

Problem 6.84

Calculate V^R , H^R , and S^R for each of the following using the generalized virial method:

(e) Ethylbenzene at 620 K and 20 bar.

(f) Methane at 250 K and 90 bar.

Solution Part (e) - Ethylbenzene at 620 K and 20 bar

```

In[*]:= Quit[];

R1 = 8.314 (*R for enthalpy and entropy -  $\frac{\text{J}}{\text{mol}\cdot\text{K}}$  *);
R2 = 83.14; (*R for molar volume calcs -  $\frac{\text{cm}^3\cdot\text{bar}}{\text{mol}\cdot\text{K}}$  *)
T = 620.; (*K*);
P = 20.; (*bar*)
 $\omega$  = 0.303;
Tc = 617.2; (*from appendix B in K*)
Pc = 36.06; (*from appendix B in bar*)
Tr = T / Tc;
Pr = P / Pc;

In[*]:= B0 = 0.083 - .422 / Tr1.6; (*Eq 3.61*)
B1 = 0.139 - 0.172 / Tr4.2; (*Eq 3.62*)
dB0 = 0.675 / Tr2.6; (*Eq 6.70*)
dB1 = 0.722 / Tr5.2; (*Eq 6.71*)
Hr = R1 * Tc * Pr * (B0 - Tr * dB0 +  $\omega$  * (B1 - Tr * dB1)) (*Eq 6.68*)
Sr = -R1 * Pr * (dB0 +  $\omega$  * dB1) (*Eq 6.69*)

Z = 1 + (B0 +  $\omega$  * B1) * (Pr / Tr);
Vr = (R2 * T / P) * (Z - 1)

Out[*]:=
-3499.90569776

Out[*]:=
-4.06145502934

Out[*]:=
-490.901789785

(*// ANS (e)*)
(*units in order: Hr:  $\frac{\text{J}}{\text{mol}}$  Sr:  $\frac{\text{J}}{\text{mol}\cdot\text{K}}$  Vr:  $\frac{\text{cm}^3}{\text{mol}}$  *)

```

Solution Part (f) - Methane at 250 K and 90 bar

```

In[ ]:= Quit[];

R1 = 8.314; (*R for enthalpy and entropy -  $\frac{\text{J}}{\text{mol}\cdot\text{K}}$  *)
R2 = 83.14; (*R for molar volume calcs -  $\frac{\text{cm}^3\cdot\text{bar}}{\text{mol}\cdot\text{K}}$  *)
P = 90.; (*bar*)
T = 250.; (*K*);
 $\omega$  = 0.012;
Tc = 190.6; (*from appendix B in K*)
Pc = 45.99; (*from appendix B in bar*)
Tr = T / Tc;
Pr = P / Pc;

In[ ]:= B0 = 0.083 - .422 / Tr1.6; (*Eq 3.61 *)
B1 = 0.139 - 0.172 / Tr4.2; (*Eq 3.61*)
dB0 = 0.675 / Tr2.6; (*Eq 6.70*)
dB1 = 0.722 / Tr5.2; (*Eq 6.71*)
Hr = R1 * Tc * Pr * (B0 - Tr * dB0 +  $\omega$  * (B1 - Tr * dB1)) (*Eq 6.68*)
Sr = -R1 * Pr * (dB0 +  $\omega$  * dB1) (*Eq 6.69*)

R2 = 83.14; (*appropriate R for molar volume calcs -  $\frac{\text{cm}^3\cdot\text{bar}}{\text{mol}\cdot\text{K}}$  *)
Z = 1 + (B0 +  $\omega$  * B1) * (Pr / Tr);
Vr = (R2 * T / P) * (Z - 1)

Out[ ]:=
-1952.08298558

Out[ ]:=
-5.45900059793

Out[ ]:=
-65.2592040108

(*// ANS (d)*) (*units in order: Hr:  $\frac{\text{J}}{\text{mol}}$  Sr:  $\frac{\text{J}}{\text{mol}\cdot\text{K}}$  Vr:  $\frac{\text{cm}^3}{\text{mol}}$  *)

```

Problem 6.101

Use the API mixture rules in slide 11 to estimate the critical temperature and pressure of air at 50% relative humidity, 25 deg C, and 1 bar total pressure. Check your answers with CHEMCAD (CC).

