Thermotools memo

Documentation of the binary-XY code in thermopack

Thermotools
Location:
Trondheim
NORWAY

https://thermotools.github.io/thermopack/index.html

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1 Introduction

The equations required to describe an binary Txy or Pxy plot.

2 Governing equations

The equation system $\mathbf{F}(\mathbf{X}) = \mathbf{0}$, is defined by equation (1) to (8).

$$
\begin{align}
f_i &= \ln K_i + \ln \hat{\varphi}_i\left(\mathbf{y}\right) - \ln \hat{\varphi}_i\left(\mathbf{x}\right) = 0, \quad i = 1,2 \tag{1} \\
f_{i+2} &= y_i - K_i x_i = 0, \quad i = 1,2 \tag{2} \\
f_5 &= x_1 + x_2 - 1 = 0 \tag{3} \\
f_6 &= y_1 + y_2 - 1 = 0 \tag{4} \\
f_7 &= S - S_{\text{spec}} = 0 \tag{5} \\
& \tag{6}
\end{align}
$$

$$
\mathbf{F} = \begin{pmatrix} f_1 \\ \vdots \\ f_7 \end{pmatrix} \tag{7}
$$

The last variable will be $\ln T$ or $\ln P$, for simplicity the equations are written out for a Txy binary plot. The temperature is therefore constant. The last variable is therefore $\ln P$. The Pxy problem can be developed in the same manner.

$$
\mathbf{X} = \begin{pmatrix} \ln \mathbf{K} \\ \mathbf{x} \\ \mathbf{y} \\ \ln P \end{pmatrix} \tag{8}
$$

2.1 Changing the specification

Differentiating, we get:

$$
\begin{align}
\frac{\mathrm{d}\mathbf{F}(\mathbf{X})}{\mathrm{d}\mathbf{X}} \frac{\mathrm{d}\mathbf{X}}{\mathrm{d}S_{\text{spec}}} + \frac{\mathrm{d}\mathbf{F}(\mathbf{X})}{\mathrm{d}S_{\text{spec}}} &= \mathbf{0} \tag{9} \\
\frac{\mathrm{d}\mathbf{F}(\mathbf{X})}{\mathrm{d}\mathbf{X}} \frac{\mathrm{d}\mathbf{X}}{\mathrm{d}S_{\text{spec}}} &= \begin{pmatrix} \mathbf{0} \\ 1 \end{pmatrix} \tag{10}
\end{align}
$$

We are therefore able to produce new initial guesses when we change the specification, S_{spec}.

2.2 Termination

The binaryXY routine need to terminate when one of the following situations occur:

1. One of the components become zero.
2. Critical point or azeotrope is reached. $(\mathbf{x} = \mathbf{y})$
3. User given maximum in pressure or minimum in temperature is reached.

