## Problem 7

a) Estimate the residual properties using Lee/Kessler generalized correlations
$\mathrm{T}=200^{\circ} \mathrm{C}=473.15 \mathrm{~K}$
$\mathrm{P}=1400 \mathrm{kPa}=1400 * \mathrm{bar} / 100 \mathrm{kPa}=14 \mathrm{bar}$

The critical conditions of water from Table B. 1
$\mathrm{T}_{\mathrm{c}}=647.1 \mathrm{~K}$
$\mathrm{P}_{\mathrm{c}}=220.55 \mathrm{bar}$
$\omega=0.345$
$\mathrm{M}=18.015$
The reduced temperature and pressure
$\mathrm{T}_{\mathrm{r}}=473.15 / 647.1=0.73$
$\mathrm{P}_{\mathrm{r}}=14 / 220.55=0.0635$

Use Tables in Appendix to get $Z^{0}, Z^{1}$ by interpolation (see solution of problem 5 for how to do linear interpolation)

Note: The values in the table are not italic which means that the fluid at the conditions given is in the vapor phase. We already know from the reduced variables that we are not in the supercritical region.
$Z^{0}=0.9431$
$Z^{1}=-0.0542$
$\mathrm{Z}=0.9431+0.345^{*}(-0.0542)=0.9244$

$$
\begin{aligned}
& \mathrm{V}^{\mathrm{R}}=\mathrm{V}-\mathrm{V}^{\mathrm{ig}}=\mathrm{Z} \frac{\mathrm{RT}}{\mathrm{P}}-\frac{\mathrm{RT}}{\mathrm{P}}=(\mathrm{Z}-1) \frac{\mathrm{RT}}{\mathrm{P}} \\
& =(0.9244-1) * \frac{83.14\left(\frac{\mathrm{~cm}^{3} \mathrm{bar}}{\mathrm{~mol} \mathrm{~K}}\right) * 473.15 \mathrm{~K}}{14 \mathrm{bar}}=-212.4 \frac{\mathrm{~cm}^{3}}{\mathrm{~mol}}
\end{aligned}
$$

Repeat the above procedure for the enthalpy

$$
\begin{gathered}
\frac{\left(\mathrm{H}^{\mathrm{R}}\right)^{\mathrm{c}}}{\mathrm{RT}_{\mathrm{c}}}=-0.1207 \\
\frac{\left(\mathrm{H}^{\mathrm{R}}\right)}{\mathrm{RT}_{\mathrm{c}}}=-0.2106 \\
\frac{\mathrm{H}^{\mathrm{R}}}{\mathrm{RT}_{\mathrm{c}}}=-0.1207+0.345 *(-0.2106)=-0.1934 \\
\mathrm{H}^{\mathrm{R}}=-0.1934 * 8.314 \frac{\mathrm{~J}}{\mathrm{molK}} * 647.1 \mathrm{~K}=-1040.2 \frac{\mathrm{~J}}{\mathrm{~mol}}
\end{gathered}
$$

Do the same for the entropy

$$
\begin{aligned}
& \frac{\left(S^{R}\right)^{\rho}}{R}=-0.1110 \\
& \frac{\left(S^{R}\right)}{R}=-0.2395 \\
& \frac{S^{R}}{R}=-0.1110+0.345 *(-0.2395)=-0.1936 \\
& S^{R}=-0.1936 * 8.314 \frac{\mathrm{~J}}{\mathrm{molK}}=-1.6098 \frac{\mathrm{~J}}{\mathrm{~mol} \mathrm{~K}}
\end{aligned}
$$

b) Repeat part (a) using the steam tables

Here, we will use the definition of the residual property

$$
M^{R}(T, P)=M(T, P)-M^{i g}(T, P)
$$

There are two types of steam tables: saturated and superheated. The saturated steam tables give information about the two-phase region while the superheated tables give information about the vapor phase. Since we know from part (a) that our point lies in the vapor phase, we will use the superheated steam tables. If we looked first at the saturated steam table, we would have found that the saturated pressure is 1554.5 kPa (p. 671). Since we are interested in a lower pressure, we make out that our point lies in the vapor phase.

