Chemical Thermodynamics for Process Simulation
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Example 02.06 Isobaric Heating of Ethylene Using a High Precision Equation of State

Problem:

Ethylene from a pipeline (50 t/h, 70 bar, 5°C) passes a heat exchanger and is heated up to 45°C. The pressure drop is negligible. As usual, in the data sheet of the heat exchanger the c_P values at inlet and outlet are given:

c_P (5°C, 70 bar) = 3.984 J/g*K

c_P (45°C, 70 bar) = 3.783 J/g*K

Calculate the heat to be exchanged

a) by estimation with an average c_P

b) using a high-precision equation of state

Which solution shall be preferred?

Definitions and Constants:

$R := 8.31433 \frac{J}{mol \cdot K}$

$cm := 0.01m$ $kmol := 1000mol$ $kPa := 1000Pa$ $bar := 10^5 Pa$

$dm := 0.1m$ $g := 0.001kg$ $MPa := 10^6 Pa$ $h := 3600s$

$MW := 10^6 W$

Theory

Component Selection and Model Parameters:

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

name = "ethylene"

ispolar := 0

c =

0.9096223
-2.4641015
0.56175311
-0.019688013
0.078831145
0.00021478776
0.23151337
-0.037804454
-0.20122739
-0.044960157
-0.02834296
0.012652824

$$c_{id} = \begin{pmatrix} 1 \\ 100.6795534 \\ 3.466324 \\ 18.867981 \\ -1.584956 \\ 6.3700828 \\ 0.0000544 \\ -0.0000307 \\ 0 \end{pmatrix}$$

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

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

Different Thermodynamic Functions of T and v:

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

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

v as function of P (liquid) $\quad v_{L_eos}(T,P) := \left| \begin{array}{l} v \leftarrow 0.38 \cdot v_c \\ root\left[\frac{(P_{eos}(T,v) - P)}{P}, v\right] \end{array} \right.$

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.

h as function of T and v $\quad h_{eos}(T,v) := -R \cdot T \cdot \left[T \cdot \left(\frac{d}{dT}\alpha(\tau(T),\delta(v))\right) + v \cdot \left(\frac{d}{dv}\alpha(\tau(T),\delta(v))\right) + 1\right]$

Solution:

Conditions:

$T_{in} := (5 + 273.15)K \qquad \tau(T_{in}) = 1.015$

$T_{out} := (45 + 273.15)K \qquad \tau(T_{out}) = 0.887$

$P := 70bar \qquad m_{flow} := 50000\,\frac{kg}{h}$

a) In the first step the mean heat capacity in the temperature range between 5 and 45°C is calculated:

$c_{P_av} := \frac{(3.984 + 3.783)}{2}\,\frac{J}{g \cdot K} \qquad c_{P_av} = 3.883\,\frac{J}{g \cdot K}$

The heat stream to be supplied by the heat exchanger can then be calculated via:

$Q_{flow} := m_{flow} \cdot (T_{out} - T_{in}) \cdot c_{P_av} \qquad Q_{flow} = 2.157\,MW$

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

$v_{in} := v_{L_eos}(T_{in}, P)$ $\quad v_{in} = 0.077 \frac{dm^3}{mol}$ $\quad h_{eos}(T_{in}, v_{in}) = -5.355 \times 10^5 \frac{J}{mol}$

$v_{out} := v_{L_eos}(T_{out}, P)$ $\quad v_{out} = 0.223 \frac{dm^3}{mol}$ $\quad h_{eos}(T_{out}, v_{out}) = -5.285 \times 10^5 \frac{J}{mol}$

Although in the supercritical state, the root function does not succeed to find 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.

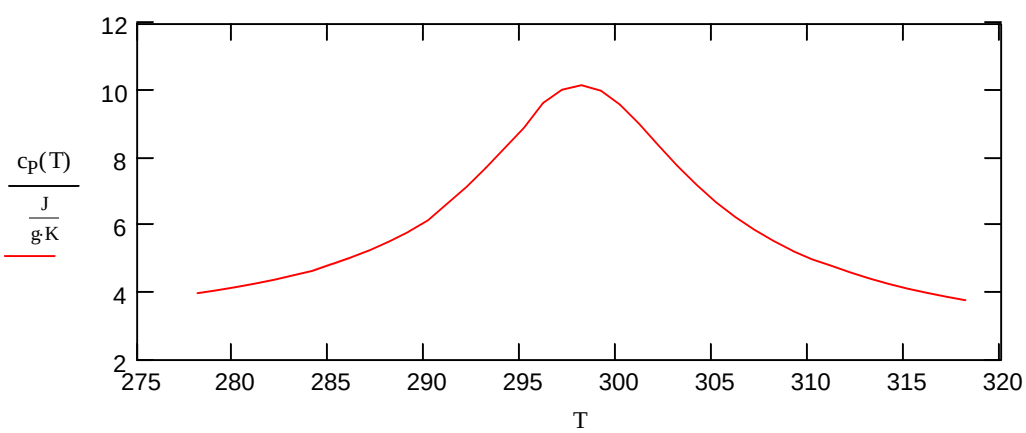
In the next step the molar and total enthalphy difference between inlet and outlet stream is calculated:

$\Delta h := h_{eos}(T_{out}, v_{out}) - h_{eos}(T_{in}, v_{in})$ $\quad \Delta h = 6960.506 \frac{J}{mol}$

$n_{flow} := \frac{m_{flow}}{mw}$ $\quad n_{flow} = 1782.277 \frac{kmol}{h}$

$Q_{flow} := \Delta h \cdot n_{flow}$ $\quad Q_{flow} = 3.446\,MW$

There is a large difference between the two results. Although the c_P values are correct, approach a) does not yield a reasonable result. The problem is that c_P has a sharp maximum in the area in the vicinity of the critical point, as the following plot illustrates:

$T := 278.15K, 279.15K .. 318.15K$

$$c_P(T) := -\frac{h_{eos}(T - 0.05K, v_{L_eos}(T - 0.05K, P)) - h_{eos}(T + 0.05K, v_{L_eos}(T + 0.05K, P))}{0.1K \cdot mw}$$