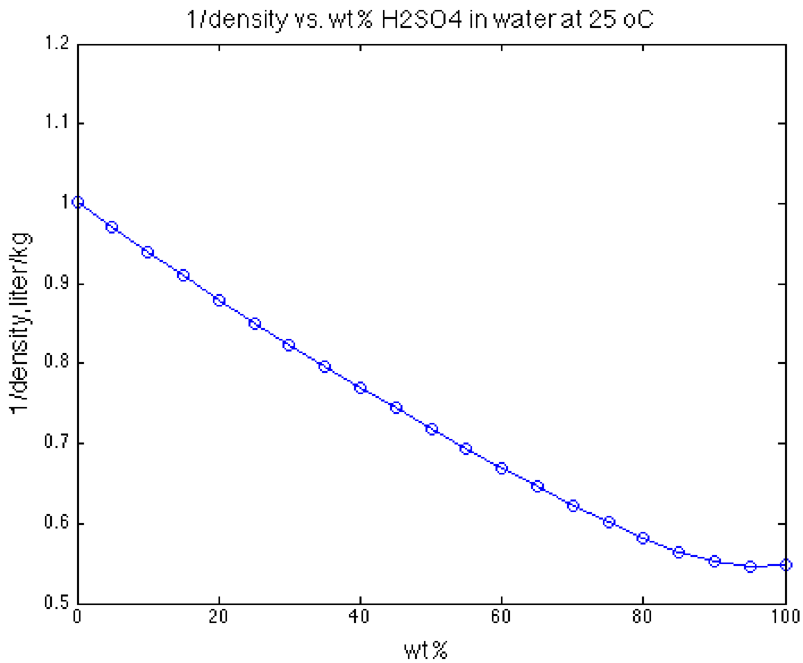
CBE 20255

HW5 sotluion

1 Looking for ideal solution..



1.

Matlab script is attached in the end of solution.

2.

Average molar weight of the mixture

$$\overline{MW} = \frac{1}{\frac{wt\%\ of\ H2SO4}{MW_{H2SO4}} + \frac{wt\%\ of\ water}{MW_{H2O}}}$$

