follows from the Hessian matrix being at least positive-semidefinite, as shown below:

$$B_{ij} = \frac{\partial^2 Q}{\partial \beta_j \partial \beta_k} = \sum_{i=1}^{C} \frac{N_i}{E_i^2 \varphi_{ij}\varphi_{ik}} = \sum_{i=1}^{C} U_{ki}U_{ji}N_i, \tag{12}$$

where the $F \times C$ matrix U is given by

$$U_{ki} = \frac{1}{E_i \varphi_{ik}}.$$

The Hessian matrix **B** can thus be written $\mathbf{B} = \mathbf{UNU}^T$ where **N** is diagonal, with elements $N_i$. When the $F \times C$ matrix **U** is of rank $F$ ($\leq C$) **B** will be positive-definite, and $Q$ is a strictly convex function. With rare exceptions (azeotropic or critical mixtures) U will be of rank $F$ whenever the number of components equals or exceeds the number of phases.

The minimum of a strictly convex function is unique (Fletcher, 1981) and Newton's method with linesearch is well suited for locating the minimum.

If the number of phases exceeds the number of components **B** will only be positive-semidefinite. This requires that one of the phases is eliminated in order to yield a result with the appropriate number of phases.

As mentioned above, a few degenerate cases exist, such as azeotropic mixtures, critical mixtures or pure components at their saturation point. Here we obtain a continuous set of solutions, characterized by identical phase composition but undeterminable phase amounts.

For two-phase calculations the conventional Rachford–Rice procedure is of course simpler than the minimization approach, since only one independent variable is required. It is also possible in the present approach to eliminate one of the independent variables by substituting:

$$\beta_F = \sum_{i=1}^{C} N_i - \sum_{j=1}^{F-1} \beta_j, \tag{13}$$

and it is readily shown that use of this relation reduces the gradient condition in the two-phase calculation to the Rachford–Rice equation. With more phases potentially present, however, the reduction from $F$ to $F-1$ variables is slightly inconvenient. Precautions must be taken to handle situations where the "dependent" phase $F$ might vanish, and it therefore seems preferable to maintain the full set of equations.

### PHYSICAL EQUILIBRIUM WITH PURE PHASES

In many practically important problems involving more than two phases, many of the phases will often

be pure or almost pure phases, such as solid phases, or liquid phases with low solubility for other components, such as water in a hydrocarbon mixture. Pure phases can be handled with the general version of the multiphase procedure, but the dimension of the problem can be reduced as follows:

To simplify the notation we shall for convenience assume that the components indexed $1, 2, \ldots f$ may form pure phases indexed $1, 2, \ldots f$. In pure phase $k$ the fugacity coefficients of all components, except the component forming the phase, are infinite.

The gradient relation [equation (10)] for a pure phase thus becomes:

$$\frac{\partial Q}{\partial \beta_k} = 1 - \sum_{i=1}^{C} \frac{N_i}{\varphi_{ik} E_i} = 1 - \frac{N_k}{\varphi_{kk} E_k} = 0 \qquad (14)$$

or

$$\varphi_{kk} E_K = N_k. \qquad (15)$$

Substituting

$$E_k = \sum_{j=1}^{F} \frac{\beta_j}{\varphi_{kj}} = \frac{\beta_k}{\varphi_{kk}} + \sum_{j=f+1}^{F} \frac{\beta_j}{\varphi_{kj}}, \qquad (16)$$

we arrive at

$$\beta_k = N_k - \varphi_{kk} \sum_{j=f+1}^{F} \frac{\beta_j}{\varphi_{kj}}. \qquad (17)$$

If, at the current iteration, all $\beta_k$ $(k = 1, 2, \ldots, f)$ calculated from equation (17) are positive, we can substitute equations (17) and (15) into the expression for $Q$ to obtain:

$$Q = \sum_{i=1}^{f} N_i (\ln \varphi_{ii} - \ln N_i + 1) + \sum_{j=f+1}^{F} \beta_j \left( 1 - \sum_{k=1}^{f} \frac{\varphi_{kk}}{\varphi_{jk}} \right)$$
$$- \sum_{i=f+1}^{C} N_i \ln E_i, \qquad (18)$$

where we note that:

$$E_i = \sum_{j=1}^{F} \frac{\beta_j}{\varphi_{ij}} = \sum_{j=f+1}^{F} \frac{\beta_j}{\varphi_{ij}}, \quad (i > f), \qquad (19)$$

since

$$\frac{1}{\varphi_{ij}} = 0$$

for $j \leq f$.

