

Memo

Thermodynamic equilibrium algorithms - Reimplemented in a new framework.

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1 Introduction

In the project CO₂ Dynamics, the overall aim is to provide knowledge about safe and efficient design and operation of CO₂-pipeline transport and injection systems. To achieve this, models capable of predicting the thermophysical properties of multiphase CO₂-mixtures are needed. Since evaluation of transient CO₂-pipeline operation is made with fluid dynamical models connected to thermodynamic models and phase-calculations, a high degree of robustness and accuracy is necessary for numerical stability. State-of-the-art algorithms are thus needed for the phase calculations. Another reason to implement the best routines for phase-calculations is the need of a flexible framework capable of handling multiple liquid-phases and solids such as dry-ice. The latest algorithms proposed by [Michelsen and Mollerup \(2007\)](#) have been implemented as part of the development of the new flexible workbench for thermodynamics, called ThermoPack, documented in the Memo DA1201. The underlying equations and algorithms used to solve the phase equilibrium between two-phase vapour and liquid with specified temperature and pressure (*TP*-flash), specified enthalpy and pressure (*HP*-flash) and specified entropy and pressure (*SP*-flash) will be described.

Many systems in CCS contain several phases. [Austegard et al. \(2006\)](#) for instance, investigated thermodynamic models for H₂O-CO₂-CH₄ mixtures. In their Fig. 8, for the system H₂O-CO₂-CH₄ at 298K, a three-phase system occurs between 70-72 bar in which one water rich liquid-phase forms, one CO₂ rich liquid-phase forms and a CH₄ rich vapour-phase is formed. To be able to predict when a CO₂-rich system will consist of several liquid-phases and also to calculate the composition of them, a multiphase flash routine has been implemented in ThermoPack. In this memo, it will be shown that the implementation can successfully predict phase-diagrams with more than one liquid phase for two relevant mixtures.

All the code has been implemented in a Fortran 90/95-syntax and a Mercurial version control has been used to track changes and merge the developments in the source-code of ThermoPack. The same test functionality in the COTT-code developed in Task B and C of this project has been used to test the code. To have an active and up-to-date documentation, comments have been added in a syntax used by the popular program Doxygen. The algorithms and equations used may be found in Section 2. Results from tests and comparisons are located in Section 4, while conclusions and suggestions for further work can be found in Section 5.

2 Algorithms and equations

2.1 Chemical potential

Chemical potential, μ , of a fluid, i , with composition z_i , is given by the following equation,

$$\frac{\partial G}{\partial n_i} = \mu_i = \mu_i^0 + RT \ln\left(\frac{f_i}{P^0}\right) \quad (1)$$

$$f_i = z_i \varphi_i P \quad (2)$$

Where f is the fugacity and φ is the fugacity factor.

2.2 Wilson-K factors

Wilson-K factors are used as initial values in the TP -flash, and are given as

$$K_i^{Wilson} = \frac{P_i^c}{P} \exp\left(5.373(1 + \omega_i)\left(1 - \frac{T_i^c}{T}\right)\right). \quad (3)$$

P^c , T^c and ω are component specific parameters.

2.3 Phase stability

Phase stability is calculated using the tangent plane criterion method, as described by [Michelsen and Mollerup \(2007\)](#).

The modified tangent plane criterion is given as

$$t_{Mod}(\mathbf{W}) = 1.0 + \sum_i W_i (\ln W_i + \ln \varphi(\mathbf{W}) - d_i - 1), \quad (4)$$

$$d_i = \ln z_i + \ln \varphi(\mathbf{z}) \quad (5)$$

$$(6)$$

For the two-phase TP -flash, \mathbf{z} , is the overall composition, feed. For a multiphase flash, \mathbf{z} initially is the feed, but as more phases are added, \mathbf{z} is one of the equilibrium phases.

The optimisation problem (modified tangent plane criterion) is solved by first trying successive substitution, and switching to a Newton-Raphson solver if it fails to converge in 3 iterations.

2.3.1 Successive substitution

The successive substitution approach used to solve the modified tangent plane criterion is given by Equation 7.

$$\ln W_i^{(k+1)} = d_i - \ln \varphi_i(\mathbf{W}^{(k)}) \quad (7)$$

2.3.2 Newton-Raphson solver

In order to solve the modified tangent plane criterion using a Newton-Raphson, a variable transformation is introduced,

$$\boldsymbol{\alpha} = 2\sqrt{\mathbf{W}}. \quad (8)$$

The differential of the modified tangent plane criterion then becomes:

$$g_i = \frac{\partial t_{Mod}}{\partial \alpha_i} = \sqrt{W_i} (\ln W_i + \ln \varphi(\mathbf{W}) - d_i), \quad (9)$$

$$H_{ij} = \frac{\partial g_i}{\partial \alpha_j} = \delta_{ij} + \sqrt{W_i W_j} \Phi_{ij} + \frac{1}{2} (\ln W_i + \ln \varphi(\mathbf{W}) - d_i), \quad (10)$$

$$\Phi_{ij} = \frac{\partial \ln \varphi_i}{\partial W_j}, \quad (11)$$

$$\delta_{ij} = \begin{cases} 1 & i = j \\ 0 & i \neq j \end{cases}. \quad (12)$$

We see that $\ln W_i + \ln \varphi(\mathbf{W}) - d_i$ will be zero at the solution of the tangent plane minimisation. It can therefore be removed from the second derivative, without affecting the convergence properties.

2.4 The two-phase TP -flash

The two-phase TP -flash is solved as follows:

- Initialise a two phase mixture, using the Wilson K -factors.
- Try solving the Rachford-Rice equation in 10 iterations.
- If no solution found do stability check. If single phase stable exit. Otherwise switch to Newton-Raphson solver.

2.4.1 Rachford-Rice

The Rachford-Rice equation to be solved:

$$g(\beta) = \sum_i^n (y_i - x_i) = \sum_i^n \frac{z_i(K_i - 1)}{1 - \beta + \beta K_i} = 0. \quad (13)$$

g is a monotonous function in β , and is solved using a Newton-Raphson method combined with bracketing.

$$\frac{\partial g}{\partial \beta} = -\sum_i^n z_i \left(\frac{K_i - 1}{1 - \beta + \beta K_i} \right)^2 < 0. \quad (14)$$

To avoid problems for $\beta \approx 1.0$, the problem is instead solved for $1.0 - \beta$.