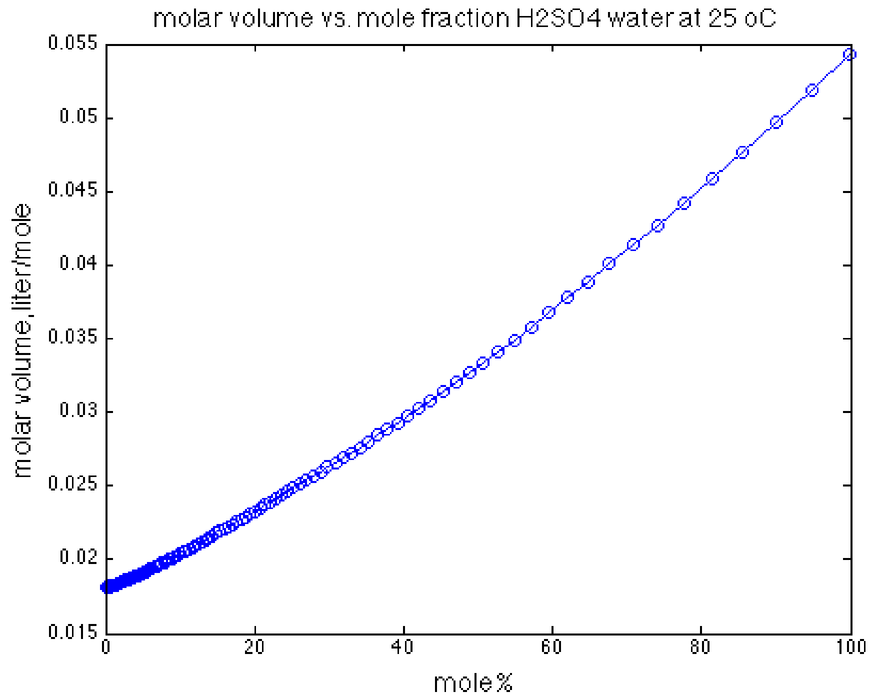
Mole fraction of H_2SO_4

$$mol\% = \frac{wt\%\ of\ H2SO4}{MW_{H2SO4}}\ \overline{MW}$$

Molar volume

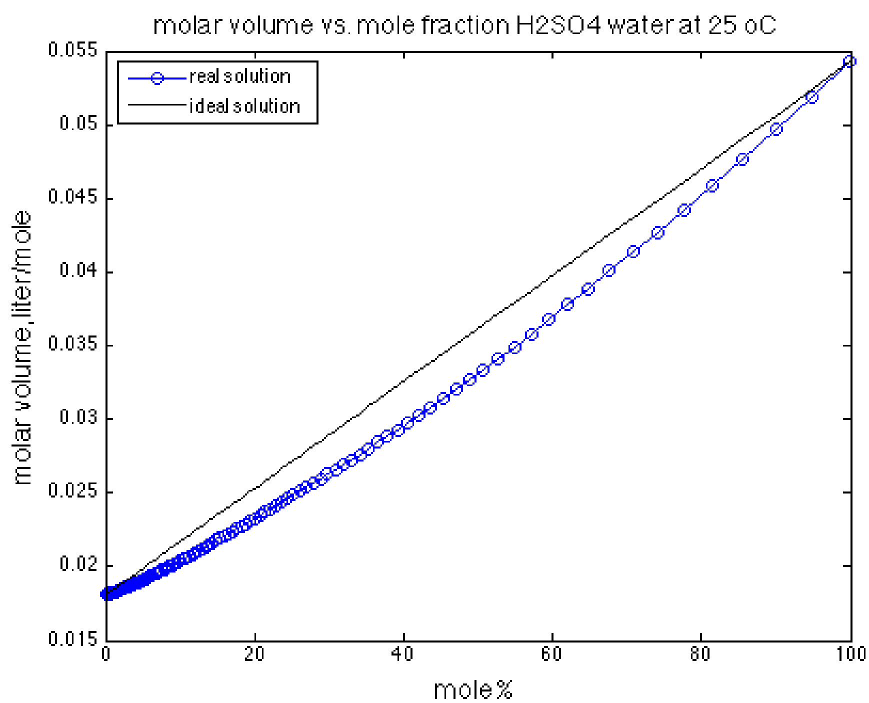
$$MV = \frac{1}{density/\overline{\overline{MW}}}$$

After processing the data, we can plot



3.

Properties of ideal solution should be linear combinations of two different liquids. For example, in this problem, the molar volume of ideal solution can be expressed as a straight line between pure sulfuric acid and pure water.



By comparison, we can see the real solution lies below the ideal solution, suggesting that the real solution is not ideal and it deviates negatively from ideality.

2. ... and I found it. ☆

1. $P_{He} = 35\% \cdot 2.00\ atm = 0.70\ atm$

$P_{CH_4} = 20\% \cdot 2.00\ atm = 0.40\ atm$

$P_{N_2} = 45\% \cdot 2.00\ atm = 0.90\ atm$

2. According to ideal gas law

$$PV = nRT$$

$$\text{molar volume} = \frac{V}{n} = \frac{RT}{P}$$

$$= \frac{0.08208\ L\ atm\ K^{-1}\ mol^{-1} \cdot (90 + 273.15)K}{2.00\ atm}$$

$$= 15\ L/mol$$

3. Standard conditions:

~~$P^\circ = 1\ bar = 0.98692\ atm$~~ $P^\circ = 1\ atm$

$T^\circ = 273.15K$

For different conditions, numbers of mole are the same,

So

$$n = \frac{PV_1}{RT} = \frac{P^\circ V_2}{RT^\circ} \longrightarrow V_2 = \frac{P}{P^\circ}\frac{T^\circ}{T}V_1$$

$$= \frac{2\ atm}{1\ atm}\ \frac{273.15K}{363.15K} \cdot 100\ L$$

$$= 150\ L = 0.15\ SCM$$

4.

