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# Computation of Phase Equilibrium in Reservoir Simulation and Optimization ⋆

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**Abstract:** In this paper, we discuss mathematical models and computational methods for computation of vapor-liquid equilibrium in systems relevant to reservoir simulation and optimization. We formulate the phase equilibrium problem as an optimization problem and discuss the UV-flash, the TV-flash, and the PT-flash. The UV-flash occurs for thermal and compositional dynamical simulation problems, the TV-flash occurs for compositional dynamical simulation problems, and the PT-flash occurs for steady-state problems.

*Keywords:* Thermodynamics, Vapor-Liquid Equilibrium, Oil & Gas, Simulation, Optimization

## 1. INTRODUCTION

The operation of off-shore oil and gas fields in terms of e.g. controlling and optimizing the flow in the reservoir, the flow of oil and gas from the well to the well-head, the flow from the well-head to the riser, and the flow from the riser to the topside and separation plant all involve operation of two- or multi-phase systems. Consequently, reservoir simulation and optimization for digitalization and automation of off-shore oil and gas operations require efficient and reliable computation of phase equilibrium in vapor-liquid systems. Vapor-liquid phase equilibrium computations are also important for construction of the digital twin (a simulator) for oil and gas systems.

In this paper, we combine the second law of thermodynamics, optimization theory, and the implicit function theorem to discuss the computation of phase equilibrium and their sensitivities in vapor-liquid equilibrium systems relevant for the oil and gas industry. The sensitivities are needed when the phase equilibrium computation is embedded as part of a gradient-based method, i.e. typically a Newton-based method, for optimization, dynamic simulation, or steady-state simulation. We present and discuss the UV-flash, the TV-flash, and the PT-flash problems as well as numerically efficient ways of computing their solutions.

### 1.1 Literature

Several authors describe the simulation and optimization of models, related to the oil and gas industry, that incorporate phase equilibrium constraints. Li and Johns (2006) describe a method for improving the efficiency of flash calculations in compositional reservoir simulations, and Zaydullin et al. (2014) describe a fully thermal and compositional reservoir flow model. Hammer and Morin (2014) and Qiu et al. (2014) simulate two-phase pipe flow systems, and Laiglecia et al. (2012) solve a dynamic optimization problem for a natural gas separation process. It is common to solve dynamic optimization problems with single-shooting algorithms. Such algorithms combine numerical simulation with numerical optimization algorithms. Efficient optimization algorithms require gradients of the objective function. Such gradients can be computed with adjoint methods (Jørgensen, 2007). Kourounis et al. (2014) use an adjoint method for solving production optimization problems for compositional reservoir models. Støren and Hertzberg (1997) describe an alternative method for efficient estimation of gradients based on approximate local thermodynamic models. Dynamic models that incorporate phase equilibrium constraints consist of 1) conservation equations (differential equations) and 2) phase equilibrium conditions (algebraic equations). Numerical algorithms for solving such differential-algebraic equations either solve the algebraic equations simultaneously with the conservation equations, or in a nested inner loop. Lima et al. (2008) use a simultaneous approach to simulate a dynamic UV-flash process, and Ritschel et al. (2017a,c,d) conclude that a simultaneous approach is faster than a nested approach for dynamic optimization of a UV-flash process. Wilhelmsen et al. (2013) find that a simultaneous approach is faster for dynamic simulation of a UV-flash process, but not for a steady-state PH-flash process.

### 1.2 Mathematics for the nested formulation

In the nested formulation for dynamic simulation, steady-state simulation, and optimization, the phase equilibrium is represented and solved as the optimization problem

$$y = y(x) = \arg\min_{y}\{f(y;x) : g(y;x) = 0\}. \tag{1}$$

In this formulation, $x$ denotes the states, while $y$ are variables related to the solution of the vapor-liquid equilibrium. It is important to notice that $y = y(x)$ is regarded as a function of $x$.

$$y_x = y_x(x) = \frac{\partial y}{\partial x}(x) \tag{2}$$

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In dynamic simulation, the initial value problem (IVP),

$$x(t_0) = x_0, \tag{3a}$$
$$\dot{x}(t) = F(y(x(t))), \tag{3b}$$

may be solved numerically using the implicit Euler method. In the implicit Euler method, the states, $x_{k+1}$, are computed by solving the residual equations

$$R(x_{k+1}) = x_{k+1} - \Delta t F(y(x_{k+1})) - x_k = 0, \tag{4}$$

using a variant of Newton's method. Newton's method requires computation of the derivative

$$\frac{\partial}{\partial x_{k+1}} R(x_{k+1}) = I - \Delta t \frac{\partial F}{\partial y}(y(x_{k+1})) \frac{\partial y}{\partial x}(x_{k+1}). \tag{5}$$

Consequently, it is obvious that simulation by the implicit Euler method requires evaluation of $y = y(x)$ and $y_x = y_x(x)$. Similarly, computation of the steady-state, $x_s$, by solution of

$$\dot{x}(t) = F(y(x_s)) = 0, \tag{6}$$

using Newton's method,

$$F(y(x_s^{[k]})) + \left[\frac{\partial F}{\partial y}(y(x_s^{[k]})) \frac{\partial y}{\partial x}(x_s^{[k]})\right] \Delta x_s^{[k]} = 0, \tag{7a}$$
$$x_s^{[k+1]} = x_s^{[k]} + \Delta x_s^{[k]}, \tag{7b}$$

requires evaluation of $y = y(x)$ and $y_x = y_x(x)$.