The values given in the steam tables are the real values, which can be used for the first term of the residual property definition. So let us get the three real values from the steam table at $\mathrm{T}=200^{\circ} \mathrm{C}$ and $\mathrm{P}=1400$ kPa .
$\mathrm{V}=142.94 \mathrm{~cm}^{3} \mathrm{~g}^{-1}$
$\mathrm{H}=2801.4 \mathrm{~kJ} \mathrm{~kg}^{-1}$
$\mathrm{S}=6.4941 \mathrm{~kJ} \mathrm{~kg}^{-1} \mathrm{~K}^{-1}$
(Units are given in the first table p.668)
Now we need to get the hypothetical ideal values of the properties at the same temperature and pressure. But the tables only give real values and not ideal ones. However, we can get the ideal values at the same temperature and very low pressure because we know that the ideal gas is a very good approximation at low pressures. So from the steam table, we get those properties at $\mathrm{P}=1 \mathrm{kPa}$ and the same temperature.
$V^{i g}(1 \mathrm{kPa})=218350 \mathrm{~cm}^{3} \mathrm{~g}^{-1}$
$\mathrm{H}^{\mathrm{ig}}(1 \mathrm{kPa})=2880.1 \mathrm{~kJ} \mathrm{~kg}^{-1}$
$\mathrm{S}^{\mathrm{ig}}(1 \mathrm{kPa})=9.9679 \mathrm{~kJ} \mathrm{~kg}^{-1} \mathrm{~K}^{-1}$
But we need the ideal properties at $\mathrm{P}=1400 \mathrm{kPa}$ and not at 1 kPa . For the volume, we can use the ideal gas low for an isothermal process.
$\mathrm{P}_{1} \mathrm{~V}_{1}=\mathrm{P}_{2} \mathrm{~V}_{2}$
$\mathrm{V}^{\mathrm{ig}}(1400 \mathrm{kPa})=218350 * 1 / 1400=155.96 \mathrm{~cm}^{3} \mathrm{~g}^{-1}$
For the enthalpy, we know that
$\mathrm{dH}^{\mathrm{ig}}=\mathrm{Cp} \mathrm{dT}$ (i.e. enthalpy is not a function of pressure for an ideal gas)

Therefore,
$\mathrm{H}^{\mathrm{ig}}(1 \mathrm{kPa})=\mathrm{H}^{\mathrm{ig}}(1400 \mathrm{kPa})=2880.1 \mathrm{~kJ} \mathrm{~kg}^{-1}$
For the entropy, we know that

$$
\mathrm{d}^{\mathrm{ig}}=\mathrm{C}_{\mathrm{p}}^{\mathrm{ig}} \frac{\mathrm{dT}}{\mathrm{~T}}-\mathrm{R} \frac{\mathrm{dP}}{\mathrm{P}}
$$

For an isothermal process, we can write

$$
\Delta \mathrm{S}^{\mathrm{ig}}=-\mathrm{R} \int_{\mathrm{P}_{1}}^{\mathrm{P}_{2}} \frac{\mathrm{dP}}{\mathrm{P}}=-\mathrm{R} \ln \left(\frac{\mathrm{P}_{2}}{\mathrm{P}_{1}}\right)
$$

Therefore

$$
\begin{aligned}
& S^{\mathrm{ig}}(1400 \mathrm{kPa})=\mathrm{S}^{\mathrm{ig}}(1 \mathrm{kPa})+\Delta \mathrm{S}^{\mathrm{ig}}=\mathrm{S}^{\mathrm{ig}}(1 \mathrm{kPa})-8.314 \frac{\mathrm{~J}}{\mathrm{~mol} \mathrm{~K}} \ln \left(\frac{1400}{1}\right) \\
& \mathrm{S}^{\mathrm{ig}}(1400 \mathrm{kPa})=9.9679 \frac{\mathrm{~kJ}}{\mathrm{~kg} \mathrm{~K}}-8.314 \frac{\mathrm{~J}}{\mathrm{~mol} \mathrm{~K}} \frac{\mathrm{~kJ}}{1000 \mathrm{~J}} \frac{\mathrm{~mol}}{18.015 \mathrm{~g}} \frac{1000 \mathrm{~g}}{\mathrm{~kg}} \ln (1400) \\
= & 6.6247 \frac{\mathrm{~kJ}}{\mathrm{~kg} \mathrm{~K}}
\end{aligned}
$$