To simplify your answer, use the air pseudo-component in CC so that your mixture has two components (air and water).

Solution

```
(*Water vapor pressure from Antoine Equation, p. 666*)
(*This Antoine Equation has T in deg C and P in kPa.*)
a = 16.3872;
b = 3885.70;
c = 230.170;
t = 25;

Pw = .5 * Exp[a - b / (t + c)] *  $\frac{1}{100}$  (*picket fence: kPa*  $\frac{1 \text{ bar}}{100 \text{ kPa}}$  *)
```

Out[*]=

0.0159387080874

```
ln[*]:= tc = {132.45, 647.35}; (*Tc of air & water from CC in K*)
pc = {37.74, 221.182}; (*Pc of air & water from CC in bar*)
vc = {91.5, 63.494}; (*Vc of air & water from CC in cm3/mol*)
w = {-0.0078798, .348}; (*w of air, water from CHEMCAD*)
x = {1 - Pw, Pw}
```

Out[*]=

{0.984061291913, 0.0159387080874}

```
ln[*]:= tpc = Plus @@ (x * tc) (*pseudocritical T of mixture*)
```

Out[*]=

140.656840794

```
ln[*]:= ppc = Plus @@ (x * pc) (*pseudocritical P of mixture*)
```

Out[*]=

40.663828489

```
ln[*]:= vpc = Plus @@ (x * vc) (*molar average critical volume*)
```

Out[*]=

91.0536205413

```
ln[*]:= theta = x * vc / vpc (*volume fractions*)
```

Out[*]=

{0.988885534422, 0.0111144655785}

```
ln[*]:= wavg = Plus @@ (x * w) (*average acentric factor*)
```

Out[*]=

-0.0022075357536

```
tcm = Plus@@ (θ * tc) (*true critical temp of mixture*)
```

```
Out[ ]:=
```

```
138.172838326
```

```
In[ ]:= (*true critical pressure of mixture*)
```

$$P_{cm} = p_{pc} + p_{pc} * (5.808 + 4.93 * \omega_{avg}) * \left(\frac{t_{cm} - t_{pc}}{t_{pc}} \right)$$

```
Out[ ]:=
```

```
36.5007798653
```

```
(*API results:*)
```

```
(*The critical T of the mixture is 138.173 K//ANS*)
```

```
(*The critical P of the mixture is 36.5008 bar//ANS*)
```

```
(*CHEMCAD results:*)
```

```
(*Tc=138.1733 K //ANS*)
```

```
(*Pc=36.5007 bar //ANS*)
```

Problem 6.14

Estimate the entropy change of vaporization of benzene at 50 deg C. The vapor pressure of benzene is given by the equation:

$$\ln(P^{\text{sat}}/\text{kPa}) = 13.8858 - \frac{2,788.51}{(t/\text{degC}) + 220.79}$$

(a) Use Eq. 6.86 with an estimated value of ΔV^{lv} .

(b) Use the Clausius-Clapeyron equation of Example 6.6.

Solution to Part (a)

Equation 6.86 is: $\frac{dP^{\text{sat}}}{dT} = \frac{\Delta H^{\text{lv}}}{T\Delta V^{\text{lv}}}$ and Equation 6.84 is $\Delta H^{\text{lv}} = T\Delta S^{\text{lv}}$, so $\Delta S^{\text{lv}} = \frac{\Delta H^{\text{lv}}}{T}$.

