Chemical Thermodynamics for Process Simulation
Jürgen Gmehling, Bärbel Kolbe, Michael Kleiber and Jürgen Rarey
WILEY-VCH

Example 02.05 Density of Supercritical Ethylene Using a High Precision Equation of State

Problem:

At 293.15 K, ethylene is already in a supercritical state (T_c = 282.35 K). How much ethylene is in a pressurized bottle (50 dm^3), if the pressure on the manometer is P = 20 MPa?

Definitions and Constants:

$R := 8.31433 \frac{J}{mol \cdot K}$ $\quad cm := 0.01m \quad kmol := 1000mol \quad kPa := 1000Pa \quad bar := 10^5 Pa$

$dm := 0.1m \quad g := 0.001kg \quad MPa := 10^6 Pa$

Theory

Like reference equations, state-of-the-art technical equations of state are formulated in terms of the Helmholtz energy, which is split into an ideal gas part and a residual part. Instead of the specific volume, the density is used as a variable:

$$\frac{a(T,\rho)}{RT} = \frac{a^{id}(T,\rho) + a^{R}(T,\rho)}{RT} = \alpha^{id}(\tau,\delta) + \alpha^{R}(\tau,\delta) \qquad 2.104$$

with $\tau = T_c/T$ and $\delta = \rho / \rho_c$.

To calculate α^{id}, an expression for the ideal gas heat capacity is required. In Appendix A parameters for the following expressions are given:

$$\frac{c_P^{id}}{R} = B + (C-B)y^2\left[1 + (y-1)(D + Ey + Fy^2 + Gy^3)\right] \quad , \quad y = \frac{T}{A+T} \qquad 3.70$$

$$\frac{c_P^{id}}{J/(kmol\ K)} = A + B\left(\frac{C/T}{\sinh(C/T)}\right)^2 + D\left(\frac{E/T}{\cosh(E/T)}\right)^2 \qquad 3.69$$

The resulting expressions for α^{id} can be derived using eq. 2.105 and the antiderivatives given in Appendix C (F4 - Antiderivatives of cPid correlations):

$$\begin{aligned} a^{id}(T,v) &= u^{id}(T) - Ts^{id}(T,v) \\ &= \int_{T_0}^{T} c_v^{id}\,dT - T\int_{T_0}^{T} c_v^{id}\frac{dT}{T} - RT\ln\frac{v}{v_0} + a(T_0,v_0) \end{aligned} \qquad 2.105$$

For eq. 3.70 the following antiderivatives are given:

$$\begin{aligned}\int c_P^{id}\,dT = RBT + R(C-B)*\\ *[T-(D+E+F+G+H+2)A\ln\frac{A+T}{K}\\ -(2D+3E+4F+5G+6H+1)\frac{A^2}{A+T}\\ +(D+3E+6F+10G+15H)\frac{A^3}{2(A+T)^2}\\ -(E+4F+10G+20H)\frac{A^4}{3(A+T)^3}\\ +(F+5G+15H)\frac{A^5}{4(A+T)^4}\\ -(G+6H)\frac{A^6}{5(A+T)^5}\\ +H\frac{A^7}{6(A+T)^6}]+const.\end{aligned} \qquad \text{C.197}$$

$$\begin{aligned}\int \frac{c_P^{id}}{T}\,dT = RB\ln\frac{T}{K} + R(C-B)*\\ *[\ln\frac{A+T}{K}+(1+D+E+F+G+H)\frac{A}{A+T}\\ -\left(\frac{D}{2}+E+\frac{3F}{2}+2G+\frac{5}{2}H\right)\frac{A^2}{(A+T)^2}\\ +\left(\frac{E}{3}+F+2G+\frac{10}{3}H\right)\frac{A^3}{(A+T)^3}\\ -\left(\frac{F}{4}+G+\frac{5}{2}H\right)\frac{A^4}{(A+T)^4}\\ +\left(\frac{G}{5}+H\right)\frac{A^5}{(A+T)^5}\\ -\frac{H}{6}\frac{A^6}{(A+T)^6}]+const.\end{aligned} \qquad \text{C.198}$$

