B.M.S. COLLEGE OF ENGINEERING, BENGALURU-19

Autonomous Institute, Affiliated to VTU

Department of Chemical Engineering

Tutorial Sheets

Course: PROCESS ENGINEERING THERMODYNAMICS-II

Course Code: 19CH4DCTD2

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UNIT – I: Thermodynamic Properties of Pure Fluids

Problem 1: Calculate the vapor pressure of water at 363 K. The vapor pressure at 373 K is 101.3 kPa. The mean heat of vaporization in this temperature range is 2275 kJ/kg.

Problem 2: Mercury has a density of 13690 kg/m^3 in the liquid state and 14193 kg/m^3 in the solid state, both measured at the melting point of 234.33 K at 1 bar. If the heat of fusion of mercury is 9.7876 kJ/kg, what is the melting point of mercury at 10 bars?

Problem 3: Calculate the internal energy, enthalpy, entropy, and free energy for one mole of nitrogen at 773 K and 100 bars assuming that nitrogen behaves as an ideal gas. The molal heat capacity of nitrogen at 1 bar is given as $CP = 27.3 + 4.2\text{x}10^{-3}$ T, where T is in K and C_P is in J/mol K. Enthalpy of nitrogen is zero at 273 K and 1 bar. The entropy of nitrogen is 192.4 J/mol K at 298 K and 1 bar.

Problem 4: A gas obeys the equation of state $P(V - B) = RT + (AP^2)/T$, where A and B are constants. The mean specific heat (C_P) at atmospheric pressure is 33.6 J/mol K. If $A = 0.001$ m^3 K/(bar) mol; $B = 8.0\text{ x}10^{-5}$ m^3/mol. Calculate

i. The entropy change when the state of the gas is changed from state 1 (4 bars, 300 K) to state 2 (12 bars, 400 K).

ii. The mean heat capacity at 12 bars.

Problem 5: The melting point of benzene is found to increase from 278.5 K to 278.78 K, when the external pressure is increased by 100 bar. Heat of fusion of benzene is 128 kJ/kg. What is the change in volume per kg accompanying the fusion of benzene?

Problem 6: Calculate the change in internal energy, enthalpy, entropy, and free energy when one kmol hydrogen gas at 300 K and 1 bar is heated and compressed to 500 K and 100 bars. The entropy of hydrogen in the initial state is 131.5 kJ/kmol K. Enthalpy at 273 K may be taken to be zero. Assume $CP = 27.3 + 4.2 \times 10^{-3}\ T$ at 1 bar where CP is in kJ/kmol K and T is in K. Hydrogen may be treated as ideal gas.

Problem 7: Superheated steam originally at P_1 = 1000 kPa and T_1 = 533.15 K expands through a nozzle to an exhaust pressure P_2 = 200 kPa. Assuming the process is reversible and adiabatic, and that equilibrium is attained. Estimate the state of the steam at the exit of the nozzle.

Problem 8: A tank of volume 1.5 m^3 contains 500 kg of liquid water in equilibrium with pure eater vapor which is fills the rest of the volume in the tank. The temperature and pressure inside the tank were 373 K and 101.33 kPa. 750 Kg of fresh liquid water was feed into the tank at a pressure of 101.33 kPa using a water line. The temperature of the fresh liquid was 343 K. If the temperature and pressure inside the tank are not changed due to the process, how much energy as heat must be supplied to the tank.

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Unit-II: Residual Properties

Problem 1: Derive an expression for the fugacity coefficient of a gas obeying the equation of state $P(V - b) = RT$ and estimate the fugacity of ammonia at 10 bar and 298 K, given that $b = 3.707 \times 10^{-5}\ m^3/mol$.

Problem 2: Determine the fugacity and fugacity coefficient of steam at 623 K and 1000 kPa using enthalpy and entropy values from steam tables. Assume that steam behaves ideally at 101.3 kPa.

Problem 3: Calculate the fugacity of n-butane in the liquid state at 350 K and 60 bar. The vapour pressure of n-butane at 350 K is 9.35 bar. The molar volume of saturated liquid at 350 K is $0.1072 \times 10^{-3}\ m^3/mol$. The fugacity coefficient for the saturated vapour at 350 K is 0.834.

Problem 4: At 300 K and 1 bar, the volumetric data for a liquid mixture of benzene and cyclohexane are represented by $V = 109.4 \times 10^{-6} - 16.8 \times 10^{-6}x - 2.64 \times 10^{-6}x^2$, where x is the mole fraction of benzene and V has the units of m3/mol. Find expressions for the partial molar volumes of benzene and cyclohexane.

Problem 5: The Henry's law constant for oxygen in water at 298 K is 4.4×10^4 bar. Estimate the solubility of oxygen in water at 298 K for a partial pressure of oxygen at 0.25 bar.

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Unit 3: Vapour Liquid Equilibrium

Problem 1:

Binary system acetonitrile(1)/nitromethane(2) conforms closely to Raoult's law. Vapor pressures for the pure species are given by the following Antoine equations:

$$\ln P_1^{sat}/\text{kPa} = 14.2724 - \frac{2945.47}{T - 49.15}$$

$$\ln P_2^{sat}/\text{kPa} = 14.2043 - \frac{2972.64}{T - 64.15}$$

(*a*) Prepare a graph showing P vs. x_1 and P vs. y_1 for a temperature of 348.15 K (75°C).

