

## Problem Set 11 - Solutions

### 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.

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

$R1 = 8.314$  (\*R for enthalpy and entropy -  $\frac{J}{mol \cdot K}$  \*) ;

$R2 = 83.14$ ; (\*R for molar volume calcs -  $\frac{cm^3 \cdot bar}{mol \cdot K}$  \*)

$T = 620.$ ; (\*K\*) ;

$P = 20.$ ; (\*bar\*)

$\omega = 0.303$ ;

$T_c = 617.2$ ; (\*from appendix B in K\*)

$P_c = 36.06$ ; (\*from appendix B in bar\*)

$T_r = T / T_c$ ;

$P_r = P / P_c$ ;

$\ln[\ast] := B0 = 0.083 - .422 / T_r^{1.6}$ ; (\*Eq 3.61\*)

$B1 = 0.139 - 0.172 / T_r^{4.2}$ ; (\*Eq 3.62\*)

$dB0 = 0.675 / T_r^{2.6}$ ; (\*Eq 6.70\*)

$dB1 = 0.722 / T_r^{5.2}$ ; (\*Eq 6.71\*)

$Hr = R1 \ast T_c \ast P_r \ast (B0 - T_r \ast dB0 + \omega \ast (B1 - T_r \ast dB1))$  (\*Eq 6.68\*)

$Sr = -R1 \ast P_r \ast (dB0 + \omega \ast dB1)$  (\*Eq 6.69\*)

$Z = 1 + (B0 + \omega \ast B1) \ast (P_r / T_r)$  ;

$Vr = (R2 \ast T / P) \ast (Z - 1)$

$Out[\ast] =$

-3499.90569776

$Out[\ast] =$

-4.06145502934

$Out[\ast] =$

-490.901789785

The residual enthalpy is  $-3,499.91 \frac{J}{mol}$ . //ANS

The residual entropy is  $-4.06146 \frac{J}{mol \cdot K}$ . //ANS

The residual volume is  $-490.902 \frac{cm^3}{mol}$ . //ANS

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

$R1 = 8.314; (*R \text{ for enthalpy and entropy} - \frac{J}{mol \cdot K} *)$

$R2 = 83.14; (*R \text{ for molar volume calcs} - \frac{cm^3 \cdot bar}{mol \cdot K} *)$

$P = 90.; (*bar*)$

$T = 250.; (*K*)$

$\omega = 0.012;$

$T_c = 190.6; (*from \text{appendix B in K}*)$

$P_c = 45.99; (*from \text{appendix B in bar}*)$

$T_r = T / T_c;$

$P_r = P / P_c;$

$In[*]:= B0 = 0.083 - .422 / T_r^{1.6}; (*Eq 3.61 *)$

$B1 = 0.139 - 0.172 / T_r^{4.2}; (*Eq 3.61*)$

$dB0 = 0.675 / T_r^{2.6}; (*Eq 6.70*)$

$dB1 = 0.722 / T_r^{5.2}; (*Eq 6.71*)$

$Hr = R1 * T_c * P_r * (B0 - T_r * dB0 + \omega * (B1 - T_r * dB1)) (*Eq 6.68*)$

$Sr = -R1 * P_r * (dB0 + \omega * dB1) (*Eq 6.69*)$

$R2 = 83.14; (*appropriate R \text{ for molar volume calcs} - \frac{cm^3 \cdot bar}{mol \cdot K} *)$

$Z = 1 + (B0 + \omega * B1) * (P_r / T_r);$

$Vr = (R2 * T / P) * (Z - 1)$

$Out[*]=$

-1952.08298558

$Out[*]=$

-5.45900059793

$Out[*]=$

-65.2592040108

The residual enthalpy is  $-1,952.08 \frac{J}{mol}$ . //ANS

The residual entropy is  $-5.459 \frac{J}{mol \cdot K}$ . //ANS

The residual volume is  $-65.2592 \frac{cm^3}{mol}$ . //ANS

## 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 °C, and 1 bar total pressure.

Check your answers with CHEMCAD (CC). Use the air pseudo-component in CC so that your mixture has two components (air and water).

