Quiz 12 Chemical Engineering Thermodynamics
April 6, 2017

In the Kalina cycle system (KCS) an ammonia (1) –water (2) mixture is used in a power generation cycle as the working fluid. For geothermal or solar power generation the Kalina cycle has improved efficiency by a factor of 1.6 over a steam-based Rankine cycle. It can improve efficiency by 1.25 in a waste heat recovery system. This improvement in efficiency is achieved by taking advantage of the broad range of boiling temperatures for the binary mixture that can more closely match the heat source compared to a steam system. The Kalina cycle usually uses an ammonia-water mixture as the working fluid, which is a "zeotropic mixture" meaning that there is no azeotrope. (http://shodhganga.inflibnet.ac.in/handle/10603/37842 *Thermodynamic optimization of Kalina cycle systems at low medium and high temperature heat recoveries, N. Shankar Ganesh (VIT University, India 2015).* Ganesh notes that the first step in designing the Kalina system is to calculate the bubble and dew pressures. Ganesh reports an equilibrium point of P=35 Bar, T = 90°C, x_1=0.709 and y_1 = 0.871. Use these values to calculate the Margules coefficient (Ammonia (1), Water (2)).

a) Use these values to calculate the one parameter Margules coefficient.
b) Calculate the Margules Acid Base (MAB) coefficient at 90°C. How does it compare to part a?
c) Using the one-parameter Margules coefficient from part "a" calculate the dew pressure at 30°C for an equimolar mixture. Proceed until convergence (a maximum of two iterations after the initial guess using Raoult's Law).
d) Using the one-parameter Margules coefficient from part "a" calculate the bubble pressure at 30°C (303°K) for an equimolar mixture.

$$\frac{G^E}{RT} = A_{12} x_1 x_2 = x_1 \ln\gamma_1 + x_2 \ln\gamma_2$$

R = 8.314 J/(mole °K)

	α (J/cm^3)$^{1/2}$	β (J/cm^3)$^{1/2}$	V (cm^3/mole)
(1) Ammonia	2.11	8.44	23.3
(2) Water	50.1	15.1	18.0

$$A_{12} = (\alpha_2 - \alpha_1)(\beta_2 - \beta_1)(V_1 + V_2)/(4RT) \qquad 11.9$$

Antoine Constants (*T in °K P in Bar*)

	A	B	C	T_{Min}(°K)	T_{Max} (°K)
(1) Ammonia	4.87	1110	-10.4	240	372
(2) Water	3.56	644	-198	379	573
(2) Water	4.65	1440	-64.8	256	373