### 1.3 Mathematics for the simultaneous formulation

In the simultaneous formulation, the phase equilibrium problem,

$$\min_y \quad f(y; x), \tag{8a}$$
$$s.t. \quad g(y; x) = 0, \tag{8b}$$

is represented by its first order optimality conditions denoted as the algebraic equations

$$G(x, y, \lambda) = 0, \tag{9}$$

where $\lambda$ denotes Lagrange multipliers associated with (8). Dynamic simulation using the simultaneous formulation is conducted by numerical solution of the initial value index-1 differential algebraic equation system

$$x(t_0) = x_0, \tag{10a}$$
$$\dot{x}(t) = F(y(t)), \tag{10b}$$
$$G(x(t), y(t), \lambda(t)) = 0. \tag{10c}$$

Solution of this system using the implicit Euler method involves solution of

$$R_{k+1} = \begin{bmatrix} D_{k+1} \\ G_{k+1} \end{bmatrix} = \begin{bmatrix} x_{k+1} - \Delta t F(y_{k+1}) - x_k \\ G(x_{k+1}, y_{k+1}, \lambda_{k+1}) \end{bmatrix} = 0, \tag{11}$$

by a Newton method. Let $w = [x; y; \lambda]$. The Newton method requires computation of the derivative

$$\frac{\partial R_{k+1}}{\partial w_{k+1}} = \begin{bmatrix} I & -\Delta t \frac{\partial F}{\partial y} & 0 \\ \frac{\partial G}{\partial x} & \frac{\partial G}{\partial y} & \frac{\partial G}{\partial \lambda} \end{bmatrix}. \tag{12}$$

Similarly, the steady state, $(x_s, y_s, \lambda_s)$, is computed by solution of

$$R = \begin{bmatrix} \dot{x}(t) \\ G \end{bmatrix} = \begin{bmatrix} F(y_s) \\ G(x_s, y_s, \lambda_s) \end{bmatrix} = 0, \tag{13}$$

using a variant of Newton's method. Newton's method requires computation of the derivatives

$$\frac{\partial R}{\partial w} = \begin{bmatrix} 0 & \frac{\partial F}{\partial y} & 0 \\ \frac{\partial G}{\partial x} & \frac{\partial G}{\partial y} & \frac{\partial G}{\partial \lambda} \end{bmatrix}. \tag{14}$$

Consequently, the simultaneous method requires evaluation of the function, $G = G(x, y, \lambda)$, in the algebraic equations and computation of the derivatives, $\partial G/\partial x$, $\partial G/\partial y$, and $\partial G/\partial \lambda$.

### 1.4 Perspective

The formulations that we present in this paper are valid when all phases are nonempty at the solution. It is not always possible to determine the exact number of nonempty phases before solving the flash problem. This is particularly true for complex models that may require the solution of several flash problems. Consequently, the solutions to the flash problems that we describe in this paper will be incorrect if the number of specified phases is incorrect. It is difficult to incorporate the disappearance of phases because it makes the problem non-smooth. There are two approaches which can extend the formulations that we present in this paper such that the solution is correct even when some phases are empty. The first approach recasts the flash problem using non-smooth equations and solves them with non-smooth methods (Stechlinski and Barton, 2017; Watson et al., 2017; Sahlodin et al., 2016; Barton and Lee, 2002). The second approach requires the solution of a mathematical program with complementarity constraints (MPCC) (Biegler, 2010; Baumrucker et al., 2008; Raghunathan et al., 2004). Such a mathematical program belongs to the class of mathematical programs with equilibrium constraints (Outrata et al., 2013; Luo et al., 1996). Both approaches combine equations that are valid in single-phase regions with the equations that are valid in the two-phase region. Both approaches therefore extend the formulations that we present in this paper.

### 1.5 Paper organization

The remaining part of the paper is organized as follows. Section 2 presents methods for computation of the minimizer and its sensitivities for the unconstrained optimization problem, while Section 3 presents similar methods for the equality-constrained optimization problem. Section 4 presents the evaluation of the required thermodynamic functions using an open-source library, `www.psetools.org`. We discuss different flash problems, their use, and their equivalence in Section 5. Section 6 discusses the Rachford-Rice method for solution of the PT-flash. Section 7 presents numerical examples, and Section 8 contains the conclusions.

## 2. UNCONSTRAINED OPTIMIZATION

The unconstrained optimization problem

$$\min_y f(y; x) \tag{15}$$

has the solution denoted as

$$y = y(x) = \arg\min_y f(y; x). \tag{16}$$

In this section, we discuss the solution of this problem when $f(y; x)$ is smooth.

### 2.1 Optimality conditions

The first-order optimality condition for a minimizer of (15) are

$$\nabla_y f(y; x) = 0. \tag{17}$$

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### 2.2 Newton's method and the Hessian matrix

The first-order optimality conditions (17) are solved using Newton's method. Each iteration in Newton's method involves solution of the linear system of equations

$$\nabla^2_{yy} f(y;x)\Delta y = -\nabla_y f(x;y), \tag{18}$$

using a Cholesky factorization of the Hessian matrix, $LL' = H = \nabla^2_{yy} f(y;x)$. This factorization also reveals if the Hessian matrix is positive definite.

### 2.3 Sensitivity

Application of the implicit function theorem to (17) provides the following equation

$$\nabla^2_{yy} f(y;x) y_x = -\left[\nabla_{yx} f(y;x)\right]', \tag{19}$$

for computation of the sensitivities

$$y_x = y_x(x) = \frac{\partial y}{\partial x}(x) = \left[\nabla_x y(x)\right]'. \tag{20}$$

It is important to notice that the existing Cholesky factorization, $LL' = H = \nabla^2_{yy} f(y;x)$, can be re-used in this computation.