Rearrange 6.84 and combine with 6.86 to give $\Delta S^{\text{lv}} = \frac{dP^{\text{sat}}}{dT} \Delta V^{\text{lv}}$.

Estimate ΔV^{lv} by assuming the vapor is an ideal gas at pressure P^{sat} and the molar volume of the liquid is negligible compared to the vapor. Get P^{sat} from the Antoine equation.

$$P^{\text{sat}}[t_] = E^{13.8858 - \frac{2788.51}{(t - 273.15) + 220.79}}; \text{ (*Antoine equation with T in Kelvins*)}$$

In[]:= P_{sat}[323.15]

Out[]:=

36.1658552072

(*Estimate ΔV^{lv} by assuming molar volume of liquid is ~ 0 that the vapor is ideal gas with $PV=RT \rightarrow V = \frac{RT}{P}$ *)

$$R = 8314.; \text{ (* } \frac{\text{kPa} \cdot \text{cm}^3}{\text{mol} \cdot \text{K}} \text{ *)}$$

$$T = 50 + 273.15;$$

$$P = P^{\text{sat}}[T];$$

$$V = R * T / P; \text{ (*units are cm}^3/\text{mol*)}$$

$$\Delta V^{\text{lv}} = V - 0$$

Out[]:=

74287.4483295

(*Rearrange 6.84 and combine with 6.86 to give $\Delta S^{\text{lv}} = \frac{dP^{\text{sat}}}{dT} \Delta V^{\text{lv}}$ *)

$$\Delta S^{\text{lv}}[t_] = \partial_t P^{\text{sat}}[t] * \Delta V^{\text{lv}};$$

$$\Delta S^{\text{lv}}[T] \text{ (*Units are } \frac{\text{kPa} \cdot \text{cm}^3}{\text{mol} \cdot \text{K}} \text{ *)}$$

Out[]:=

102169.470398

(*Convert $\frac{\text{kPa} \cdot \text{cm}^3}{\text{mol} \cdot \text{K}}$ to $\frac{\text{J}}{\text{mol} \cdot \text{K}}$ *)

$$\Delta S^{\text{lv}}[T] * \frac{\text{kPa} * \text{cm}^3}{\text{mol} * \text{K}} * \frac{1 \text{ m}^3}{10^6 \text{ cm}^3} * \frac{1000 \text{ Pa}}{1 \text{ kPa}} * \frac{1 \text{ J}}{1 \text{ m}^3 * \text{ Pa}}$$

Out[]:=

102.169470398 J
K mol

(*The entropy of vaporization at 50 degrees C from equation 6.86 is 102.169 $\frac{\text{J}}{\text{mol} \cdot \text{K}}$. //ANS*)

Solution to Part (b)

The Clausius-Clapeyron equation is found on p. 237: $\Delta H^{lv} = -R \frac{d \ln P^{sat}}{d(1/T)}$, so by equation 6.84, $\Delta S^{lv} = \frac{-R}{T} \frac{d \ln P^{sat}}{d(1/T)}$

Part (b) is very similar to part (a) but we have to find $\ln P^{sat}$ as a function of $1/T$. This is shown below.

```
In[ ]:= Psatx[x_] = Psat[1 / x]; (*Substituted x=1/t *)
```

```
In[ ]:= Psatx[1 / T] (*Check answer*)
```

```
Out[ ]:=
36.1658552072
```

```
In[ ]:= NatLogPsatx[x_] = Log[Psatx[x]]; 
```

```
In[ ]:= ΔSlvb[x_] = -R * x * ∂xNatLogPsatx[x]; (*C-C equation with equation 6.84*)
```

```
ΔSlvb[1 / T] (*Units are  $\frac{\text{kPa} \cdot \text{cm}^3}{\text{mol} \cdot \text{K}}$  *)
```

```
Out[ ]:=
102169.470398
```

```
(*  $\frac{\text{kPa} \cdot \text{cm}^3}{\text{mol} \cdot \text{K}}$  → convert units to  $\frac{\text{kJ}}{\text{mol} \cdot \text{K}}$  *)
```

```
In[ ]:= ΔSlvb[1 / T] *  $\frac{\text{kPa} \cdot \text{cm}^3}{\text{mol} \cdot \text{K}}$  *  $\frac{1 \text{ m}^3}{10^6 \text{ cm}^3}$  *  $\frac{1000 \text{ Pa}}{1 \text{ kPa}}$  *  $\frac{1 \text{ J}}{1 \text{ m}^3 \cdot \text{Pa}}$ 
```

```
Out[ ]:=
102.169470398 J
      K mol
```

```
(*The entropy of vaporization at 50 C from the Clausius
-Clapeyron equation is 102.169  $\frac{\text{J}}{\text{mol} \cdot \text{K}}$ . //ANS*)
```

