

Memo

Documentation of the binary-XY code in thermopack

Thermotools

Location:
Trondheim
NORWAY

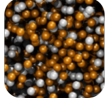
<https://thermotools.github.io/thermopack/index.html>

AUTHOR
Morten Hammer

DATE
2024-12-05

Contents

1	Introduction	2
2	Governing equations	2
2.1	Changing the specification	2
2.2	Termination	2
3	Results	3
A	Jacobian	3



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).

$$f_i = \ln K_i + \ln \hat{\varphi}_i(\mathbf{y}) - \ln \hat{\varphi}_i(\mathbf{x}) = 0, \quad i = 1, 2 \quad (1)$$

$$f_{i+2} = y_i - K_i x_i = 0, \quad i = 1, 2 \quad (2)$$

$$f_5 = x_1 + x_2 - 1 = 0 \quad (3)$$

$$f_6 = y_1 + y_2 - 1 = 0 \quad (4)$$

$$f_7 = S - S_{\text{spec}} = 0 \quad (5)$$

$$(6)$$

$$\mathbf{F} = \begin{pmatrix} f_1 \\ \vdots \\ f_7 \end{pmatrix} \quad (7)$$

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.

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

2.1 Changing the specification

Differentiating, we get:

$$\frac{d\mathbf{F}(\mathbf{X})}{d\mathbf{X}} \frac{d\mathbf{X}}{dS_{\text{spec}}} + \frac{d\mathbf{F}(\mathbf{X})}{dS_{\text{spec}}} = \mathbf{0} \quad (9)$$

$$\frac{d\mathbf{F}(\mathbf{X})}{d\mathbf{X}} \frac{d\mathbf{X}}{dS_{\text{spec}}} = \begin{pmatrix} \mathbf{0} \\ 1 \end{pmatrix} \quad (10)$$

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.

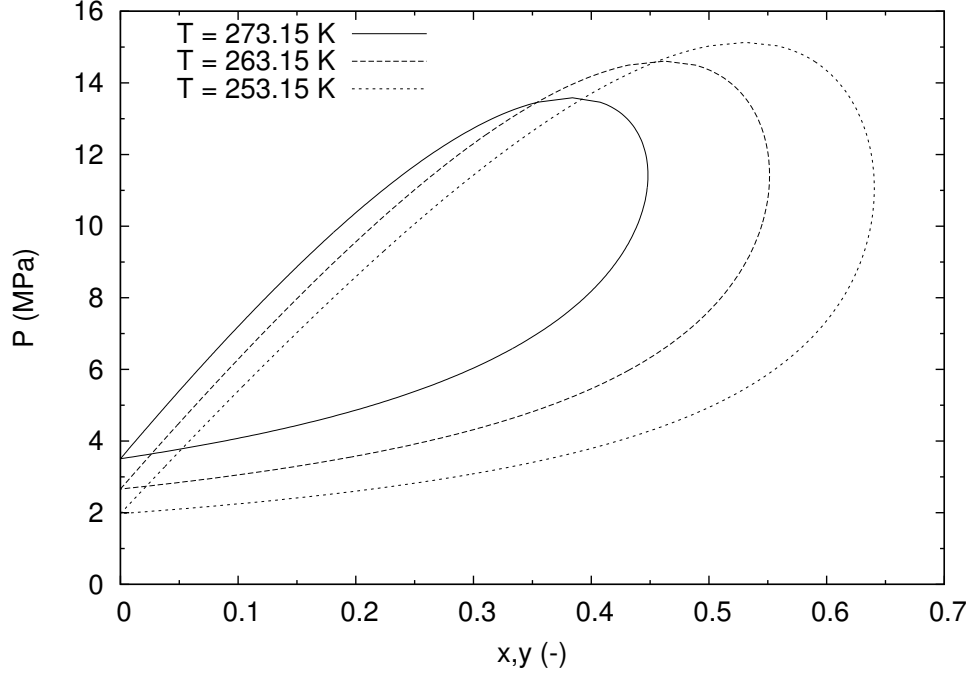
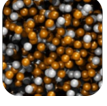


Figure 1: Mole fraction of NO in anCO₂-NO mixture with SRK and $k_{ij} = 0$.