## Solution

Determine mole fractions:

```
In[*]:= (*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

In[*]:= 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}
```

Determine mixture pseudocritical constants:

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

Out[*]=
140.656840794

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

Out[*]=
40.663828489

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

Out[*]=
91.0536205413
```

```
In[*]:=  $\theta = x * v_c / v_{pc}$  (*volume fractions*)
```

```
Out[*]:= {0.988885534422, 0.0111144655785}
```

```
In[*]:=  $\omega_{avg} = \text{Plus}@@(x * \omega)$  (*average acentric factor*)
```

```
Out[*]:= -0.0022075357536
```

Determine mixture critical constants:

```
In[*]:=  $t_{cm} = \text{Plus}@@(\theta * t_c)$  (*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:

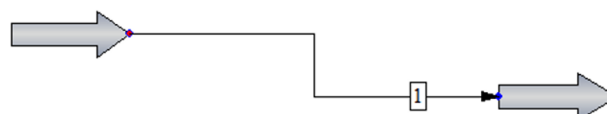
The critical temperature of the mixture is 138.1728 K. //ANS

The critical pressure of the mixture is 36.50078 bar. //ANS

CHEMCAD Results:

T<sub>c</sub> = 138.1728 K //ANS

P<sub>c</sub> = 36.5008 bar //ANS



Stream No.	1
Name	
-- Overall --	
Temp K	298.1500
Pres bar	1.0000
Enth MJ/sec	-0.0038643
Tc K	138.1728
Pc bar	36.5008
-- Vapor only --	
Rel. Humidity %	50.2838
Component mole fractio	
Air	0.984061
Water	0.015939

## Problem 6.14

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

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

- (a) Use Eq. 6.86 with an estimated value of  $\Delta V^{\text{lv}}$ .  
 (b) Use the Clausius-Clapeyron equation of Example 6.6.

Report your answers in J/mol·K.

### Solution, 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  $\Delta V^{\text{lv}}$  by assuming the vapor is an ideal gas at pressure  $P^{\text{sat}}$  and the molar volume of the liquid is negligible compared to the vapor.

Get  $P^{\text{sat}}$  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[\*]:= Psat[323.15]

Out[\*]=

36.1658552072

Estimate  $\Delta V^{\text{lv}}$  by assuming molar volume of liquid is ~0 and that the vapor is an ideal gas with  $PV = RT$

$$\rightarrow V = \frac{RT}{P} :$$

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

$$T = 50 + 273.15;$$

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

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

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

Out[\*]=

74287.4483295

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

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

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

Out[\*]=

102169.470398

Convert units from  $\frac{\text{kPa} \cdot \text{cm}^3}{\text{mol} \cdot \text{K}}$  to  $\frac{\text{J}}{\text{mol} \cdot \text{K}}$  :

$$\begin{aligned} \text{In[*]} &:= \Delta S_{lv}[T] * \frac{\text{kPa} * \text{cm}^3}{\text{mol} * \text{K}} * \frac{1 \text{ m}^3}{10^6 \text{ cm}^3} * \frac{1000 \text{ Pa}}{1 \text{ kPa}} * \frac{1 \text{ J}}{1 \text{ m}^3 * \text{Pa}} \\ \text{Out[*]} &= \frac{102.169470398 \text{ J}}{\text{K mol}} \end{aligned}$$

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

## Solution, Part (b)

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

$$\Delta S^{lv} = \frac{-R}{T} \frac{d \ln P^{\text{sat}}}{d(1/T)}$$

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

$$\begin{aligned} \text{In[*]} &:= \text{Psatx}[x\_] = \text{Psat}[1/x]; (*\text{Substituted } x = \frac{1}{t} *) \\ \text{In[*]} &:= \text{Psatx}[1/T] (*\text{Check answer} *) \\ \text{Out[*]} &= 36.1658552072 \\ \text{In[*]} &:= \text{NatLogPsatx}[x\_] = \text{Log}[\text{Psatx}[x]]; \\ \text{In[*]} &:= \Delta S_{lvb}[x\_] = -R * x * \partial_x \text{NatLogPsatx}[x]; (*\text{C-C equation with equation 6.84} *) \\ \Delta S_{lvb}[1/T] &(*\text{Units are } \frac{\text{kPa} \cdot \text{cm}^3}{\text{mol} \cdot \text{K}} *) \\ \text{Out[*]} &= 102169.470398 \end{aligned}$$

Convert units from  $\frac{\text{kPa} \cdot \text{cm}^3}{\text{mol} \cdot \text{K}}$  to  $\frac{\text{J}}{\text{mol} \cdot \text{K}}$  :

$$\begin{aligned} \text{In[*]} &:= \Delta S_{lvb}[1/T] * \frac{\text{kPa} * \text{cm}^3}{\text{mol} * \text{K}} * \frac{1 \text{ m}^3}{10^6 \text{ cm}^3} * \frac{1000 \text{ Pa}}{1 \text{ kPa}} * \frac{1 \text{ J}}{1 \text{ m}^3 * \text{Pa}} \\ \text{Out[*]} &= \frac{102.169470398 \text{ J}}{\text{K mol}} \end{aligned}$$

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 °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 in the example.