### 2.4 Summary

The solution

$$y = y(x) = \arg\min_y f(y;x), \tag{21}$$

to the unconstrained optimization problem is a solution of the nonlinear first-order optimality conditions (17). Its sensitivities are

$$y_x = y_x(x) = -\left[\nabla^2_{yy} f(y;x)\right]^{-1}\left[\nabla_{yx} f(y;x)\right]'. \tag{22}$$

## 3. EQUALITY CONSTRAINED OPTIMIZATION

We denote the solution to the equality constrained optimization problem

$$\min_y \quad f(y;x), \tag{23a}$$

$$s.t. \quad g(y;x) = 0, \tag{23b}$$

as

$$y = y(x) = \arg\min_y \left\{f(y;x) : \, g(y;x) = 0\right\}. \tag{24}$$

### 3.1 Optimality conditions

The Lagrangian function is

$$\mathcal{L}(y,\lambda;x) = f(y;x) - \lambda' g(y;x), \tag{25}$$

where $\lambda$ are Lagrange multipliers. The Karush-Kuhn-Tucker (KKT) conditions (first-order optimality conditions) for a minimizer of (23) require that the gradients of the Lagrangian with respect to $y$ are zero and that the equality constraints are satisfied:

$$\nabla_y \mathcal{L}(y,\lambda;x) = \nabla_y f(y;x) - \nabla_y g(y;x)\lambda = 0, \tag{26a}$$

$$g(y;x) = 0. \tag{26b}$$

### 3.2 Newton's method and the KKT-matrix

We solve the KKT conditions (26) for both the minimizer, $y$, and the Lagrange multipliers, $\lambda$. We use Newton's method. Each Newton iteration requires the solution of the linear system of equations

$$\begin{bmatrix} \nabla^2_{yy}\mathcal{L}(y,\lambda;x) & -\nabla_y g(y;x) \\ -\nabla_y g(y;x)' & 0 \end{bmatrix} \begin{bmatrix} \Delta y \\ \Delta\lambda \end{bmatrix} = -\begin{bmatrix} \nabla_y \mathcal{L}(y,\lambda;x) \\ g(y;x) \end{bmatrix}, \tag{27}$$

where the Hessian of the Lagrangian is

$$\nabla^2_{yy}\mathcal{L}(y,\lambda;x) = \nabla^2_{yy} f(y;x) - \sum_i \lambda_i \nabla^2_{yy} g_i(y;x). \tag{28}$$

The Newton update is

$$\bar{y} = y + \Delta y, \tag{29a}$$

$$\bar{\lambda} = \lambda + \Delta\lambda. \tag{29b}$$

It is possible to reformulate the linear system (27) such that its solution contains $\bar{\lambda}$ instead of $\Delta\lambda$:

$$\begin{bmatrix} \nabla^2_{yy}\mathcal{L}(y,\lambda;x) & -\nabla_y g(y;x) \\ -\nabla_y g(y;x)' & 0 \end{bmatrix} \begin{bmatrix} \Delta y \\ \bar{\lambda} \end{bmatrix} = -\begin{bmatrix} \nabla_y f(y;x) \\ g(y;x) \end{bmatrix}. \tag{30}$$

The system matrix in (27) and (30) is called the KKT matrix,

$$K = \begin{bmatrix} \nabla^2_{yy}\mathcal{L}(y,\lambda;x) & -\nabla_y g(y;x) \\ -\nabla_y g(y;x)' & 0 \end{bmatrix}. \tag{31}$$

The KKT matrix is indefinite. We therefore use an LDL factorization, $LDL' = K$, when solving (30).

### 3.3 Sensitivity equations

The sensitivity equations result from the application of the implicit function theorem to (26):

$$\begin{bmatrix} \nabla^2_{yy}\mathcal{L}(y,\lambda;x) & -\nabla_y g(y;x) \\ -\nabla_y g(y;x)' & 0 \end{bmatrix} \begin{bmatrix} y_x \\ \lambda_x \end{bmatrix} = -\begin{bmatrix} \left[\nabla^2_{yx} f(y;x)\right]' \\ \left[\nabla^2_{yx} g(y;x)\right]' \end{bmatrix}. \tag{32}$$

The solution of (32) gives the sensitivities of both the minimizer and the Lagrange multipliers,

$$y_x = y_x(x) = \frac{\partial y}{\partial x}(x) = \left[\nabla_x y(x)\right]', \tag{33a}$$

$$\lambda_x = \lambda_x(x) = \frac{\partial \lambda}{\partial x}(x) = \left[\nabla_x \lambda(x)\right]'. \tag{33b}$$

We reuse the LDL factorization of the KKT matrix from the solution of (30).