The TP -flash is converged using successive substitution for the K -values. In order to speed up the convergence, a dominant eigenvalue method is used.

2.4.2 Newton-Raphson solver

The objective function, $f_{T,P}$, is the dimensionless change in Gibbs energy when splitting the single phase feed, \mathbf{z} , in a liquid, ℓ , and gas, \mathbf{v} , phase.

$$f_{T,P} = \frac{\Delta G}{RT} = \frac{\sum_i v_i \mu_i^g + \sum_i l_i \mu_i^\ell - \sum_i z_i \mu_i^z}{RT} = \sum_i v_i \ln(y_i \varphi_i^g) + l_i \ln(x_i \varphi_i^\ell) - z_i \ln(z_i \varphi_i^z) \quad (15)$$

φ_i^z is the single phase solution with the smallest Gibbs free energy. A requirement for a stable two-phase split, is a negative $f_{T,P}$.

The differential of $f_{T,P}$ is

$$g_i = \frac{\partial f_{T,P}}{\partial v_i} = \ln \frac{y_i}{x_i} + \ln \varphi_i^g - \ln \varphi_i^\ell. \quad (16)$$

The second differential of $f_{T,P}$ is

$$H_{ij} = \frac{\partial g_i}{\partial v_j} = \frac{1}{\beta(1 - \beta)} \left(\frac{z_i}{x_i y_i} \delta_{ij} - 1 + \beta \Phi_{ij}^\ell + (1 - \beta) \Phi_{ij}^g \right), \quad (17)$$

$$\Phi_{ij} = \frac{\partial \ln \varphi_i}{\partial v_j}, \quad (18)$$

$$\delta_{ij} = \begin{cases} 1 & i = j \\ 0 & i \neq j \end{cases}. \quad (19)$$

2.5 The multiphase TP -flash

If we use three phase LLV as an example, the multi-phase TP -flash problem can be illustrated. Assuming a gas composition, \mathbf{w} , and the liquid phase compositions, \mathbf{l} and \mathbf{v} . The overall composition is \mathbf{z} .

The equilibrium condition then become:

$$\min g_l(\mathbf{l}) + g_w(\mathbf{w}) + g_v(\mathbf{v}) \quad (20)$$

$$\text{st. } \mathbf{z} - \mathbf{w} - \mathbf{l} - \mathbf{v} = 0 \quad (21)$$

Where the Gibbs energies are given as:

$$g_x(\mathbf{x}) = \sum_i^n x_i \mu_i(\mathbf{x}). \quad (22)$$

It is common practice to remove the linear constraints by substituting then into the nonlinear Gibbs equations. Here \mathbf{w} is removed:

$$\min g_l(\mathbf{l}) + g_w(\mathbf{z} - \mathbf{l} - \mathbf{v}) + g_v(\mathbf{v}). \quad (23)$$

The overall phase fractions are defined as follows:

$$W = \sum_i^n w_i, \quad L = \sum_i^n l_i, \quad V = \sum_i^n v_i. \quad (24)$$

Differentiating the objective functions, $g = g_l + g_w + g_v$, with respect to \mathbf{l} and \mathbf{v} :

$$\frac{\partial g}{\partial l_i} = \frac{\partial g^l}{\partial l_i} + \frac{\partial g^w}{\partial w_i} \frac{\partial w_i}{\partial l_i} = \frac{\partial g^l}{\partial l_i} - \frac{\partial g^w}{\partial w_i} = \ln\left(\frac{l_i \varphi_i^l}{L}\right) - \ln\left(\frac{w_i \varphi_i^w}{W}\right) \quad (25)$$

$$\frac{\partial g}{\partial v_i} = \frac{\partial g^v}{\partial v_i} + \frac{\partial g^w}{\partial w_i} \frac{\partial w_i}{\partial v_i} = \frac{\partial g^v}{\partial v_i} - \frac{\partial g^w}{\partial w_i} = \ln\left(\frac{v_i \varphi_i^v}{V}\right) - \ln\left(\frac{w_i \varphi_i^w}{W}\right) \quad (26)$$

Differentiating once more to get the Hessian:

$$\frac{\partial^2 g}{\partial l_i^2} = \frac{1}{l_i} - \frac{1}{L} + \frac{\partial \ln \varphi_i^l}{\partial l_i} + \frac{1}{w_i} - \frac{1}{W} + \frac{\partial \ln \varphi_i^w}{\partial w_i} \quad (27)$$

$$\frac{\partial^2 g}{\partial v_i^2} = \frac{1}{v_i} - \frac{1}{V} + \frac{\partial \ln \varphi_i^v}{\partial v_i} + \frac{1}{w_i} - \frac{1}{W} + \frac{\partial \ln \varphi_i^w}{\partial w_i} \quad (28)$$

$$\frac{\partial^2 g}{\partial l_i \partial v_i} = \frac{\partial^2 g}{\partial v_i \partial l_i} = \frac{1}{w_i} - \frac{1}{W} + \frac{\partial \ln \varphi_i^w}{\partial w_i} \quad (29)$$

We see from Equation 29 that a small w_i will give an ill-conditioned Hessian. At the same time the calculation of w_i will be prone to numerical error,

$$w_i = z_i - l_i - v_i, \quad (30)$$

because we are subtracting numbers that are almost equal to get a much smaller number.

The suggested way to handle the numerical issues, are to select the dependent variables as:

$$d_i = \max_{k \in 1 \dots F} n_i^k. \quad (31)$$

This introduce considerable administrative effort when calculation the Hessian.

2.5.1 Dropping phase from flash iterations

The phase with the smallest phase fraction, j_{\min} , is combined with all the other phases one by one. If one combination, $j_{\min} + k$, gives a reduction in Gibbs energy, the j_{\min} phase is removed. The removed phase is added to phase k .

2.5.2 The multiphase TP -flash – Successive substitution

The multiphase Rachford-Rice equation to be solved,

$$q(\boldsymbol{\beta}, \mathbf{z}) = \sum_k^F \beta_k - \sum_i^n z_i \ln E_i, \quad E_i = \sum_k^F \frac{\beta_k}{\varphi_{ik}} \quad (32)$$

The equation is constrained by $\beta_k \geq 0$.