$$n = \frac{PV_1}{RT} = \frac{2\,atm \cdot 100\,L}{0.08208\,L \cdot atm\,K^{-1}\,mol^{-1} \cdot (90+273.15)\,K}$$

$$= 6.7\ mol$$

$$\text{Total mass} = 35\%\ n \cdot MW_{He} + 20\%\ n \cdot MW_{CH_4} + 45\%\ n \cdot MW_{N_2}$$

$$= (0.36 \cdot 6.7 \cdot 4.00 + 0.20 \cdot 6.7 \cdot 16.04 + 0.45 \cdot 6.7 \cdot 28.01)\ gram$$

$$= 120\ gram$$

3 NO, NO and still NO!

1. For an isothermal batch reactor, T and V are constant.

If reactants are products are all ideal gas,

$$n_{0,total} = \frac{P_0 V}{RT}$$

$$n_{t,total} = \frac{P_t V}{RT}$$

$$n_{0,NO} = \frac{P_0 V \cdot 20.0\%}{RT}$$

$$n_{0,O_2} = \frac{P_0 V \cdot 80.0\% \cdot 21\%}{RT}$$

$$n_{0,inert} = \frac{P_0 V \cdot 80.0\% \cdot 79.0\%}{RT}$$

$$NO(g) + \tfrac{1}{2}O_2(g) \rightleftharpoons NO_2(g)$$

Initial $\frac{0.200 P_0 V}{RT}$ $\frac{0.168 P_0 V}{RT}$ 0

Reaction $-\frac{0.200 P_0 V}{RT} \cdot 90\%$ $-\frac{0.200 P_0 V}{RT} \cdot 90\% \cdot \frac{1}{2}$ $\frac{0.200 P_0 V}{RT} \cdot 90\%$

Final $\frac{0.200 P_0 V}{RT} \cdot 10\%$ $\frac{0.078 P_0 V}{RT}$ $\frac{0.180 P_0 V}{RT}$

$$n_{t,total} = \frac{0.0200 P_0 V}{RT} + \frac{0.078 P_0 V}{RT} + \frac{0.180 P_0 V}{RT} + \frac{0.632 P_0 V}{RT} = \frac{0.91 P_0 V}{RT}$$

$$\begin{cases} X_{NO} = \frac{0.02}{0.91} = 2.2\% \\ X_{O_2} = \frac{0.078}{0.91} = 8.6\% \\ X_{NO_2} = \frac{0.180}{0.91} = 19.7\% \\ X_{inert} = 69.5\% \end{cases}$$

2. From part 1, we know

$$n_{1,total} = \frac{P_1 V}{RT} = \frac{0.91 P_0 V}{RT}$$

$$\longrightarrow P_1 = 0.91 P_0$$

$$= 0.91 \cdot 380\,kPa = 346\,kPa$$

3. Assume conversion of $NO = X$ at equilibrium,

$$n_{t,total} = \frac{360\,kPa}{380\,kPa} n_{0,total}$$

$$n_{t,total} = \frac{0.200 P_0 V}{RT}(1-X) + \frac{0.168 P_0 V}{RT} - \frac{0.200 P_0 V}{RT}\frac{1}{2}X + \frac{0.200 P_0 V}{RT} X + \frac{0.632 P_0 V}{RT}$$

$$= \frac{P_0 V}{RT} - \frac{0.100 P_0 V}{RT} X = \frac{360}{380}\frac{P_0 V}{RT}$$

So $X = 0.526$

$$n_{t,NO} = \frac{0.200 P_0 V}{RT}(1-0.526) \longrightarrow \boxed{\begin{aligned} P_{t,NO} &= 0.200(1-0.526) P_0 \\ &= 36\,kPa \end{aligned}}$$

$$n_{t,O_2} = \frac{0.168 P_0 V}{RT} - \frac{0.200 P_0 V}{RT}\frac{1}{2} \cdot 0.526 \longrightarrow \boxed{\begin{aligned} P_{t,O_2} &= (0.168 - 0.200 \cdot \tfrac{1}{2} \cdot 0.526) P_0 \\ &= 44\,kPa \end{aligned}}$$

$$n_{t,NO_2} = \frac{0.200 P_0 V}{RT} \cdot 0.526 \longrightarrow \boxed{P_{t,NO_2} = 0.200 \cdot 0.526 P_0 = 40\,kPa}$$

$$n_{t,inert} = \frac{0.632 P_0 V}{RT} \longrightarrow \boxed{P_{t,inert} = 0.632 P_0 = 239\,kPa}$$