(*b*) Prepare a graph showing t vs. x_1 and t vs. y_1 for a pressure of 70 kPa.

a. P-X-Y Diagram:

1. Find the values of P_1^{sat} = 83.2069 kPa and P_2^{sat} = 41.9827kPa

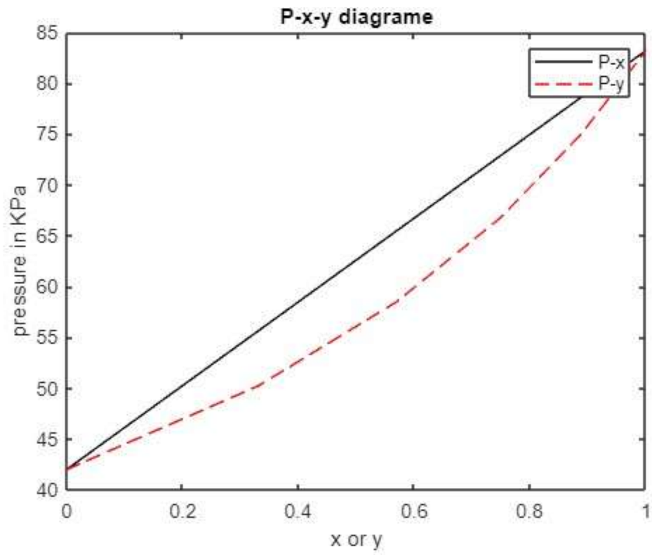
Assume the values of x1 and find P and y1.

For ideal solutions from raoult's law $y_1 P = x_1 P_1^{sat}$; from Dolton's law $P = p_1 + p_2$.

$p_1 = partial\ pressure\ of\ component\ 1$

$P = p_1 + p_2$, $P = x_1 P_1^{sat} + x_2 P_2^{sat}$, $P = x_1 P_1^{sat} + (1 - x_1) P_2^{sat}$ and $y_1 = \frac{x_1 P_1^{sat}}{P}$

x_1	0	0.2	0.4	0.6	0.8	1.0
y_1	0	0.3313	0.5692	0.7483	0.8880	1.0000
P	41.9827	50.2275	58.4724	66.7172	74.9620	83.2069



b. T-X-Y Diagram:

1. Find the values of T_1^{sat} =342.9946 K and $T_2^{sat} = 362.7336$ K using rearranged Antoine equation, $lnP_i^{sat} = A_i - \frac{B_i}{T+C_i}$, where i= no of components, when T= T_i^{sat}, then $P_i^{sat} = P$.

Use these equations to find

$$T_1^{sat} = \frac{B_1}{A_1 - lnP} - C_1 \,;\, T_2^{sat} = \frac{B_2}{A_2 - lnP} - C_2$$

Assume the values of x1, find T, P_1^{sat} and y1.

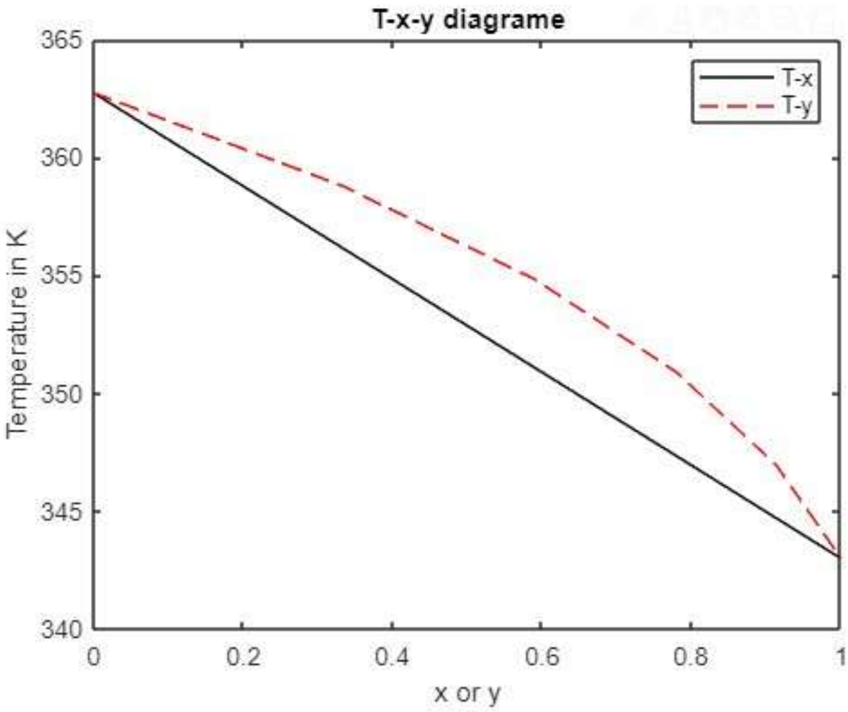
For ideal solutions from raoult's law $y_1 P = x_1 P_1^{sat}$; from Dolton's law $P = p_1 + p_2$.

$$p_1 = partial\ pressure\ of\ component\ 1$$

.

$$T = x_1 T_1^{sat} + x_2 T_2^{sat},\ P = x_1 T_1^{sat} + (1 - x_1) T_2^{sat} \text{ and } y_1 = \frac{x_1 P_1^{sat}}{P}$$

x_1	0	0.2	0.4	0.6	0.8	1.0
y_1	0	0.333	0.589	0.779	0.9137	1.0
T	362.73	358.78	354.83	350.89	346.94	342.99



Problem 2: *n*-Heptane and toluene form ideal solution. At 373 K, their vapour pressures are 106 and 74 kPa respectively. Determine the composition of the liquid and vapour in equilibrium at 373 K and 101.3 kPa.