The gradient vector elements of q ,

$$g_k = \frac{\partial q}{\partial \beta_k} = 1 - \sum_i^n \frac{z_i}{E_i \varphi_{ik}}. \quad (33)$$

The Hessian matrix elements of q ,

$$H_{kl} = \frac{\partial g_k}{\partial \beta_l} = \sum_i^n \frac{z_i}{E_i^2 \varphi_{il} \varphi_{ik}} \quad (34)$$

The minimum condition for the Rachford-Rice equation are:

$$g_k = 0, \quad \beta_k > 0 \quad \text{or} \quad g_k > 0, \quad \beta_k = 0 \quad (35)$$

2.5.3 Initial guess

The multiphase flash generates initial guesses for the \mathbf{K} -values by testing the stability of a pure liquid and a pure gas. If the stability calculation for gas is negative, $\text{tm}_g < 0$, we will get a phase with fugacity coefficients $\boldsymbol{\varphi}_g^{\text{tm}}$. The single phase fugacity coefficient with the minimum Gibbs energy is denoted: $\boldsymbol{\varphi}_z^{\text{gmin}}$. The \mathbf{K} -values are calculated from the results of the stability calculations.

$$\mathbf{K} = \begin{cases} \boldsymbol{\varphi}_\ell^{\text{tm}} / \boldsymbol{\varphi}_g^{\text{tm}} & \text{tm}_\ell < 0 \ \& \ \text{tm}_g < 0 \\ \boldsymbol{\varphi}_\ell^{\text{tm}} / \boldsymbol{\varphi}_z^{\text{gmin}} & \text{tm}_\ell < 0 \ \& \ \text{tm}_g \geq 0 \\ \boldsymbol{\varphi}_z^{\text{gmin}} / \boldsymbol{\varphi}_g^{\text{tm}} & \text{tm}_\ell \geq 0 \ \& \ \text{tm}_g < 0 \\ \mathbf{K}^{\text{Wilson}} & \text{otherwise} \end{cases} \quad (36)$$

2.5.4 Phase stability

Trial compositions for the stability analysis. Liquid trials are given the subscript, ℓ , and the gas trial phase is given the subscript, g . If as gas phase is already present, the gas trial is omitted.

$$\mathbf{w}_g = \mathbf{x} \boldsymbol{\varphi}_x, \quad (37)$$

$$\mathbf{w}_{\ell,1} = (1, 0, \dots, 0)^T, \quad (38)$$

$$\vdots \quad (39)$$

$$\mathbf{w}_{\ell,n} = (0, 0, \dots, 1)^T, \quad (40)$$

$$\mathbf{w}_{\ell,n+1} = \mathbf{z}. \quad (41)$$

$$(42)$$

Where \mathbf{x} is one of the phases already found.

2.5.5 Inclusion of solid phases

The inclusion of a pure solid phase only represent one new variable, while hydrates are a mixture of water and a host molecule, and therefore represent more than one variable. To get a general framework, it is found best to include all components of the solid phase as variables in the equation system. The variables can also be selected as before, treating the solid mole number both as a dependent and independent variable. This will for dry ice introduce $n - 1$ dummy variables. The only adaption needed for solid is the special treatment of these dummy variables. The special treatment includes setting differentials to zero, and setting diagonal elements to unity.

2.6 The *PS*-flash and *PH*-flash

Both the *PS*-flash and *PH*-flash can be solved using a nested loop approach. The inner loop is a *PT*-flash flash, while the outer loop is a equation for entropy or enthalpy. The method is based on the methods of [Michelsen \(1999\)](#).

The outer loop specification for the *PH*-flash is

$$F_{h,p}\left(\frac{1}{T}\right) = -\frac{g - h_{\text{spec}}}{T}. \quad (43)$$

The differentials then become

$$\frac{\partial F_{h,p}}{\partial\left(\frac{1}{T}\right)} = -h + h_{\text{spec}}, \quad (44)$$

$$\frac{\partial^2 F_{h,p}}{\partial\left(\frac{1}{T}\right)^2} = T^2 \frac{\partial h}{\partial T}. \quad (45)$$

The outer loop specification for the *PS*-flash is

$$F_{s,p}(T) = -(g + Ts_{\text{spec}}). \quad (46)$$

The differentials then become

$$\frac{\partial F_{h,p}}{\partial T} = s - s_{\text{spec}}, \quad (47)$$

$$\frac{\partial^2 F_{h,p}}{\partial T^2} = \frac{1}{T} \frac{\partial h}{\partial T}. \quad (48)$$

2.6.1 Mixture $\frac{\partial h}{\partial T}$

In order to calculate the differential of the mixture enthalpy wrpt. the temperature the Jacobian for the *PH*-flash is required.

$$\mathbf{F}_{h,p}(\mathbf{v}, T) = \begin{pmatrix} g_1 \\ \vdots \\ g_N \\ a_T \end{pmatrix} \quad (49)$$

$$a_T = \frac{1}{RT} (h_{\text{spec}} - h) \quad (50)$$

Differentiating the equation system $\mathbf{F}_{h,P}$ in Equation 49 with respect to h_{spec} gives:

$$\frac{\partial \mathbf{F}_{h,P}}{\partial \mathbf{X}} \frac{\partial \mathbf{X}}{\partial h_{\text{spec}}} + \frac{\partial \mathbf{F}_{h,P}}{\partial h_{\text{spec}}} = 0, \quad (51)$$

$$\frac{\partial \mathbf{F}_{h,P}}{\partial \mathbf{X}} \frac{\partial \mathbf{X}}{\partial h_{\text{spec}}} = \left[0, \dots, 0, -\frac{1}{RT} \right]^T. \quad (52)$$

Solving this linear system we will get the following temperature differential wrpt. enthalpy.

2.7 The UV-flash

In order to solve the UV-flash fast and reliable, a combination of a full Newton-Raphson solver and a nested loop is required. See [Hammer and Giljarhus \(2011\)](#).

2.7.1 Nested-loop

The UV-flash problem is formulated as a constrained maximisation of S .

$$\begin{aligned} \max \quad & S(T, P, n_g, n_l) \\ \text{st.} \quad & \\ & U - U_{\text{spec}} = 0 \\ & V - V_{\text{spec}} = 0 \\ & n_g + n_l - z = 0 \end{aligned} \quad (53)$$

The linear constraints are usually substituted into the entropy function to yield $S(T, P, n_g, z - n_g)$. In the same manner the nonlinear constraints are modified. But maximising a nonlinear function, S , with two nonlinear constraints is very difficult. It is no way to formulate this problem that guarantees convergence.