Problem 6.25

Steam at 2,100 kPa and 260 deg C expands at constant enthalpy (as in a throttling process) to 125 kPa. What is the temperature of the steam in its final state and what is its entropy change? What would be the final temperature and entropy change for an ideal gas?

Solution

This problem uses the steam tables in Appendix E, and is similar to Example 6.9, which used the fact that entropy is constant from state 1 to state 2. This allowed enthalpy in state 2 to be calculated. Example 6.9 is somewhat more complicated than problem 25 because state 2 is a 2-phase mixture of saturated water and steam. The premise of the example was to use S_2 , S^{liquid} and S^{vapor} to calculate x^{liquid} and x^{vapor} , which are then used to calculate H^{liquid} , H^{vapor} , and H_2 . Problem 6.25 is somewhat simpler because we will see that state 2 is superheated steam (one phase), so no calculation of x^{liquid} and x^{vapor} is needed.

Quit [] ;

First, solve for the entropy and enthalpy at $P_1 = 2100$ kPa and $T_1 = 260$ degC by interpolation of data in Table E.2, page 717. The data must be interpolated between 250 and 275 deg C:

$$\text{eq1} = \frac{260 - 250}{275 - 250} = \frac{S1 - 6.5162}{6.6356 - 6.5162};$$

Solve [eq1, S1] (* $\frac{\text{kJ}}{\text{kg} \cdot \text{K}}$ *)

{ {S1 → 6.56396} }

$$\text{eq2} = \frac{260 - 250}{275 - 250} = \frac{H1 - 2897.9}{2961.9 - 2897.9};$$

Solve [eq2, H1] (*kJ/kg*)

{ {H1 → 2923.5} }

Next, carefully study Table E.2 on page 707. Observe that the enthalpy value at 125 kPa is comparable to H_1 . That is, at 225 deg C, the enthalpy is 2923.9 kJ/kg, and at 200 deg C it is 2874.2 kJ/kg. We can see that $2874.2 < H_1 < 2923.9$. Since H_1 is between these two values, we conclude that state 2 is indeed superheated steam. Therefore, we can interpolate this data to find the temperature:

$$\text{eq3} = \frac{T2 - 200}{225 - 200} = \frac{2923.5 - 2874.2}{2923.9 - 2874.2};$$

Solve [eq3, T2] (*deg C*)

{ {T2 → 224.798792757} }

(* //ANS*)

Now, using Table E.2 on page 707, find entropy data at 125 kPa. Interpolate the entropy data using the known enthalpies to find the unknown entropy S_2 :

$$\text{eq3} = \frac{S2 - 7.7300}{7.8324 - 7.7300} = \frac{2923.5 - 2874.2}{2923.9 - 2874.2};$$

Solve [eq3, S2]

{ {S2 → 7.83157585513} }

Next, calculate ΔS :

$$\Delta S = 7.8316 - 6.5640 \left(* \frac{\text{kJ}}{\text{kg} \cdot \text{K}} * \right)$$

$$1.2676$$

$$(*\text{The entropy change is } 1.268 \frac{\text{kJ}}{\text{kg} \cdot \text{K}} . //\text{ANS}*)$$