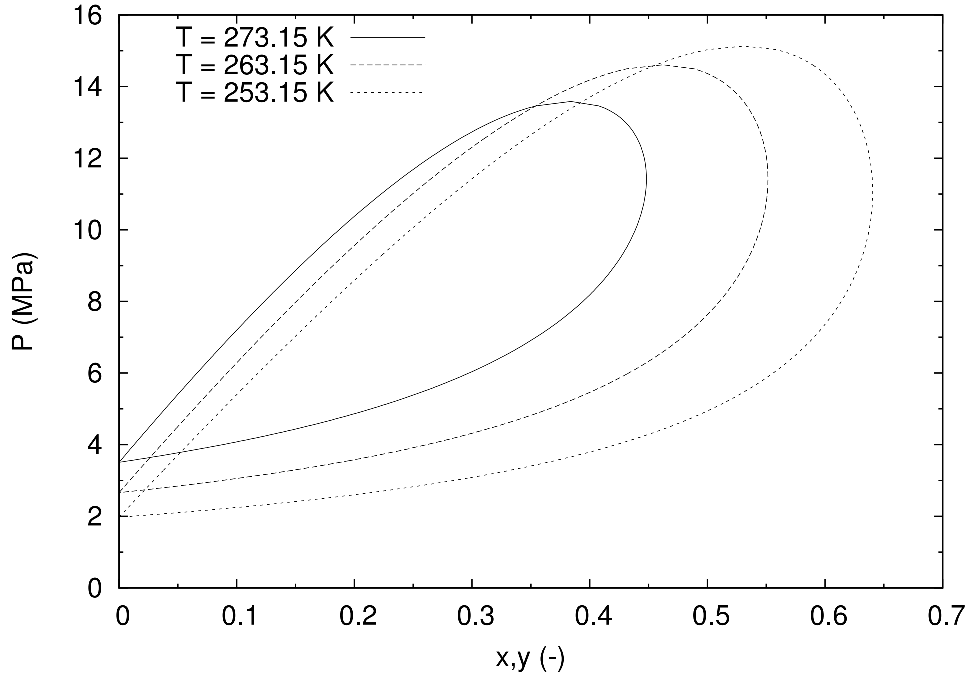

Figure 1: Mole fraction of NO in anCO_2-NO mixture with SRK and $k_{ij} = 0$.

3 Results

Have tested the mixture CO_2-NO with SRK and PR. Both have been tested with the binary interaction parameters $k_{ij} = 0$ and $k_{ij} = -0.105$. The plots have been initialised at the CO_2 bubble point.

See Figure 1, 2, 3 and 4.

A Jacobian

The Jacobian required for a Newton solver of the equation system in section 2.

$$\frac{\partial f_1}{\partial \ln K_1} = 1 \tag{11}$$

$$\frac{\partial f_1}{\partial \ln K_2} = 0 \tag{12}$$

$$\frac{\partial f_1}{\partial x_i} = -\frac{\partial \ln \hat{\varphi}_1(\mathbf{x})}{\partial x_i}, \quad i = 1, 2 \tag{13}$$

$$\frac{\partial f_1}{\partial y_i} = \frac{\partial \ln \hat{\varphi}_1(\mathbf{y})}{\partial y_i}, \quad i = 1, 2 \tag{14}$$

$$\frac{\partial f_1}{\partial \ln P} = P\left(\frac{\partial \ln \hat{\varphi}_1(\mathbf{y})}{\partial P} - \frac{\partial \ln \hat{\varphi}_1(\mathbf{x})}{\partial P}\right) \tag{15}$$

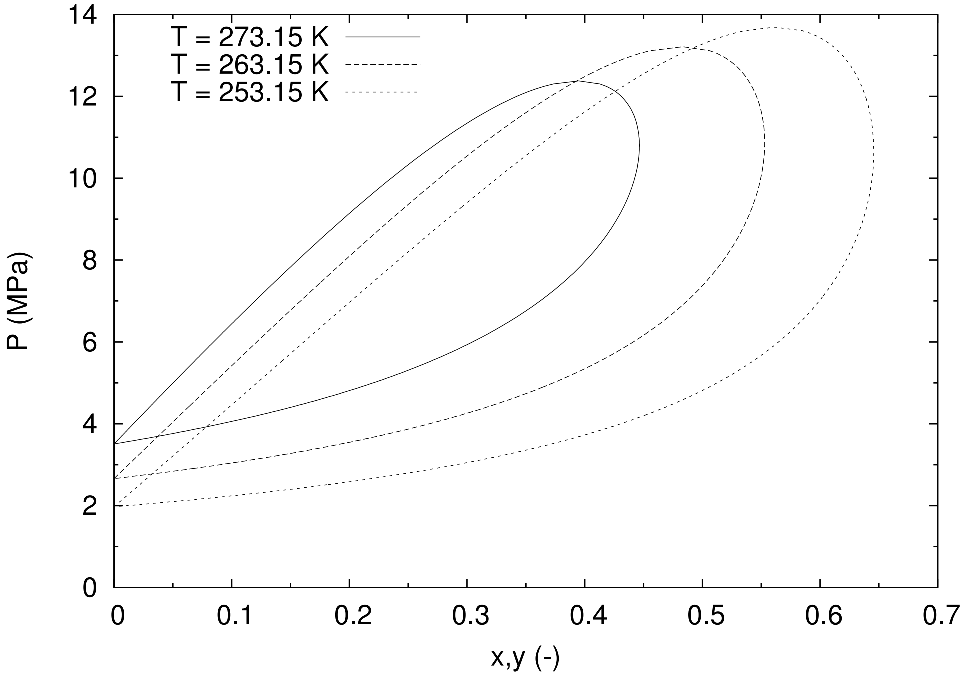

Figure 2: Mole fraction of NO in anCO_2-NO mixture with SRK and $k_{ij} = -0.119$.

