Problem Set J

Problem 33

a) $\frac{G^E}{RT} = 0.95\,x_1 x_2$

$$\frac{\bar{G}_1^E}{RT} = \ln \gamma_1 = \left[\frac{\partial (n G^E/RT)}{\partial n_1}\right]_{T,P,n_2}$$

$$= \frac{\partial}{\partial n_1}\left\{0.95\,\frac{n_1}{n}\cdot\frac{n_2}{n}\cdot n\right\}$$

$$= \frac{\partial}{\partial n_1}\left(0.95\,\frac{n_1 n_2}{n_1+n_2}\right)$$

$$= 0.95\,n_2 \cdot \frac{\partial}{\partial n_1}\left(\frac{n_1}{n_1+n_2}\right)$$

$$= 0.95\,n_2 \cdot \left[\frac{-n_1}{(n_1+n_2)^2} + \frac{1}{n_1+n_2}\right]$$

$$= 0.95\,x_2(1-x_1)$$

$$= 0.95\,x_2^2$$

$$\frac{\bar{G}_2^E}{RT} = \ln \gamma_2$$

from $\frac{G^E}{RT} = \sum_i x_i \ln \gamma_i = x_1 \ln\gamma_1 + x_2 \ln\gamma_2$

$$\therefore \ln\gamma_2 = \left(\frac{G^E}{RT} - x_1 \ln\gamma_1\right)\cdot\frac{1}{x_2}$$

$$= \left(0.95\,x_1 x_2 - x_1 \cdot 0.95\,x_2^2\right)\cdot\frac{1}{x_2}$$

$$= 0.95\,x_1 - 0.95\,x_1 x_2$$

$$= 0.95\,x_1^2$$

From $y_i P = \gamma_i x_i P_i^{sat}$ => modified Raoult's law

=> here we assume that the gas behave ideally , ϕ_i

$$\Sigma y_i P = \Sigma \gamma_i x_i P_i^{sat} = \gamma_1 x_1 P_1^{sat} + \gamma_2 x_2 P_2^{sat}$$, sir

$$\therefore P = \gamma_1 x_1 P_1^{sat} + \gamma_2 x_2 P_2^{sat}$$

since we know $\ln \gamma_1$ and $\ln \gamma_2$ as a function of

$\therefore$ given x_1, and x_2, we can calculate γ_1, and γ_2

P_{Bubble} and P_{Dew}

At $x_1 = 0.5$ $\quad \ln \gamma_1 = 0.2375 \quad \therefore \gamma_1 = 1.268$

$\ln \gamma_2 = 0.2375 \quad \gamma_2 = 1.268$

$$\therefore P_{bubble} = (1.268 \times 0.5 \times 79.8) + (1.268 \times 0.5 \times 40.5)$$

$$\boxed{P_{Bubble} = 76.3 \text{ kPa}}$$

and $y_1 P = \gamma_1 x_1 P_1^{sat}$

$$\therefore y_1 = \frac{\gamma_1 x_1 P_1^{sat}}{P} = \frac{1.268 \times 0.5 \times 79.8}{76.3}$$

$$\boxed{y_1 = 0.66}$$

b) $y_1 = 0.5 \quad y_2 = 0.5$, $\quad y_i P = \gamma_i x_i P_i^{sat} \quad \therefore \quad x_i =$

$$\sum x_i = \sum \frac{y_i P}{\gamma_i P_i^{sat}} \quad \therefore \quad P = \frac{1}{\frac{y_1}{\gamma_1 P_1^{sat}} + \frac{y_2}{\gamma_2 P_2^{sat}}}$$

$\therefore$ need γ_1 and γ_2, but since we don't know γx_i we need to do the calculations iteratively

- First assume $\gamma_1 = 1$, $\gamma_2 = 1$, then calculate P_{Dew} using e
- With that value of P_{Dew}, use $x_1 = \frac{y_1 P_{Dew}}{\gamma_1 P_1^{sat}}$ and

  to calculate x_1 and x_2
- With these x_1 and x_2, recalculate γ_1 and γ_2.
- Repeat until converge

	γ_1	γ_2	P_{Dew}	x_1	x_2
	1	1	53.7	0.337	0.663
	1.52	1.11	65.7	0.271	0.729
	⋮	⋮	⋮	⋮	⋮
after ~ 6 steps	1.745	1.054	65.3	0.235	0.765