Solution : $P = x_1 P_1{}^{sat} + (1 - x_1) P_2{}^{sat}; P - P_2{}^{sat} = x_1 (P_1{}^{sat} - P_2{}^{sat}); x_1 = \frac{P - P_2{}^{sat}}{P_1{}^{sat} - P_2{}^{sat}}$;

And $y_1 = \frac{x_1 P_1{}^{sat}}{P}; final\ answers$; x1= 0.8539; y1= 0.8933

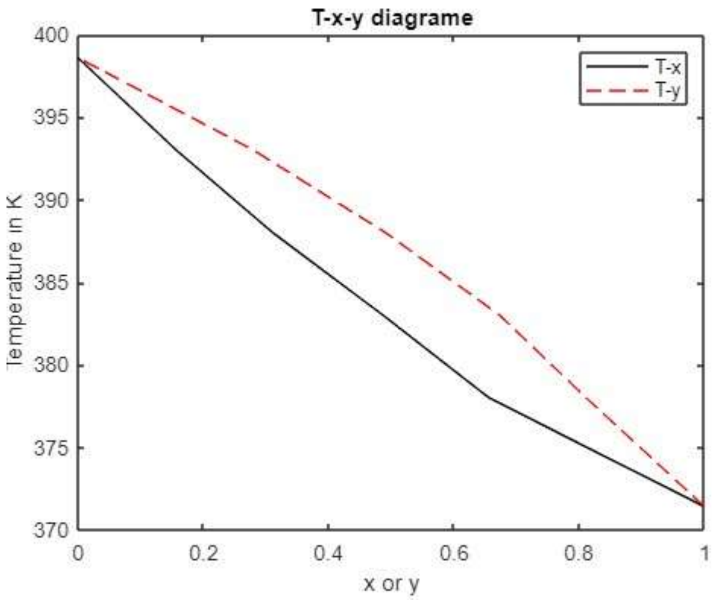
Problem 3: Mixtures of *n*-Heptane (A) and *n*-Octane (B) are expected to behave ideally. The total pressure over the system is 101.3 kPa. Using the vapour pressure data given below,

Construct the boiling point diagram (T-X-Y diagram) and
The equilibrium diagram

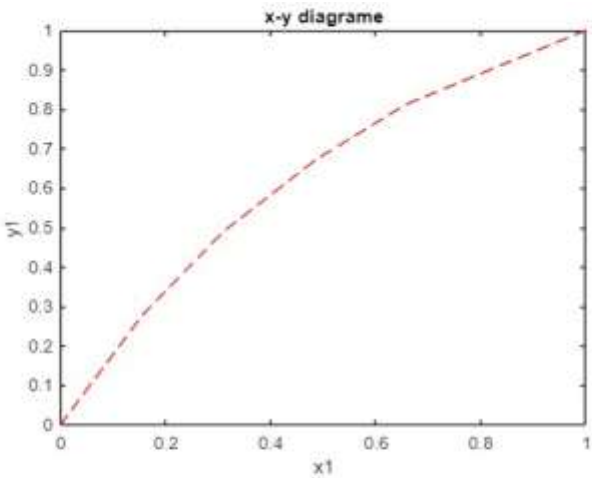
T, K	371.4	378	383	388	393	398.6
$P^S{}_A$, kPa	101.3	125.3	140.0	160.0	179.9	205.3
$P^S{}_B$, kPa	44.4	55.6	64.5	74.8	86.6	101.3

Solution: $x_1 = \frac{P - P_2^{sat}}{P_1^{sat} - P_2^{sat}}$ and $y_1 = \frac{x_1 P_1^{sat}}{P}$

T, K	371.4	378	383	388	393	398.6
x_A	1.000	0.656	0.487	0.312	0.157	0
y_A	1.000	0.811	0.674	0.492	0.279	0



b. Equilibrium Diagram



Problem 4: The vapour pressures of benzene and toluene are given below. Calculate the equilibrium data for the system at 101.3 kPa and formulate an equation for the equilibrium diagram in terms of average relative volatility.

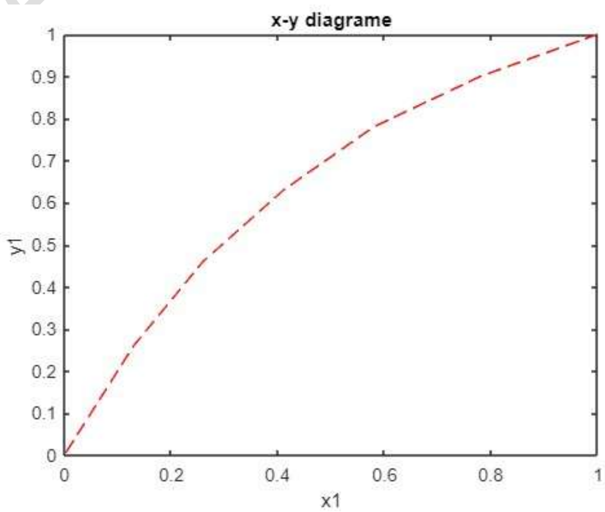
T, K	353.1	358	363	368	373	378	383	383.6
P_A^S, kPa	101.3	116.9	135.4	155.7	179.1	204.2	233.0	240.0
P_B^S, kPa	39.6	46.0	54.0	63.3	74.2	86.0	99.0	101.3