*Special case:* In the case where $f(y;x) = f(y)$ and $g(y;x) = g(y) - h(x)$, the sensitivity equations become

$$\begin{bmatrix} \nabla^2_{yy}\mathcal{L}(y,\lambda;x) & -\nabla g(y) \\ -\nabla g(y)' & 0 \end{bmatrix} \begin{bmatrix} y_x \\ \lambda_x \end{bmatrix} = \begin{bmatrix} 0 \\ h_x(x) \end{bmatrix}. \tag{34}$$

### 3.4 Summary

The solution to the equality constrained optimization problem,

$$y = y(x) = \arg\min_y \left\{f(y;x) : \, g(y;x) = 0\right\}, \tag{35}$$

is a solution to the nonlinear KKT conditions (26). The sensitivities of the solution, $y$, and the associated Lagrange multipliers, $\lambda$, are

$$\begin{bmatrix} y_x \\ \lambda_x \end{bmatrix} = \begin{bmatrix} \nabla^2_{yy}\mathcal{L}(y,\lambda;x) & -\nabla_y g(y;x) \\ -\nabla_y g(y;x)' & 0 \end{bmatrix}^{-1} \begin{bmatrix} \left[\nabla^2_{yx} f(y;x)\right]' \\ \left[\nabla^2_{yx} g(y;x)\right]' \end{bmatrix}. \tag{36}$$

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## 4. THERMODYNAMIC FUNCTIONS

The evaluation of thermodynamic functions is central to phase equilibrium computations. In this section, we discuss the relations between thermodynamic state functions, and we describe the relation between the fugacity coefficients and Gibbs energy. The methods described in Section 2 and Section 3 require the first and second order derivatives of thermodynamic functions. For that reason, Ritschel et al. (2017b, 2016) developed an open-source thermodynamic library, ThermoLib, which provides routines for evaluating the enthalpy, entropy, and volume as well as their first and second order derivatives with respect to temperature, pressure, and the composition vector. We use ThermoLib in this work. For more information on thermodynamic functions, we refer the reader to introductory texts on chemical engineering thermodynamics by Smith et al. (2005), Gmehling et al. (2012), Koretsky (2014), and Walas (1985).

### *4.1 Gibbs energy and thermodynamic functions*

The temperature, $T$, pressure, $P$, and phase composition vector, $n$, completely specify a phase. The thermodynamic model in ThermoLib provides expressions for enthalpy, entropy, and volume:

$$H = H(T, P, n), \tag{37a}$$
$$S = S(T, P, n), \tag{37b}$$
$$V = V(T, P, n). \tag{37c}$$

We compute the remaining thermodynamic functions, internal energy, Gibbs energy, and Helmholtz energy, from the fundamental thermodynamic relations,

$$U = U(T, P, n) = H(T, P, n) - PV(T, P, n), \tag{38a}$$
$$G = G(T, P, n) = H(T, P, n) - TS(T, P, n), \tag{38b}$$
$$A = A(T, P, n) = U(T, P, n) - TS(T, P, n). \tag{38c}$$

When Gibbs energy is expressed as a function of its canonical variables, $(T, P, n)$, it plays the role of a *generating function*, i.e. all other thermodynamic functions can be computed from it by simple mathematical operations such as differentiation and elementary algebra. Therefore, Gibbs energy implicitly represents *complete* property information:

$$H = H(T, P, n) = G(T, P, n) - T\frac{\partial G}{\partial T}(T, P, n), \tag{39a}$$
$$S = S(T, P, n) = -\frac{\partial G}{\partial T}(T, P, n), \tag{39b}$$
$$V = V(T, P, n) = \frac{\partial G}{\partial P}(T, P, n). \tag{39c}$$

### *4.2 Chemical potential*

We introduce the chemical potential in order to define the fugacity. The chemical potential of component $i$ in a mixture is the partial derivative of the Gibbs energy of that mixture with respect to the $i$'th mole number:

$$\mu_i(T, P, n) = \frac{\partial G}{\partial n_i}(T, P, n). \tag{40}$$

The definition of the fugacity of component $i$ involves 1) the $i$'th chemical potential of an ideal gas mixture, $\mu_i^{ig}(T, P, n) = \partial G^{ig}/\partial n_i(T, P, n)$, and 2) the chemical potential of a pure component ideal gas that only contains $n_i$ moles of component $i$, $\mu_i^{pc,ig}(T, P, n_i) = \partial G_i^{pc,ig}/\partial n_i(T, P, n_i)$. The latter is independent of the mole number, i.e. $\mu_i^{pc,ig}(T, P, n_i) = \mu_i^{pc,ig}(T, P)$. The $i$'th chemical potential of an ideal gas mixture is

$$\mu_i^{ig}(T, P, n) = \frac{\partial G^{ig}}{\partial n_i}(T, P, n) = \mu_i^{pc,ig}(T, P_0) + RT \ln \frac{z_i P}{P_0}, \tag{41}$$

where $P_0$ is a reference pressure, and $z_i = n_i / \sum_i n_i$ is the mole fraction of component $i$.

### *4.3 Fugacity*

The fugacity is implicitly defined such that the chemical potential of nonideal mixtures, $\mu_i(T, P, n)$, is given by the right-hand side of (41) where the fugacity, $f_i(T, P, n)$, replaces $z_i P$:

$$\begin{aligned}\mu_i(T, P, n) &= \frac{\partial G}{\partial n_i}(T, P, n) \\ &= \mu_i^{pc,ig}(T, P_0) + RT \ln \frac{f_i(T, P, n)}{P_0}.\end{aligned} \tag{42}$$

We subtract (41) from (42):

$$RT \ln \frac{f_i(T, P, n)}{z_i P} = \frac{\partial}{\partial n_i}\left(G(T, P, n) - G^{ig}(T, P, n)\right). \tag{43}$$

The difference between the actual Gibbs energy of a mixture and the Gibbs energy of that mixture if it was an ideal gas is defined as the residual Gibbs energy, $G^R(T, P, n) = G(T, P, n) - G^{ig}(T, P, n)$. We also introduce the fugacity coefficients, $\phi_i(T, P, n) = f_i(T, P, n)/(z_i P)$. With these two definitions, we obtain the following expression for the logarithm of the fugacity coefficients:

$$\ln \phi_i(T, P, n) = \frac{1}{RT}\frac{\partial G^R}{\partial n_i}(T, P, n). \tag{44}$$