$\therefore$ $\boxed{P_{Dew} = 65.3 \text{ kPa}}$ $\quad \boxed{x_1 = 0.235}$

$*$ or use $\frac{y_1 P}{y_2 P} = \frac{\gamma_1 x_1 P_1^{sat}}{\gamma_2 x_2 P_2^{sat}}$ to eliminate P and solve f

c) At azeotrope, $y_1 = x_1$ and $y_2 = x_2$

and $P_{Bubble} = P_{dew}$

$$\therefore \quad \gamma_1 x_1 P_1^{sat} + \gamma_2 x_2 P_2^{sat} = \frac{1}{\frac{y_1}{\gamma_1 P_1^{sat}} + \frac{y_2}{\gamma_2 P_2^{sat}}}$$

$$\gamma_1 x_1 P_1^{sat} + \gamma_2 (1-x_1) P_2^{sat} = \frac{1}{\frac{x_1}{\gamma_1 P_1^{sat}} + \frac{(1-x_1)}{\gamma_2 P_2^{sat}}}$$

with $\ln \gamma_1 = 0.95(1-x_1)^2$ and $\ln \gamma_2 = 0.95\, x_1^2$

we have an equation that has only x_1 as an unknow

solve this equation to get $x_1 = 0.857$

$$\therefore \quad \boxed{\begin{array}{ll} \text{Composition} & y_1 = x_1 = 0.857 \\ & y_2 = x_2 = 0.143 \end{array}}$$

and $P = \gamma_1 x_1 P_1^{sat} + \gamma_2 x_2 P_2^{sat}$

$$\boxed{P = 81.4 \text{ kPa}}$$

* or you can use $\frac{y_1 P}{y_2 P} = \frac{\gamma_1 x_1 P_1^{sat}}{\gamma_2 x_2 P_2^{sat}}$ to eliminate P , ar

Problem 34

a) $\frac{G^E}{RT} = 0.64\, x_1 x_2$

following procedures used in problem 33

$$\ln \gamma_1 = 0.64\, x_2^2$$
$$\ln \gamma_2 = 0.64\, x_1^2$$

from modified Raoult's law $\quad y_i P = \gamma_i x_i P_i^{sat}$

$$\therefore \quad P_{Bubble} = \sum_i \gamma_i x_i P_i^{sat} = \gamma_1 x_1 P_1^{sat} + \gamma_2 x_2 P_2^{sat}$$

Using Antoine equation $\quad \ln P^{sat} = A - \frac{B}{t+C} \quad P^{sat}$ in kPa

For acetone (1) $\quad A = 14.3916 \quad B = 2795.82 \quad C = 230$

For methanol (2) $\quad A = 16.5938 \quad B = 3644.3 \quad C = 239.76$

$\therefore$ At 50°C $\quad P_1^{sat} = 82.0$ kPa $\quad P_2^{sat} = 55.5$ kPa

To construct Pxy diagram

- Pick a value of x_1, then calculate γ_1 and γ_2
- Calculate P_{Bubble} using eqn. (B)
- Using eqn (A), calculate $y_1 = \frac{\gamma_1 x_1 P_1^{sat}}{P_{Bubble}}$, this

mole fraction of acetone in the vapor that is in equilibr

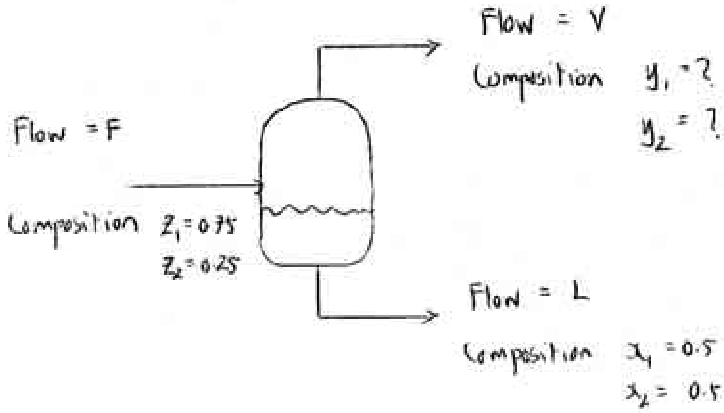
liquid of composition x_1 at $P = P_{Bubble}$

b) To construct a Txy diagram

- Set P at 75 kPa
- Pick a value of x_1
- Using eqn (B) with $P_{Bubble} = 75$ kPa, calculate T, since P_1^{sat} and P_2^{sat} are function by Antoine equations
- Knowing T, hence P_i^{sat}, we can calculate y_1 using

or you can pick T, and get P_i^{sat} from Antoine eqns; then x_1

c)