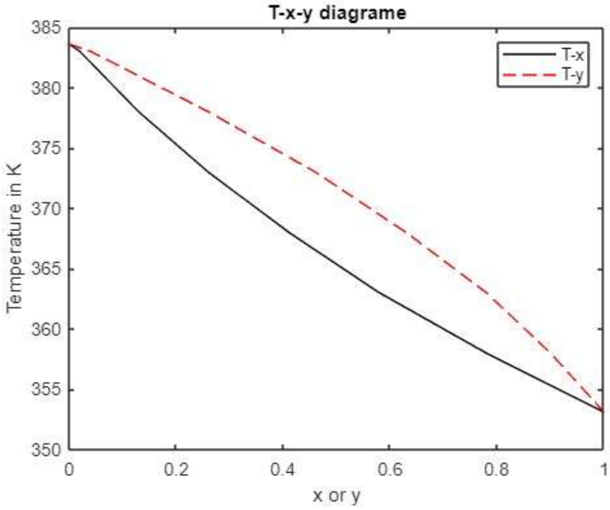
Solution: relative volatility; $\propto = \frac{P_1{}^{sat}}{P_2{}^{sat}}$; $y_1 = \frac{x_1 P_1{}^{sat}}{P}$; $y_2 = \frac{x_2 P_2{}^{sat}}{P}$ and $\frac{y_1}{1-y_1} = \propto \frac{x_1}{1-x_1}$

$y_1 = \frac{\propto x_1}{1+(\propto-1)x_1}$. $x_1 = \frac{P-P_2{}^{sat}}{P_1{}^{sat}-P_2{}^{sat}}$

Find the $\propto$value first, find x1 value and find the y1 value.

T	x1	PS1	PS2	y1
353.1	1.00	101.3	39.6	1.00
358	0.78	116.9	46	0.90
363	0.58	135.4	54	0.78
368	0.41	155.7	63.3	0.63
373	0.26	179.1	74.2	0.46
378	0.13	204.2	86	0.26
383	0.02	233	99	0.04
383.6	0.00	240	101.3	0.00





Problem 5: The binary system, acetone (1)–acetonitrile (2) conforms closely to Raoult's law. Using the vapour pressure data given below plot the following a. P-$x1$ and P-$y1$ curves at 323 K
b. T-$x1$ and T-$y1$ curves at 53.32 kPa

T, K	311.45	315	319	323	327	331	335.33
P_1^S, kPa	53.32	61.09	70.91	81.97	94.36	108.2	124.95
P_2^S, kPa	21.25	24.61	28.90	33.79	39.35	45.62	53.32

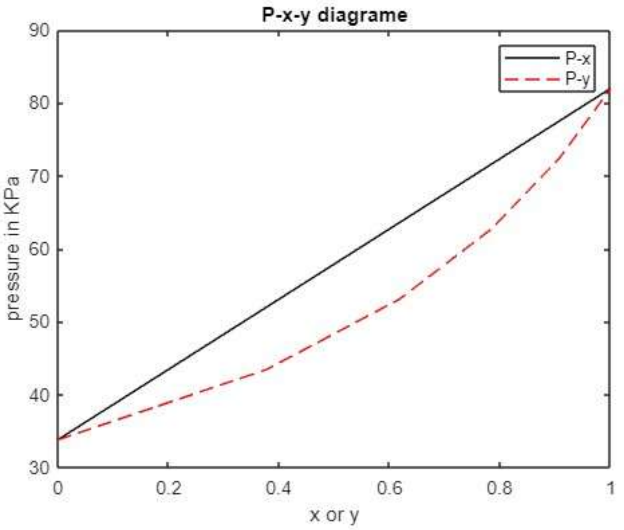
a. P-X-Y Diagram:

1. Find the values from table of P_1^{sat} = 81.97 kPa and P_2^{sat} = 33.79kPa

Assume the values of x1 and find P and y1. For ideal solutions from raoult's law $y_1 P = x_1 P_1^{sat}$; from Dolton's law $P = p_1 + p_2$. $p_1 = partial\ pressure\ of\ component\ 1$.

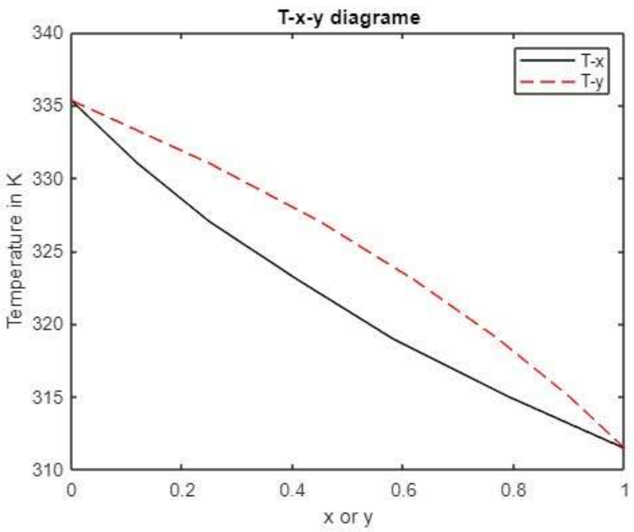
$P = p_1 + p_2$, $P = x_1 P_1^{sat} + x_2 P_2^{sat}$, $P = x_1 P_1^{sat} + (1 - x_1) P_2^{sat}$ and $y_1 = \frac{x_1 P_1^{sat}}{P}$

x_1	0	0.2	0.4	0.6	0.8	1.0
y_1	0	0.377	0.618	0.784	0.906	1.0
P	33.79	43.42	53.06	62.69	72.33	81.97