3 Results

Have tested the mixture CO₂-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 CO₂ 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.

$$\frac{\partial f_1}{\partial \ln K_1} = 1 \quad (11)$$

$$\frac{\partial f_1}{\partial \ln K_2} = 0 \quad (12)$$

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

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

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

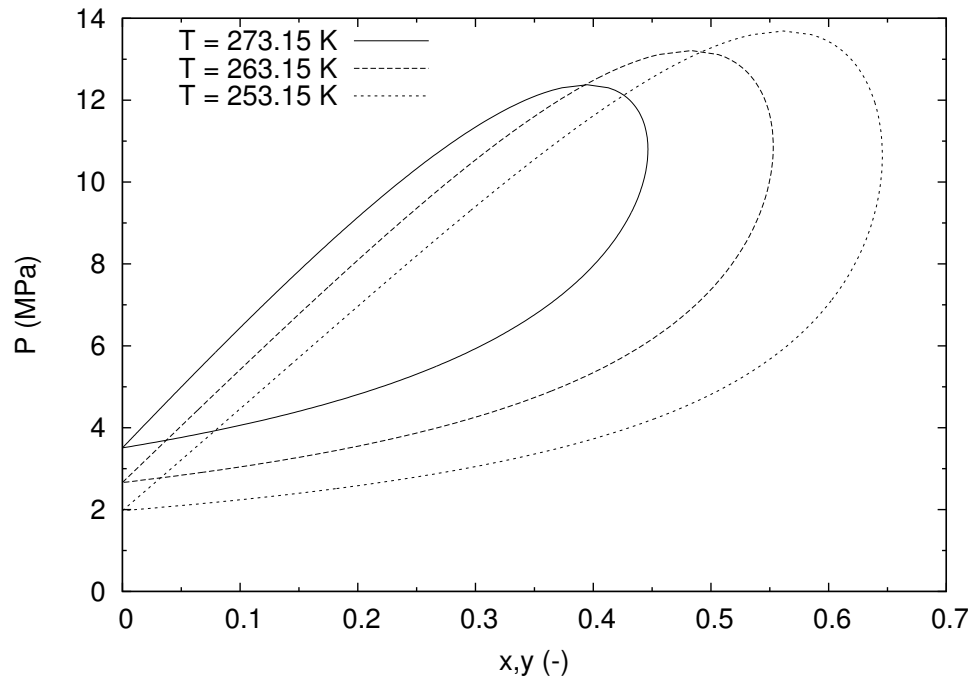


Figure 2: Mole fraction of NO in anCO₂-NO mixture with SRK and $k_{ij} = -0.119$.

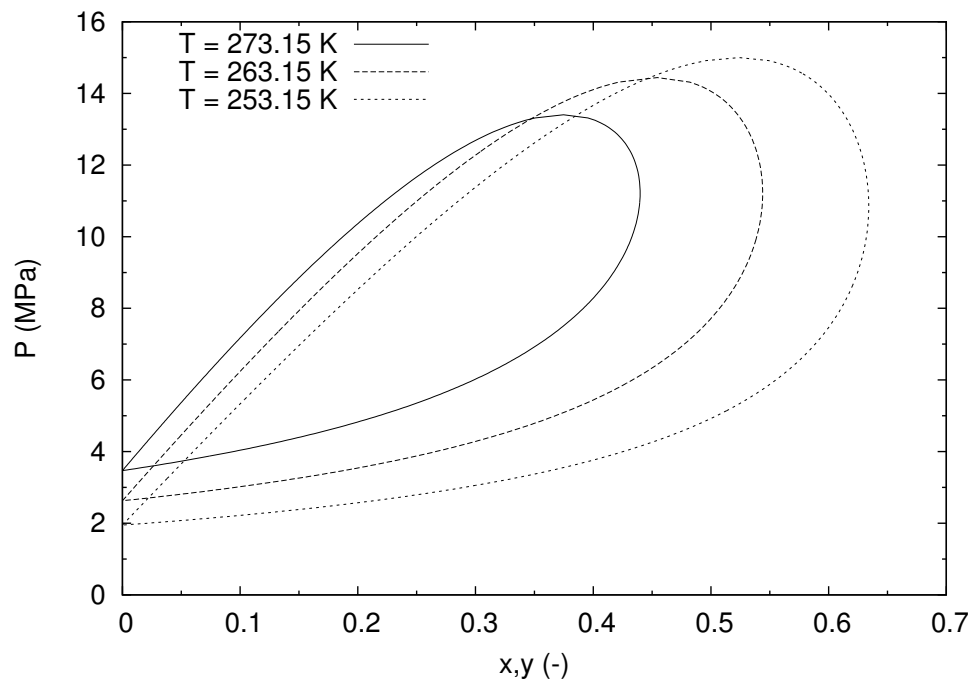


Figure 3: Mole fraction of NO in anCO₂-NO mixture with PR and $k_{ij} = 0$.