P = 100 kPa

Using $P_{Bubble} = \gamma_1 x_1 P_1^{sat} + \gamma_2 x_2 P_2^{sat}$

$$100 = \exp(0.64 \cdot 0.5^2) \times 0.5 \times \exp\left[14.3916 - \frac{2795.82}{t+230}\right]$$

$$+ \exp(0.64 \cdot 0.5^2) \times 0.5 \times \exp\left[16.5938 - \frac{3644.3}{t+239.76}\right]$$

solve this equation to get $\boxed{t = 55.6\ ^\circ C}$

$$\therefore\ y_1 = \frac{\gamma_1 x_1 P_1^{sat}}{P} = \frac{\exp(0.64 \cdot 0.5^2) \times 0.5 \times \exp\left[14.3916 - \frac{27}{55.6}\right.}{100}$$

$$\boxed{y_1 = 0.58}$$

Performing material balances on

Total $\quad F = V + L$

Component 1 $\quad 0.75F = 0.58V + 0.5L$

$$\therefore \quad 0.75(V+L) = 0.58V + 0.5L$$

$$0.25L = -0.17V$$

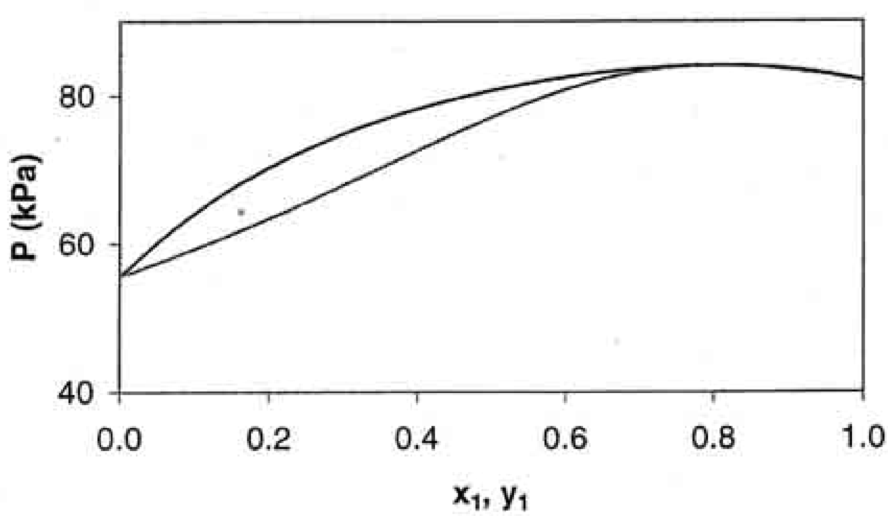
$$\boxed{\frac{L}{V} = -0.68}$$

this is not possible as we have a negative flow, we want to flow in the V stream

(a)

	Acetone 1	Methanol 2
A	14.3916	16.5938
B	2795.82	3644.3
C	230	239.76
t	50	50
P^{sat} (kPa)	81.98	55.53

x_1	γ_1	γ_2	P	y_1
0.00	1.896	1.000	55.53	0.00
0.05	1.782	1.002	60.14	0.12
0.10	1.679	1.006	64.06	0.21
0.15	1.588	1.015	67.41	0.29
0.20	1.506	1.026	70.27	0.35
0.25	1.433	1.041	72.72	0.40
0.30	1.368	1.059	74.83	0.45
0.35	1.310	1.082	76.64	0.49
0.40	1.259	1.108	78.20	0.53
0.45	1.214	1.138	79.54	0.56
0.50	1.174	1.174	80.68	0.60
0.55	1.138	1.214	81.65	0.63
0.60	1.108	1.259	82.46	0.66
0.65	1.082	1.310	83.10	0.69
0.70	1.059	1.368	83.59	0.73
0.75	1.041	1.433	83.89	0.76
0.80	1.026	1.506	84.01	0.80
0.85	1.015	1.588	83.92	0.84
0.90	1.006	1.679	83.58	0.89
0.95	1.002	1.782	82.96	0.94
1.00	1.000	1.896	81.98	1.00