T-X-Y Data

T	x1	PS1	PS2	y1
311.45	1.00	53.32	21.25	1.00
315	0.79	61.09	24.61	0.90
319	0.58	70.91	28.9	0.77
323	0.41	81.97	33.79	0.62
327	0.25	94.36	39.35	0.45
331	0.12	108.2	45.62	0.25
335.33	0.00	124.95	53.32	0.00



Problem 6: The vapour pressures of acetone (1) and acetonitrile (2) can be evaluated by the Antoine equations

$$\ln P_1^S = 14.5463 - \frac{2940.46}{T - 35.93}$$

$$\ln P_2^S = 14.2724 - \frac{2945.47}{T - 49.15}$$

Where T is in K and P is in kPa. Assuming that the solutions formed by these are ideal, calculate

a. x_1 and y_1 at 327 K and 65 kPa
b. T and y_1 at 65 kPa and $x_1 = 0.4$
c. P and y_1 at 327 K and $x_1 = 0.4$
d. T and x_1 at 65 kPa and $y_1 = 0.4$
e. P and x_1 at 327 K and $y_1 = 0.4$

Solution:

a. $P = x_1 P_1^{sat} + (1 - x_1)P_2^{sat}$;find $P_1^{sat} = 85.12\ kPa$; $P_2^{sat} = 39.31\ kPa$

$x_1 = \frac{P - P_2^{sat}}{P_1^{sat} - P_2^{sat}} = \frac{65-39.31}{85.12-39.31} = 0.5608$ and $y_1 = \frac{x_1 P_1^{sat}}{P} = \frac{0.568*85.12}{65} = 0.7344$

b. Here T= bubble point or bubble temperature, this is calculated by trial and error, because P_1^{sat} and P_2^{sat}, are function of temperature. The feed condition given is liquid solution. Hence here the phase change is from liquid-vapour. If the given system is at its boiling point than the sum of vapour fractions of all the components will be equal to 1, i.e. $y_1 + y_2 = 1$ for the given problem.

i. First, assume initial guess value for temperature. That will be $T = x_1 T_1^{sat} + x_2 T_2^{sat}$
$T_1^{sat} = boiling\ point\ of\ component\ 1$ and $T_2^{sat} = boiling\ point\ of\ component\ 2$.

ii. Find the P_1^{sat} and P_2^{sat} for the initial temperature and verify if P=65 kPa, $P = x_1 P_1^{sat} + (1 - x_1)P_2^{sat}$.

iii. Check if $y_1 + y_2 = 1$ at the end.

$T = 332.2757\ K$, initial guess, calculate P_1^{sat} and P_2^{sat} ; finally Bubble Temp = 330.3692 K

$P_1^{sat} = 95.55 kPa$ and $P_2^{sat} = 44.6330 kPa$; $y_1 = 0.5880$, ; $y_2 = 0.412$ and $y = 1.0$

c. $P = x_1 P_1^{sat} + (1 - x_1)P_2^{sat} = 57.634\ kPa$; find $P_1^{sat} = 85.12\ kPa$; $P_2^{sat} = 39.31\ kPa$

$x_1 = 0.4$ and $y_1 = \frac{x_1 P_1^{sat}}{P} = \frac{0.4*85.12}{57.634} = 0.591$. This P= bubble pressure

d. Here T= Dew point or Dew temperature, this is calculated by trial and error, because P_1^{sat} and P_2^{sat}, are function of temperature. The feed condition given is vapour. Hence here the phase change is from liquid-vapour. If the given system is at its boiling point than the sum of vapour fractions of all the components will be equal to 1, i.e. $x_1 + x_2 = 1$ for the given problem.

i. First, assume initial guess value for temperature. That will be $T = y_1 T_1{}^{sat} + y_2 T_2{}^{sat}$
$T_1{}^{sat} = Melting\ point\ of\ component\ 1$ and $T_2{}^{sat} = Melting\ point\ of\ component\ 2$.

ii. Find the $P_1{}^{sat}$ and $P_2{}^{sat}$ for the initial temperature and verify if P=65 kPa, $x_1 + x_2 = 1$
$\frac{1}{P} = \frac{y_1}{P_1{}^{sat}} + \frac{(1-y_1)}{P_2{}^{sat}}$.

iii. Check if $x_1 + x_2 = 1$ at the end.