The entropy state function maximisation is transformed to a maximisation of a state function Q . The maximisation of Q is solved by a nested loop where the minimum gibbs energy, G_{\min} , is calculated by a TP-flash in the inner loop. In the outer loop T and P is used to maximise Q in T and P .

$$Q = \frac{1}{T} (G_{\min} - U_{\text{spec}} - PV_{\text{spec}}) \quad (54)$$

$$\begin{aligned} G_{\min}(T, P, z) = \min \quad & G(T, P, z) \\ \text{st.} \quad & \\ & T = T_{\text{spec}} \\ & P = P_{\text{spec}} \end{aligned} \quad (55)$$

z is the overall molar composition. The inner loop, TP-flash, does a stability check of its solution. The outer loop uses the results from the inner loop, and no stability check is therefore required for the outer loop.

By differentiating Q in T and P we see that the stationary point of Q satisfies the flash specifications. The full differentiation of Q is shown in appendix 2.7.1, Equation 57. The results are summarised in Equation 56. Differentiating with respect to n_g will give a requirement for identical chemical potentials in gas and liquid for the stationary point. This requirement is ensured by the PT-flash calculation.

$$\begin{aligned} \left. \frac{\partial Q}{\partial P} \right|_T = 0 &\Leftrightarrow V - V_{\text{spec}} = 0 \\ \left. \frac{\partial Q}{\partial T} \right|_P = 0 &\Leftrightarrow H - U_{\text{spec}} - PV_{\text{spec}} = 0 \end{aligned} \quad (56)$$

To solve the maximisation of Q , a Newton method for unconstrained minimisation is used. The method is described by [Dennis and Schnabel \(1996\)](#), section 5.5. The search direction is modified to always be decent. (An indefinite second derivative matrix of Q is modified to have positive eigenvalues). To guarantee reduction in the objective function, $-Q$, in every iteration, a Wolfe line search is used. The Wolfe line search is described by [Nocedal and Wright \(1999\)](#).

In order to optimise the state function, Q , defined in Equation 54, the first and second differentials are required. To document the implementation of the state function optimisation, the Q differentials are included here.

$$\nabla Q = \begin{pmatrix} \frac{\partial Q}{\partial T} \Big|_{P,z} \\ \frac{\partial Q}{\partial P} \Big|_{T,z} \end{pmatrix} = \begin{pmatrix} -\frac{1}{T^2} (H_{\min} - U_s - PV_s) \\ \frac{1}{T} (V_{\min} - V_s) \end{pmatrix} \quad (57)$$

$$\nabla^2 Q = \begin{pmatrix} \frac{\partial^2 Q}{\partial T^2} & \frac{\partial^2 Q}{\partial T \partial P} \\ \frac{\partial^2 Q}{\partial P \partial T} & \frac{\partial^2 Q}{\partial P^2} \end{pmatrix} \quad (58)$$

$$\frac{\partial^2 Q}{\partial T^2} = -\frac{1}{T^2} \frac{\partial H_{\min}}{\partial T} \Big|_{P,z} \quad (59)$$

$$\frac{\partial^2 Q}{\partial P^2} = \frac{1}{T} \frac{\partial V_{\min}}{\partial P} \Big|_{T,z} \quad (60)$$

$$\frac{\partial^2 Q}{\partial T \partial P} = \frac{\partial^2 Q}{\partial P \partial T} = \frac{1}{T} \frac{\partial V_{\min}}{\partial T} \Big|_{P,z} \quad (61)$$

This requires the following mixture differentials:

$$\frac{\partial H}{\partial T} \Big|_{P,z} = \frac{\partial H_g}{\partial T} + \frac{\partial H_l}{\partial T} + \sum_{i=1}^N \left[\frac{\partial H_g}{\partial n_{g,i}} - \frac{\partial H_l}{\partial n_{l,i}} \right] \frac{\partial n_{g,i}}{\partial T} \quad (62)$$

$$\frac{\partial V}{\partial P} \Big|_{T,z} = \frac{\partial V_g}{\partial P} + \frac{\partial V_l}{\partial P} + \sum_{i=1}^N \left[\frac{\partial V_g}{\partial n_{g,i}} - \frac{\partial V_l}{\partial n_{l,i}} \right] \frac{\partial n_{g,i}}{\partial P} \quad (63)$$

$$\frac{\partial V}{\partial T} \Big|_{P,z} = \frac{\partial V_g}{\partial T} + \frac{\partial V_l}{\partial T} + \sum_{i=1}^N \left[\frac{\partial V_g}{\partial n_{g,i}} - \frac{\partial V_l}{\partial n_{l,i}} \right] \frac{\partial n_{g,i}}{\partial T} \quad (64)$$

$\partial H/\partial T$ is calculated as shown in section 2.6.1. $\partial V/\partial T$ and $\partial V/\partial P$ can be calculated in a similar manner, specifying an equilibrium condition for a VP -flash and VT -flash respectively.

2.7.2 The Newton approach

The UV -flash can in the multi-phase case can be formulated as a non-linear system of equations suitable for a Newton–Raphson iteration. Note however that in this case both the number of variables and their scaling can change between iterations.

As for the two-phase case we can use the fact that the molar fractions sum up to unity to reduce the number of independent variables. For an F -phase, C -component system we can assert

$$n_{iF} = z_i - \sum_{k=1}^{F-1} n_{ik}. \quad (65)$$

The equilibrium conditions for the system can then be written as

$$\mathbf{F}_{U,V}(\mathbf{n}_1, \dots, \mathbf{n}_{F-1}, T, P) = \begin{pmatrix} g_{11} \\ \vdots \\ g_{C1} \\ g_{12} \\ \vdots \\ g_{C2} \\ \vdots \\ g_{1(F-1)} \\ \vdots \\ g_{C(F-1)} \\ r_T \\ r_P \end{pmatrix} \quad (66)$$

where

$$g_{ik} = \frac{\partial Q}{\partial n_{ik}} \quad (67)$$

and Q is the objective function for the minimization of the Gibbs energy

$$Q = \sum_{i=1}^C \sum_{k=1}^F n_{ik} \ln \phi_i^{(k)} \quad (68)$$

However, as discussed by [Michelsen and Mollerup \(2007\)](#), the choice (65) might lead to numerical difficulties in round-off when the reference phase F is present only in very small quantities. As an alternative, one can choose a component-specific reference phase M_i and let