For eq. 3.69 the antiderivatives are:

$$\int c_P^{id}\,dT = AT + BC\coth\left(\frac{C}{T}\right) - DE\tanh\left(\frac{E}{T}\right) + const. \qquad \text{C.195}$$

$$\int \frac{c_P^{id}}{T}\,dT = A\ln\frac{T}{K} + B\left[\frac{C}{T}\coth\left(\frac{C}{T}\right) - \ln\sinh\left(\frac{C}{T}\right)\right] - \qquad \text{C.196}$$
$$- D\left[\frac{E}{T}\tanh\left(\frac{E}{T}\right) - \ln\cosh\left(\frac{E}{T}\right)\right] + const.$$

The constants cancel out when using the expressions in eq. 2.105, which also adds the value at a reference point. Usually, h_{ref} and s_{ref} are set to be zero at the ideal gas state at T_{ref} = 298.15 K and P_{ref} = 101325 Pa, even if this reference point is fictitious and the fluid regarded is in the liquid state.

The residual part is different for non-polar and polar fluids:

For non-polar fluids (methane, ethane, propane, n-butane, n-pentane, n-hexane, n-heptane, n-octane, argon, oxygen, nitrogen, ethylene, isobutane, cyclohexane, sulfur hexafluoride, carbon monoxide, carbonyl sulfide, n-decane, hydrogen sulfide, isopentane, neopentane, isohexane, krypton, n-nonane, toluene, xenon and R116):

$$\begin{aligned}\alpha^{\mathrm{R}}(\tau,\delta) = {} & \mathrm{n}_1\delta\tau^{0.25} + \mathrm{n}_2\delta\tau^{1.125} + \mathrm{n}_3\delta\tau^{1.5} + \mathrm{n}_4\delta^2\tau^{1..375} + \mathrm{n}_5\delta^3\tau^{0.25} + \mathrm{n}_6\delta^7\tau^{0.875} \\ & + \mathrm{n}_7\delta^2\tau^{0.625}\mathrm{e}^{-\delta} + \mathrm{n}_8\delta^5\tau^{1.75}\mathrm{e}^{-\delta} + \mathrm{n}_9\delta\tau^{3.625}\mathrm{e}^{-\delta^2} + \mathrm{n}_{10}\delta^4\tau^{3.625}\mathrm{e}^{-\delta^2} \\ & + \mathrm{n}_{11}\delta^3\tau^{14.5}\mathrm{e}^{-\delta^3} + \mathrm{n}_{12}\delta^4\tau^{12}\mathrm{e}^{-\delta^3}\end{aligned}$$

For polar fluids (R11, R12, R22, R32, R113, R123, R125, R134a, R143a, R152a, carbon dioxide, ammonia, acetone, nitrous oxide, sulfur dioxide, R141b, R142b, R218 and R245fa):

$$\begin{aligned}\alpha^{\mathrm{R}}(\tau,\delta) = {} & \mathrm{n}_1\delta\tau^{0.25} + \mathrm{n}_2\delta\tau^{1.25} + \mathrm{n}_3\delta\tau^{1.5} + \mathrm{n}_4\delta^3\tau^{0.25} + \mathrm{n}_5\delta^7\tau^{0.875} + \mathrm{n}_6\delta\tau^{2.375}\mathrm{e}^{-\delta} \\ & + \mathrm{n}_7\delta^2\tau^2\mathrm{e}^{-\delta} + \mathrm{n}_8\delta^5\tau^{2.125}\mathrm{e}^{-\delta} + \mathrm{n}_9\delta\tau^{3.5}\mathrm{e}^{-\delta^2} + \mathrm{n}_{10}\delta\tau^{6.5}\mathrm{e}^{-\delta^2} \\ & + \mathrm{n}_{11}\delta^4\tau^{4.75}\mathrm{e}^{-\delta^2} + \mathrm{n}_{12}\delta^2\tau^{12.5}\mathrm{e}^{-\delta^3}\end{aligned}$$

References:
R. Span; W. Wagner; Int. J. Thermophys. 24(1), 41-109 (2003).
E. W. Lemmon; R. Span; J. Chem. Eng. Data 24(1), 41-109 (2006).
R. Span; W. Wagner; Int. J. Thermophys. 24(1), 111-162 (2003).
E. C. Ihmels; E. W. Lemmon; Fluid Phase Equilib. 207, 111-130 (2003).

