

Chemical Engineering Thermodynamics

Vapor/Liquid Equilibrium: Introduction and Application

Mohammad Fadil Abdul Wahab

Consider a multicomponent system in a VLE condition, the fugacity (to be defined in Chapter 11) of species i for each phase is given by,

For vapor mixture
$$\hat{f}_i^v = \hat{\phi}_i y_i P$$

For liquid solution
$$\hat{f}_i^l = \gamma_i x_i f_i$$

VLE criteria (to be shown/derived in chapter 11),

$$\hat{f}_i^l = \hat{f}_i^v$$

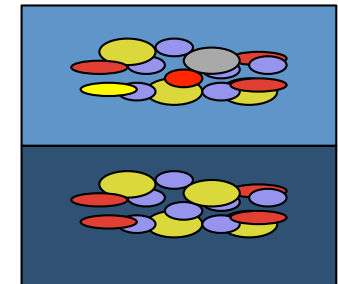
so
$$\hat{\phi}_i y_i P = \gamma_i x_i f_i$$

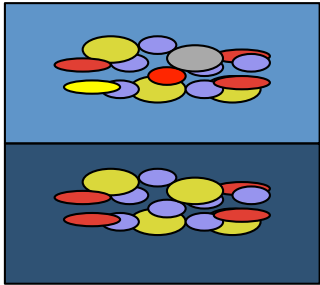
where,

$\hat{\phi}_i$ fugacity coefficient species i in gas mixture

f_i fugacity of pure species i

γ_i activity coefficient of species i in liquid solution





Raoult's Law

$$\hat{\phi}_i = 1$$

For ideal gas vapor mixture in
equilibrium with ideal liquid solution

$$\gamma_i = 1$$

equation becomes

$$y_i P = x_i f_i$$

and also for pure species in equilibrium and ideal gas vapor,

$$f_i = f_i^l = f_i^v = P = P_i^{sat}$$

we get,

$$y_i P = x_i P_i^{sat} \quad \text{Raoult's Law} \quad (10.1)$$

Modified Raoult's Law

$$\hat{\phi}_i = 1$$

For ideal-gas mixture in equilibrium with non-ideal liquid solution

~~$$\hat{\phi}_i y_i P = \gamma_i x_i f_i$$~~

$$y_i P = \gamma_i x_i P_i^{\text{sat}} \quad \text{Modified Raoult's Law} \quad (10.5)$$

where γ_i is a function of T and x_i .

K-value (K_i)

$$K_i = \frac{y_i}{x_i} \quad (10.10)$$

If Raoult's Law is valid,

$$y_i P = x_i P_i^{sat}$$

$$K_i = \frac{P_i^{sat}}{P} \quad (10.11)$$

If Modified Raoult's Law is valid,

$$y_i P = x_i \gamma_i P_i^{sat}$$

$$K_i = \frac{\gamma_i P_i^{sat}}{P} \quad (10.12)$$

K-value Using DePriester Chart

For light hydrocarbon mixture (commonly found in industry),

K_i is essentially function of T and P only.

K_i are tabulated in a chart called the DePriester chart.

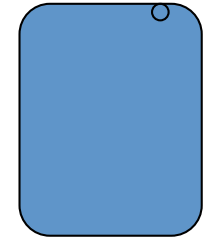
Bubblepoint & Dewpoint Calculations

BUBL P: Calculate $\{y_i\}$ and P, given $\{x_i\}$ and T

To calculate the P when the 1st bubble appear as a result of decrease in P at constant T. Also calculate the bubble's composition $\{y_i\}$.

or

To calculate the P when the last bubble disappear as a result of increase in P at constant T. Also calculate the composition $\{y_i\}$ of this bubble.



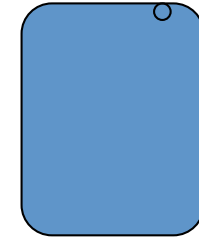
DEW P: Calculate $\{x_i\}$ and P , given $\{y_i\}$ and T

To calculate the P when the 1st dew (a drop of liquid) appear as a result of increase in P at constant T . Also calculate the composition $\{x_i\}$ of this dew.

or



To calculate the P when the last dew disappear as a result of decrease in P at constant T . Also calculate the composition $\{x_i\}$ of this dew.