$$n_{iM_i} = z_i - \sum_{k \neq M_i}^F n_{ik}. \quad (69)$$

M_i should be chosen to be the phase for which the component is present in the largest amount ([Michelsen and Mollerup \(2007\)](#)). Furthermore, for better conditioning, the phase variables are scaled by the overall composition by setting

$$\tilde{n}_i = \frac{n_i}{z_i}. \quad (70)$$

In terms of individually chosen reference phases M_i , the equilibrium conditions become

$$\mathbf{F}_{U,V}(\tilde{\mathbf{n}}_1, \dots, \tilde{\mathbf{n}}_C, T, P) = \begin{pmatrix} g_1 \\ \vdots \\ g_C \\ r_T \\ r_P \end{pmatrix} \quad (71)$$

where

$$\mathbf{g}_i = \begin{pmatrix} \frac{\partial Q}{\partial \tilde{n}_{i0}} \\ \vdots \\ \frac{\partial Q}{\partial \tilde{n}_{i(M_i-1)}} \\ \frac{\partial Q}{\partial \tilde{n}_{i(M_i+1)}} \\ \vdots \\ \frac{\partial Q}{\partial \tilde{n}_{iF}} \end{pmatrix} \quad (72)$$

and

$$\frac{\partial Q}{\partial \tilde{n}_{ik}} = z_i \left(\ln \phi_i^{(k)} - \ln \phi_i^{(M_i)} \right). \quad (73)$$

The Newton iteration then uses the formulation

$$\begin{pmatrix} \mathbf{M}_{11} & \dots & \mathbf{M}_{1C} & \mathbf{g}_{1T} & \mathbf{g}_{1P} \\ \vdots & \ddots & \vdots & \vdots & \vdots \\ \mathbf{M}_{C1} & \dots & \mathbf{M}_{CC} & \mathbf{g}_{CT} & \mathbf{g}_{CP} \\ \mathbf{g}_{1T}^T & \dots & \mathbf{g}_{CT}^T & E_{TT} & E_{TP} \\ \mathbf{g}_{1P}^T & \dots & \mathbf{g}_{CP}^T & E_{PT} & E_{PP} \end{pmatrix} \begin{pmatrix} \Delta \tilde{\mathbf{n}}_1 \\ \vdots \\ \Delta \tilde{\mathbf{n}}_C \\ \Delta \ln T \\ \Delta \ln P \end{pmatrix} = \begin{pmatrix} \mathbf{g}_1 \\ \vdots \\ \mathbf{g}_C \\ r_T \\ r_P \end{pmatrix}, \quad (74)$$

where

$$r_T = \frac{1}{RT} (U^{\text{spec}} + PV^{\text{spec}} - H), \quad r_P = \frac{P}{RT} (V - V^{\text{spec}}), \quad (75)$$

$$\mathbf{M}_{ij} = \frac{\partial \mathbf{g}_i}{\partial \tilde{\mathbf{n}}_j}, \quad (76)$$

$$E_{TT} = -\frac{C_p}{R}, \quad E_{TP} = \frac{P}{R} \frac{\partial V}{\partial T}, \quad E_{PP} = \frac{P^2}{RT} \frac{\partial V}{\partial P}, \quad (77)$$

$$\mathbf{g}_{iT,j} = T \left(\frac{\partial (\ln \phi_i^{(j)})}{\partial T} - \frac{\partial (\ln \phi_i^{(M_i)})}{\partial T} \right), \quad (78)$$

$$\mathbf{g}_{iP,j} = P \left(\frac{\partial (\ln \phi_i^{(j)})}{\partial P} - \frac{\partial (\ln \phi_i^{(M_i)})}{\partial P} \right), \quad (79)$$

where $j = 1, \dots, F-1$ and

$$\tilde{\mathbf{n}}_i = \begin{pmatrix} \tilde{n}_{i0} \\ \vdots \\ \tilde{n}_{i(M_i-1)} \\ \tilde{n}_{i(M_i+1)} \\ \vdots \\ \tilde{n}_{iF} \end{pmatrix}. \quad (80)$$

A NR iteration then becomes:

$$\nabla_X \mathbf{F}_{U,V} \Delta \mathbf{X} + \mathbf{F}_{U,V} = 0 \quad (81)$$

The search direction is limited to yield valid component masses. The gas masses must be positive, and are upwards limited by the overall composition.

$$0 \leq \tilde{n}_{ij} \leq 1, \quad i \in \{1, \dots, C\} \quad \text{and} \quad j \in \{1, \dots, F-1\} \quad (82)$$

To guaranty reduction of the function residual, a simple line search is applied.

2.8 Symmetry in the second derivative of Q

Using mole numbers as variables, the second derivative of Q becomes symmetric. This follows from the thermodynamic identity,

$$\frac{1}{RT} \frac{\partial H^R}{\partial n_i} \Big|_{T,P} = - \frac{\partial \phi_i}{\partial \ln T} \Big|_{P,n}, \quad (83)$$

where the relation between the residual enthalpy $H_i^R = \frac{\partial H^R}{\partial n_i}$ and overall enthalpy H_i is given from,

$$H_i = H_i^R + H_i^{\text{Id}}. \quad (84)$$

The ideal contribution for one component is simply a temperature function, $H_i^{\text{Id}} = H_i^{\text{Id}}(T)$. Differentiating r_T with respect to mole numbers, using phase indices as as earlyer, therefor give,

$$\frac{\partial r_T}{\partial n_i^{(j)}} = - \left(\frac{H_i^{(j)}}{RT} - \frac{H_i^{(M_i)}}{RT} \right) = - \frac{H_i^{R,(j)}}{RT} + \frac{H_i^{R,(M_i)}}{RT}. \quad (85)$$

Using the thermodynamic identity, Equation 83, it is seen that

$$\frac{\partial r_T}{\partial n_i^{(j)}} = g_{iT}^{(j)}. \quad (86)$$

There exist a similar theremodynamic identity for resudial volume,

$$\frac{P}{RT} \frac{\partial V^R}{\partial n_i} \Big|_{T,P} = \frac{\partial \phi_i}{\partial \ln P} \Big|_{T,n}. \quad (87)$$

Overall this give a symmetric second derivative of Q .