We have thus reduced $Q$ to a function of $F-f$ variables, with gradient and Hessian given by:

$$\frac{\partial Q}{\partial \beta_j} = 1 - \sum_{k=1}^{f} \frac{\varphi_{kk}}{\varphi_{kj}} - \sum_{i=f+1}^{C} \frac{N_i}{E_i \varphi_{ij}} \qquad (20)$$

and

$$\frac{\partial^2 Q}{\partial \beta_j \partial \beta_k} = \sum_{i=f+1}^{C} \frac{N_i}{E_i^2 \varphi_{ij} \varphi_{ik}} = \sum_{i=f+1}^{C} N_i U_{ji} U_{ki}. \qquad (21)$$

It is worthwhile to notice that $f$ may well change during the iterative minimization. Correction of the fluid phase $\beta$-values may lead to negative $\beta_k$ in equation (17), in which case the pure phase vanishes, or the correction of the fluid phase amounts may lead to formation of new pure phases. Regardless of the final outcome it is evident that the potential presence of pure phases except for a modest amount of bookkeeping does not increase the size or complexity of the minimization problem.

Finally, it is important to realize that the phase molar amounts defined by:

$$n_{ij} = \beta_j y_{ij} = \frac{N_i}{E_i} \frac{\beta_j}{\varphi_{ij}}, \qquad (22)$$

satisfy the overall material balance $\Sigma_j n_{ij} = N_i$ for any value of $\beta$. A successive substitution procedure requires repeated evaluations of physical properties and determination of the phase distribution at each step, but a very accurate determination of the phase distribution is not required provided the approximate solution satisfies the material balance. Considering that the overall rate of convergence for successive substitution in nonideal mixtures is linear, a single iterative step for the minimization, where a second order convergence procedure is applied, may well be adequate, in particular when we are close to overall convergence.

## EXAMPLES

The component fugacity coefficients used in the following examples are all taken at equilibrium compositions, using the Soave–Redlich–Kwong equation of state (Soave, 1972).

### Example 1

A mixture of light hydrocarbons and water is flashed at $T = 280$ K, $P = 5$ atm. The solubility of the hydrocarbons in the water phase is negligible. Fugacity coefficients and the equilibrium distribution are given in Table 1. An average of 6 iterations (error $< 10^{-10}$) was required to converge the phase distribution calculation from initial estimates of $(\beta_l, \beta_v) = (0, 1)$ and $(1, 0)$, respectively.

Table 1

| Molar composition | ln $\varphi_i$ | | |
| --- | --- | --- | --- |
| | Vapour | Liquid | Water |
| $C_2$: 0.20 | −0.040 | 1.429 | — |
| $C_3$: 0.50 | −0.096 | 0.032 | — |
| $C_4$: 0.20 | −0.153 | −1.343 | — |
| $H_2O$: 0.10 | 0.012 | 2.461 | −6.61 |
| Equilibrium amount | 0.619 | 0.282 | 0.099 |

Table 2a

| Molar composition | ln $\varphi_i$ ($P = 20$ atm) | | | |
|---|---|---|---|---|
|  | Vapour | Liquid 1 | Liquid 2 | Solid |
| $C_1$: 0.66 | −0.211 | 2.066 | 0.128 | — |
| $C_2$: 0.03 | −0.642 | −1.903 | −3.368 | — |
| $C_3$: 0.01 | −1.008 | −4.258 | −6.020 | — |
| $CO_2$: 0.05 | −0.402 | −2.130 | −2.137 | −4.768 |
| $H_2S$: 0.25 | −0.532 | −5.373 | −3.624 | −5.571 |
| Equilibrium amount | 0.390 | 0.243 | 0.366 | 0.0013 ($CO_2$) |

Table 2b

| Molar composition | ln $\varphi_i$ ($P = 40$ atm) | | | |
|---|---|---|---|---|
|  | Vapour | Liquid 1 | Liquid 2 | Solid |
| $C_1$: 0.66 | −0.413 | 1.535 | −0.556 | — |
| $C_2$: 0.03 | −1.282 | −2.404 | −3.911 | — |
| $C_3$: 0.01 | −2.012 | −4.694 | −6.477 | — |
| $CO_2$: 0.05 | −0.804 | −2.681 | −2.645 | −5.410 |
| $H_2S$: 0.25 | −1.065 | −6.040 | −4.022 | −6.220 |
| Equilibrium amount | 0.000 | 0.142 | 0.818 | 0.0400 ($H_2S$) |

*Example 2*

A mixture of $C_1$, $C_2$, $C_3$, $CO_2$ and $H_2S$ is flashed at $T = 174$ K and at various pressures. Under these conditions the mixture may form two liquid phases, and in addition solid $CO_2$ and $H_2S$ can precipitate. Conditions are given in Tables 2a and b. Each example was calculated, using as initial estimate that one of the mixed phases, in turn, was equal to the total feed, while the remaining were absent. An average of 10 iterations was required for this example.