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  $S_2$ ,  $S^{\text{liquid}}$  and  $S^{\text{vapor}}$  to calculate  $x^{\text{liquid}}$  and  $x^{\text{vapor}}$ , which are then used to calculate  $H^{\text{liquid}}$ ,  $H^{\text{vapor}}$ , and  $H_2$ .

Problem 6.25 is somewhat simpler than the example because we will see that state 2 is superheated steam (one phase), so no calculation of  $x^{\text{liquid}}$  and  $x^{\text{vapor}}$  is needed.

`Quit[];`

First, solve for the entropy and enthalpy at  $P_1 = 2100$  kPa and  $T_1 = 260$  °C by interpolation of data in Table E.2, page 717. The data must be interpolated between 250 and 275 °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] (*  $\text{kJ/kg}$  *)`

`{ {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 °C, the enthalpy is 2923.9 kJ/kg, and at 200 °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} }

The final temperature of the steam is 224.80 °C. //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  $S_2$ :

$$\text{eq3} = \frac{S_2 - 7.7300}{7.8324 - 7.7300} = \frac{2923.5 - 2874.2}{2923.9 - 2874.2};$$

**Solve[eq3, S2]**

{ {S2 → 7.83157585513} }

Next, calculate  $\Delta S$ :

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

1.2676

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

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

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

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

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:

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

Out[\*]=

$$\frac{1.30207849357 \text{ kJ}}{\text{K kg}}$$

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



## Problem 6.28

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

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

0.0314590113242

The mole fraction of water vapor in air that is saturated with water at 25 °C and 101.33 kPa is 0.031459.

//ANS

At 50 °C:

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

0.12242434827

The mole fraction of water vapor in air that is saturated with water at 50 °C and 101.33 kPa is 0.122424.

//ANS

## Problem 6.83

An equimolar mixture of methane and propane is discharged from a compressor at 5,500 kPa and 90 °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?

### Solution

Instructor's thought process:

**(Identify)** Molar volume comes from the EOS. If molar volume is in  $\text{cm}^3/\text{mol}$  and molar flow rate in  $\text{mol}/\text{sec}$  were available, I could multiply them and get the volumetric flow rate.

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

**(Identify)** Mass flow rate is given. Molar flow rate comes from the mass flow rate divided by molar mass:

$$\begin{aligned} \text{In[*]} &:= \frac{\frac{\text{kg}}{\text{sec}} * \frac{\text{g}}{\text{kg}}}{\frac{1 \text{ g}}{\text{mol}}} \\ \text{Out[*]} &= \frac{\text{mol}}{\text{sec}} \end{aligned}$$

**(Identify)** Velocity is given. If volumetric flow rate is in  $\text{cm}^3/\text{sec}$  and velocity is in  $\text{cm}/\text{sec}$  were available, I could divide and get area:

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

**(Formulate)** Molar volume from the equation of state can be formulated with Table 3.1 and equations 3.41, 3.44, and 3.45 to give molar volume.

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

Now proceed to the 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 given velocity and calculated volumetric flow rate to find area, and use the area to find the diameter.

```
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 equations 6.78-6.82 with the SRK equation:

```
 $\omega = 0.5 * 0.012 + 0.5 * 0.152$  ; (*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*)
 $\Psi = 0.42748$  ;
 $\sigma = 1$  ;
 $\epsilon = 0$  ;
 $\alpha = (1 + (0.480 + 1.574 * \omega - 0.176 * \omega^2) * (1 - \sqrt{T_{pr}}))^2$  ;
 $a = \Psi \frac{\alpha * R^2 * T_{pc}^2}{P_{pc}}$  ; (*Eq 3.45*)
 $b = \Omega * \frac{R * T_{pc}}{P_{pc}}$  ; (*Eq 3.44*)
eq1 = P ==  $\frac{R * T}{V - b} - \frac{a}{(V + \epsilon * b) * (V + \sigma * b)}$  ; (*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
```

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

```
Out[*]=  $\frac{20924.017293 \text{ cm}^3}{\text{sec}}$ 
```

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

```
Out[*]= 6.97467243099 cm2
```

```
In[*]:= 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