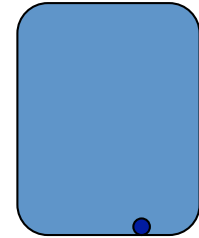


BUBL T: Calculate $\{y_i\}$ and T, given $\{x_i\}$ and P

To calculate the T when the 1st bubble appear as a result of increase in T at constant P. Also calculate the composition $\{y_i\}$ of this bubble.

or

To calculate the T when the last bubble disappear as a result of decrease in T at constant P. Also calculate the composition $\{y_i\}$ of this bubble.



DEW T: Calculate $\{x_i\}$ and T, given $\{y_i\}$ and P

To calculate the T when the 1st dew (a drop of liquid) appear as a result of decrease in T at constant P. Also calculate the composition $\{x_i\}$ of this dew.

or

To calculate the T when the last dew disappear as a result of increase in T at constant P. Also calculate the composition $\{x_i\}$ of this dew.

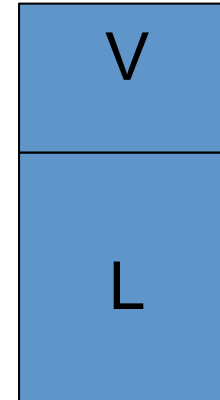
Derivation

Overall mole balance

$$T = L + V$$

Component mole balance,

$$Tz_i = Lx_i + Vy_i$$



Let $T=1$ mol, so V and L are mole fractions,

$$z_i = Lx_i + Vy_i$$

$$z_i = (1 - V)x_i + Vy_i \quad (\text{A})$$

Note: z_i is overall composition.

Substitute $y_i = K_i x_i$ into (A),

$$z_i = (1 - V)x_i + K_i x_i V = x_i(1 - V + VK_i) = x_i(1 + V(K_i - 1))$$

$$x_i = \frac{z_i}{1 + V(K_i - 1)}$$

Substitute $x_i = \frac{y_i}{K_i}$ into (A),

$$z_i = (1 - V)\frac{y_i}{K_i} + y_i V \qquad z_i K_i = (1 - V)y_i + y_i V K_i$$

$$y_i = \frac{z_i K_i}{1 + V(K_i - 1)} \qquad (10.16)$$

Also,

$$\sum x_i - \sum y_i = 0$$

$$\sum \frac{z_i}{1+V(K_i-1)} - \sum \frac{z_i K_i}{1+V(K_i-1)} = 0$$

$$\sum \frac{z_i - z_i K_i}{1+V(K_i-1)} = 0$$

Bubblepoint Calculation

At bubble point (practically all liquid) $L=1$, $V=0$ and $z_i = x_i$

$$\sum \frac{z_i - z_i K_i}{1 + V(K_i - 1)} = 0 \text{ becomes,}$$

$$\sum (x_i - x_i K_i) = 0$$

$$\sum x_i = \sum x_i K_i$$

$$\sum x_i K_i = 1 \quad (10.13) \quad \text{Bubblepoint criteria}$$

If Raoult's Law valid,

$$\sum x_i K_i = \sum x_i \frac{P_i^{sat}}{P} = 1 \quad \text{so,} \quad P = \sum x_i P_i^{sat} \quad (10.2)$$

see example 10.1

If Modified Raoult's Law valid,

$$\sum x_i K_i = \sum x_i \frac{\gamma_i P_i^{sat}}{P} = 1 \quad \text{so,} \quad P = \sum x_i \gamma_i P_i^{sat} \quad (10.6)$$

see example 10.3

Dewpoint Calculation

At dewpoint (practically all vapor): $L=0$, $V=1$ and $z_i = y_i$

$$\sum \frac{z_i - z_i K_i}{1 + V(K_i - 1)} = 0 \quad \text{becomes,}$$

$$\sum \frac{y_i - y_i K_i}{K_i} = 0$$

$$\sum \frac{y_i}{K_i} - \sum y_i = 0$$

$$\sum \frac{y_i}{K_i} = 1 \quad (10.14)$$

Dewpoint criteria

If Raoult's Law valid,

$$\sum \frac{y_i}{K_i} = \sum \frac{y_i}{\frac{P_i^{sat}}{P}} = 1 \quad P = \frac{1}{\sum \frac{y_i}{P_i^{sat}}} \quad (10.3),$$