2.9 Maintained symmetry when using scaled mole numbers as variables

Using scaled variables \tilde{n} we get,

$$\tilde{M}_{ij} = Z_i Z_j M_{ij}, \quad (88)$$

and the symmetry of \mathbf{M} remains.

With scaled variables one get

$$\tilde{g}_i = Z_i g_i, \quad (89)$$

further

$$\frac{1}{RT} \frac{\partial H^R}{\partial \tilde{n}_i} \Big|_{T,P} = \frac{Z_i}{RT} \frac{\partial H^R}{\partial n_i} \Big|_{T,P} = -Z_i \frac{\partial \phi_i}{\partial \ln T} \Big|_{P,n}, \quad (90)$$

and the symmetry remains.

Since E_{TP} and E_{PT} are unaffected by the mole number scaling, the full symmetry remains.

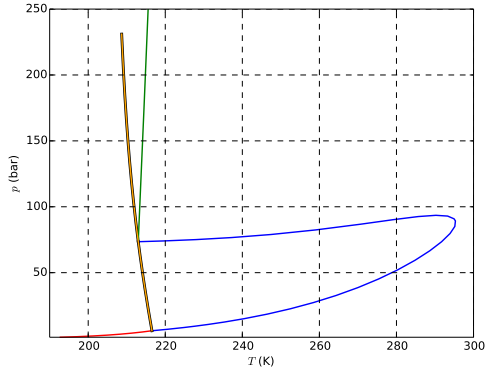
3 Special issues in single and two-component fluids

Write about single phase and integrate with rest of text.

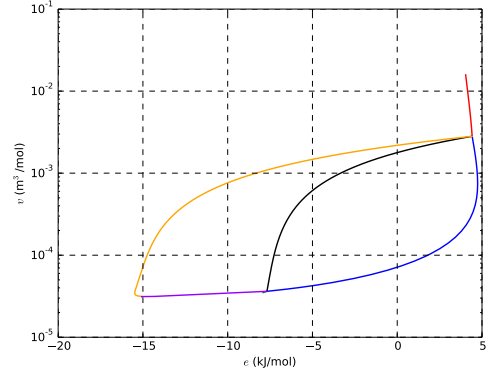
Solving the internal-energy–volume flash for a two component CO₂rich mixture involves solving along the triple line. The triple line behaves in this case, much as the saturation line for single component, ie. the phase transition can not be plotted in temperature-pressure space alone. Other variables must be used, like the phase fraction of one of the phases.

This three-phase line is illustrated in Figure 1a. Figure 1 show three phase diagrams of a mixture containing 87.5 % CO₂ and 12.5 % N₂.

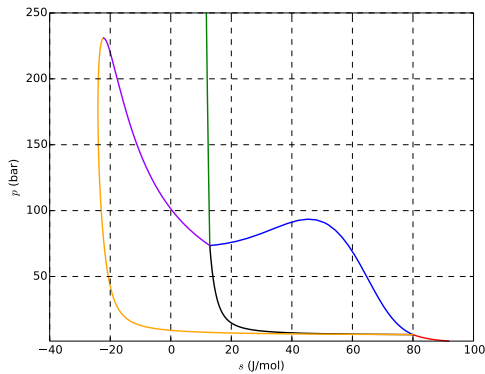
Here we choose the use of pressure and solid phase fraction. As the temperature is fairly constant along the three-phase line, it is considered better to use pressure. The strategy when solving is to search along the three-phase line, implying that temperature ($T = T(p)$), gas phase composition ($\mathbf{Y} = \mathbf{Y}(T(p), p)$) and liquid phase composition ($\mathbf{X} = \mathbf{X}(T(p), p)$) are known from the pressure alone.



- (a) Phase diagram for the temperature–pressure space. The blue and the black line encircle the vapor–liquid region. Above the red line and left of the orange line we have the vapor solid region. The green line is the solid appearance line in from the liquid phase. It is seen that there is no three-phase area, only a line, as the orange and black line coincide, ending in a critical point.



- (b) Phase diagram for the internal-energy–volume space.



- (c) Phase diagram for the pressure–entropy space. Here the three phase line in the temperature–pressure space represent an area enclosed by the black, purple and yellow line. The pressure maximum of this region coincide with a critical point.

Figure 1: Phase diagrams for a $\text{CO}_2\text{-N}_2$ mixture. The mole fraction vector of the mixture is $[0.875, 0.125]$

3.1 Three-phase line

3.1.1 The UV-flash

The equations required to calculate the three phase line is given in the envelope memo, and best calculated for $\beta_{\text{sol}} = 0$. Not that at a given temperature and pressure, changing $\beta_{\text{sol}} = 0$, do not change the phase composition of the gas or liquid phase.

The enthalpy, specific volume and internal energy of a gas-liquid-solid mixture is described as,

$$h_{\text{mix}} = \beta_g h_g + \beta_\ell h_\ell + \beta_{\text{sol}} h_{\text{sol}}, \quad (91)$$

$$v_{\text{mix}} = \beta_g v_g + \beta_\ell v_\ell + \beta_{\text{sol}} v_{\text{sol}}, \quad (92)$$

$$e_{\text{mix}} = h_{\text{mix}} - p v_{\text{mix}}. \quad (93)$$

Differentiating the mixture enthalpy along the three-phase line, using pressure and solid fraction as variables, yields,

$$\frac{\partial h_{\text{mix}}}{\partial p} = \frac{\partial h_{\text{mix}}}{\partial p} + \frac{\partial h_{\text{mix}}}{\partial t} \frac{\partial t}{\partial p} + \frac{\partial (\beta_g h_g)}{\partial \mathbf{n}_g} \frac{\partial \mathbf{n}_g}{\partial p} + \frac{\partial (\beta_\ell h_\ell)}{\partial \mathbf{n}_\ell} \frac{\partial \mathbf{n}_\ell}{\partial p}, \quad (94)$$

$$\frac{\partial h_{\text{mix}}}{\partial \beta_{\text{sol}}} = h_{\text{sol}} + \frac{\partial (\beta_g h_g)}{\partial \mathbf{n}_g} \frac{\partial \mathbf{n}_g}{\partial \beta_{\text{sol}}} + \frac{\partial (\beta_\ell h_\ell)}{\partial \mathbf{n}_\ell} \frac{\partial \mathbf{n}_\ell}{\partial \beta_{\text{sol}}}. \quad (95)$$

