Memo

Phase envelope modelling

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Contents

1 Introduction

The intention of this memo is to describe the equations used for mapping phase envelopes in thermopack.

2 Liquid-Vapor envelopes

The equations:

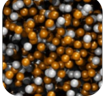$$g_i = \ln K_i + \ln \varphi_i^{\text{vap}} - \ln \varphi_i^{\text{liq}}, \quad i = 1, \dots, n \tag{1}$$

$$g_{n+1} = \sum_{i=1}^{n} \left(Y_i - X_i \right), \tag{2}$$

$$g_{n+2} = S - S_{\text{spec}}. \tag{3}$$

Relation between overall composition and phase compositions:

$$\boldsymbol{X} = \frac{\boldsymbol{Z}}{1 - \beta + \beta \boldsymbol{K}}, \tag{4}$$

$$\boldsymbol{Y} = \frac{\boldsymbol{K}\boldsymbol{Z}}{1 - \beta + \beta \boldsymbol{K}}. \tag{5}$$

Vector form of the equations:

$$G\left(\boldsymbol{W}\right) = \begin{pmatrix} g_1 \\ \vdots \\ g_{n+2} \end{pmatrix} \tag{6}$$

Variables:

$$\boldsymbol{W} = \begin{pmatrix} \ln \boldsymbol{K} \\ \ln T \\ \ln P \end{pmatrix} \tag{7}$$

2.1 Differentials

The Jacobean matrix needs the following differentials:

$$\frac{\partial X_i}{\partial \ln K_i} = -\frac{K_i Z_i \beta}{(1 - \beta + \beta K_i)^2} = -\frac{K_i X_i \beta}{(1 - \beta + \beta K_i)} = -\beta \frac{Y_i X_i}{Z_i}. \tag{8}$$

$$\frac{\partial Y_i}{\partial \ln K_i} = -K_i \frac{K_i Z_i \beta}{(1 - \beta + \beta K_i)^2} + K_i \frac{Z_i \beta}{(1 - \beta + \beta K_i)} = -\frac{(1 - \beta)}{\beta} \frac{\partial X_i}{\partial K_i} = (1 - \beta) \frac{Y_i X_i}{Z_i}. \tag{9}$$

$$\frac{\partial g_i}{\partial \ln K_j} = \delta_{ij} + \left((1 - \beta) \frac{\partial \ln \varphi_i^{\text{vap}}}{\partial Y_j} + \beta \frac{\partial \ln \varphi_i^{\text{liq}}}{\partial X_j} \right) \frac{X_j Y_j}{Z_j}. \tag{10}$$

$$\frac{\partial g_{n+1}}{\partial \ln K_j} = \frac{X_j Y_j}{Z_j}. \tag{11}$$

3 Extension to include solids

Since β will vary along the saturation lines, it must be included as a variable. The same applies for β_{sol}. Typically one of these will be fixed to zero when mapping a three-phase line, while the other is a variable.

The equation set must be extended with the following equilibrium relation:

$$g_{n+3} = \ln \varphi_s^{\text{vap}} + \ln Y_s - \ln \varphi^{\text{sol}}. \tag{12}$$

Earlier it was assumed, $\beta_{\text{vap}} = \beta$, and $\beta_{\text{liq}} = 1 - \beta$. There are three options when extending to include solids, (1) to continue to assume this within the vapor-liquid part of the mixture, or (2) to use $\beta_{\text{liq}} = 1 - \beta - \beta_{\text{sol}}$, or (3) to introduce a new variable for β_{liq}. Since we typically need to specify one of the phase fractions to be zero, only the first and the last option can be used.

For the first option, the corrected fluid composition, Z_i^*, becomes,

$$Z_i^* = \begin{cases} \frac{Z_i - \beta_{\text{sol}}}{1 - \beta_{\text{sol}}}, & \text{if } i = s \\ \frac{Z_i}{1 - \beta_{\text{sol}}}, & \text{otherwise.} \end{cases} \tag{13}$$

For the third option, the new mass balance for the solid component, Z_s, becomes:

$$Z_i = \begin{cases} \beta_{\text{vap}} Y_i + \beta_{\text{liq}} X_i + \beta_{\text{sol}}, & \text{if } i = s \\ \beta_{\text{vap}} Y_i + \beta_{\text{liq}} X_i, & \text{otherwise.} \end{cases} \tag{14}$$

Equation 6 for the fluid equilibrium then changes form completely. To simplify, it is therefore suggested to use the first approach.
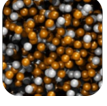
Substituting Equation 13 into equations 4 we get,

$$X_i = \begin{cases} \frac{Z_i - \beta_{\text{sol}}}{(1-\beta_{\text{sol}})(1-\beta+\beta K_{\text{s}})}, & \text{if } i = s \\ \frac{Z_i}{(1-\beta_{\text{sol}})(1-\beta+\beta K_{\text{s}})}, & \text{otherwise.} \end{cases} \tag{15}$$