see example 10.1

If Modified Raoult's Law valid,

$$\sum \frac{y_i}{K_i} = \sum \frac{y_i}{\frac{\gamma_i P_i^{sat}}{P}} = 1 \quad P = \frac{1}{\sum \frac{y_i}{\gamma_i P_i^{sat}}} \quad (10.7),$$

see example 10.3

Relative Volatility

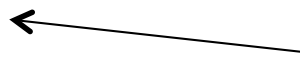
$$\alpha_{ik} = \frac{y_i/x_i}{y_k/x_k} = \frac{K_i}{K_k}$$

at azeotrope $\alpha_{ik} = \frac{1}{1} = 1$

$\alpha_{ik} > 1$ Species i is relatively more volatile
 $\alpha_{ik} < 1$ Species k is relatively more volatile

If Raoult's Law valid,

$$\alpha_{12} = \frac{P_1^{sat}/P}{P_2^{sat}/P} = \frac{P_1^{sat}}{P_2^{sat}}$$



Note: for higher vapor pressure means more volatile $\alpha_{12} > 1$

If Modified Raoult's Law valid,

$$\alpha_{12} = \frac{\gamma_1 P_1^{sat}/P}{\gamma_2 P_2^{sat}/P} = \frac{\gamma_1 P_1^{sat}}{\gamma_2 P_2^{sat}}$$

Example 10.1

Plot Px_1y_1 at $T=75^\circ\text{C}$

Mixture: Acetonitrile(1)/Nitromethane(2)

Antoine Eqn,

$$\ln P_1^{sat} / kPa = 14.2724 - \frac{2945.47}{T / ^\circ\text{C} + 224.00}$$

$$\ln P_2^{sat} / kPa = 14.2043 - \frac{2972.64}{T / ^\circ\text{C} + 209.00}$$

calculate at 75°C ,

$$P_1^{sat} = 83.21kPa \quad P_2^{sat} = 41.98kPa$$

Note: Acetonitrile(1) is more volatile.

Calculate P and y_1 , given a set of x_1 and $T=75^\circ\text{C}$.
This is BUBL P calculation.

$$\sum x_i K_i = 1 \quad (10.13) .$$

Let us assume Raoult's Law is valid , $P = P_b = \sum x_i P_i^{sat}$ (10.2)

$$P = x_1 P_1^{sat} + x_2 P_2^{sat} = x_1 P_1^{sat} + (1 - x_1) P_2^{sat}$$

$$P = (P_1^{sat} - P_2^{sat})x_1 + P_2^{sat} \quad \text{Eqn A} \quad \text{note: a linear line (y=mx+c)}$$

$$\text{also, } y_1 = \frac{x_1 P_1^{sat}}{P} \quad \text{Eqn B}$$

So,

Calculate P for a set of x_1 (Eqn A) and then calculate y_1 (Eqn B)

Given or Set

Calculate

$$P = P_b = (P_1^{sat} - P_2^{sat})x_1 + P_2^{sat}$$

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

| T (°C) | x_1 | $P=P_b$ (kPa) | y_1 |
|--------|-------|-------------------|--------|
| 75 | 0 | 41.98 P_2^{sat} | 0 |
| 75 | 0.2 | 50.23 | 0.3313 |
| 75 | 0.4 | 58.47 | 0.5692 |
| 75 | 0.6 | 66.72 | 0.7483 |
| 75 | 0.8 | 74.96 | 0.8880 |
| 75 | 1 | 83.21 P_1^{sat} | 1 |

Point b

So now plot Px_1 and Py_1 on Pxy diagram!!

Ex: Calculate P_d and x_1 , given $y_1=0.6$ and $T=75^\circ\text{C}$

(i.e. what is the dew P for gas mixture at 75°C and 60% acetonitrile)

This is point c in previous Px_1y_1 diagram.

Dew P calculation (Note: $z_1=y_1$).

$$\sum \frac{y_i}{K_i} = 1 \quad (10.14), \quad \text{If Raoult's Law valid,} \quad P_d = \frac{1}{\sum \frac{y_i}{P_i^{sat}}} \quad (10.3)$$

$$P_d = \frac{1}{\frac{0.6}{83.21} + \frac{0.4}{41.98}} = 59.74 \text{ kPa}$$

Compare with values from Pxy diagram.