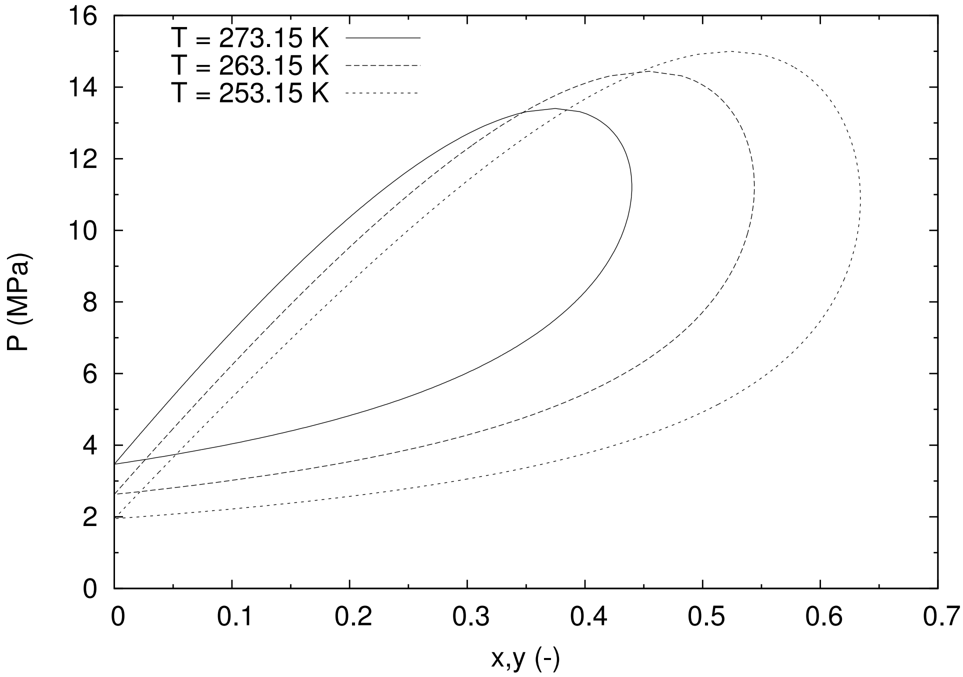

Figure 3: Mole fraction of NO in anCO_2-NO mixture with PR and $k_{ij} = 0$.