The fugacity coefficients play an important role in isothermal and isobaric (constant temperature and pressure) vapor-liquid equilibrium problems as we discuss in Section 6. The logarithm of the fugacity coefficients of ideal gas mixtures are by definition zero, i.e. $\ln \phi_i^{ig}(T, P, n^v) = 0$. For ideal liquid mixtures, the logarithm of the fugacity coefficients are (Ritschel and Jørgensen, 2017)

$$\ln \phi_i^{id}(T, P, n^l) = \frac{P_i^{sat}(T)}{P} \exp\left(\frac{v_i^l(T)(P - P_i^{sat}(T))}{RT}\right). \tag{45}$$

$v_i^l(T)$ is the liquid volume, and $P_i^{sat}(T)$ is the saturation pressure. We see that the ideal liquid fugacity coefficients are independent of composition, i.e. $\ln \phi_i^{id}(T, P, n^l) = \ln \phi_i^{id}(T, P)$. ThermoLib uses cubic equations of state for nonideal mixtures. It is outside the scope of this work to describe the corresponding fugacity coefficients. However, both Ritschel et al. (2016) and Ritschel and Jørgensen (2017) provide expressions for them.

## 5. FLASH PROBLEMS

Table 1 shows the specified variables, the state function that is minimal at equilibrium, and relevant types of models for different flash problems (Paterson, 2017). We demonstrate that the UV-, the TV-, and the PT-flash problems can be formulated as unconstrained (15) and

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Table 1. Examples of flash problems

| Spec. | State function | Example of relevant model |
|---|---|---|
| $(P,T)$ | $G$ | Isothermal-isobaric steady-state flow |
| $(T,V)$ | $A$ | Isothermal unsteady-state flow |
| $(P,H)$ | $-S$ | Thermal steady-state flow |
| $(U,V)$ | $-S$ | Thermal unsteady-state flow |
| $(P,S)$ | $H$ | Reversible expansion/compression |

constrained (23) optimization problems (Michelsen, 1999; Michelsen and Mollerup, 2007). We use a single-stage dynamic model to illustrate the use of the flash problems in dynamic models. Typically, more complex models can be formulated as interconnected single-stage models. The PT-flash is of particular interest because 1) it can be formulated as unconstrained optimization, and 2) other types of flash problems are equivalent to a combination of algebraic constraints and the PT-flash. The PT-flash is therefore often used in unsteady-state computations using a nested approach. We discuss both of these aspects.

### 5.1 UV-flash problem

The UV-flash problem is considered difficult to solve (Saha and Carroll, 1997; Castier, 2009). However, it is a key component in rigorous models of vapor-liquid equilibrium processes such as fluid vessels (Castier, 2010), distillation columns (Flatby et al., 1994), and thermal- and compositional oil recovery. We consider a single-stage model, essentially a fluid vessel, that contains a vapor-liquid mixture. A feed stream ($f$) supplies mass, and therefore energy, to the mixture. A vapor stream ($v$) and a liquid stream ($l$) extract mass and energy from the mixture. Furthermore, a heat input, $Q$, supplies energy to the mixture. The mass and energy conservation equations are

$$\dot{n}_i = f_i - l_i - v_i, \tag{46a}$$

$$\dot{U} = H_f - H_l - H_v + Q, \tag{46b}$$

where $n_i$ is the moles of component $i$, and $U$ is the internal energy of the mixture. The mixture temperature, $T$, pressure, $P$, and vapor-liquid composition, $n^v$ and $n^l$, completely specify the vapor-liquid streams, i.e.

$$l_i = l_i(T, P, n^l), \tag{47a}$$

$$v_i = v_i(T, P, n^v), \tag{47b}$$

and

$$H_l = H_l(T, P, n^l), \tag{48a}$$

$$H_v = H_v(T, P, n^v). \tag{48b}$$

We assume that the vapor phase and the liquid phase are in equilibrium at all times. The conservation equations (46) specify the internal energy, $U$, and the total moles of each chemical component, $n$. The volume of the tank, $V$, is fixed. $U$, $V$, and $n$ completely specify the temperature, $T$, pressure, $P$, and phase compositions of the vapor-liquid mixture, $n^v$ and $n^l$. That is because the second law of thermodynamics states that the entropy, $S$, of a closed system is maximal at equilibrium, or equivalently that $-S$ is minimal:

$$\min_{T,P,n^v,n^l} \quad -S = -\left(S^v(T,P,n^v) + S^l(T,P,n^l)\right), \tag{49a}$$

$$s.t. \quad U^v(T,P,n^v) + U^l(T,P,n^l) = U, \tag{49b}$$

$$V^v(T,P,n^v) + V^l(T,P,n^l) = V, \tag{49c}$$

$$n_i^v + n_i^l = n_i, \quad i = 1,\ldots,N_C. \tag{49d}$$

We use the linear mass balance constraint (49d) to eliminate the liquid mole numbers, $n^l = n - n^v$:

$$\min_{T,P,n^v} \quad -S = -\left(S^v(T,P,n^v) + S^l(T,P,n-n^v)\right), \tag{50a}$$

$$s.t. \quad U^v(T,P,n^v) + U^l(T,P,n-n^v) = U, \tag{50b}$$

$$V^v(T,P,n^v) + V^l(T,P,n-n^v) = V. \tag{50c}$$

### 5.2 TV-flash problem

We again consider the single-stage model (46). We assume that the internal energy is constant:

$$\dot{n}_i = f_i - l_i - v_i, \tag{51a}$$

$$\dot{U} = H_f - H_l - H_v + Q = 0. \tag{51b}$$

The dynamic equations therefore only consist of the mass conservation equations:

$$\dot{n}_i = f_i - l_i - v_i. \tag{52}$$

The condition of constant internal energy requires that the heat input precisely matches the difference between the enthalpies of the feed and the vapor-liquid streams:

$$Q = H_l + H_v - H_f = \Delta H. \tag{53}$$

When the temperature is constant, the condition of maximal entropy is equivalent to a condition of minimal Helmholtz energy, $A$:

$$\min_{P,n^v,n^l} \quad A = A^v(T,P,n^v) + A^l(T,P,n^l), \tag{54a}$$

$$s.t. \quad V^v(T,P,n^v) + V^l(T,P,n^l) = V, \tag{54b}$$

$$n_i^v + n_i^l = n_i, \quad i = 1,\ldots,N_C. \tag{54c}$$

$T$, $V$, and $n$ therefore completely specify $P$, $n^v$, and $n^l$. Again, we eliminate the liquid mole numbers:

$$\min_{P,n^v} \quad A = A^v(T,P,n^v) + A^l(T,P,n-n^v), \tag{55a}$$

$$s.t. \quad V^v(T,P,n^v) + V^l(T,P,n-n^v) = V. \tag{55b}$$

### 5.3 PT-flash problem

We consider the single-stage model (46) again. Isothermal and isobaric processes (constant temperature and pressure) are relevant to steady state processes:

$$\dot{n}_i = f_i - l_i - v_i = 0, \tag{56a}$$

$$\dot{U} = H_f - H_l - H_v + Q = 0. \tag{56b}$$

The heat input exactly matches the difference in enthalpy of the feed and the vapor-liquid streams,

$$Q = H_l + H_v - H_f = \Delta H, \tag{57}$$

and the molar flow rates of the vapor-liquid streams exactly match those of the feed stream:

$$l_i + v_i = f_i. \tag{58}$$

The condition of maximal entropy is equivalent to a condition of minimal Gibbs energy when both temperature and pressure are constant:

$$\min_{n^v,n^l} \quad G = G^v(T,P,n^v) + G^l(T,P,n^l), \tag{59a}$$

$$s.t. \quad n_i^v + n_i^l = n_i, \quad i = 1,\ldots,N_C. \tag{59b}$$

$T$, $P$, and $n$ thus completely specify $n^v$ and $n^l$. We eliminate the liquid mole numbers and obtain an unconstrained minimization problem:

$$\min_{n^v} G = G^v(T,P,n^v) + G^l(T,P,n-n^v). \tag{60}$$

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### 5.4 Equivalence of different flash problems

The UV-flash problem (50) is equivalent to a combination of the PT-flash (60) and constraints on $U$ and $V$ as in (50b)-(50c). The UV constraints are thereby effectively moved outside of the optimization problem at the cost of changing the objective function. The VT flash problem (55) is also equivalent to the PT-flash (60) combined with a constraint on $V$ as in (55b). That means that it is possible to solve UV- and TV-flash problems with unconstrained optimization methods. It also means that existing software for PT-flash problems can be reused when solving the more complex flash problems.

## 6. THE RACHFORD-RICE EQUATIONS

The Rachford-Rice equations are often used to solve PT-flash problems. We outline the associated computation and the computations of the needed sensitivities.

### 6.1 Vapor-liquid equilibrium constant

The PT-flash problem can be formulated as the unconstrained optimization problem

$$\min_{n^v} G = G^v(T,P,n^v) + G^l(T,P,n-n^v), \tag{61}$$

for which the first-order optimality conditions are

$$\frac{\partial G}{\partial n_i^v} = \frac{\partial G^v}{\partial n_i^v}(T,P,n^v) - \frac{\partial G^l}{\partial n_i^l}(T,P,n^l) = 0, \tag{62}$$

for all $i$ and with the liquid phase mole numbers being $n^l = n - n^v$. The chemical potentials of the vapor and liquid phases are defined as

$$\mu_i^v(T,P,n^v) = \frac{\partial G^v}{\partial n_i^v}(T,P,n^v), \tag{63a}$$

$$\mu_i^l(T,P,n^l) = \frac{\partial G^l}{\partial n_i^l}(T,P,n^l). \tag{63b}$$

The equilibrium conditions (62) are therefore

$$\mu_i^v(T,P,n^v) = \mu_i^l(T,P,n^l). \tag{64}$$

Because of the definition of the fugacities (42), the condition of equal chemical potentials (64) is equivalent to

$$f_i^v(T,P,n^v) = f_i^l(T,P,n^l). \tag{65}$$

Let $x_i = n_i^l/\sum_i n_i^l$ and $y_i = n_i^v/\sum_i n_i^v$ be the mole fractions of the liquid and vapor phase, respectively. Because of the definition of the fugacity coefficients, the equality of fugacities (65) is equivalent to $\phi_i^v(T,P,n^v)y_iP = \phi_i^l(T,P,n^l)x_iP$ or equivalently

$$\phi_i^v(T,P,n^v)y_i = \phi_i^l(T,P,n^l)x_i. \tag{66}$$

The equilibrium constants (sometimes referred to as equilibrium ratios) are defined as $K_i = y_i/x_i$. We use (66) to derive an expression for the equilibrium constants:

$$K_i(T,P,n^v,n^l) = \frac{y_i}{x_i} = \frac{\phi_i^l(T,P,n^l)}{\phi_i^v(T,P,n^v)}. \tag{67}$$