T is in °K and P is in Bar

$\log_{10}(P) = A - (B / (T + C))$

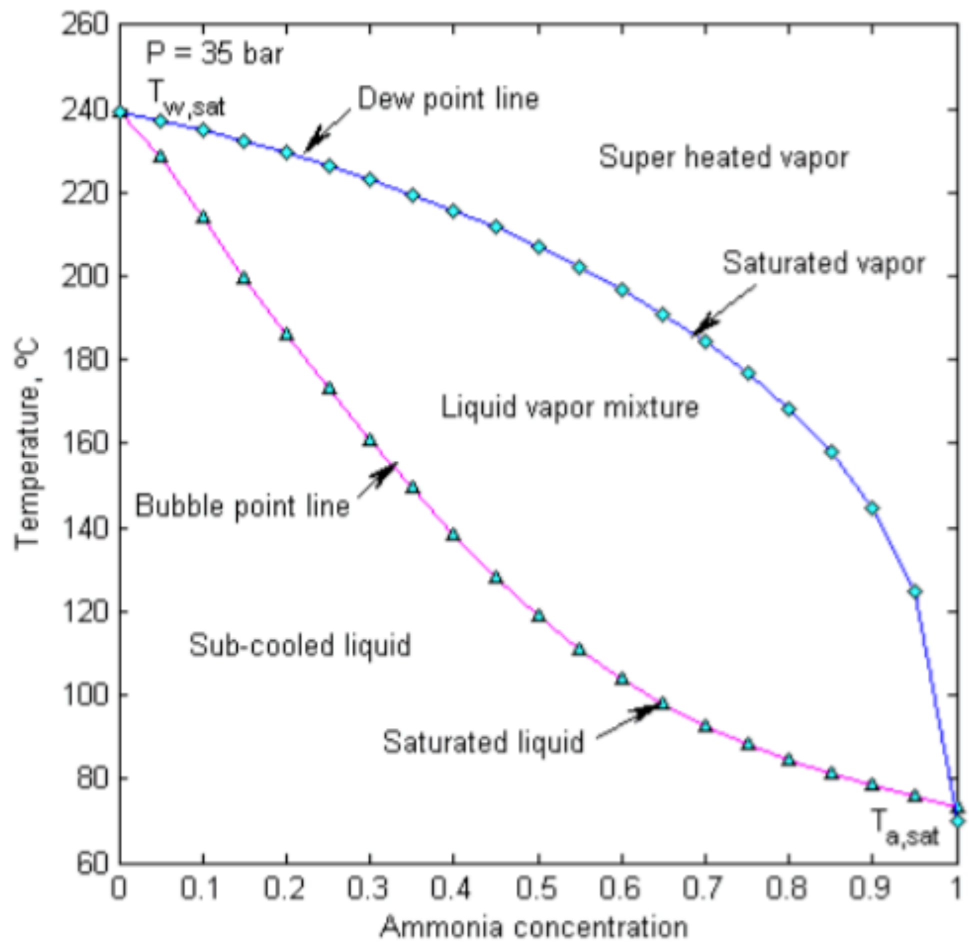


Fig.A.1 Property regions on temperature-concentration diagram for ammonia-water mixture at constant pressure

http://shodhganga.inflibnet.ac.in/handle/10603/37842

Modified Raoult's law.

$$\boxed{y_i P = x_i \gamma_i P_i^{sat}} \quad \text{or} \quad \boxed{K_i = \frac{\gamma_i^L P_i^{sat}}{P}} \qquad 11.18$$

