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## 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

```

In[=]:= (*Temperature and Pressure*)
t = 620. (*K*);
p = 20. (*bar*);

(*Ethylbenzene properties from Table B.1, p.664*)
tc = 617.2 (*K*);
pc = 36.06 (*bar*);
ω = 0.303;

(*Reduced T and P*)
tr = t / tc;
pr = p / pc;

(*Equation of state supporting information*)
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*);

(*Solve for Z and VR)
R2 = 83.14 (*R2 is the gas constant for molar volume calcs -  $\frac{\text{cm}^3 \cdot \text{bar}}{\text{mol} \cdot \text{K}}$ *);
Z = 1 + (B0 + ω * B1) * (pr / tr);
Vr = (R2 * t / p) * (Z - 1);

(*Solve for Residuals HR and SR)
R1 = 8.314 (*R1 is the gas constant for enthalpy and entropy -  $\frac{\text{J}}{\text{mol} \cdot \text{K}}$ *);
Hr = R1 * tc * pr * (B0 - tr * dB0 + ω * (B1 - tr * dB1)) (*Eq 6.68*);
Sr = -R1 * pr * (dB0 + ω * dB1) (*Eq 6.69*)

Out[=]=
-490.9018

Out[=]=
-3499.906

Out[=]=
-4.061455

VR = -490.902  $\frac{\text{cm}^3}{\text{mol}}$ , HR = -3,499.910  $\frac{\text{J}}{\text{mol}}$ , and SR = -4.061  $\frac{\text{J}}{\text{mol} \cdot \text{K}}$ . //ANS

```

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

```
In[ ]:= (*Temperature and Pressure*)
t = 250. (*K*);
p = 90. (*bar*);

(*Methane properties from Table B.1, p.663*)
tc = 190.6 (*K*);
pc = 45.99 (*bar*);
ω = 0.012;

(*Reduced T and P*)
tr = t / tc;
pr = p / pc;

(*Equation of state supporting information*)
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*);

(*Solve for Z and VR*)
R2 = 83.14 (*R2 is the gas constant for molar volume calcs -  $\frac{\text{cm}^3 \cdot \text{bar}}{\text{mol} \cdot \text{K}}$ *);
Z = 1 + (B0 + ω * B1) * (pr / tr);
Vr = (R2 * t / p) * (Z - 1);

(*Solve for Residuals HR and SR*)
R1 = 8.314 (*R1 is the gas constant for enthalpy and entropy -  $\frac{\text{J}}{\text{mol} \cdot \text{K}}$ *);
Hr = R1 * tc * pr * (B0 - tr * dB0 + ω * (B1 - tr * dB1)) (*Eq 6.68*);
Sr = -R1 * pr * (dB0 + ω * dB1) (*Eq 6.69*)

Out[ ]=
-65.2592

Out[ ]=
-1952.083

Out[ ]=
-5.459001

VR = -65.259  $\frac{\text{cm}^3}{\text{mol}}$ , HR = -1,952.080  $\frac{\text{J}}{\text{mol}}$ , and SR = -5.459  $\frac{\text{J}}{\text{mol} \cdot \text{K}}$ . //ANS
```

## Solution Grid

Out[ $\circ$ ] =

	$V^R$ $\frac{cm^3}{mol}$	$H^R$ $\frac{J}{mol}$	$S^R$ $\frac{J}{mol \cdot K}$
(a)	490.9020	-3,499.910	-4.061
(b)	-65.2592	-1,952.080	-5.459

## 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

```
In[0]:= Clear["Global`*"]
```

Determine the mole fractions in the mixture:

```
In[0]:= (*Water vapor pressure from Antoine Equation, p. 666*)
(*The temperature and pressure units in the appendix are °C and kPa.*)
a = 16.3872;
b = 3885.70;
c = 230.170;
t = 25(*°C*);

Pw = .5 * Exp[a - b / (t + c)] *  $\frac{1}{100}$  (*picket fence: kPa *  $\frac{1 \text{ bar}}{100 \text{ kPa}}$ *);
(*Partial pressure is 50% of saturation.*)
(*Partial pressure is also equal to the mole fraction from*)
(*Dalton's Law of Partial Pressures.*)
x = {1 - Pw, Pw}

Out[0]= {0.9840613, 0.01593871}
```

```
In[0]:= (*Book Values, Table B.1, page 665*)
tc = {132.20, 647.10} (*Tc of air & water from Table B.1 in K*);
pc = {37.45, 220.55} (*Pc of air & water from Table B.1 in bar*);
vc = {84.8, 55.9} (*Vc of air & water from Table B.1 in cm³/mol*);
w = {0.035, 0.345} (*w of air & water from Table B.1, dimensionless*);

(*CHEMCAD Values*)
(*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={-0.0078798,0.348}*) (*w of air & water from CC, dimensionless*);
```