To calculate $\boldsymbol{Y}$, we still use, $Y_i = K_i X_i$. To calculate the real gas $(\tilde{\beta}_{\text{vap}})$ and liquid $(\tilde{\beta}_{\text{liq}})$ phase fractions, the mass balance for the solid component yields,

$$\tilde{\beta}_{\text{vap}} = \frac{Z_{is} - X_{is} + \beta_{\text{sol}}(X_{is} - 1)}{Y_{is} - X_{is}} \tag{16}$$

$$\tilde{\beta}_{\text{liq}} = 1 - \tilde{\beta}_{\text{vap}} - \beta_{\text{sol}} \tag{17}$$

3.1 Additional differentials

$$\frac{\partial X_i}{\partial \beta} = -\frac{Z_i^*(K_i - 1)}{(1 - \beta + \beta K_i)^2} = -\frac{X_i(Y_i - X_i)}{Z_i^*}. \tag{18}$$

$$\frac{\partial Y_i}{\partial \beta} = -\frac{K_i Z_i^*(K_i - 1)}{(1 - \beta + \beta K_i)^2} = -\frac{Y_i(Y_i - X_i)}{Z_i^*}. \tag{19}$$

$$\frac{\partial X_i}{\partial \beta_{\text{sol}}} = \begin{cases} \frac{X_i}{(1-\beta_{\text{sol}})}\left(1 - \frac{1}{Z_i^*}\right), & \text{if } i = s \\ \frac{X_i}{(1-\beta_{\text{sol}})}, & \text{otherwise.} \end{cases} \tag{20}$$

$$\frac{\partial Y_i}{\partial \beta_{\text{sol}}} = K_i \frac{\partial X_i}{\partial \beta_{\text{sol}}}. \tag{21}$$

$$\frac{\partial g_i}{\partial \beta} = -\sum_{j=1}^{n}\left(\frac{\partial \ln \varphi_i^{\text{vap}}}{\partial Y_j}Y_j - \frac{\partial \ln \varphi_i^{\text{liq}}}{\partial X_j}X_j\right)\frac{(Y_i - X_i)}{Z_i^*} \tag{22}$$

$$\frac{\partial g_{n+1}}{\partial \beta} = \sum_{i=1}^{n}(K_i - 1)\frac{\partial X_i}{\partial \beta}. \tag{23}$$

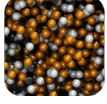The differential with regards to β_{sol} will have the same shape.

$$\frac{\partial g_{n+3}}{\partial \ln K_i} = \left(\frac{\partial \ln \varphi_{\text{s}}^{\text{vap}}}{\partial Y_i} + \frac{\delta_{is}}{Y_{\text{s}}}\right)\frac{\partial Y_i}{\partial \ln K_j} = \left(\frac{\partial \ln \varphi_{\text{s}}^{\text{vap}}}{\partial Y_i} + \frac{\delta_{is}}{Y_{\text{s}}}\right)(1 - \beta)\frac{Y_i X_i}{Z_i^*}. \tag{24}$$

$$\frac{\partial g_{n+3}}{\partial \ln T} = T\left(\frac{\partial \ln \varphi_{\text{s}}^{\text{vap}}}{\partial T} - \frac{\partial \ln \varphi^{\text{sol}}}{\partial T}\right). \tag{25}$$

$$\frac{\partial g_{n+3}}{\partial \ln P} = P\left(\frac{\partial \ln \varphi_{\text{s}}^{\text{vap}}}{\partial P} - \frac{\partial \ln \varphi^{\text{sol}}}{\partial P}\right). \tag{26}$$

$$\frac{\partial g_{n+3}}{\partial \beta} = \sum_{i=1}^{n}\frac{\partial \ln \varphi_{\text{s}}^{\text{vap}}}{\partial Y_i}\frac{\partial Y_i}{\partial \beta} + \frac{1}{Y_{\text{s}}}\frac{\partial Y_{\text{s}}}{\partial \beta}. \tag{27}$$

The differential with regards to β_{sol} will have the same shape.