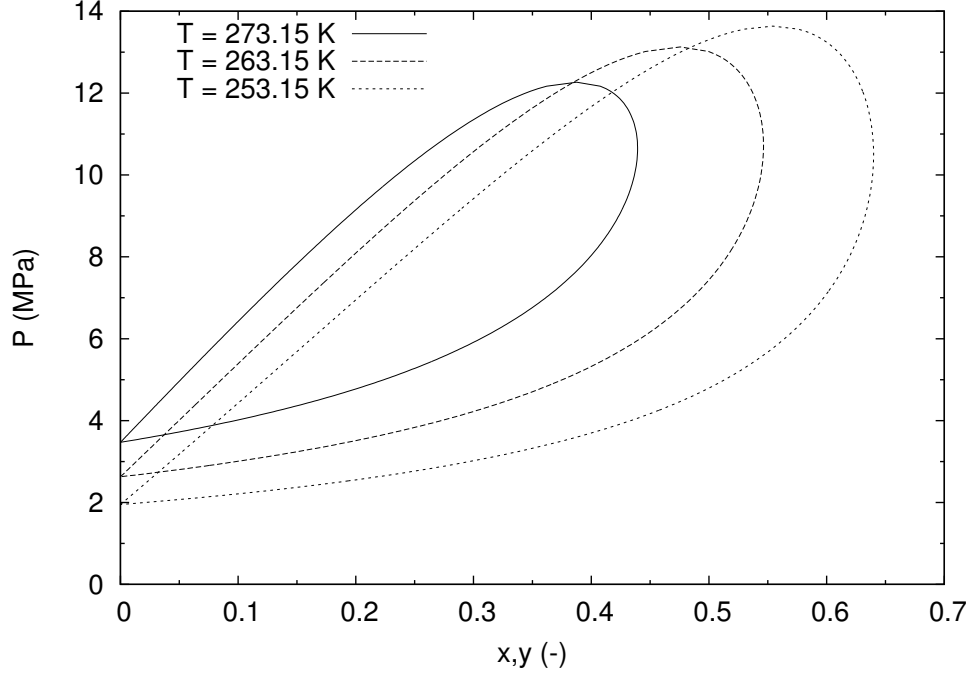
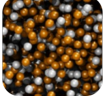


Figure 4: Mole fraction of NO in anCO₂-NO mixture with PR and $k_{ij} = -0.105$.

$$\frac{\partial f_2}{\partial \ln K_1} = 0 \quad (16)$$

$$\frac{\partial f_2}{\partial \ln K_2} = 1 \quad (17)$$

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

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

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

$$\frac{\partial f_3}{\partial \ln K_1} = -K_1 x_1 \quad (21)$$

$$\frac{\partial f_3}{\partial \ln K_2} = 0 \quad (22)$$

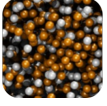
$$\frac{\partial f_3}{\partial x_1} = -K_1 \quad (23)$$

$$\frac{\partial f_3}{\partial x_2} = 0 \quad (24)$$

$$\frac{\partial f_3}{\partial y_1} = 1 \quad (25)$$

$$\frac{\partial f_3}{\partial y_2} = 0 \quad (26)$$

$$\frac{\partial f_3}{\partial \ln P} = 0 \quad (27)$$



$$\frac{\partial f_4}{\partial \ln K_1} = 0 \quad (28)$$

$$\frac{\partial f_4}{\partial \ln K_2} = -K_2 x_2 \quad (29)$$

$$\frac{\partial f_4}{\partial x_1} = 0 \quad (30)$$

$$\frac{\partial f_4}{\partial x_2} = -K_2 \quad (31)$$

$$\frac{\partial f_4}{\partial y_1} = 0 \quad (32)$$

$$\frac{\partial f_4}{\partial y_2} = 1 \quad (33)$$

$$\frac{\partial f_4}{\partial \ln P} = 0 \quad (34)$$

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

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

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

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

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