Determine the true critical temperature and pressure of the mixture:

```
In[=]:= tpc = x.tc(*pseudocritical T of mixture*);
ppc = x.pc(*pseudocritical P of mixture*);
vpc = x.vc(*molar average critical volume*);
θ = x * vc / vpc (*volume fractions*);
Tcm = θ.tc(*true Tc of mixture*)
wavg = x.ω;
Pcm = ppc + ppc * (5.808 + 4.93 * wavg) *  $\left( \frac{Tcm - tpc}{tpc} \right)$  (*true Pc of mixture*)
(*Pro Tip: The "." or "period" operator is the same as Plus@@*)
(*This is handy for working with lists.*)
(*It does a pair-wise multiplication of the list elements*)

Out[=]=
137.6395

Out[=]=
35.59061
```

API Results with Textbook Critical Constants:

The critical temperature of the mixture is 137.6395 K. //ANS

The critical pressure of the mixture is 35.5906 bar. //ANS

API Results with CHEMCAD Critical Constants:

(Re-run above calculation with CHEMCAD constants to obtain these results)

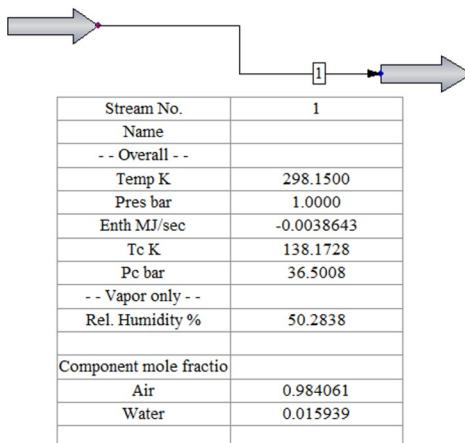
The critical temperature of the mixture is 138.1728 K. //ANS

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

CHEMCAD Results for comparison:

Tc = 138.1728 K //ANS

Pc = 36.5008 bar //ANS



CC uses a different vapor pressure equation, which is why relative humidity is slightly off.

## 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)

Method:

$$\frac{dP^{\text{sat}}}{dT} = \frac{\Delta H^{\text{lv}}}{T\Delta V^{\text{lv}}} \text{ from equation 6.86.}$$

$$\Delta H^{\text{lv}} = \frac{dP^{\text{sat}}}{dt} T\Delta V^{\text{lv}} \text{ from re-arranging equation 6.86.(A)}$$

$$\Delta H^{\text{lv}} = T\Delta S^{\text{lv}} \text{ from equation 6.84.}$$

$$\Delta S^{\text{lv}} = \frac{\Delta H^{\text{lv}}}{T} \text{ from re-arranging equation 6.84. (B)}$$

$$\Delta S^{\text{lv}} = \frac{dP^{\text{sat}}}{dt} \Delta V^{\text{lv}} \text{ from substituting (A) into (B).}$$

$\Delta V^{\text{lv}} = V^{\text{v}} - V^{\text{l}}$ . Estimate  $\Delta V^{\text{lv}}$  by assuming the vapor is an ideal and ignoring the molar volume of the liquid.

$P^{\text{sat}}$  as a function of T is the Antoine equation.