Component Selection and Model Parameters:

Parameter vectors for the ideal gas heat capacity (c_{id}) and for the real part of the Helmholtz energy (c) are stored in separate files and are imported as references. In the ideal heat capacity parameter vector, the first element denotes the equation to be used (1 - 3.70, 2 - 3.69).

Reference:H:\Th-Ex\02. PvT Behavior of Pure Components\Examples\02.EOS-ethylene.mcd(R)

name = "ethylene"

ispolar := 0

$$c = \begin{pmatrix} 0.9096223 \\ -2.4641015 \\ 0.56175311 \\ -0.019688013 \\ 0.078831145 \\ 0.00021478776 \\ 0.23151337 \\ -0.037804454 \\ -0.20122739 \\ -0.044960157 \\ -0.02834296 \\ 0.012652824 \end{pmatrix} \qquad c_{id} = \begin{pmatrix} 1 \\ 100.6795534 \\ 3.466324 \\ 18.867981 \\ -1.584956 \\ 6.3700828 \\ 0.0000544 \\ -0.0000307 \\ 0 \end{pmatrix}$$

$T_c = 282.35\,K$ $\quad P_c = 50.418\,bar$ $\quad v_c = 130.947\,\frac{cm^3}{mol}$ $\quad mw = 28.054\,\frac{g}{mol}$

α^{id} and α^R Functions, Auxiliary Functions

c_P^{id} function 3.70 and the two different integrals required for calculation of α_{id}.

$$y370(T) := \frac{T}{c_{id_2} \cdot K + T}$$

$$cpid370(T) := \begin{bmatrix} R \cdot c_{id_3} \ldots \\ + R \cdot \left(c_{id_4} - c_{id_3}\right) \cdot y370(T)^2 \cdot \begin{bmatrix} 1 \ldots \\ + \left(y370(T) - 1\right) \cdot \begin{pmatrix} c_{id_5} \ldots \\ + c_{id_6} \cdot y370(T) \ldots \\ + c_{id_7} \cdot y370(T)^2 \ldots \\ + c_{id_8} \cdot y370(T)^3 \ldots \\ + c_{id_9} \cdot y370(T)^4 \end{pmatrix} \end{bmatrix} \end{bmatrix}$$

$$
\begin{aligned}
\mathrm{intcpdt370}(T) := {} & R \cdot c_{id_3} \cdot T \ldots \\
& + R \cdot K \cdot \left(c_{id_4} - c_{id_3}\right) \cdot \left[\begin{array}{l}
\dfrac{T}{K} \ldots \\
+ -\left[\left(c_{id_5} + c_{id_6} + c_{id_7} + c_{id_8} + c_{id_9} + 2\right) \cdot c_{id_2} \cdot \ln\left(c_{id_2} + \dfrac{T}{K}\right)\right] \ldots \\
+ -\left(2 \cdot c_{id_5} + 3 \cdot c_{id_6} + 4 \cdot c_{id_7} + 5 \cdot c_{id_8} + 6 \cdot c_{id_9} + 1\right) \cdot \dfrac{\left(c_{id_2}\right)^2}{c_{id_2} + \dfrac{T}{K}} \ldots \\
+ \left(c_{id_5} + 3 \cdot c_{id_6} + 6 \cdot c_{id_7} + 10 \cdot c_{id_8} + 15 \cdot c_{id_9}\right) \cdot \dfrac{\left(c_{id_2}\right)^3}{2 \cdot \left(c_{id_2} + \dfrac{T}{K}\right)^2} \ldots \\
+ -\left[\left(c_{id_6} + 4 \cdot c_{id_7} + 10 \cdot c_{id_8} + 20 \cdot c_{id_9}\right) \cdot \dfrac{\left(c_{id_2}\right)^4}{3 \cdot \left(c_{id_2} + \dfrac{T}{K}\right)^3}\right] \ldots \\
+ \left(c_{id_7} + 5 \cdot c_{id_8} + 15 \cdot c_{id_9}\right) \cdot \dfrac{\left(c_{id_2}\right)^5}{4 \cdot \left(c_{id_2} + \dfrac{T}{K}\right)^4} \ldots \\
+ -\left[\left(c_{id_8} + 6 \cdot c_{id_9}\right) \cdot \dfrac{\left(c_{id_2}\right)^6}{5 \cdot \left(c_{id_2} + \dfrac{T}{K}\right)^5}\right] \ldots \\
+ \left(c_{id_9}\right) \cdot \dfrac{\left(c_{id_2}\right)^7}{6 \cdot \left(c_{id_2} + \dfrac{T}{K}\right)^6}
\end{array}\right]
\end{aligned}
$$