*Example 3*

A binary mixture of methane and hexane is flashed at $T = 187$ K, $P = 40$ atm, very close to conditions at which this mixture forms 3 phases. Fugacity coefficients are given in Table 3. For this example, the Hessian matrix is rank deficient when all phases are assumed to be present (the number of phases exceeding the number of components). A diagonal correction of $10^{-7}$ was added to the Hessian to ensure full rank while essentially preserving

Table 3

| Molar composition | ln $\varphi_i$ | | |
|---|---|---|---|
|  | Vapour | Liquid | Liquid 2 |
| $C_1$: 0.90 | −0.372 | −0.355 | −0.254 |
| $C_6$: 0.10 | −4.773 | −10.62 | −12.46 |
| Equilibrium amount | 0 | 0.128 | 0.872 |

second order convergence. This lead to rapid elimination of the extraneous phase, the average iteration count being 10. An initial estimate of vapour only, however, required 18 iterations.

### EXTENSION TO CHEMICALLY REACTING MIXTURES

The present formulation can be extended to include chemical equilibrium. When $R$ independent chemical reactions occur, the overall material balance can be written:

$$N_i = N_{i0} + \sum_{m=1}^{R} v_{im}\zeta_m, \quad i = 1, 2, \ldots, C, \quad (23)$$

where the $v_{im}$ are stoichiometric coefficients and $\zeta_m$ the extent of the $m$th reaction.

The additional equilibrium conditions derived from the condition of minimal Gibbs energy, are:

$$\sum_{i=1}^{C} v_{im}\frac{\mu_i}{RT} = 0, \quad m = 1, 2, \ldots, R, \quad (24)$$

where

$$\frac{\mu_i}{RT} = \frac{\mu_i^0}{RT} + \ln P + \ln \varphi_{ij} + \ln y_{ij}, \quad j = 1, 2, \ldots, F, \quad (25)$$

or equivalently,

$$\frac{\mu_i}{RT} = \alpha_i + \ln \varphi_{ij} + \ln y_{ij}, \quad (26)$$

with

$$\alpha_i = \frac{\mu_i^0}{RT} + \ln P.$$

The objective function is extended as follows:

$$Q_R(\beta, \zeta) = Q(\beta) + \sum_{i=1}^{C} N_i(\ln N_i + \alpha_i - 1) \quad (27)$$

from which we obtain:

$$\frac{\partial Q_R}{\partial \beta_j} = \frac{\partial Q}{\partial \beta_j} = 1 - \sum_{i=1}^{C} \frac{N_i}{E_i \varphi_{ij}} \quad (28)$$

and

$$\frac{\partial Q_R}{\partial \zeta_m} = \sum_{i=1}^{C} v_{im}(\alpha_i + \ln N_i - \ln E_i). \quad (29)$$

When the conditions:

$$\frac{\partial Q}{\partial \beta_j} = 0, \quad j = 1, 2, \ldots, F,$$

are satisfied we have shown earlier that:

$$\frac{N_i}{E_i} = y_{i1}\varphi_{i1} = y_{i2}\varphi_{i2} = \cdots = y_{iF}\varphi_{iF}$$

and hence

$$\ln\frac{N_i}{E_i} = \ln(y_{i1}\varphi_{i1}) = \cdots = \ln(y_{iF}\varphi_{iF})$$

and simultaneous satisfaction of the gradient conditions thus implies that:

$$\sum_{i=1}^{c} v_{im}\frac{\mu_i}{RT} = 0, \quad m = 1, 2, \ldots, R, \qquad (30)$$

i.e. that all conditions for physical and chemical equilibrium are satisfied at a stationary point of $Q_R$.

$Q_R$ is at least semiconvex. The elements of the Hessian matrix are given by:

$$\frac{\partial^2 Q_R}{\partial\beta_j\partial\beta_k} = \sum_{i=1}^{c}\frac{N_i}{E_i^2\varphi_{ij}\varphi_{ik}} = \sum_{i=1}^{c} U_{ki}U_{ji}N_i, \qquad (31)$$

$$\frac{\partial^2 Q_R}{\partial\zeta_m\partial\zeta_n} = \sum_{i=1}^{c}\frac{v_{im}v_{in}}{N_i} \qquad (32)$$