For entropy change for an ideal gas, $\Delta S/R$ is given by equation 5.10 on page 188. But recall that the enthalpy is held constant in the problem statement. The only way for this to be possible is if T_1 is equal to T_2 . This means the integral term in equation 5.10 is zero.

$$\Delta S_{\text{ig}} = \left(\int_{T_1}^{T_2} \frac{C_p}{T} dT - \text{Log} \left[\frac{P_2}{P_1} \right] \right) * R$$

$$\text{In}[]:= R = 8.314; \left(* \frac{\text{J}}{\text{mol} \cdot \text{K}} * \right)$$

$$\text{In}[]:= \Delta S_{\text{ig}} = \left(-\text{Log} \left[\frac{125}{2100} \right] \right) * R$$

$$\text{Out}[]:= 23.4569440616$$

The units are in J per mol per K, and must be converted to kJ per kg per K to compare with values from the steam tables:

$$\text{In}[]:= \Delta S_{\text{ig}} * \frac{\text{J}}{\text{mol} \cdot \text{K}} * \frac{1 \text{ mol}}{18.015 \text{ g}} * \frac{1000 \text{ g}}{1 \text{ kg}} * \frac{1 \text{ kJ}}{1000 \text{ J}}$$

$$\text{Out}[]:= \frac{1.30207849357 \text{ kJ}}{\text{K kg}}$$

$$(*\text{The entropy change for the ideal gas is } 1.302 \frac{\text{kJ}}{\text{kg} \cdot \text{K}} . //\text{ANS}*)$$

Problem 6.28

What is the mole fraction of water vapor in air that is saturated with water at 25 deg C and 101.33 kPa? At 50 deg C and 101.33 kPa?

Solution

Use the Antoine equation with constants from Table B.2 on p. 666. In the instructor's version of the book, Psat is in kPa and T is in deg C.

(*Water vapor pressure from Antoine Equation, p. 666*)

(*This Antoine Equation has T in deg C and P in kPa.*)

(*This was also given in Problem 6.101.*)

a = 16.3872;

b = 3885.70;

c = 230.170;

$$P_{\text{sat}}[T_] = e^{a - \frac{b}{T+c}};$$

(*From Dalton's Law, at 25 degC:*)

$$y_{\text{water}} = \frac{P_{\text{sat}}[25]}{101.33}$$

0.0314590113242

(*At 50 degC*)

$$y_{\text{water}} = \frac{P_{\text{sat}}[50]}{101.33}$$

0.12242434827

Problem 6.83

An equimolar mixture of methane and propane is discharged from a compressor at 5,500 kPa and 90 deg C at a rate of 1.4 kg/sec. If the velocity in the discharge line is not to exceed 30 m/sec, what is the minimum diameter of the discharge line?

Thought Process:

(Identify) If volumetric flow rate is in cm^3/sec and velocity is in cm/sec were available, I could divide and get area:

$$\frac{\text{cm}^3 / \text{sec}}{\text{cm} / \text{sec}} \\ \text{cm}^2$$

If molar volume is in cm^3/mol and molar flow rate in mol/sec were available, I could multiply them and get the volumetric flow rate.

$$\frac{\text{cm}^3}{\text{mol}} * \frac{\text{mol}}{\text{sec}} \\ \text{cm}^3 \\ \text{sec}$$

Molar flow rate comes from the mass flow rate divided by molar mass:

$$\frac{\text{kg}}{\text{sec}} * \frac{\text{g}}{\text{kg}} * \frac{1 \text{ mol}}{\text{g}} \\ \text{mol} \\ \text{sec}$$

(Formulate) Molar volume from the equation of state can be formulated with Table 3.1 and equations 3.42, 3.45, and 3.46 to give molar volume.