$T = 332.2757\ K$, initial guess, calculate $P_1{}^{sat}$ and $P_2{}^{sat}$; finally Bubble Temp = 334.155K
$P_1{}^{sat} = 108.4664\ kPa$ and $P_2{}^{sat} = 51.2959\ kPa$; $x_1 = 0.2397$, ; $x_2 = 0.7603$ and $x = 1.0$

e. $x_1 = \frac{P-P_2{}^{sat}}{P_1{}^{sat}-P_2{}^{sat}}$, sub for P, $P = \frac{x_1 P_1{}^{sat}}{y_1}$; $x_1 = \frac{x_1 P_1{}^{sat} - y_1 P_2{}^{sat}}{y_1(P_1{}^{sat}-P_2{}^{sat})}$

$x_1 y_1 (P_1{}^{sat} - P_2{}^{sat}) = x_1 P_1{}^{sat} - y_1 P_2{}^{sat}$; $x_1 P_1{}^{sat} - x_1 y_1 (P_1{}^{sat} - P_2{}^{sat}) = y_1 P_2{}^{sat}$

Final Equation $x_1 = \frac{y_1 P_2{}^{sat}}{P_1{}^{sat} - y_1(P_1{}^{sat}-P_2{}^{sat})}$; $P_1{}^{sat} = 85.12\ kPa$; $P_2{}^{sat} = 39.31\ kPa$

$x_1 = 0.2354$; $x_2 = 0.7646$ and $P = \frac{x_1 P_1{}^{sat}}{y_1} = 50.093\ kPa$

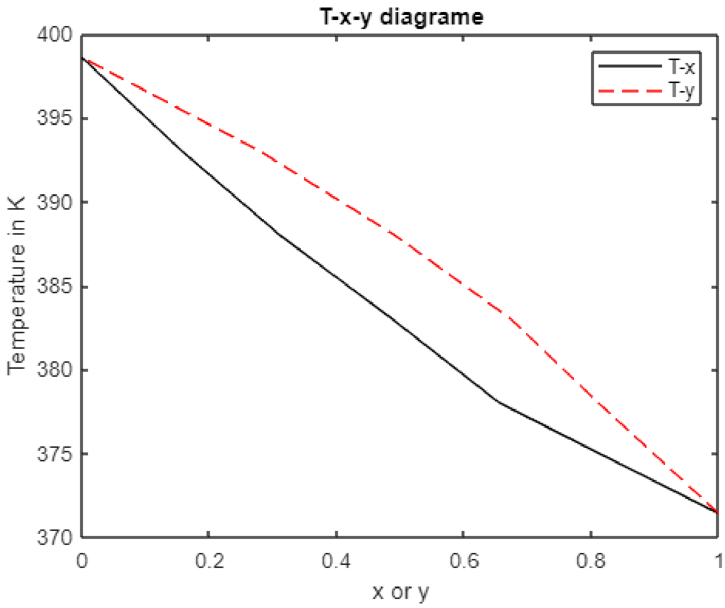
Problem 7: Mixtures of *n*-Heptane (*A*) and *n*-Octane (*B*) are expected to behave ideally. The total pressure over the system is 101.3 kPa. Using the vapour pressure data given below,
(a) Construct the boiling point diagram
(b) The equilibrium diagram
(c) Deduce an equation for the equilibrium diagram using an arithmetic average 'α' value.

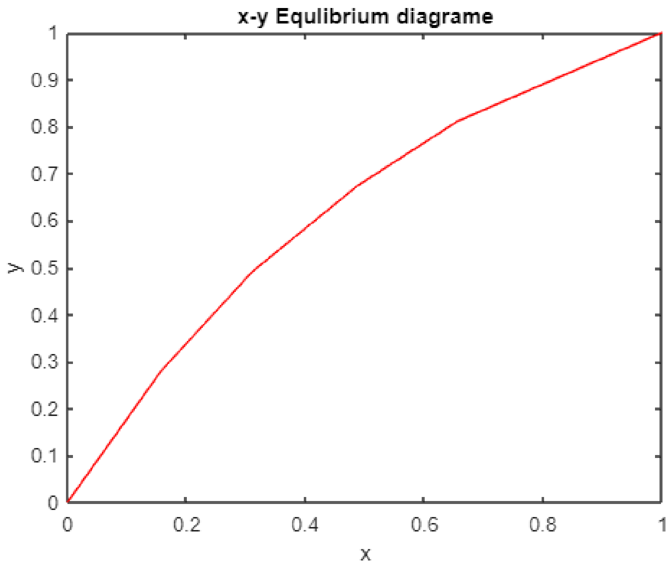
T, K	371.4	378	383	388	393	398.6
P_A^S , kPa	101.3	125.3	140.0	160.0	179.9	205.3
P_B^S , kPa	44.4	55.6	64.5	74.8	86.6	101.3

Solution: a. Find the $x_A = \frac{P-P_B{}^{sat}}{P_A{}^{sat}-P_B{}^{sat}}$, $\alpha = \frac{P_A^S}{P_B^S}$ and $y_A = \frac{x_A P_A{}^{sat}}{P}$

T	x1	PS1	PS2	y1	α
371.4	1.00	101.3	44.4	1.00	2.282
378	0.66	125.3	55.6	1.54	2.254
383	0.49	140	64.5	1.28	2.171
388	0.31	160	74.8	0.93	2.139