and

$$\frac{\partial^2 Q_R}{\partial\beta_j\partial\zeta_m} = -\sum_{i=1}^{c}\frac{v_{im}}{E_i\varphi_{ij}} = -\sum_{i=1}^{c} U_{ji}v_{im} \qquad (33)$$

and the Hessian matrix be written

$$\mathbf{B}_R = \mathbf{V}\mathbf{V}^T \qquad (34)$$

where the elements of the $(F + R) \times C$ matrix $\mathbf{V}$ are:

$$V_{ki} = U_{ki}N_i^{1/2}, \quad k = 1, 2, \ldots, F,$$

$$V_{F+k,i} = -v_{ik}N_i^{-1/2}, \quad k = 1, 2, \ldots, R \qquad (35)$$

and thus $\mathbf{B}_R$ is at least positive semidefinite and, with exceptions as for the physical equilibrium case, positive definite when the number of components $C$ equals or exceeds $R + F$.

The minimization of $Q_R$ is performed subject to the constraints:

$$\beta_j \geq 0, \quad j = 1, 2, \ldots, F,$$
$$N_i \geq 0, \quad i = 1, 2, \ldots, C, \qquad (36)$$

where the equality constraint for $N_i$ can become active only if component $i$ can only appear as a pure phase.

When $f$ pure phases are present the convex minimization problem of dimension $R + F$ can be reduced to dimension $R + F - f$ in a similar manner as for the nonreactive equilibrium calculation.

We may finally notice that at the minimum $Q_R$ is equal to the reduced Gibbs energy of the mixture. $Q_R$ can be written:

$$Q_R(\beta, \zeta) = \sum_{j=1}^{F}\beta_j - \sum_{i=1}^{C} N_i + \sum_{i=1}^{C} N_i(\ln N_i - \ln E_i + \alpha_i).$$
$$(37)$$

At the minimum $\Sigma_j\beta_j = \Sigma_i N_i$ and $\ln(N_i/E_i) = \ln y_{ij} + \ln\varphi_{ij}$ and from equation (25) we obtain:

$$Q_{R,\text{min}} = \sum_{i=1}^{c} N_i\frac{\mu_i}{RT} = \frac{G}{RT}, \qquad (38)$$

which is valid for the reactive as well as the nonreactive case.

In contrast to the physical equilibrium calculation the chemical equilibrium calculation cannot be started from arbitrary initial estimates. The presence of logarithmic terms in the molar amounts requires an initial composition where all mixed phase molar amounts are positive. This should not present problems when the suggested procedure is used in connection with successive substitution, where initial estimates are available from the previous iteration, but it may be advantageous to employ an alternative initialization procedure for the very first calculation of the equilibrium distribution.

As for the nonreactive mixtures the proposed formulation for calculation of chemical equilibrium has the advantageous property that all material balance constraints are satisfied at each iteration.

## CONCLUSION

A procedure for calculating the equilibrium distribution in multiphase mixtures, where physical properties are assumed composition independent, has been developed. The procedure is second-order, globally convergent and capable of automatic determination of the correct phase distribution. The number of independent variables equals the number of fluid phases present at equilibrium, and the computational effort is likely to be very modest as compared with that required for evaluation of physical properties.

An extension of the procedure to chemically reacting mixtures has been suggested. This extension shares the compactness and the capabilities of the procedure for calculation of physical equilibrium but has not at present been extensively tested.

## NOMENCLATURE

$\mathbf{B}, \mathbf{B}_R$ = Hessian matrix
$C$ = No. of components in mixture
$E$ = Vector with elements defined in equation (5)
$f$ = No. of pure phases
$F$ = Total No. of phases
$G$ = Gibbs energy of mixture
$i$ = Component index
$j, k$ = Phase indices
$m, n$ = Reaction indices
$n_{ij}$ = Moles of component $i$ in phase $j$
$N_i$ = Moles of component $i$ in equilibrium mixture
$N_{i0}$ = Moles of component $i$ in feed
$Q, Q_R$ = Objective function

$R$ = Gas constant, or No. of independent reactions
$T$ = Temperature
$P$ = Pressure
$U$ = Matrix defined in equation (12)
$V$ = Matrix defined in equation (35)
$y_{ij}$ = Mole fraction of component $i$ in phase $j$

*Greek*

$\alpha_i$ = Modified chemical potential, equation (26)
$\beta_j$ = Amount of phase $j$
$\nu_{im}$ = Stoichiometric coefficient
$\mu_i$ = Chemical potential of component $i$
$\mu_{i0}$ = Chemical potential of component $i$, pure ideal gas, 1 atm
$\varphi_{ij}$ = Fugacity coefficient of component $i$ in phase $j$
$\zeta_m$ = Extent of reaction for $m$th reaction

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