(Solve) Solve the equation of state for the molar volume using Mathematica and use molar volume, molar mass, and mass flow rate to get volumetric flow rate, then use volumetric flow rate to get area and radius.

Solution

We will calculate the molar volume of the mixture, use molar volume and given mass flow rate to find volumetric flow rate. Then use specified velocity and volumetric flow rate to find area, and use the area to find the diameter.

`In[]:= Quit[] ;`

`In[]:= R = 83.14 (* $\frac{\text{cm}^3 \cdot \text{bar}}{\text{mol} \cdot \text{K}}$ *) ;`
`P = 55. (*bar*) ;`
`T = 363.15 (*K*) ;`

Use pseudocritical parameters from eqs 6.78-6.82 with the SRK equation:

```

In[ ]:=  $\omega = 0.5 * 0.012 + 0.5 * 0.152$ ; (*Eq. 6.78*)
 $T_{pc} = 0.5 * 190.6 + 0.5 * 369.8$ ; (*K*) (*Eq. 6.79*)
 $P_{pc} = 0.5 * 45.99 + 0.5 * 42.48$ ; (*bar*) (*Eq. 6.80*)
 $T_{pr} = T / T_{pc}$ ; (*Eq. 6.81*)
 $P_{pr} = P / P_{pc}$ ; (*Eq. 6.82*)

 $\Omega = 0.08664$ ; (*Table 3.1, SRK*)
 $\Psi = 0.42748$ ;
 $\sigma = 1$ ;
 $\epsilon = 0$ ;
 $\alpha = \left(1 + (0.480 + 1.574 * \omega - 0.176 * \omega^2) * \left(1 - \sqrt{T_{pr}}\right)\right)^2$ ;

```

$$a = \Psi \frac{\alpha * R^2 * T_{pc}^2}{P_{pc}}; \text{ (*Eq 3.45*)}$$

$$b = \Omega * \frac{R * T_{pc}}{P_{pc}}; \text{ (*Eq 3.44*)}$$

$$\text{eq1} = P == \frac{R * T}{V - b} - \frac{a}{(V + \epsilon * b) * (V + \sigma * b)}; \text{ (*Eq 3.41*)}$$

```
Quiet[sol1 = Solve[eq1, V]]
```

```
Out[ ]:=
```

```

{{V -> 49.7662433482 - 75.1235893056 I},
 {V -> 49.7662433482 + 75.1235893056 I}, {V -> 449.418258758}}

```

```

In[ ]:=  $V = 449.418$  (*molar volume of mixture in  $\frac{\text{cm}^3}{\text{mol}}$  *);

```

```

In[ ]:=  $MW = 0.5 * 16.043 + 0.5 * 44.097$  (*molar mass of mixture in  $\frac{\text{g}}{\text{mol}}$  *)

```

```
Out[ ]:=
```

```
30.07
```

$$\text{vdot} = V * \frac{\text{cm}^3}{\text{mol}} * \frac{1}{MW} * \frac{\text{mol}}{\text{g}} * \frac{1000 \text{ g}}{1 \text{ kg}} * \frac{1.4 \text{ kg}}{\text{sec}}$$

```
Out[ ]:=
```

$$\frac{20924.017293 \text{ cm}^3}{\text{sec}}$$

```

In[ ]:=  $\text{area} = \frac{\text{vdot}}{\frac{30 \text{ m}}{\text{sec}} * \frac{100 \text{ cm}}{\text{m}}}$ 

```

```
Out[ ]:=
```

$$6.97467243099 \text{ cm}^2$$

```

In[ ]:=  $\text{eq2} = \pi * r^2 == \text{area} / \text{cm}^2$ ;

```

```
In[ ]:= Solve[eq2, r]
```

```
Out[ ]:= {{r -> -1.49000241197}, {r -> 1.49000241197}}
```

(*The minimum diameter is $2 \times 1.49 \text{ cm} = 2.98 \text{ cm}$ // ANS*)