# Exercise 10

## 1. Computation of enthalpy and entropy from cubic EOS

The objective of this exercise is to use residual enthalpy and residual entropy obtained from an equation of state (EOS) along with the enthalpy and entropy of the ideal state to compute the actual $\Delta_{12}H$ and $\Delta_{12}S$ between states 1 and 2. The Soave-Redlich-Kwong EOS will be used in this exercise. The chemical compound to be considered is Ethylene.

### Part I

The Soave-Redlich-Kwong EOS is given by

$$P = \frac{RT}{V-b} - \frac{a}{V(V+b)} \tag{1}$$

where

$$a = 0.42748\frac{(RT_c)^2}{P_c}[1+\Omega(1-\sqrt{T_r})]^2, \quad b = 0.08664\frac{RT_c}{P_c}, \quad \Omega = 0.48 + 1.57\omega - 0.17\omega^2 \tag{2}$$

$P$ is the pressure, $T$ is the temperature, and $v$ is the molar volume. $a$ and $b$ are model parameters. The subscript $c$ denotes *critical*. $T_r = T/T_c$ is reduced temperature and $\omega$ is acentric factor. The gas constant is represented by $R$.

Given the following units:

| | | |
|---|---|---|
| $P$ | [=] | MPa |
| $T$ | [=] | K |
| $V$ | [=] | $cm^3$/mol |

c) From the information given above, determine the units of $a$ and $b$.

d) Given $R = 8.31447 \cdot 10^{-5}$ $m^3$-bar/mol-K. Adjust $R$ such that it's units is consistent with the remaining EOS (1)–(2).

c) Looking at the SRK EOS, in the second term, we have V+b in the denominator for this to make sense, $[b]=[V]=cm^3/mol$. Furthermore, the unit of each term must be equal to the unit of P

$$\Rightarrow [P] = \left[\frac{a}{V(V+b)}\right]$$

$$MPa = \frac{[a]}{(cm^3/mol)^2}$$

$$\Rightarrow [a] = \frac{MPa \cdot cm^6}{mol^2}$$

$$\boxed{[a] = \frac{MPa \cdot cm^6}{mol^2}, \quad [b] = \frac{cm^3}{mol}}$$

d) $\Omega$ and $T_r$ are unitless, as we know the unit of a, we need this to be true:

$$[a] = \left[\frac{R^2T_c^2}{P_c}\right] = \frac{MPa \cdot cm^6}{mol^2}$$

$$\Rightarrow [R]^2 = \frac{MPa \cdot cm^6}{mol^2} \cdot \frac{MPa}{K^2} = \frac{MPa^2 \cdot cm^6}{mol^2 \cdot K^2}$$

$$[R] = \frac{MPa \cdot cm^3}{mol \cdot K}$$

Need to convert R into these units

$$\Rightarrow \frac{m^3 \cdot bar}{mol \cdot K} \quad \text{to} \quad \frac{MPa \cdot cm^3}{mol \cdot K}$$

$m^3$ to $cm^3$: $1\ m^3 = 10^6\ cm^3$

bar to MPa: $1\ bar = 10^5\ Pa = 10^{-1}\ MPa$

$\Rightarrow$ Multiply by $10^6 \cdot 10^{-1} = 10^5$

$$\Rightarrow \text{Adjusted } R = 8,31447\ \frac{MPa \cdot cm^3}{mol \cdot K}$$

## Part II

The critical constants of ethylene are

$$P_c = 5.0418 \text{ [MPa]}$$
$$T_c = 282.35 \text{ [K]}$$

and the acentric factor is $\omega = 0.0866$ [−]. State 1 is specified by $T_1 = 250$ K and $P_1 = 3.0$ MPa.

a) Compute the values of $a$ and $b$ at state $T_1$ and $P_1$.

Let's introduce the definitions

$$A = \frac{aP}{(RT)^2}, \qquad B = \frac{bP}{RT} \tag{3}$$

b) Compute the values of $A$ and $B$ at state $T_1$ and $P_1$.