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

In[ ]:= Psat[323.15]

Out[ ]= 36.16586

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

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

$$T = 50 + 273.15;$$

$$P = \text{Psat}[T];$$

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

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

Out[ ]= 74287.45

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

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

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

Out[ ] =  
102169.5

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

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

Out[ ] =  
$$\frac{102.1695 \text{ J}}{\text{K mol}}$$

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:  $\Delta H^{lv} = -R \frac{d \ln P_{sat}}{d(1/T)}$ , 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.

$$\ln[ ] := \text{Psatx}[x_] = \text{Psat}[1/x]; (*\text{Substituted } x = \frac{1}{t} *)$$

$$\ln[ ] := \text{Psatx}[1/T] (*\text{Check answer}*)$$

Out[ ] =  
36.16586

$$\ln[ ] := \text{NatLogPsatx}[x_] = \text{Log}[\text{Psatx}[x]];$$

$$\ln[ ] := \Delta S_{lvb}[x_] = -R * x * \partial_x \text{NatLogPsatx}[x]; (*\text{C-C equation with equation 6.84}*)$$

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

Out[ ] =  
102169.5

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

$$\ln[ ] := \Delta S_{lvb}[1/T] * \frac{\text{kPa} \cdot \text{cm}^3}{\text{mol} \cdot \text{K}} * \frac{1 \text{ m}^3}{10^6 \text{ cm}^3} * \frac{1000 \text{ Pa}}{1 \text{ kPa}} * \frac{1 \text{ J}}{1 \text{ m}^3 \cdot \text{Pa}}$$

Out[ ] =  
$$\frac{102.1695 \text{ J}}{\text{K mol}}$$

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°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 is very similar to Example 6.10. In that example, entropy is constant from state 1 to state 2, allowing enthalpy in state 2 to be calculated using the steam tables.

Example 6.10 is somewhat more complicated because in that problem, state 2 is a two-phase mixture containing saturated liquid water and steam. The premise of the example is to use  $S_2$ ,  $S^{\text{liquid}}$  and  $S^{\text{vapor}}$  to calculate liquid and vapor qualities  $x^{\text{liquid}}$  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 because we can deduce that state 2 is superheated steam (one phase), so no calculations of  $x^{\text{liquid}}$  and  $x^{\text{vapor}}$  are needed.

Any steam tables can be used. The calculations below refer to the steam tables in Appendix E of the textbook.

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. To find the values at 260°C, the steam table entries must be interpolated between 250 and 275 °C:

$$\text{eq1} = \frac{260 - 250}{275 - 250} = \frac{S_1 - 6.5162}{6.6356 - 6.5162};$$

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

$$\{ \{ S1 \rightarrow 6.56396 \} \}$$

$$\text{eq2} = \frac{260 - 250}{275 - 250} = \frac{H_1 - 2897.9}{2961.9 - 2897.9};$$

$$\text{Solve[eq2, H1]} (*\text{kJ}/\text{kg}* )$$

$$\{ \{ H1 \rightarrow 2923.5 \} \}$$

Next, carefully study the superheated steam table E.2 on page 705, specifically the 125 kPa row corresponding to  $P_2$  and recall that this is a constant enthalpy expansion, so  $H_2 = H_1$ . Observe that the enthalpy value at 225°C (2923.9 kJ/kg) is very close to but slightly greater than  $H_1$  (or  $H_2$ ), and that the enthalpy value at 200°C (2874.2 kJ/kg) is significantly less than  $H_1$  (or  $H_2$ ). This means that the unknown temperature  $T_2$  must be between 200 and 225°C and very close to 225°C.

We can also see that the enthalpy is 2923.9 kJ/kg at 225°C and at 200°C it is 2874.2 kJ/kg. That is,  $2874.2 < H_1 < 2923.9$ . Since  $H_1$  is between these two values, we conclude that state 2 is indeed superheated steam with a temperature between 200 and 225°C. An interpolation is needed to find the exact value:

$$\text{eq3} = \frac{T_2 - 200}{225 - 200} = \frac{2923.5 - 2874.2}{2923.9 - 2874.2};$$

**Solve[eq3, T2] (\*°C\*)**

$$\{\{T_2 \rightarrow 224.7988\}\}$$

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]**

$$\{\{S_2 \rightarrow 7.831576\}\}$$

Next, calculate  $\Delta S$ :

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

$$1.2676$$

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.