$$\text{intcp_Tdt370}(T) := R \cdot c_{id_3} \cdot \ln\left(\frac{T}{K}\right) \ldots$$
$$+ R \cdot \left(c_{id_4} - c_{id_3}\right) \cdot \left[\ln\left(c_{id_2} + \frac{T}{K}\right) \ldots \right.$$
$$+ \left(1 + c_{id_5} + c_{id_6} + c_{id_7} + c_{id_8} + c_{id_9}\right) \cdot \frac{c_{id_2}}{c_{id_2} + \frac{T}{K}} \ldots$$
$$+ - \left[\left(\frac{c_{id_5}}{2} + c_{id_6} + \frac{3 \cdot c_{id_7}}{2} + 2 \cdot c_{id_8} + \frac{5 \cdot c_{id_9}}{2} \right) \cdot \left(\frac{c_{id_2}}{c_{id_2} + \frac{T}{K}} \right)^2 \right] \ldots$$
$$+ \left(\frac{c_{id_6}}{3} + c_{id_7} + 2 \cdot c_{id_8} + \frac{10 \cdot c_{id_9}}{3} \right) \cdot \left(\frac{c_{id_2}}{c_{id_2} + \frac{T}{K}} \right)^3 \ldots$$
$$+ - \left[\left(\frac{c_{id_7}}{4} + c_{id_8} + \frac{5 \cdot c_{id_9}}{2} \right) \cdot \left(\frac{c_{id_2}}{c_{id_2} + \frac{T}{K}} \right)^4 \right] \ldots$$
$$+ \left(\frac{c_{id_8}}{5} + c_{id_9} \right) \cdot \left(\frac{c_{id_2}}{c_{id_2} + \frac{T}{K}} \right)^5 \ldots$$
$$\left. + - \left[\frac{c_{id_9}}{6} \cdot \left(\frac{c_{id_2}}{c_{id_2} + \frac{T}{K}} \right)^5 \right] \right]$$

c_P^{id} function 3.69 and the two different integrals required for calculation of α_{id}.

$$\text{cpid369}(T) := \left[c_{id_2} + c_{id_3} \cdot \left(\frac{\frac{c_{id_4} \cdot K}{T}}{\sinh\left(\frac{c_{id_4} \cdot K}{T}\right)} \right)^2 + c_{id_5} \cdot \left(\frac{\frac{c_{id_6} \cdot K}{T}}{\cosh\left(\frac{c_{id_6} \cdot K}{T}\right)} \right)^2 \right] \cdot \frac{J}{kmol \cdot K}$$

$$\text{intcpdt369}(T) := \left[\left(c_{id_2} \cdot \frac{T}{K} + c_{id_3} \cdot c_{id_4} \cdot \coth\left(\frac{c_{id_4} \cdot K}{T}\right) - c_{id_5} \cdot c_{id_6} \cdot \coth\left(\frac{c_{id_6} \cdot K}{T}\right) \right) \cdot \frac{J}{kmol} \right]$$

$$\text{intcp_Tdt369}(T) := \left[\begin{array}{l} c_{id_2} \cdot \ln\left(\frac{T}{K}\right) \ldots \\ + c_{id_3} \cdot \left(\frac{c_{id_4} \cdot K}{T} \cdot \coth\left(\frac{c_{id_4} \cdot K}{T}\right) - \ln\left(\sinh\left(\frac{c_{id_4} \cdot K}{T}\right)\right)\right) \ldots \\ + -\left[c_{id_5} \cdot \left(\frac{c_{id_6} \cdot K}{T} \cdot \coth\left(\frac{c_{id_6} \cdot K}{T}\right) - \ln\left(\sinh\left(\frac{c_{id_6} \cdot K}{T}\right)\right)\right)\right] \end{array} \right] \cdot \frac{J}{kmol \cdot K}$$

Set the correct functions for c_P^{id} and the two different integrals depending on the function used.