The specific volume differentials take the same form. The required differentials along the three-phase line therefore becomes,

$$\left. \frac{\partial t}{\partial p} \right|_{\beta_{\text{sol}}}, \left. \frac{\partial \mathbf{n}_g}{\partial p} \right|_{\beta_{\text{sol}}}, \left. \frac{\partial \mathbf{n}_\ell}{\partial p} \right|_{\beta_{\text{sol}}}, \left. \frac{\partial \mathbf{n}_g}{\partial \beta_{\text{sol}}} \right|_p, \left. \frac{\partial \mathbf{n}_\ell}{\partial \beta_{\text{sol}}} \right|_p \quad (96)$$

The envelope solver give the gas phase fraction, $\tilde{\beta}_g$, given a zero solid phase $\tilde{\beta}_{\text{sol}} = 0$. To calculate the real gas (β_g) and liquid (β_ℓ) phase fractions, the mass balance for the solid component yields,

$$\beta_g = \frac{Z_{is} - X_{is} + \beta_{\text{sol}} (X_{is} - 1)}{Y_{is} - X_{is}}, \quad (97)$$

$$\beta_\ell = 1 - \tilde{\beta}_g - \beta_{\text{sol}}. \quad (98)$$

The relation between mole numbers and mole fractions are as follows,

$$\mathbf{n}_g = \mathbf{Y} \beta_g, \quad (99)$$

$$\mathbf{n}_\ell = \mathbf{X} (1 - \beta_g - \beta_{\text{sol}}). \quad (100)$$

The differentials at constant pressure therefore becomes,

$$\frac{\partial \mathbf{n}_g}{\partial \beta_{\text{sol}}} = \mathbf{Y} \frac{\partial \beta_g}{\partial \beta_{\text{sol}}}, \quad (101)$$

$$\frac{\partial \mathbf{n}_\ell}{\partial \beta_{\text{sol}}} = -\mathbf{X} \left(\frac{\partial \beta_g}{\partial \beta_{\text{sol}}} + 1 \right). \quad (102)$$

From Equation 97 we have,

$$\frac{\partial \beta_g}{\partial \beta_{\text{sol}}} = \frac{X_{is} - 1}{Y_{is} - X_{is}}. \quad (103)$$

The envelope three-phase line linearisation will provide information on how the temperature, composition and gas phase fraction changes with pressure, ie. $\partial T / \partial \ln p$, $\partial \ln K / \partial \ln p$ and $\partial \beta_g / \partial \ln p$. These can be used to construct the required pressure differentials.

The relation between K and $\tilde{\beta}_g$ and the gas and liquid composition, are

$$X = \frac{Z}{1 - \tilde{\beta}_g + \tilde{\beta}_g K}, \quad (104)$$

$$Y = KX. \quad (105)$$

The differentials of the compositions then become,

$$\frac{\partial X}{\partial K} = -\frac{\tilde{\beta}_g Z}{(1 - \tilde{\beta}_g + \tilde{\beta}_g K)^2} = -\frac{\tilde{\beta}_g X}{1 - \tilde{\beta}_g + \tilde{\beta}_g K}, \quad (106)$$

$$\frac{\partial Y}{\partial K} = X - \frac{\tilde{\beta}_g Y}{1 - \tilde{\beta}_g + \tilde{\beta}_g K}, \quad (107)$$

$$\frac{\partial X}{\partial \tilde{\beta}_g} = -\frac{Z(K-1)}{(1 - \tilde{\beta}_g + \tilde{\beta}_g K)^2} = -\frac{X(K-1)}{1 - \tilde{\beta}_g + \tilde{\beta}_g K}, \quad (108)$$

$$\frac{\partial Y}{\partial \tilde{\beta}_g} = -\frac{Y(K-1)}{1 - \tilde{\beta}_g + \tilde{\beta}_g K}. \quad (109)$$

From Equation 99, the mole number differentials can be derived,

$$\frac{\partial \mathbf{n}_g}{\partial p} = \tilde{\beta}_g \left(\frac{\partial Y}{\partial K} + \frac{\partial Y}{\partial K} \right) \frac{\partial K}{\partial p} + Y \frac{\partial \tilde{\beta}_g}{\partial p} \quad (110)$$

3.1.2 The PS-flash

The three-phase line must also be treated separately for two-component mixtures. By locating the three-phase line point for the specified pressure, the entropies at $\beta_{sol} = 0$, $s_{[\beta_{sol}=0]}$, and $\beta_\ell = 0$, $s_{[\beta_\ell=0]}$, will determine if the solution resides on the three-phase line.

The solid and gas phase fractions at zero liquid phase fraction is found from Equation 97 and Equation 98, when setting $\beta_\ell = 0$,

$$\beta_{sol} = \frac{Z_{is} - Y_{is}}{1 - Y_{is}}, \quad (111)$$

$$\beta_g = 1 - \beta_{sol}. \quad (112)$$

If the specified entropy, s_s , satisfies,

$$s_{[\beta_\ell=0]} \leq s_s \leq s_{[\beta_{sol}=0]}, \quad (113)$$

the solution resides on the three-phase line. In this case, the phase fractions must be determined from the following equation,

$$s_s = \beta_g s_g + \beta_\ell s_\ell + \beta_{sol} s_{sol}. \quad (114)$$

Combining Equation 114 with the equations 97 and 98, the problem is reduced to solving for β_{sol} ,

$$\beta_{\text{sol}} = \frac{\left(s_s - s_\ell\right)\left(Y_{is} - X_{is}\right) - \left(s_g - s_\ell\right)\left(Z_{is} - X_{is}\right)}{\left(s_g - s_\ell\right)\left(X_{is} - 1\right) + \left(s_{\text{sol}} - s_\ell\right)\left(Y_{is} - X_{is}\right)}. \quad (115)$$

4 Results

In order to test the new implementation, TPLib and a thermodynamic library from Danmarks Tekniske Universitet (DTU), is used. This work could therefore be performed in parallel with the new implementation for the equation of state with mixing rules.

The algorithms are tested on a temperature-pressure grid, for multiple compositions.

4.1 Testing *TP*-flash

The main testing of the *TP*-flash, has been to solve the flash problem on large temperature-pressure grid, and compare the phase envelope and results with TPLib.

Multiple CO₂ rich mixtures of CO₂-CH₄-N₂ have been tested.