3.2 Liquid-solid or vapor-solid equilibrium

One equilibrium and on specification equation is required,

$$g_1 = \ln \varphi_s^{\text{vap}} + \ln Y_s - \ln \varphi^{\text{sol}}, \tag{28}$$

$$g_2 = S - S_{\text{spec}}. \tag{29}$$

Variables:

$$\boldsymbol{W} = \begin{pmatrix} \ln T \\ \ln P \end{pmatrix} \tag{30}$$

One of the variables must be specified, and β_{sol} must be set. The fluid mole fractions then become,

$$Y_i = \begin{cases} \frac{Z_s - \beta_{\text{sol}}}{1 - \beta_{\text{sol}}}, & \text{if } i = s \\ \frac{Z_i}{1 - \beta_{\text{sol}}}, & \text{otherwise.} \end{cases} \tag{31}$$

For Y_i the differentials are,

$$\frac{\partial Y_i}{\partial \beta_{\text{sol}}} = \begin{cases} \frac{Y_i - 1}{1 - \beta_{\text{sol}}}, & \text{if } i = s \\ \frac{Y_i}{1 - \beta_{\text{sol}}}, & \text{otherwise.} \end{cases} \tag{32}$$

Using these the other differentials are simple.

4 Illustrations

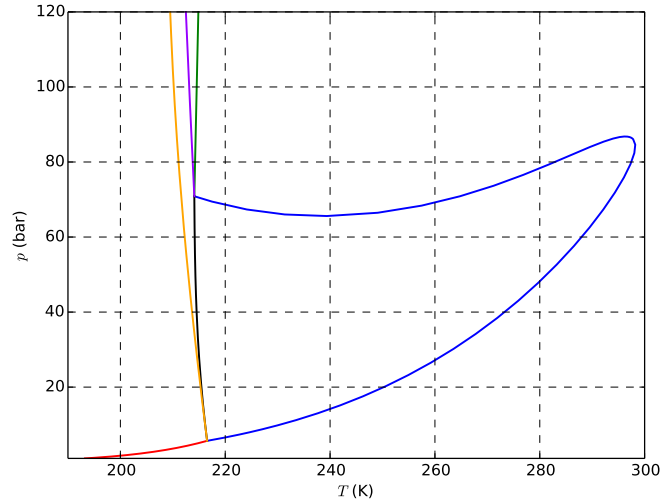Figure 1 show an example of the phase diagram of a multicomponent mixture with approximately 91% CO_2.

Figure 1: Illustration of a multicomponent mixture (CO_2-H_2-N_2-O_2-CH_4) with all its phase areas. 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. Right of the orange and left of the black and brown line there is a vapor-liquid-solid line. Between the purple and green line there is a liqid solid region. The mole fraction vector of the mixture is $[0.9094, 0.0103, 0.0402, 0.0184, 0.0217]$

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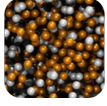
5 Two-component system

For a two-component system there is no three phase area, only a three phase line. This means, that at the same temperature and pressure, several equilibrium states can be found. The state differ only in different solid fraction and different fluid phase fractions. That is; while dry-ice freeze, the phase compositions are constant. The chemical potential of the component freezing then remain constant, as seen from Equation 12.

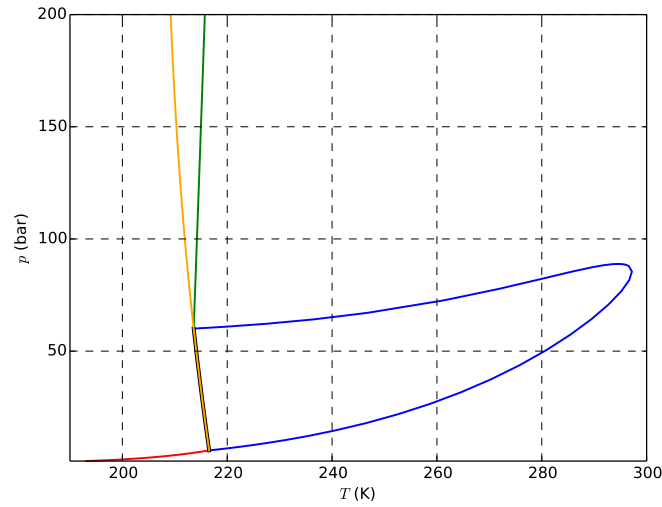This is illustrated in Figure 2. Figure 2 show the phase diagram of a mixture containing 87.5% CO_2 and 12.5% N_2.

Figure 2: Illustration of a binary mixture (CO_2-N_2) with all its phase areas. 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. The mole fraction vector of the mixture is $[0.875, 0.125]$

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The Gibbs' phase rule, state that the degree of freedom (F) is given as number of components (C) and number of phases (P),

$$F = C - P + 2. \tag{33}$$

For three phases and two components, the degree of freedom become 1. That is; the it is not possible to change the temperature independently of the pressure, giving a three-phase line in temperature-pressure space.

Applying the same rule to pure CO_2, no degree of freedom is seen for the three-phase region, giving a triple point in temperature-pressure space.