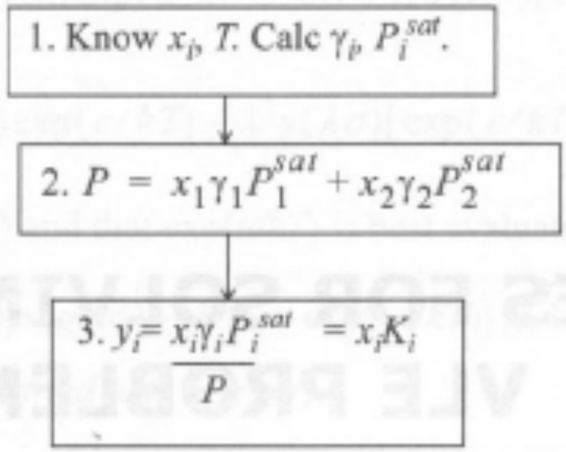
$$\ln \gamma_1 = A_{12} x_2^2$$

$$\ln \gamma_2 = A_{12} x_1^2$$

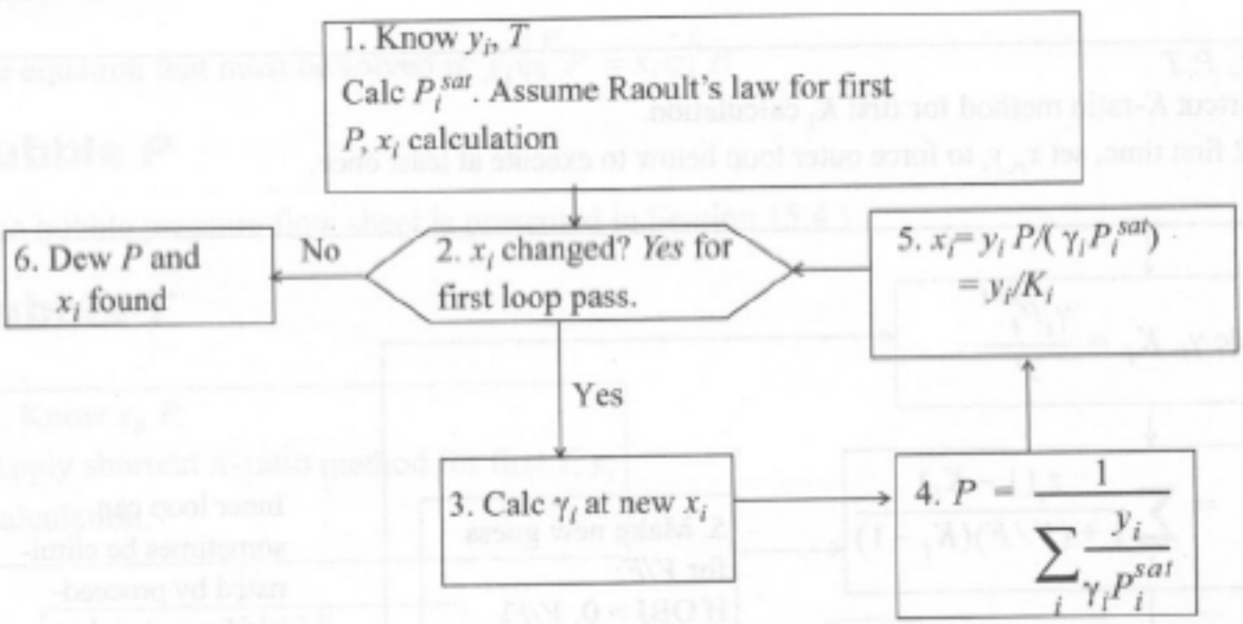
C.1 MODIFIED RAOULT'S LAW METHODS

The equation that must be solved is: $y_i P = x_i \gamma_i P_i^{sat}$

Bubble *P*



Dew *P*



Answers Quiz 12 CHE Thermo

a)4.28
b) 1.09
c) 0.00534 bar
d) 17.4 bar

a) $\frac{G^E}{RT} = A_{12} x_1 x_2 = x_1 \ln \gamma_1 + x_2 \ln \gamma_2$

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

$P_1^{sat\ 90°C} = 10^\wedge\left(4.87 - \frac{1110}{90°C + 273°K - 10.4}\right) = 52.7 \text{ bar}$

$P_2^{sat\ 90°C} = 10^\wedge\left(3.56 - \frac{644}{90°C + 273°K - 198}\right) = 0.454 \text{ bar}$

$\gamma_1 = \frac{0.871}{0.709} \frac{35 \text{ bar}}{52.7 \text{ bar}} = 0.816$

$\gamma_2 = \frac{(1-.871)}{(1-0.709)} \frac{35 \text{ bar}}{0.454 \text{ bar}} = 34.2$

$A_{12} = \frac{x_1 \ln \gamma_1 + x_2 \ln \gamma_2}{x_1 x_2} = 4.28$

b) $A_{12\,MAB} = \frac{\left(50.1\left(\frac{J}{cm^3}\right)^{1/2} - 2.11\left(\frac{J}{cm^3}\right)^{1/2}\right)\left(15.1\left(\frac{J}{cm^3}\right)^{1/2} - 8.49\left(\frac{J}{cm^3}\right)^{1/2}\right)\left(23.3 \frac{cm^3}{mol} + 18 \frac{cm^3}{mol}\right)}{4 \cdot 8.314\ J/mol°K \cdot 363\ °K}$

$A_{12\,MAB} = 1.09$

The two calcs differ

c) $T = 30\ °C \quad y_1 = y_2 = 0.50 \quad \Sigma x = 1$

$P = \frac{1}{\frac{y_1}{\gamma_1 P_1^{sat}} + \frac{y_2}{\gamma_2 P_2^{sat}}}$

$P_1^{sat} = 10^\wedge\left(4.87 - \frac{1110}{30°C + 273°K - 10.4}\right) = 11.9 \text{ bar}$

$P_2^{sat} = 10^\wedge\left(3.56 - \frac{644}{30°C + 273°K - 198}\right) = 0.00267 \text{ bar}$

Assume Raoult's Law for initial values $\gamma_1 = \gamma_2 = 1$

$$P = \frac{1}{\frac{0.5}{11.9\,bar} + \frac{0.5}{0.00267\,bar}} = 0.00534\,bar$$

$$x_1 = \frac{y_1 P}{\gamma_1 P_1^{sat}} = \frac{y_1 P}{P_1^{sat}} = \frac{0.5 \cdot 0.00534\,bar}{11.9\,bar}$$

$$= 0.000224$$

$$x_2 = \frac{y_2 P}{\gamma_2 P_2^{sat}} = \frac{y_2 P}{P_2^{sat}} = \frac{(0.5)\,0.00534\,bar}{0.00267\,bar}$$

$$= 0.9998$$

1'st Iteration

$$\gamma_1 = \exp(A_{12} x_2^2) = \exp(4.28 \cdot 1)$$

$$= 72.2$$

$$\gamma_2 = \exp(A_{12} x_1^2) = \exp(4.28 \cdot 0.000224)$$

$$= 1.00$$

$$P = \frac{1}{\frac{0.5}{72.2(11.9\,bar)} + \frac{0.5}{(1)(0.00267\,bar)}}$$

$$= 0.00534\,bar$$

$$x_1 = \frac{0.5\,(0.00534\,bar)}{72.2(11.9\,bar)} = 3.11e^{-6}$$

$$x_2 = 1.00$$

No change in P so the relation has converged

$P = 0.00534$ bar

d) Bubble Pressure $\Sigma y = 1$

$x_1 = x_2 = 0.5$

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

$\gamma_1 = \exp(4.28(.25)) = 2.92$

$\gamma_2 = \exp(4.28(.25)) = 2.92$

$P_1^{sat\,30°C} = 11.9$ bar

$P_2^{sat\,30°C} = 0.00267$ bar

$P = .5(2.92)\,11.9\text{ bar} + 0.5(2.92)\,0.00267\text{ bar}$

$= 17.4$ bar

$y_1 = \dfrac{x_1 \gamma_1 P_1^{sat}}{P} = 1.00 \qquad y_2 = \dfrac{x_2 \gamma_2 P_2^{sat}}{P} = 2.24e^{-4}$