Problem 35

a) Henry's law $y_i P = p_i = H_i x_i$

$P_{O_2} = 1$ atm

In 1 liter of $(C_4F_9)_3N$, we have 384 ml of O_2 dissolved in

assuming ideal gas $PV^t = nRT$
1atm, 25°C

$$n = \frac{PV^t}{RT} = \frac{\overset{(Pa)}{1.01325 \times 10^5} \times \overset{(m^3)}{384 \times 10^{-6}}}{\underset{(J/mol\,K)}{8.314} \times \underset{(K)}{298}}$$

$$= 0.0157 \text{ moles of } O_2$$

we have $1.883 \times 1000 = 1883g$ of solvents in a liter

ie. $$\frac{1883}{3\times\{\underset{C}{(12\times4)}+\underset{F}{(19\times9)}\} + \underset{N}{14}} = 2.806 \text{ moles of } (C_4F_9$$

$$\therefore H_{O_2} = \frac{P_{O_2}}{x_{O_2}} = \frac{1}{0.0157/(0.0157+2.806)}$$

$$\boxed{H_{O_2} = 180 \text{ atm}}$$

b) In 1 liter of Oxypherol => 0.2 liters of $(C_4F_9)N$
0.8 liters of water

Air consists of ~ 20% O_2

$\therefore$ oxygen partial pressure in air at 1atm is 0.

$\therefore P_{O_2} = 0.2$

For $(C_4F_9)_3N$

$$x_{O_2}^{(C_4F_9)_3N} = \frac{P_{O_2}}{H_{O_2}^{(C_4F_9)_3N}} = \frac{0.2}{180} = 0.0011$$

we have $1.883 \times 0.2 \times 1000 = 376.6\ g$ $(C_4F_9)_3N$

or $\frac{376.6}{671} = 0.561$ moles of $(C_4F_9)_3N$

hence we have $$0.0011 = \frac{n_{O_2}^{(C_4F_9)_3N}}{n_{O_2}^{(C_4F_9)_3N} + 0.561}$$

$$n_{O_2}^{(C_4F_9)_3N} = 0.000624 \text{ moles}$$

For water

$$x_{O_2}^{H_2O} = \frac{P_{O_2}}{H_{O_2}^{H_2O}} = \frac{0.2}{4.38\times10^4} = 4.57\times10^{-6}$$

we have $1 \times 0.8 \times 1000 = 800\ g$ of water

$\rho = 1 g/mL$

or $\frac{800}{18} = 44.44$ moles of H_2O

$$\therefore \quad 4.57\times10^{-6} = \frac{n_{O_2}^{H_2O}}{n_{O_2}^{H_2O} + 44.44}$$

$$n_{O_2}^{H_2O} = 0.000203 \text{ moles}$$

$$\therefore \quad n_{O_2}^{total} = 0.000624 + 0.000203 = 0.000827 \text{ moles}$$

At 1atm, 25°C, this has volume $$V^t = \frac{nRT}{P} = \frac{0.000827 \times 8.314}{1.01325\times10}$$

$$= 2.02\times10^{-5}\ m$$

$$\boxed{V_{dissolve} = 20.2 \text{ ml}}$$

c) For 1 liter of water

ie. 1000g H_2O or $\frac{1000}{18} = 55.56$ moles of H_2O

$$4.57 \times 10^{-6} = \frac{n_{O_2}^{H_2O}}{n_{O_2}^{H_2O} + 55.56}$$

$$\therefore \quad n_{O_2}^{H_2O} = 0.000254 \text{ moles.}$$

At 1atm, 25°C $\qquad V^t = \frac{0.000254 \times 8.314 \times 298}{1.01325 \times 10^5} \times 10^6$

$$\boxed{V = 6.2 \text{ ml}}$$