4.2 Multiphase *TP*-flash

The main testing of the multiphase *TP*-flash algorithm has been on the following two mixtures.

4.2.1 Test case 1 - Multiphase *TP*-flash

A 5 component mixture (66% CH₄, 3% C₂H₆, 3% C₃H₈, 5% CO₂ and 25% H₂S), is selected because it is known to produce multiple phases (LLV, LV and LL).

Figure 2 shows the number of stable phases found for this test mixtures in the *T-P* space.

4.2.2 Test case 2 - Multiphase *TP*-flash

A 3 component mixture (5% CH₄, 90% CO₂ and 5% H₂O), is selected because it is known to produce multiple phases (LLV, LV and LL).

Figure 3 shows the number of stable phases found for this test mixtures in the *T-P* space.

4.3 Testing *HP*-flash and *SP*-flash

Test procedure for the *HP*-flash and *SP*-flash:

1. Perform a *TP*-flash.
2. Calculate enthalpy or entropy.
3. Set a random initial value for the temperature. $120 \geq T_{\text{init}} \geq 999$ K.
4. Perform a *HP*-flash or *SP*-flash, and compare the resulting temperature with the specified temperature.

Multiple CO₂ rich mixtures of CO₂-CH₄-N₂ have been tested.

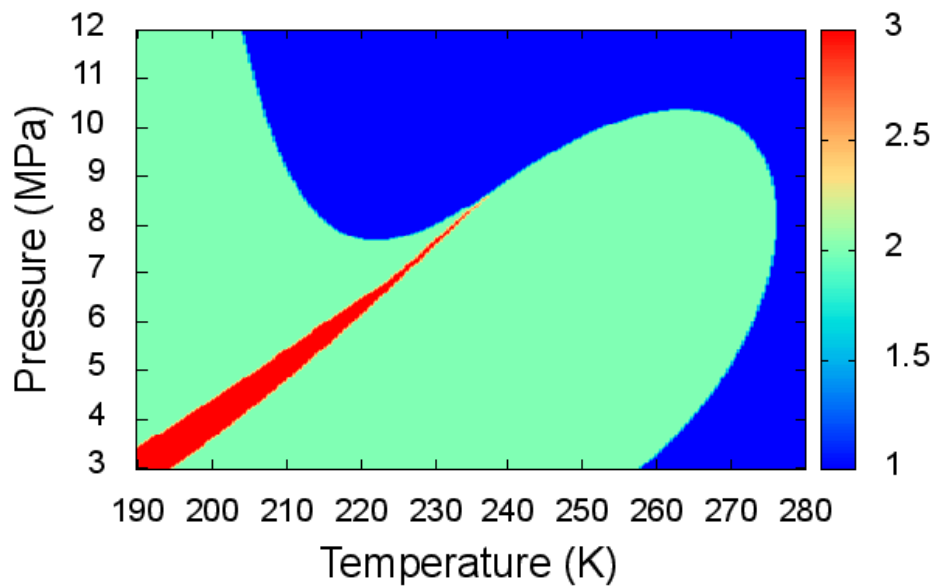


Figure 2: 5 component test mixture. The red area is LLV. The blue area is single phase. The green area to the left is LL, and the other green area is LV.

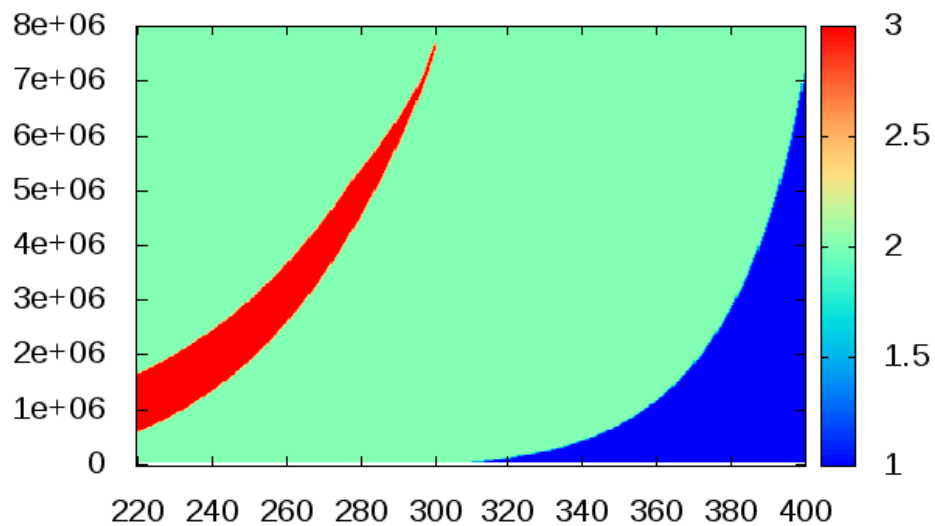


Figure 3: 3 component test mixture. The red area is LLV. The blue area is single phase. The green area to the left is LL, and the other green area is LV.

4.4 Testing *UV*-flash

Test procedure for the *UV*-flash:

1. Perform a *TP*-flash, for (T^*, P^*) .
2. Calculate internal energy and specific volume.
3. Set an random initial value for the temperature. $T^* - 50 \geq T_{\text{init}} \geq T^* + 50$ K.
4. Set a random initial value for the pressure. $P^* - 5e5 \geq P_{\text{init}} \geq P^* + 5e5$ K.
5. Perform a *UV*-flash, and compare the resulting temperature and pressure with the specified temperature and pressure.

Multiple CO₂ rich mixtures of CO₂-CH₄-N₂ have been tested.

5 Conclusion and future work

In this memo, it has been described how state-of-the-art algorithms for the *TP*-flash, *HP*-flash, *SP*-flash and *UV*-flash have been implemented in the new flexible thermodynamic workbench developed at SINTEF: "ThermoPack". A new multiphase-flash capable of handling several liquid phases has also been implemented. The multiphase-flash implementation successfully predicted the phase diagrams for two relevant mixtures.

Future work for the multiphase-flash will be to validate that it calculates accurately for other mixtures relevant for CCS, and use it to predict for which mixtures and temperature, pressure ranges multiphase systems should be expected. In addition, formation of solids should be implemented as part of the multiphase-flash.

Due to improvement of the other flash calculations it is expected that the new *UV*-flash is faster and more robust than the previous implementation.

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