Then calculate x_1 using,

$$x_1 = \frac{y_1 P_d}{P_1^{sat}} = \frac{0.6(59.74)}{83.21} = 0.43$$

- We could also plot Pxy diagram using DEW pressure calculation.
- Set y_i , calculate P_d and x_i .
- Plot Pxy using $P_d x_i y_i$
- DIY.....

Plot Tx_1y_1 at $P=70\text{kPa}$

Mixture: Acetonitrile(1)/Nitromethane(2)

Antoine Eqn,

$$T_1^{sat} / ^\circ\text{C} = \frac{2945.47}{14.2724 - \ln P / \text{kPa}} - 224.00$$

$$T_2^{sat} / ^\circ\text{C} = \frac{2972.64}{14.2043 - \ln P / \text{kPa}} - 209.00$$

so at 70kPa,

$$T_1^{sat} = 69.84^\circ\text{C} \quad T_2^{sat} = 89.58^\circ\text{C}$$

As expected Acetonitrile(1) is more volatile

$$\sum x_i K_i = 1 \quad (10.13)$$

For Raoult's Law, $P = P_b = \sum x_i P_i^{sat} \quad (10.2)$

$$P = x_1 P_1^{sat} + x_2 P_2^{sat} = x_1 P_1^{sat} + (1 - x_1) P_2^{sat}$$

$$x_1 = \frac{P - P_2^{sat}}{P_1^{sat} - P_2^{sat}} \quad \text{Eqn C}$$

Note: Since we used BUBL point calculation, $T = T_b$

Choose T between T_1^{sat} and T_2^{sat} , then using Antoine eqns calculate P_1^{sat} and P_2^{sat} at the chosen T and then calculate x_1 by Eqn C.

Then calculate y_1 using,

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

Plot Tx_1y_1 at $P=70$ kPa

Given or Set

$$x_1 = \frac{P - P_2^{sat}}{P_1^{sat} - P_2^{sat}}$$

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

| P (kPa) | $T=T_b(^{\circ}\text{C})$ | x_1 | y_1 |
|---------|---------------------------|---------------|---------------|
| 70 | 69.84 T_1^{sat} | 1 ($x_2=0$) | 1 ($y_2=0$) |
| 70 | 74 | 0.7378 | 0.8484 |
| 70 | 78 | 0.5156 | 0.6759 |
| 70 | 82 | 0.3184 | 0.4742 |
| 70 | 86 | 0.1424 | 0.2401 |
| 70 | 89.58 T_2^{sat} | 0 ($x_2=1$) | 0 ($y_2=1$) |

So now plot Tx_1 and Ty_1 on a Txy diagram!!

Ex: Calculate T_b and y_1 , given $x_1=0.6$ and $P=70\text{kPa}$.
 (i.e. calculate the bubble temperature at 70kPa and 60% acetonitrile)

This is point b in previous Tx_1y_1 diagram. Note: $z_1=x_1$
Bubble temperature calculation!!

$$\sum x_i K_i = 1 \quad (10.13),$$

The solution is not straightforward as T is unknown. Let's see how to solve mathematically,

For Raoult's Law, $P_b = \sum x_i P_i^{sat} \quad (10.2)$

$$P_b = \frac{P_k^{sat}}{P_k^{sat}} \sum x_i P_i^{sat} = P_k^{sat} \sum x_i \frac{P_i^{sat}}{P_k^{sat}} = P_k^{sat} \sum x_i \alpha_{ik}$$

where k is a component that arbitrarily chosen.

$$P_b = P_k^{sat} \sum x_i \alpha_{ik}$$

where $\alpha_{ik} = \frac{P_i^{sat}}{P_k^{sat}}$ is relative volatility of i wrt k .

$$P_k^{sat} = \frac{P_b}{\sum x_i \alpha_{ik}} \quad (\text{A})$$

Also,

$$\ln \alpha_{ik} = \ln \frac{P_i^{sat}}{P_k^{sat}} = \ln P_i^{sat} - \ln P_k^{sat} = \left(A_i - \frac{B_i}{T + C_i} \right) - \left(A_k + \frac{B_k}{T + C_k} \right)$$