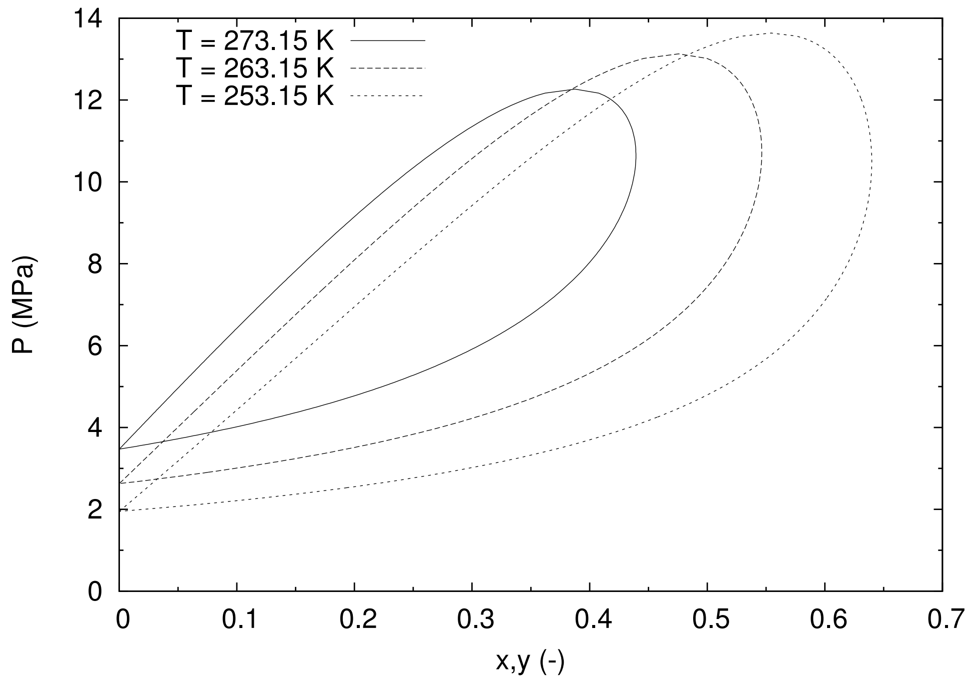

Figure 4: Mole fraction of NO in anCO_2-NO mixture with PR and $k_{ij} = -0.105$.

$$\frac{\partial f_2}{\partial \ln K_1} = 0 \tag{16}$$

$$\frac{\partial f_2}{\partial \ln K_2} = 1 \tag{17}$$

$$\frac{\partial f_2}{\partial x_i} = -\frac{\partial \ln \hat{\varphi}_2(\mathbf{x})}{\partial x_i}, \quad i = 1, 2 \tag{18}$$

$$\frac{\partial f_2}{\partial y_i} = \frac{\partial \ln \hat{\varphi}_2(\mathbf{y})}{\partial y_i}, \quad i = 1, 2 \tag{19}$$

$$\frac{\partial f_2}{\partial \ln P} = P\left(\frac{\partial \ln \hat{\varphi}_2(\mathbf{y})}{\partial P} - \frac{\partial \ln \hat{\varphi}_2(\mathbf{x})}{\partial P}\right) \tag{20}$$

$$\frac{\partial f_3}{\partial \ln K_1} = -K_1 x_1 \tag{21}$$

$$\frac{\partial f_3}{\partial \ln K_2} = 0 \tag{22}$$

$$\frac{\partial f_3}{\partial x_1} = -K_1 \tag{23}$$

$$\frac{\partial f_3}{\partial x_2} = 0 \tag{24}$$

$$\frac{\partial f_3}{\partial y_1} = 1 \tag{25}$$

$$\frac{\partial f_3}{\partial y_2} = 0 \tag{26}$$

$$\frac{\partial f_3}{\partial \ln P} = 0 \tag{27}$$

$$\frac{\partial f_4}{\partial \ln K_1} = 0 \tag{28}$$

$$\frac{\partial f_4}{\partial \ln K_2} = -K_2 x_2 \tag{29}$$

$$\frac{\partial f_4}{\partial x_1} = 0 \tag{30}$$

$$\frac{\partial f_4}{\partial x_2} = -K_2 \tag{31}$$

$$\frac{\partial f_4}{\partial y_1} = 0 \tag{32}$$

$$\frac{\partial f_4}{\partial y_2} = 1 \tag{33}$$

$$\frac{\partial f_4}{\partial \ln P} = 0 \tag{34}$$

$$\frac{\partial f_5}{\partial X_i} = 0 \quad i = 1, 2, 5, 6, 7 \tag{35}$$

$$\frac{\partial f_5}{\partial x_i} = 1 \quad i = 3, 4 \tag{36}$$

$$\frac{\partial f_6}{\partial X_i} = 0 \quad i = 1, 2, 3, 4, 7 \tag{37}$$

$$\frac{\partial f_6}{\partial y_i} = 1 \quad i = 5, 6 \tag{38}$$

$$\frac{\partial f_7}{\partial X_i} = \begin{cases} 1 & i = i_{\mathrm{spec}} \\ 0 & \text{otherwise} \end{cases} \tag{39}$$