4. $K_p = \frac{P_{NO_2}}{P_{NO} \cdot P_{O_2}^{0.5}} = \frac{40\,kPa}{36kPa \cdot (44kPa)^{0.5}} = 0.168\,(kPa)^{-0.5}$

5. $NO(g) + \frac{1}{2}O_2(g) \rightleftharpoons NO_2(g)$

Initial $\frac{0.5P_0V}{RT}$ $\frac{0.5P_0V}{RT}$

Reaction: $-\frac{0.5P_0V}{RT}X$ $-\frac{0.5P_0V}{RT}\frac{1}{2}X$ $\frac{0.5P_0V}{RT}X$

Final: $\frac{0.5P_0V}{RT}(1-X)$ $\frac{0.5P_0V}{RT}(1-\frac{1}{2}X)$ $\frac{0.5P_0V}{RT}X$

$$N_{t,total} = \frac{P_0V}{RT}(1-0.25X)$$

$$P_{t,NO_2} = \frac{0.5X}{1-0.25X}P_0$$

$$P_{t,O_2} = \frac{0.5(1-\frac{1}{2}X)}{1-0.25X}P_0$$

$$P_{t,NO} = \frac{0.5(1-X)}{1-0.25X}P_0$$

$$K_p = \frac{P_{t,NO_2}}{P_{t,NO}\ P_{t,O_2}^{\frac{1}{2}}} = \frac{0.5X}{0.5(1-X)\cdot[0.5(1-\frac{1}{2}X)]^{0.5}}P_0^{-\frac{1}{2}}\ (1-0.25X)^{\frac{1}{2}}$$

$$= 0.168$$

$\longrightarrow X = 0.674$

So $P_t = (1-0.25\cdot 0.647)P_0 = 316kPa$

$x_{t,NO_2} = \frac{0.5\cdot 0.674}{1-0.25\cdot 0.674} = 40.5\%$ $x_{t,NO} = 19.6\%$ $x_{t,O_2} = 39.9\%$

4 Don't be so critical ... ☆

1.

	Critical point		
	T_c (K)	P_c (MPa)	V_c ($m^3/kmol$)
Methane	191.1	4.64	0.0993
Ethane	305.5	4.48	0.1480
Propane	370	4.26	0.1998
Butane	425.2	3.80	0.2547

T_c and V_c increase as carbon chain length increases while P_c decreases as carbon chain length increases

2.

Methane is most "ideal".

Reasons:

① Methane is the smallest molecule among them and therefore occupies least volume, which is better consistent with ideal gas assumption that gas molecules occupy no volume.

② Methane is the smallest molecule so that van der waals interaction between molecules is weakest, which is better consistent with ideal gas assumption ~~that~~ gas molecules do not interact with each other.

5 A non-ideal state of affairs

1. $$n = \frac{PV}{RT} = \frac{m}{MW}$$

$$= \frac{75.0\,kg}{44.1\,g/mol}$$

$$= 1.70 \times 10^3\ mol$$

$$P = \frac{nRT}{V} = \frac{1.70\times10^3\,mol \cdot 8.314\,m^3\,Pa\,K^{-1}\,mol^{-1} \cdot (25+273.15)\,K}{5.0\,m^3}$$

$$= 8.4\times10^5\,Pa = 8.4\,bar$$

2. van der Waal's equation of state

$$(P + an^2/V^2)/(V - nb) = nRT$$

For propane,

$a = 9.385\ bar\,L^2/mol^2$

$b = 0.09044\ L/mol$

So $$\left[P + \frac{9.385 \cdot (1.7\times10^3\,mol)^2\,bar\,L^2/mol^2}{(5.0\times10^3\,L)^2}\right](5.0\times10^3\,L - 1.7\times10^3\,mol \cdot 0.09044\,L/mol)$$

$$= 1.70\times10^3\,mol \cdot 8.314\times10^{-2}\,L\,bar\,K^{-1}\,mol^{-1} \cdot 298.15\,K$$