The compressibility factor is defined by

$$Z = \frac{Pv}{RT} \tag{4}$$

c) Substitute (3) and (4) into (1) and manipulate till the results is on the form of a cubic polynomial $\alpha Z^3 + \beta Z^2 + \gamma Z + \delta = 0$.

d) Use the computed results above to determine the values of $\alpha$, $\beta$, $\gamma$ and $\delta$. Determine the three roots of the cubic polynomial $\alpha Z^3 + \beta Z^2 + \gamma Z + \delta = 0$.

e) From, e.g., *Perry's Handbook* we find that ethylene is compressed liquid at state $(T_1, P_1)$. Based on this information, which $Z$-root should we choose?

All code is attached in a seperate python file

a) Inserting the given parameters into the equation from part I: (Compared to the provided numerical answers I have wrong units, but by converting to the same unit as the numerical answers, my answers become correct.

$J = Pa \cdot m^3 \Rightarrow MPa \cdot cm^6 = 10^6 \cdot 10^{-12} Pa \cdot m^6 = 10^{-6} J \cdot m^3$

$cm^3 = 10^{-6} m^3$

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----- Part II -----
a) Converted to the units used in the numerical answers:
a = 0.5018026474493057 J*m^3/mol^2, b = 4.034179260856837e-05 m^3/mol
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b) Using eq 3.

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b) A = 0.3484215788164907, B = 0.0582239771510175
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c) eq 1: $P = \frac{RT}{V-b} - \frac{a}{V(V+b)}$, rearranging $/ \cdot V-b$

$$Pv - Pb = RT - \frac{a}{V+b} + \frac{ab}{V(V+b)} \quad / \cdot V$$

$$PV^2 - PbV = RTV - \frac{aV}{V+b} + \frac{ab}{V+b} \quad / \cdot V+b$$

$$PV^3 + PbV^2 - PbV^2 - Pb^2V = RTV^2 + RTbV - aV + ab$$

$$PV^3 - RTV^2 + (-RTb - Pb^2 + a)V - ab = 0 \quad / V = \frac{ZRT}{P}$$

$$\frac{R^3T^3}{P^2}Z^3 - \frac{R^3T^3}{P^2}Z^2 + \left(-\frac{R^2T^2}{P}b - RTb^2 + \frac{RT}{P}a\right)Z - ab = 0 \quad / \cdot \frac{P^2}{R^3T^3}$$

$$Z^3 - Z^2 + \left(-\frac{P}{RT}b - \frac{P^2}{R^2T^2}b^2 + \frac{P}{R^2T^2}a\right)Z - \frac{P^2}{R^3T^3}ab = 0 \quad / A = \frac{aP}{(RT)^2}, B = \frac{bP}{RT}$$

$$Z^3 - Z^2 + (A - B - B^2)Z - AB = 0$$

Then: $\alpha = 1$, $\beta = -1$, $\gamma = A - B - B^2$, $\delta = -AB$

d) Using the answer from c) and the polynomial solution method from previous exercises

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d) alpha = 1, beta = -1, gamma = 0.286807570150191, delta = -0.0202864900439328
   The roots of the system are: 0.5341874428691661, 0.3604562028894567 and 0.10535635424137736
```

e) As long as we have a liquid, we choose the smallest Z as it corresponds to the smallest V ($V = \frac{ZRT}{P}$), which again corresponds to the liquid state. $Z = 0.105356$

## Part III

For example, enthalpy can be computed by

$$H = H^{ig} + H^R \tag{5}$$

$H^{ig}$ denotes the enthalpy as if the substance were in the ideal gas state. $H^R$ is a correction (residual) enthalpy that, when added to $H^{ig}$, results in the actual enthalpy, $H$. Similarily for entropy:

$$S = S^{ig} + S^R \tag{6}$$

We can derive expressions for residual properties from cubic EOS. For the Soave-Redlich-Kwong EOS, the residual enthalpy and entropy are given by, respectively

$$H^R = RT(Z-1) + \frac{T(da/dT) - a}{b} \ln\frac{Z+B}{Z} \tag{7}$$

$$S^R = R\ln(Z-B) + \frac{da/dT}{b} \ln\frac{Z+B}{Z} \tag{8}$$

with

$$\frac{da}{dT} = -0.42748 \frac{R^2 T_c}{P_c} \frac{(1+\Omega(1-\sqrt{T_r}))\Omega}{\sqrt{T_r}} \tag{9}$$

f) Compute the residual properties $H^R$ and $S^R$ at state $(T_1, P_1)$.

g) Comment on the sign of the computed values for $H^R$ and $S^R$.

*Hint*: this is not a discussion related with exothermic/endothermic.

f) Again, inserting equations 7-9 into python, and using the smallest Z-root:

```
----- Part III -----
f) HR = -10386.618623209526 J/mol, SR = -37.61693992912422 J/mol*K
```

Units

$H^R$ will have the same unit as the $RT(Z-1)$ term, which is

$$\frac{MPa \cdot cm^3}{mol \cdot K} \cdot K = \frac{10^6\ Pa \cdot 10^{-6} m^3}{mol} = \frac{J}{mol}$$

Similarily for $S^R$, it will have the same units as $R$:

$$\frac{MPa \cdot cm^3}{mol \cdot K} = \frac{10^6\ Pa \cdot 10^{-6} m^3}{mol \cdot K} = \frac{J}{mol \cdot K}$$

g) They are both negative, this means that both $H < H^{ig}$ and $S < S^{ig}$

## Part IV

State 2 is saturated vapor at $T_2 = 170$ K and $P_2 = 0.10526$ MPa.

For a change in state, (5) and (6) yield, respectively

$$\Delta_{12}H = \Delta_{12}H^{ig} + H_2^R - H_1^R \tag{10}$$

$$\Delta_{12}S = \Delta_{12}S^{ig} + S_2^R - S_1^R \tag{11}$$

where

$$\Delta_{12}H^{ig} = \int_{T_1}^{T_2} C_P^{ig}\, dT$$

$$\Delta_{12}S^{ig} = \int_{T_1}^{T_2} \frac{C_P^{ig}}{T}\, dT - R\ln\frac{P_2}{P_1}$$

For ethylene, the heat capacity is given by

$$C_P^{ig}/R = a_0 + a_1 T + a_2 T^2 + a_3 T^3 + a_4 T^4$$

with

$$a_0 = 4.221,\ a_1 = -0.008782,\ a_2 = 0.00005795,\ a_3 = -6.729 \times 10^{-8},\ a_4 = 2.511 \times 10^{-11}$$

a) Compute $\Delta_{12}H^{ig}$ and $\Delta_{12}S^{ig}$.

a) Inserting the provided expressions into python gives:

```
----- Part IV -----
a) dHig = -2906.66560804465 J/mol, dSig = 13.902163523097O5 J/mol*K
```

## Part V

a) Compute $\Delta_{12}H$ and $\Delta_{12}S$ from (10) and (11), respectively.

b) Tabulated values for $\Delta_{12}H$ and $\Delta_{12}S$ are, respectively, 7505.57 J/mol and 51.5212 J/mol-K. Compute the error of Soave-Redlich-Kwong.

a) To do this, parts II and III was repeated for state 2 to find $H_2^R$ and $S_2^R$, the only difference is that we know that state 2 is saturated vapor, so we choose the largest Z-root instead of the little one in part III. Inserting the calculated parameters into equations 10 and 11 gives:

```
----- Part V -----
a) dH12 = 7372.290407323341 J/mol, dS12 = 51.12891748393073 J/mol*K
```

b) Using error = $\left| \frac{\text{Tabulated} - \text{Calculated}}{\text{Tabulated}} \right| \cdot 100\,\%$

=>

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b) Error in dH12 = 1.7757 %,
   Error in dS12 = 0.7614 %
```