Now we can get the residual properties

$$
\begin{aligned}
& \mathrm{V}^{\mathrm{R}}=142.94-155.96=-13.02 \mathrm{~cm}^{3} \mathrm{~g}^{-1} \\
& =-13.02 \frac{\mathrm{~cm}^{3}}{\mathrm{~g}} \frac{18 \mathrm{~g}}{\mathrm{~mol}}=-234.36 \frac{\mathrm{~cm}^{3}}{\mathrm{~mol}} \\
& \mathrm{H}^{\mathrm{R}}=2801.4-2880.1=-78.7 \mathrm{~kJ} \mathrm{~kg}^{-1} \\
& =-78.7 \frac{\mathrm{~kJ}}{\mathrm{~kg}} \frac{18 \mathrm{~g}}{\mathrm{~mol}} \frac{\mathrm{~kg}}{1000 \mathrm{~g}} \frac{1000 \mathrm{~J}}{\mathrm{~kJ}}=-1416.6 \frac{\mathrm{~J}}{\mathrm{~mol}} \\
& \mathrm{~S}^{\mathrm{R}}=6.4941-6.6247=-0.1306 \mathrm{~kJ} \mathrm{~kg}^{-1} \mathrm{~K}^{-1} \\
& =-0.1306 \frac{\mathrm{~kJ}}{\mathrm{~kg} \mathrm{~K}} \frac{18 \mathrm{~g}}{\mathrm{~mol}} \frac{\mathrm{~kg}}{1000 \mathrm{~g}} \frac{1000 \mathrm{~J}}{\mathrm{~kJ}}=-2.3508 \frac{\mathrm{~J}}{\mathrm{~mol} \mathrm{~K}}
\end{aligned}
$$

c)


## Constant temperature line

For the liquid phase and the ideal gas, the line is a vertical line because H is not a function of pressure for these two cases (see lecture notes)
Inside the dome, there is only one degree of freedom ( 2 phases). Hence for a defined T, P is set. The constant temperature line becomes a horizontal line.

## Constant entropy line

From the definition of dH
$\mathrm{dH}=\mathrm{TdS}+\mathrm{VdP}$
For constant entropy, $\mathrm{d} S=0$
Therefore,

$$
\begin{gathered}
\left(\frac{\partial \mathrm{P}}{\partial \mathrm{H}}\right)_{S}=\frac{1}{\mathrm{~V}} \\
\left(\frac{\partial \ln \mathrm{P}}{\partial \mathrm{H}}\right)_{S}=\frac{1}{\mathrm{P}}\left(\frac{\partial \mathrm{P}}{\partial \mathrm{H}}\right)_{S}=\frac{1}{\mathrm{PV}}
\end{gathered}
$$

That means that the constant entropy lines in a $\ln \mathrm{P}$ vs. H diagram always have positive slopes that are equal to $1 / \mathrm{PV}$.
d) Slope of an isotherm

We also start from dH

$$
\mathrm{dH}=\mathrm{C}_{\mathrm{p}} \mathrm{dT}+\left[\mathrm{V}-\mathrm{T}\left(\frac{\partial \mathrm{~V}}{\partial \mathrm{~T}}\right)_{\mathrm{P}}\right] \mathrm{dP}
$$

For constant T,

$$
\left(\frac{\partial \mathrm{H}}{\partial \mathrm{P}}\right)_{\mathrm{T}}=\mathrm{V}-\mathrm{T}\left(\frac{\partial \mathrm{~V}}{\partial \mathrm{~T}}\right)_{\mathrm{P}}
$$

We have

$$
\left(\frac{\partial \ln \mathrm{P}}{\partial \mathrm{H}}\right)_{\mathrm{T}}=\frac{1}{\mathrm{P}}\left(\frac{\partial \mathrm{P}}{\partial \mathrm{H}}\right)_{\mathrm{T}}
$$

Then,

$$
\left(\frac{\partial \ln \mathrm{P}}{\partial \mathrm{H}}\right)_{\mathrm{T}}=\frac{1}{\mathrm{P}} \frac{1}{\left(\frac{\partial \mathrm{H}}{\partial \mathrm{P}}\right)_{\mathrm{T}}}=\frac{1}{\mathrm{P}\left[\mathrm{~V}-\mathrm{T}\left(\frac{\partial \mathrm{~V}}{\partial \mathrm{~T}}\right)_{\mathrm{P}}\right]}
$$

e) The slope for an ideal gas

For an ideal gas we have

$$
\begin{gathered}
V=\frac{R T}{P} \\
\left(\frac{\partial V}{\partial T}\right)_{P}=\frac{R}{P}
\end{gathered}
$$

Substituting in the slope equation, we get

$$
\left(\frac{\partial \ln \mathrm{P}}{\partial \mathrm{H}}\right)_{\mathrm{T}}=\frac{1}{\mathrm{P}\left(\mathrm{~V}-\mathrm{T} \frac{\mathrm{R}}{\mathrm{P}}\right)}=\frac{1}{\mathrm{P}(\mathrm{~V}-\mathrm{V})}=\frac{1}{0}=\infty
$$

The slope the constant temperature lines of an ideal gas in a $\ln \mathrm{P}$ vs. H diagram are always vertical lines.