393	0.16	179.9	86.6	0.53	2.077
398.6	0.00	205.3	101.3	0.00	2.027

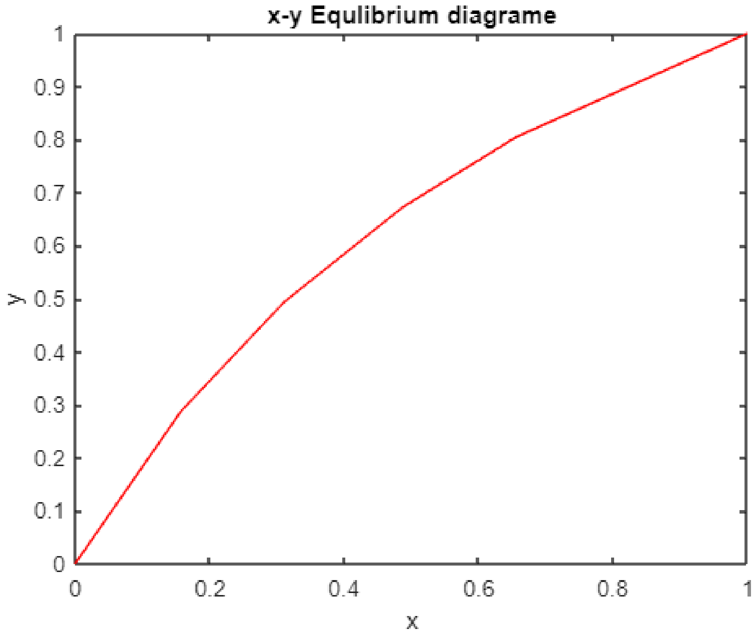




c. Find the Average Value of α and find the Equilibrium data for the x value estimated using equation $y_A = \frac{\alpha x_A}{1+(\alpha-1)x_A} = \frac{2.16x_A}{1+(2.16-1)x_A}$

T, K	371.4	378	383	388	393	398.6

x_1	1.0000	0.6557	0.4874	0.3110	0.1576	0
y_1	1.0000	0.8044	0.6726	0.4937	0.2877	0



Problem 8: A mixture contains 45% (mol) methanol (*A*), 30% (mol) ethanol (*B*) and the rest *n*-propanol (*C*). Liquid solution may be assumed to be ideal and perfect gas law is valid for the vapour phase, total pressure of 101.3 kPa. Calculate

(a) The bubble point and the vapour composition
(b) The dew point and the liquid composition.
The vapour pressures of the pure liquids are given below:

Temperature , K	333	343	353	363
P_A^S , kPa	81.97	133.29	186.61	266.58
P_B^S , kPa	49.32	73.31	106.63	166.61
P_C^S , kPa	39.32	62.65	93.30	133.29

Solution:

Step1. If the vapour phase can be treated as an ideal gas and liquid phase, an ideal solution, the K-values can be written as $K_i = \frac{y_i}{x_i} = \frac{P_i^S}{P}$.

Step2. from the Flash Calculation Criteria $\sum y_i = \sum K_i x_i = \sum \frac{x_i P_i^{sat}}{P} = 1$ at Bubble temperature. Assume the feed as saturated Liquid and all the compositions given are liquid compositions.
Step 3. Plot T Vs saturation pressure plot for interpolation.

i. First, assume initial guess value for temperature. That will be $= x_1 T_1^{sat} + x_2 T_2^{sat} + x_3 T_3^{sat}$. $T_1^{sat},\ T_2^{sat}\ and\ T_3^{sat} = boiling\ point\ of\ component\ 1{,}2\ and\ 3$

ii. Find the P_1^{sat}, P_2^{sat} and P_3^{sat} for the initial temperature and verify if P=65 kPa, $P = x_1 P_1^{sat} + x_2 P_2^{sat} + x_3 P_3^{sat}$.

iii. Check if $y_1 + y_2 + y_3 = 1$ at the end. For the obtained temperature Value from graph.

Component	x_i		$K_i = /P$	$y_i = K_i x_i$
Methanol	0.45	137.30	1.355	0.610
Ethanol	0.30	76.20	0.752	0.226
Propanol	0.25	65.40	0.646	0.162

Dew point Calculations

1. From the Flash Calculation Criteria $\sum x_i = \sum \frac{y_i}{K_i} = \sum \frac{y_i P}{P_i^{sat}} = 1$ at Bubble temperature. Assume the feed as saturated Liquid and all the compositions given are liquid compositions.

i. First, assume initial guess value for temperature. That will be $T = y_1 T_1^{sat} + y_2 T_2^{sat} + y_3 T_3^{sat}, T_1^{sat}, T_2^{sat}\ and\ T_3^{sat} = Melting\ point\ of\ component\ 1, 2\ and\ 3.$

ii. Find the P_1^{sat} and P_2^{sat} for the initial temperature and verify if P= $\frac{1}{P} = \frac{y_1}{P_1^{sat}} + \frac{y_2}{P_2^{sat}} + \frac{y_3}{P_3^{sat}}$.

iii. Check if $x_1 + x_2 + x_3 = 1$ at the end.

Component	y_i		$K_i = /P$	$x_i = y_i/K_i$
Methanol	0.45	153.28	1.5131	0.2974
Ethanol	0.30	85.25	0.8416	0.3565
Propanol	0.25	73.31	0.7237	0.3454

Problem 9: A hydrocarbon mixture contains 25% (mol) propane, 40% (mol) *n*-butane and 35% (mol) *n*-pentane at 1447.14 kPa. Assume ideal solution behaviour and calculate

(a) The bubble-point temperature and composition of the vapour

(b) The dew-point temperature and the composition of the liquid
(c) The temperature and the composition of the liquid and vapour in equilibrium when 45% (mol) of the initial mixture is vaporised. **(Refer EXAMPLE 8.26, K.V. Narayan).**

UNIT- 4: Non-Ideal solutions

Problem 1: Prove that at the azeotropic composition, the vapour and liquid have the same composition.