Solution is through iteration,

1. Start with an initial guess of T as follows,

$$T = \sum x_i T_i^{sat} \qquad T = 0.6(69.84) + 0.4(89.58) = 77.74^\circ C$$

2. Arbitrarily pick a component, e.g. Nitromethane so, k=2

3. Calculate α_{ik} ,

(note: Number of α_{ik} is equal to total number of component)

$$\ln \alpha_{ik} = \left(A_i - \frac{B_i}{T + C_i} \right) - \left(A_k + \frac{B_k}{T + C_k} \right)$$

we get,

$$\alpha_{12} = 1.9611$$

$$\alpha_{22} = 1$$

4. Calculate P_k^{sat} using eqn A,

$$P_k^{sat} = \frac{P}{\sum x_i \alpha_{ik}}$$

$$P_2^{sat} = \frac{P}{x_1 \alpha_{12} + x_2 \alpha_{22}} = \frac{70}{0.6(1.9611) + 0.4(1)} = 44.3977 \text{ kPa}$$

5. Calculate a new value of T using the Antoine eqn,

$$T = \frac{B_k}{A_k - \ln P_k^{sat}} - C_k \quad T = \frac{2972.64}{14.2043 - \ln 44.3977} - 209 = 76.53^\circ \text{ C}$$

6. Stop if this T is equal or close to earlier value of T, else use this value as a new guess. Repeat steps 3, 4 & 5 until converge.

| T | α_{12} | P_2^{sat} | T |
|-------|---------------|--------------------|-------|
| 77.74 | 1.9611 | 44.39 | 76.53 |
| 76.53 | 1.9703 | 44.24 | 76.43 |
| 76.43 | 1.9717 | 44.22 | 76.42 |

Answer
(point b)

7. Finally, calculate y_i using Raoult's law (Use the Antoine Eqn for P_i^{sat})

$$y_1 = 0.7472$$

DEW T calculation

Calculate T_d and x_1 , given y_1 and P .

Example: Calculate T_d and x_1 for $z_1 = y_1 = 0.6$ and $P = 70 \text{ kPa}$.
See page 356 for the solution (also by iteration) of DEW T calculation.

Answer: $T_d = 79.58^\circ\text{C}$
 $x_1 = 0.4351$

Example 10.4

Calculation of dew pressure and bubble pressure using K-value from DePriester chart.

Note: Why the solution is by trial and error?

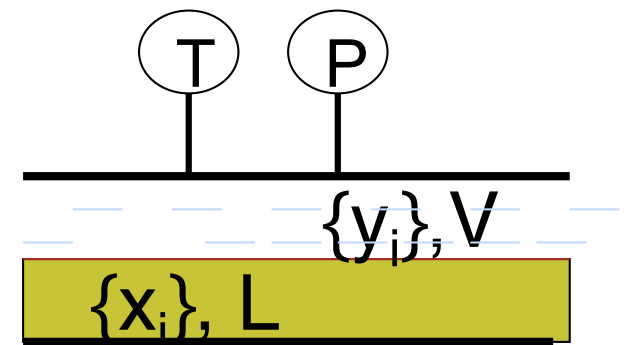
Flash Calculation

Flash Calculation

An important application of VLE!

Liquid at pressure equal or higher than P_b
“flashes” or partially evaporates when the P is reduced, thus producing a vapor and liquid.

Flash calculation is to determine
 V , L , $\{x_i\}$, and $\{y_i\}$ at
 T and P by assuming VLE.



Note: $\{x_i\}$ composition of liquid and $\{y_i\}$ composition of vapor

As derived for VLE system,

$$y_i = \frac{z_i K_i}{1 + V(K_i - 1)} \quad (10.16)$$

$$\sum y_i = 1, \quad \text{so:}$$

$$\sum \frac{z_i K_i}{1 + V(K_i - 1)} = 1 \quad (10.17)$$

Solution is by trial and error.

Guess V until the summation term equal to 1.

But.....

.....first we need to know whether the system is actually two-phase.

In general

If $P_d < P < P_b$, two phase

or

If $T_b < T < T_d$, two phase

Examples of Flash Calculation

Example 10.5:

Flash calculation for system where
Raoult's Law valid

Example 10.6:

Flash calculation using K-value from
DePriester Chart

Dewpoint T of Mixture of Water Vapor and Non-condensable Gases

This is a special case of dew T calculation.