### 6.2 The Rachford-Rice method - Ideal vapor-liquid mixture

For mixtures of an ideal gas and an ideal liquid, the vapor liquid equilibrium constant defined by (67) is

$$K_i = K_i(T,P) = \frac{P_i^{sat}(T)}{P}\exp\left(\frac{v_i^l(T)(P-P_i^{sat}(T))}{RT}\right). \tag{68}$$

In that case, the vapor-liquid equilibrium constant is independent of composition and depends only on temperature, $T$, and pressure, $P$, but not on the compositions of the liquid and vapor mixture. Define $z_i = n_i/\sum_i n_i$ such that $n_i^l + n_i^v = n_i$ can be expressed as

$$(1-\beta)x_i + \beta y_i = z_i, \tag{69}$$

where $\beta$ is the vapor fraction defined as

$$\beta = \frac{\sum_i n_i^v}{\sum_i n_i}. \tag{70}$$

The relation (69) and $K_i = y_i/x_i$ imply that

$$\begin{aligned} z_i &= (1-\beta)x_i + \beta y_i \\ &= (1-\beta)x_i + \beta K_i x_i = (1+\beta(K_i-1))\,x_i, \end{aligned} \tag{71}$$

such that

$$x_i = \frac{1}{1+\beta(K_i-1)}z_i, \tag{72a}$$

$$y_i = K_i x_i = \frac{K_i}{1+\beta(K_i-1)}z_i. \tag{72b}$$

This implies that

$$n_i^l = x_i(1-\beta)\sum_i n_i = \frac{1-\beta}{1+\beta(K_i-1)}n_i, \tag{73a}$$

$$n_i^v = y_i\beta\sum_i n_i = \frac{\beta K_i}{1+\beta(K_i-1)}n_i. \tag{73b}$$

The relations $\sum_i x_i = \sum_i y_i = 1$ imply that $\sum_i(y_i - x_i) = 0$. By combination of this observation and (72), we obtain the following relation

$$\begin{aligned} f(\beta) &= \sum_i (y_i - x_i) = \sum_i (K_i - 1)\,x_i \\ &= \sum_i \frac{K_i - 1}{1+\beta(K_i-1)}z_i = 0, \end{aligned} \tag{74}$$

for computation of $\beta$. The derivative of this function is

$$f'(\beta) = -\sum_i \left[\frac{K_i-1}{1+\beta(K_i-1)}\right]^2 z_i \le 0. \tag{75}$$

Newton's method for determination of $\beta$ is

$$\beta_{k+1} = \beta_k - \frac{f(\beta_k)}{f'(\beta_k)}. \tag{76}$$

When $\beta$ has been computed, we compute the vapor composition, $n_i^v$, from (73b) and the liquid composition from $n_i^l = n_i - n_i^v$.

*Sensitivity:* The vapor fraction is a function of temperature, pressure, and total composition, i.e. $\beta = \beta(K,n) = \beta(K(T,P),n) = \beta(T,P,n)$. The sensitivities of $\beta$ are

$$\frac{\partial\beta}{\partial T} = \sum_i \frac{\partial\beta}{\partial K_i}\frac{\partial K_i}{\partial T}, \tag{77a}$$

$$\frac{\partial\beta}{\partial P} = \sum_i \frac{\partial\beta}{\partial K_i}\frac{\partial K_i}{\partial P}, \tag{77b}$$

$$\frac{\partial\beta}{\partial n_j} = \sum_i \frac{\partial\beta}{\partial z_i}\frac{\partial z_i}{\partial n_j}, \tag{77c}$$

where

$$\frac{\partial\beta}{\partial K_i} = -\frac{\frac{\partial f}{\partial K_i}}{f'(\beta)}, \qquad \frac{\partial\beta}{\partial z_i} = -\frac{\frac{\partial f}{\partial z_i}}{f'(\beta)}. \tag{78}$$

Similarly, the vapor-liquid mole numbers, $n_i^v$ and $n_i^l$, are functions of temperature, pressure, and total composition,

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i.e. $n^v = n^v(\beta, K, n) = n^v(\beta(T, P, n), K(T, P), n) = n^v(T, P, n)$ and $n^l = n^l(n^v, n) = n^l(n^v(T, P, n), n) = n^l(T, P, n)$. In order to describe the sensitivities of $n^l$ and $n^v$, we introduce the auxiliary variables

$$\tau_i = \frac{1}{1 + \beta(K_i - 1)}, \tag{79a}$$

$$\gamma_i = K_i n_i - (K_i - 1) n_i^v. \tag{79b}$$

The sensitivities of the vapor mole numbers are

$$\frac{\partial n_i^v}{\partial T} = \tau_i \left( \frac{\partial \beta}{\partial T} \gamma_i + \beta \frac{\partial K_i}{\partial T} (n_i - n_i^v) \right), \tag{80a}$$

$$\frac{\partial n_i^v}{\partial P} = \tau_i \left( \frac{\partial \beta}{\partial P} \gamma_i + \beta \frac{\partial K_i}{\partial P} (n_i - n_i^v) \right), \tag{80b}$$

$$\frac{\partial n_i^v}{\partial n_j} = \tau_i \left( \frac{\partial \beta}{\partial n_j} \gamma_i + \beta K_i \delta_{ij} \right), \tag{80c}$$

and the sensitivities of the liquid mole numbers are

$$\frac{\partial n_i^l}{\partial T} = -\frac{\partial n_i^v}{\partial T}, \tag{81a}$$

$$\frac{\partial n_i^l}{\partial P} = -\frac{\partial n_i^v}{\partial P} \tag{81b}$$

$$\frac{\partial n_i^l}{\partial n_j} = \delta_{ij} - \frac{\partial n_i^v}{\partial n_j}. \tag{81c}$$

$\delta_{ij}$ is Kronecker's delta, i.e. $\delta_{ij} = 1$ if $i = j$ and 0 if $i \neq j$.