$$\text{cpid}(T) := \begin{cases} \text{cpid370}(T) & \text{if } c_{id_1} = 1 \\ \text{cpid369}(T) & \text{if } c_{id_1} = 2 \end{cases}$$

$$\text{intcpdt}(T) := \begin{cases} \text{intcpdt370}(T) & \text{if } c_{id_1} = 1 \\ \text{intcpdt369}(T) & \text{if } c_{id_1} = 2 \end{cases}$$

$$\text{intcp_Tdt}(T) := \begin{cases} \text{intcp_Tdt370}(T) & \text{if } c_{id_1} = 1 \\ \text{intcp_Tdt369}(T) & \text{if } c_{id_1} = 2 \end{cases}$$

$$\delta_0 := \frac{v_c \cdot 101.325kPa}{R \cdot 298.15K} \qquad \frac{1}{\delta_0} = 187 \qquad \alpha_{id}(\tau,\delta) := \frac{\text{intcpdt}\left(\frac{T_c}{\tau}\right) - \frac{T_c}{\tau} \cdot \text{intcp_Tdt}\left(\frac{T_c}{\tau}\right)}{R \cdot \frac{T_c}{\tau}} - \ln\left(\frac{\delta_0}{\delta}\right)$$

$$\begin{aligned} \alpha R_{np}(\tau,\delta) := {} & c_1 \cdot \delta \cdot \tau^{0.25} + c_2 \cdot \delta \cdot \tau^{1.125} + c_3 \cdot \delta \cdot \tau^{1.5} + c_4 \cdot \delta^2 \cdot \tau^{1.375} + c_5 \cdot \delta^3 \cdot \tau^{0.25} \ldots \\ & + c_6 \cdot \delta^7 \cdot \tau^{0.875} + c_7 \cdot \delta^2 \cdot \tau^{0.625} \cdot e^{-\delta} + c_8 \cdot \delta^5 \cdot \tau^{1.75} \cdot e^{(-\delta)} + c_9 \cdot \delta \cdot \tau^{3.625} \cdot e^{-\delta^2} \ldots \\ & + c_{10} \cdot \delta^4 \cdot \tau^{3.625} \cdot e^{-\delta^2} + c_{11} \cdot \delta^3 \cdot \tau^{14.5} \cdot e^{-\delta^3} + c_{12} \cdot \delta^4 \cdot \tau^{12} \cdot e^{-\delta^3} \end{aligned}$$

$$\begin{aligned} \alpha R_p(\tau,\delta) := {} & c_1 \cdot \delta \cdot \tau^{0.25} + c_2 \cdot \delta \cdot \tau^{1.25} + c_3 \cdot \delta \cdot \tau^{1.5} + c_4 \cdot \delta^3 \cdot \tau^{0.25} + c_5 \cdot \delta^7 \cdot \tau^{0.875} \ldots \\ & + c_6 \cdot \delta \cdot \tau^{2.375} \cdot e^{-\delta} + c_7 \cdot \delta^2 \cdot \tau^2 \cdot e^{-\delta} + c_8 \cdot \delta^5 \cdot \tau^{2.125} \cdot e^{-\delta} + c_9 \cdot \delta \cdot \tau^{3.5} \cdot e^{-\delta^2} \ldots \\ & + c_{10} \cdot \delta \cdot \tau^{6.5} \cdot e^{-\delta^2} + c_{11} \cdot \delta^4 \cdot \tau^{4.75} \cdot e^{-\delta^2} + c_{12} \cdot \delta^2 \cdot \tau^{12.5} \cdot e^{-\delta^3} \end{aligned}$$

$$\alpha_R(\tau,\delta) := \begin{cases} \alpha R_{np}(\tau,\delta) \\ \alpha R_p(\tau,\delta) & \text{if ispolar} = 1 \end{cases}$$

Auxiliary functions:

$$\alpha(\tau,\delta) := \alpha_{id}(\tau,\delta) + \alpha_R(\tau,\delta) \qquad \tau(T) := \frac{T_c}{T} \qquad \delta(v) := \frac{v_c}{v}$$

Different Thermodynamic Functions of T and v:

pressure $P_{eos}(T,v) := -R \cdot T \cdot \left(\frac{d}{dv}\alpha\left(\tau(T),\delta(v)\right)\right)$

v as function of P (vapor) $v_{V_eos}(T,P) := \left| \begin{array}{l} v \leftarrow \frac{R \cdot T}{P} \\ \text{root}\left[\frac{\left(P_{eos}(T,v) - P\right)}{P}, v\right] \end{array} \right.$

v as function of P (liquid) $v_{L_eos}(T,P) := \left| \begin{array}{l} v \leftarrow 0.4 \cdot v_c \\ \text{root}\left[\frac{\left(P_{eos}(T,v) - P\right)}{P}, v\right] \end{array} \right.$

A starting value close above the hardcore volume is usually possible and ensures finding the liquid root. As P(v) covers several orders of magnitude, the objective of the root function should be the relative deviation in pressure.