Problems 2: Liquids *A* and *B* form an azeotrope containing 46.1 mole per cent *A* at 101.3 kPa and 345 K. At 345 K, the vapour pressure of *A* is 84.8 kPa and that of *B* is 78.2 kPa. Calculate the van Laar constants.

Solution:

$$\gamma_i = \frac{P}{P_i^S} \quad \gamma_1 = \frac{P}{P_1^S} = \frac{101.3}{84.8} = 1.195, \qquad \gamma_2 = \frac{P}{P_2^S} = \frac{101.3}{78.2} = 1.295$$

$$A = \ln\gamma_1\left(1 + \frac{x_2 \ln\gamma_2}{x_1 \ln\gamma_1}\right)^2 = \ln 1.195\left(1 + \frac{0.539 \times \ln 1.295}{0.461 \times \ln 1.195}\right)^2 = 1.2955$$

$$B = \ln\gamma_2\left(1 + \frac{x_1 \ln\gamma_1}{x_2 \ln\gamma_2}\right)^2 = \ln 1.295\left(1 + \frac{0.461 \times \ln 1.195}{0.539 \times \ln 1.295}\right)^2 = 0.6530$$

Problems 3: The azeotrope of the ethanol–benzene system has a composition of 44.8% (mol) ethanol with a boiling point of 341.4 K at 101.3 kPa. At this temperature the vapour pressure of benzene is 68.9 kPa and the vapour pressure of ethanol is 67.4 kPa. What are the activity coefficients in a solution containing 10% alcohol?

Solution:

$$\gamma_1 = \frac{P}{P_1^S} = \frac{101.3}{68.9} = 1.4702, \qquad \gamma_2 = \frac{P}{P_2^S} = \frac{101.3}{67.4} = 1.5030$$

$$\ln\gamma_1 = \frac{Ax_2^2}{[(A/B)x_1 + x_2]^2} = \frac{1.3305 \times 0.1^2}{[(1.3305/1.9106)\, 0.9 + 0.1]^2} = 0.02519$$

$$\ln \gamma_2 = \frac{Bx_1^2}{[x_1 + (B/A)\, x_2]^2} = \frac{1.9106 \times 0.9^2}{[0.9 + (1.9106/1.3305)\, 0.1]^2} = 1.4210$$

Problem 4: Water (1) –hydrazine (2) system forms an azeotrope containing 58.5% (mol) hydrazine at 393 K and 101.3 kPa. Calculate the equilibrium vapour composition for a solution containing 20% (mol) hydrazine. The relative volatility of water with reference to hydrazine is 1.6 and may be assumed to remain constant in the temperature range involved. The vapour pressure of hydrazine at 393 K is 124.76 kPa.

$$P_1^S = 199.62 \text{ kPa}; \qquad P_2^S = 124.76 \text{ kPa}$$

$$\gamma_1 = \frac{P}{P_1^S} = \frac{101.3}{199.62} = 0.5075; \qquad \gamma_2 = \frac{P}{P_2^S} = \frac{101.3}{124.76} = 0.8120$$

$$A = \ln \gamma_1 \left(1 + \frac{x_2 \ln \gamma_2}{x_1 \ln \gamma_1}\right)^2 = -0.6783 \left(1 + \frac{0.585 \times (-0.2083}{0.415 \times (-0.6783}\right)^2 = -1.3927$$

$$B = \ln \gamma_2 \left(1 + \frac{x_1 \ln \gamma_1}{x_2 \ln \gamma_2}\right)^2 = -0.2083 \left(1 + \frac{0.415 \times (-0.6783}{0.585 \times (-0.2083}\right)^2 = -2.2822$$

$$\ln \gamma_1 = \frac{Ax_2^2}{[(A/B)x_1 + x_2]^2} = \frac{-1.3927 \times 0.2^2}{[0.8\,(-1.3927)/(-2.2822) + 0.2]^2} = -0.1176$$

$$\ln \gamma_2 = \frac{Bx_1^2}{[x_1 + (B/A)\, x_2]^2} = \frac{-2.2822 \times 0.8^2}{[0.8 + 0.2(-2.2822)/(-1.3927)]^2} = -1.1485$$

$$y_1 = \gamma_1 x_1 \frac{P_1^S}{P}, \qquad y_2 = \gamma_2 x_2 \frac{P_2^S}{P}$$

$$y_1 = \frac{1}{1 + \dfrac{\gamma_2 x_2 P_2^S}{\gamma_1 x_1 P_1^S}} = \frac{1}{1 + \dfrac{0.3171}{0.8891} \times \dfrac{0.2}{0.8} \times \dfrac{1}{1.6}} = 0.9472$$

Reference

1. Smith J. M. and Van Ness H.C, "Introduction to Chemical Engineering Thermodynamics", 5th edition, McGraw Hill, New York, 1996.

2. Narayanan, K. V. "Chemical Engineering Thermodynamics", Prentice Hall of India Private Limited, New Delhi, 2001.