## 2. Computation of enthalpy and entropy with cubic EOS using mixing rules

Consider the binary mixture of $CO_2$ (component 1) and normal pentane (component 2). The overall composition is $z_1 = 0.32$ ($z_2 = 0.68$). Tabulated values for the components are:

| | $CO_2$ | n-Pentane |
|---|---|---|
| $T_c$ [K] | 304.2 | 469.7 |
| $P_c$ [MPa] | 7.374 | 3.37 |
| $\omega$ [-] | 0.225 | 0.252 |

The ideal gas heat capacity coefficients are:

| | $CO_2$ | n-Pentane |
|---|---|---|
| $a_0$ | 3.259 | 7.554 |
| $a_1$ | 0.001356 | $-0.000368$ |
| $a_2$ | 0.00001502 | 0.00011846 |
| $a_3$ | $-2.374 \times 10^{-8}$ | $-1.4939 \times 10^{-7}$ |
| $a_4$ | $1.056 \times 10^{-11}$ | $5.753 \times 10^{-11}$ |

where $c_p/R = a_0 + a_1 T + a_2 T^2 + a_3 T^3 + a_4 T^4$ and $R = 8.3144$ (MPa· cm$^3$)/(mol·K).

Use the Soave-Redlich-Kwong equation of state (EOS) with the mixing rules

$$a_{\text{mix}} = \sum_i \sum_j x_i x_j \left(1 - k_{ij}\right) \left(a_i a_j\right)^{1/2}$$

$$b_{\text{mix}} = \sum_i x_i b_i$$

Here $a_i$ and $b_i$ refer to the pure component. For the $CO_2$-pentane mixture, $k_{ij} = k_{12} = 0.12$.

Compute $\Delta_{12}H$ and $\Delta_{12}S$ of the binary mixture with the states 1 and 2 specified by:

| | State 1 | State 2 |
|---|---|---|
| $T$ [K] | 277 | 300 |
| $P$ [MPa] | 1.615 | 1.615 |

Here, I heavily reused the code from problem 1, but some adaptations had to be made

Part II: I first found the a and b parameters for each component, before i found $a^{mix}$ and $b^{mix}$ using the mixing rules. We know that $k_{11}=0$, $k_{22}=0$ and $k_{12}=k_{21}=0,12$ (k is symmetric)

When finding the Z-roots, only one were found for both states so I did not have to choose.

Part III: To find $da^{mix}/dT$, I wrote out the full expression:

$$a^{mix} = Z_1^2 a_1 + 2 \cdot Z_1 \cdot Z_2 \cdot (1 - k_{12}) \cdot \sqrt{a_1 a_2} + Z_2^2 a_2$$

Then:

$$\frac{da^{mix}}{dT} = Z_1^2 \frac{da_1}{dT} + \frac{2 \cdot Z_1 \cdot Z_2 \cdot (1-k_{12}) \cdot \frac{1}{2}}{\sqrt{a_1 \cdot a_2}} \cdot \frac{d}{dT}(a_1 a_2) + Z_2^2 \frac{da_2}{dT} \quad \text{/using product rule}$$

$$= Z_1^2 \frac{da_1}{dT} + \frac{Z_1 \cdot Z_2 \cdot (1-k_{12})}{\sqrt{a_1 \cdot a_2}} \left(a_1 \frac{da_2}{dT} + a_2 \frac{da_1}{dT}\right) + Z_2 \frac{da_2}{dT}$$

Which was added into python

Part IV: To find $C_p^{mix}$ i used:

$$C_p^{mix} = Z_1 C_{p1} + Z_2 C_{p2}$$

The result of the calculations was:

```
dH12 = 3175.986988165758 J/mol, dS12 = 11.009916448370468 J/mol*K
```

I am aware that the python file is difficult to read. I wasnt sure on how to do this one, so it became «learn as you go». This resulted in a chaotic python file.

I hope it is still good enough to get the exercise approved, even though I do not have the exact answers, I can see that they are in the correct ballpark at the very least.