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

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

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

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

$$23.45694$$

The entropy units are  $\frac{\text{J}}{\text{mol}\cdot\text{K}}$  and the steam tables are in  $\frac{\text{kJ}}{\text{kg}\cdot\text{K}}$ . Convert for comparison:

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

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

$$\frac{1.302078 \text{ kJ}}{\text{K kg}}$$

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, T is in °C and P is in kPa.

$$a = 16.3872;$$

$$b = 3885.70;$$

$$c = 230.170;$$

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

From Dalton's Law of Partial Pressures at 25°C and 101.33 kPa:

$$y_{\text{water}} = \frac{P_{\text{sat}}[25]}{101.33} (*25^{\circ}\text{C}* )$$

$$0.031459\ 01$$

The mole fraction of water is 0.031459. //ANS

From Dalton's Law of Partial Pressures at 50°C and 101.33 kPa:

$$y_{\text{water}} = \frac{P_{\text{sat}}[50]}{101.33} (*50^{\circ}\text{C}* )$$

$$0.122424\ 3$$

The mole fraction of water 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. The product of molar volume and molar flow rate is 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 is mass flow rate divided by molar mass:

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

$$\frac{\text{g}}{\text{mol}}$$

$$\frac{\text{mol}}{\text{sec}}$$

Out[ ] =

**(Identify)** Area is volumetric flow rate divided by velocity and velocity is given. Divide them to get area, which leads to diameter:

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

$$\text{cm}^2$$

**(Formulate)** The equation of state can be formulated with Table 3.1 and equations 3.41, 3.44, and 3.45.

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

Now proceed to the solution. Calculate the molar volume of the mixture, then use the molar volume and the given mass flow rate to find volumetric flow rate. Then use the calculated volumetric flow rate and the given velocity to find area. Finally, use the area to find the diameter.

In[ ] := **Clear["Global`\*"]**

```
(*Temperature, Pressure, Mole Fractions, and Molar Mass Values*)
t = 90 + 273.15; (*K*)
p = 55.; (*bar*)
x = {.5, .5}; (*methane, air*)
MW = {16.043, 44.097} ; (*molar mass of methane and air in  $\frac{g}{mol}$ *)

(*Methane and Air Properties from Table B.1, p.664*)
tc = {190.6, 369.8}; (*K*)
pc = {45.99, 42.48}; (*bar*)
w = {0.012, 0.152}; (*not used in RK EOS*)

(*Mixture Properties*)
wpc = x.w; (*Eq. 6.78*)
tpc = x.tc; (*K*) (*Eq. 6.79*)
ppc = x.pc; (*bar*) (*Eq. 6.80*)

(*Reduced T and P*)
tpr = t / tpc; (*reduced temperature, Eq. 6.81*)
ppr = p / ppc; (*reduced pressure, Eq. 6.82*)

(*Equation of State Supporting Information from Table 3.1 page 100*)
σ = 1;
ε = 0;
Ω = 0.08664;
Ψ = 0.42748;
α = (1 + (0.480 + 1.574 * wpc - 0.176 * wpc2) * (1 - √tpr))2;

(*Equation of State*)
R = 83.14 (* $\frac{cm^3 \cdot bar}{mol \cdot K}$ *);
a = Ψ  $\frac{\alpha * R^2 * tpc^2}{ppc}$ ; (*Eq 3.45*)
b = Ω *  $\frac{R * tpc}{ppc}$ ; (*Eq 3.44*)
eq1 = p =  $\frac{R * t}{v - b} - \frac{a}{(v + \epsilon * b) * (v + \sigma * b)}$ ; (*Eq 3.41*)

(*Solve for Molar Volume of the Mixture*)
V = SolveValues[eq1, v] [[3]]
```

Out[ ]=

449.4183

The molar volume of the mixture is 449.418  $\frac{cm^3}{mol}$ .

(\*Molar Mass of the Mixture\*)

$$\text{MWmix} = x \cdot \text{MW} * \frac{\text{g}}{\text{mol}};$$

(\*Molar Flow Rate of the Mixture\*)

$$\dot{m} = \frac{1.4 \text{ kg}}{\text{sec}} * \frac{1000 \text{ g}}{1 \text{ kg}};$$

(\*Volumetric Flow Rate of the Mixture\*)

$$\dot{v} = V * \frac{\text{cm}^3}{\text{mol}} * \dot{m};$$

(\*Cross-Sectional Area of Pipe\*)

$$\text{area} = \frac{\dot{v}}{\frac{30 \text{ m}}{\text{sec}} * \frac{100 \text{ cm}}{\text{m}}};$$

(\*Pipe Diameter\*)

$$\text{eq2} = \frac{\pi * d^2}{4} == \text{area};$$

`SolveValues[eq2, d]`

`Out[ ]=`

$$\{-2.980006 \text{ cm}, 2.980006 \text{ cm}\}$$

The minimum diameter is 2.98 cm. // ANS