## 7. NUMERICAL EXAMPLE

In this section, we solve the UV-, TV-, and PT-flash problems for different values of the specified variables. We consider a mixture of 60% $C_1$, 8% $C_2$, 5% $C_3$, 25% n-$C_7$, and 2% $CO_2$. Figure 1 shows the solutions to the flash problems (in blue and red) in a phase diagram and as functions of the specified variables. The vapor fraction is constant along the black and gray curves. The curves meet at the critical point which is located around 425 K and 16.3 MPa. The upper and the lower black curves are the bubble-point ($\beta = 0$) and the dew-point ($\beta = 1$) curves, which together constitute the phase envelope. Ritschel and Jørgensen (2017) describe the computation of the isoparametric (constant vapor fraction) curves. The vapor fraction of the curves increases in steps of 0.1 starting from the bubble-point curve and ending in the dew-point curve. The vapor fraction depends nonlinearly on the specified variables. The pressure exhibits an inverse relationship with volume. The remaining variables are close to linear in the specified variables for this example.

## 8. CONCLUSION

We describe how the solution to the phase equilibrium problem enters into dynamic and steady-state simulations for both nested and simultaneous formulations. We formulate the phase equilibrium problems as optimization problems and present methods for their solution and computation of the needed sensitivities. In particular, we describe the UV-, and the TV-flash problems which are relevant to thermal and isothermal compositional reservoir flow models, respectively. We also describe the commonly used PT-flash and its relation to the other types of flash problems. Finally, using a numerical example, we illustrate how the solutions to the UV-, TV-, and PT-flash problems depend on the specified variables.

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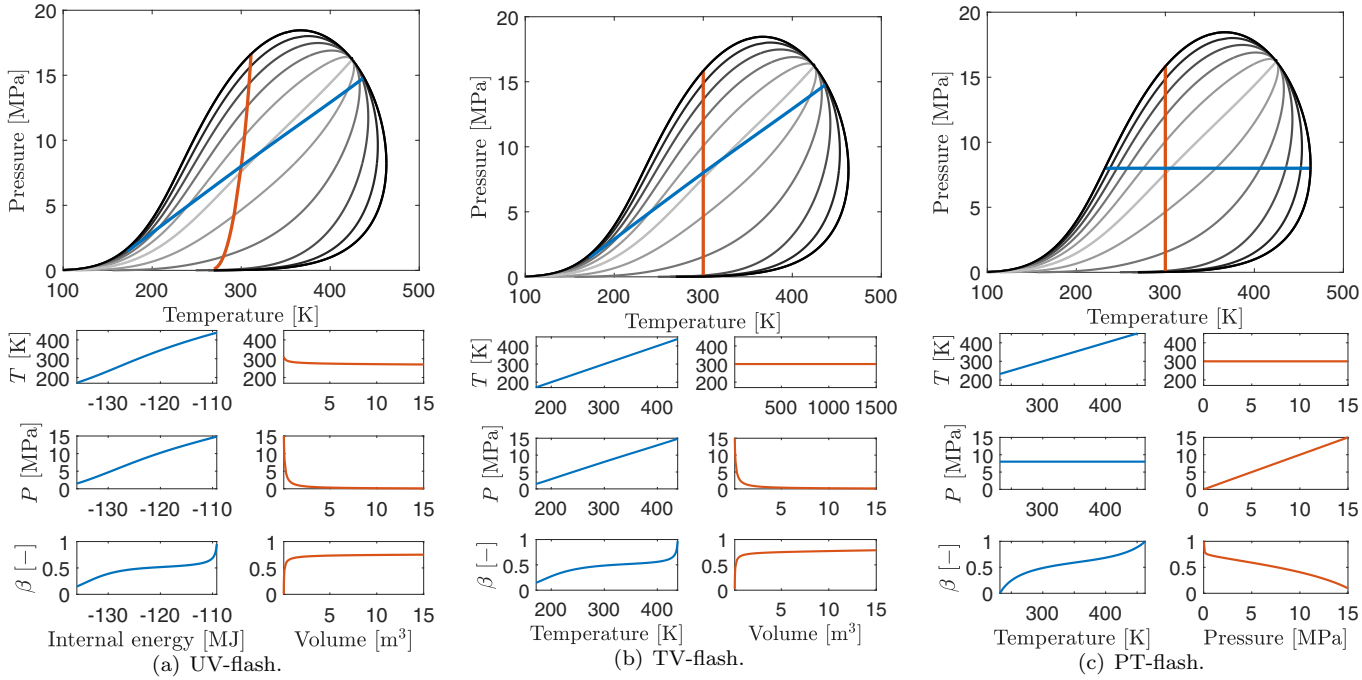


(a) UV-flash. (b) TV-flash. (c) PT-flash.

Fig. 1. Solutions to UV-, TV-, and PT-flash problems for a mixture of $C_1$-$C_3$, $C_7$, and $CO_2$.


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