Solution:

Conditions: $T := 293.15K$ $V := 50dm^3$ $P := 20MPa$

$\tau(T) = 0.963$

In the first step the molar volume of ethylene at the conditions inside the pressurized bottle has to be calculated:

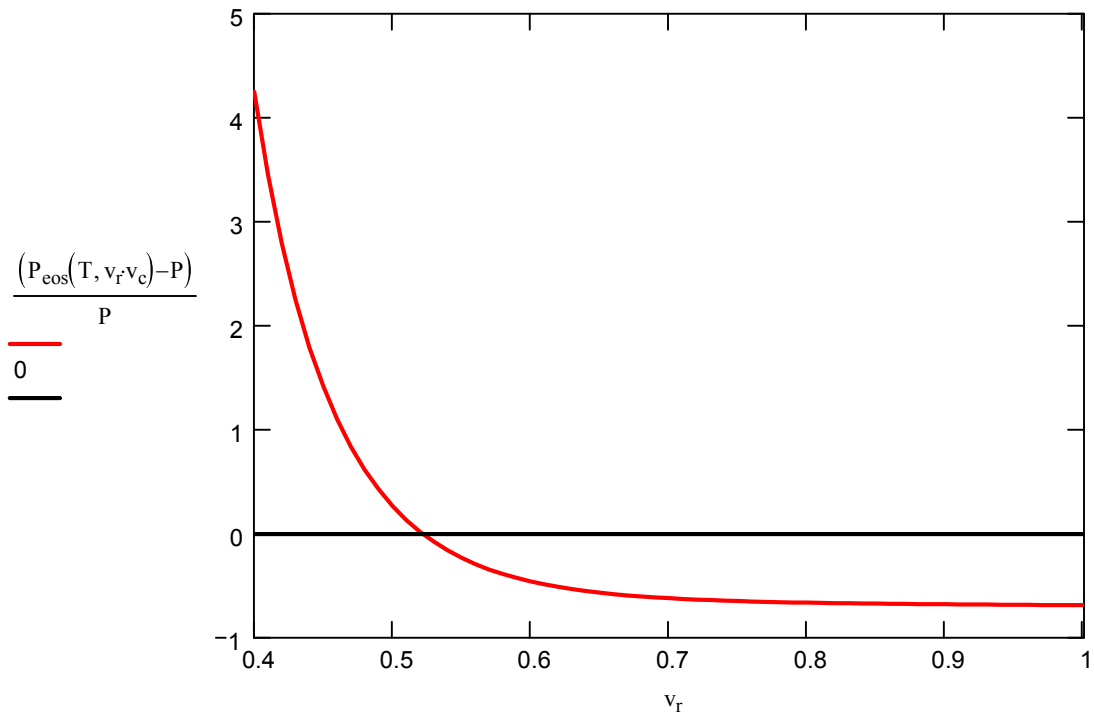
$v := v_{V_eos}(T,P)$ $v = 0.017 + 0.145i\,\frac{dm^3}{mol}$ (complex solution)

$v := v_{L_eos}(T,P)$ $v = 0.068\,\frac{dm^3}{mol}$

Although in the supercritical state, the root function found only a complex and not a real solution when starting from the ideal gas volume. The second function usually used to find the liquid volume starts at a very low liquid volume and converges to the correct solution.
Dividing the volume of the bottle by the molar volume yields the number of moles, that can be easily converted to the mass of ethylene in the bottle:

$n := \frac{V}{v}$ $n = 731.566\,mol$ $m := n \cdot mw$ $m = 20.523\,kg$

The pressurized bottle contains 20.523 kg of ethylene.

The following plot shows the dependence of the objective function of the root function on reduced volume using the high precision equation of state for ethylene:

$v_r := 0.40, 0.41 .. 1$