By solving the equation,

$$P = 7.6 \text{ bar}$$

3. Soave-Redlich-Kwong equation of state,

$$P = \frac{RT}{V_m - b} - \frac{a\alpha}{V_m(V_m + b)}$$

$$\alpha = (1 + (0.480 + 1.574\omega - 0.176\omega^2)(1 - T_r^{0.5}))^2$$

$$a = 0.42748 \frac{R^2 T_c^2}{P_c}$$

$$b = 0.08664 \frac{R T_c}{P_c}$$

For propane, $T_c = 370K$, $P_c = 42.6 \text{ bar}$, $\omega = 0.152$

At $T = 298.15K$, $T_r = \frac{298.15}{370} = 0.806$

$$\alpha = (1 + (0.480 + 1.574 \cdot 0.152 - 0.176 \cdot 0.152^2)(1 - 0.806^{0.5}))^2$$

$$= 1.152$$

$$a = 0.42748 \frac{(8.314 \times 10^{-5})^2 (370K)^2 \text{ m}^3 \text{ bar K}^{-1} \text{mol}^{-1}}{42.6 \text{ bar}} = 9.496 \times 10^{-6} \text{ K m}^3 \text{ mol}^{-1}$$

$$b = 0.08664 \frac{8.314 \times 10^{-5} \text{ m}^3 \text{ bar K}^{-1} \text{mol}^{-1} \cdot 370K}{42.6 \text{ bar}} = 6.2563 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$$

$\cancel{V_c = 0.1998 \times 10^{-3} \text{ m}^3/\text{mol}}$ $\cancel{V_m = \frac{V/n}{V = 0.1998 \times 10^{-3} \text{ m}^3/\text{mol}} \quad 5.0 \text{ m}^3/1700 \text{ mol}}$

$$V_m = \frac{5.0 \text{ m}^3}{1700 \text{ mol}} = 2.90 \times 10^{-3} \text{ m}^3/\text{mol}$$

plug in all value,

$P = 7.3 \text{ bar}$

4. $T_r = \frac{T}{T_c} = \frac{298.15K}{370K} = 0.806$

$$V_r = \frac{VP_c}{RT_c} = \frac{2.9\times10^{-3}\ m^3/mol \cdot 42.6\ bar}{8.314\times10^{-5}\ m^3\ bar\ K^{-1}\ mol^{-1} \cdot 370K}$$

$$= 4.07$$

5. From the generalized compressibility chart, it can be found that $P_r \sim 0.175$, $Z \sim 0.86$

So $P = P_r P_c = 0.175 \cdot 42.6\ bar$

$= 7.5\ bar$

Matlab script for problem 1

```
clear
A1=importdata('/problem_1.txt');
wt=A1(:,1);
density=A1(:,6);
inverse_density=1./density

for i=1:21
    position=i-1
    collect_wt(i)=wt(position*5+1);
    collect_inverse_density(i)=inverse_density(position*5+1);
end

average_MW=100./(wt/99.08+(100-wt)/18.02);

mol_vol=1./(density.*1000./average_MW);

mol_frac=100*wt./99.08./(wt/99.08+(100-wt)/18.02);



plot(collect_wt,collect_inverse_density,'-o')
title('1/density vs. wt% H2SO4 in water at 25 oC','FontSize',14)
xlabel('wt%','FontSize',14)
ylabel('1/density,liter/kg','FontSize',14)

ideal=(mol_vol(101)-mol_vol(1))/100*mol_frac+mol_vol(1);

plot(mol_frac,mol_vol,'-o')
hold on
plot(mol_frac,ideal,'-k')
title('molar volume vs. mole fraction H2SO4 water at 25 oC','FontSize',14)
xlabel('mole%','FontSize',14)
ylabel('molar volume,liter/mole','FontSize',14)
legend('real solution','ideal solution','Location','northwest')
```