Solution is straightforward by the application of Raoult's Law to the condensable component H₂O (here identified as component 2).

The system contains a dew (liquid water) in VLE with mixture of water vapor and non-condensable gases (such as N₂, CO₂, O₂ etc.).

$$y_2 P = x_2 P_2^{sat}$$

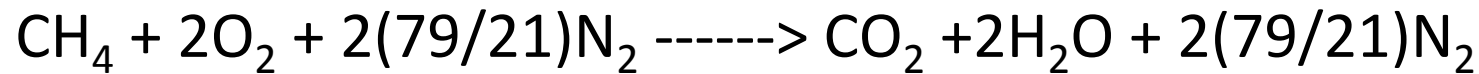
The dew is 100% H₂O, so $x_2=1$

$$\text{so } P_2^{sat} = y_2 P$$

Example

Dewpoint T of Combustion Products

For stoichiometric combustion of methane, calculate dew point T of the combustion products.



Mole fraction of H₂O is $2/(1+2+2(79/21)) = 0.19$

$$P_2^{sat} = y_2 P \quad P_2^{sat} = 0.19(101.325\text{kPa}) = 19.25\text{kPa}$$

From steam table*, $T_d = T_2^{sat} = 59.5^\circ\text{C}$

*You could also use Antoine Eqn.

Henry's Law

Henry's Law is VLE relation that is valid for ideal-gas mixture in equilibrium with a dilute solution, where we want to know the composition of dissolve gas i in the dilute solution.

For example,

a) CO₂ and H₂O system.

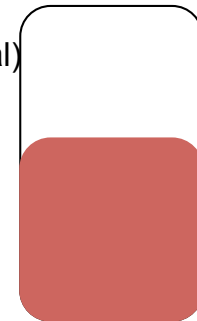
b) Air and H₂O system.

$$\cancel{\hat{\phi}_i} \overset{1}{y_i} P = \gamma_i x_i f_i$$

$$y_i P = x_i \gamma_i f_i = x_i \gamma_i P_i^{sat}$$

$$\text{let } H_i = \gamma_i f_i = \gamma_i P_i^{sat}$$

no value for dissolved (supercritical) gas at VLE conditions



H_i is Henry's constant (in bar) for dissolved gas (i).

so $y_i P = x_i H_i$ Henry's Law

$$y_i P = x_i H_i$$

So at dilute solution,
 $y_i = (H_i/P) x_i$

For constant system pressure P ,
 $y_i = (\text{Constant}) x_i$

If we plot y_i vs x_i , we get a straight line through the origin.

So Henry's constant for dissolved gas (i) can be easily determined from experiment.

In previous example of dewpoint for combustion product, we assume the liquid is all H₂O ($x_2=1$).

What if we want to know the mole fraction of dissolved CO₂ (component 1) in the dew (liquid)?

We could solve this using Henry's Law for dissolved gases (CO₂).

Apply Henry's law for component 1.

Use H_1 data from Table 10.1 (note: this actually valid at 25°C).

$$x_1 = \frac{y_1 P}{H_1} = \frac{(1 / (1 + 2 + 7.52))(1.013 \text{ bar})}{1670 \text{ bar}} = 3.4622 \times 10^{-5} \approx 0$$

As expected, only small amount of CO₂ present in liquid water.

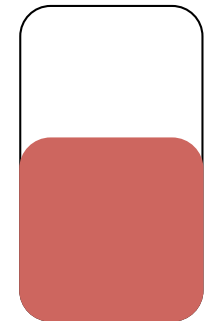
See also example 10.2

If the fugacity of i in **liquid** phase is given by Henry's Law,

$$\hat{f}_i = \gamma_i x_i f_i = x_i H_i$$

If the **gas** is ideal solution (Lewis/Randall is valid),

$$\hat{f}_i^{id} = \phi_i y_i P$$



So we get the following version of Henry's Law if gas mixture is ideal solution ,

$$\phi_i y_i P = x_i H_i$$

Extension of Example 10.3

Plot Px_1y_1 and x_1y_1 diagrams at $T=318.15\text{K}$

From bubblepoint calculation,

Set x_1

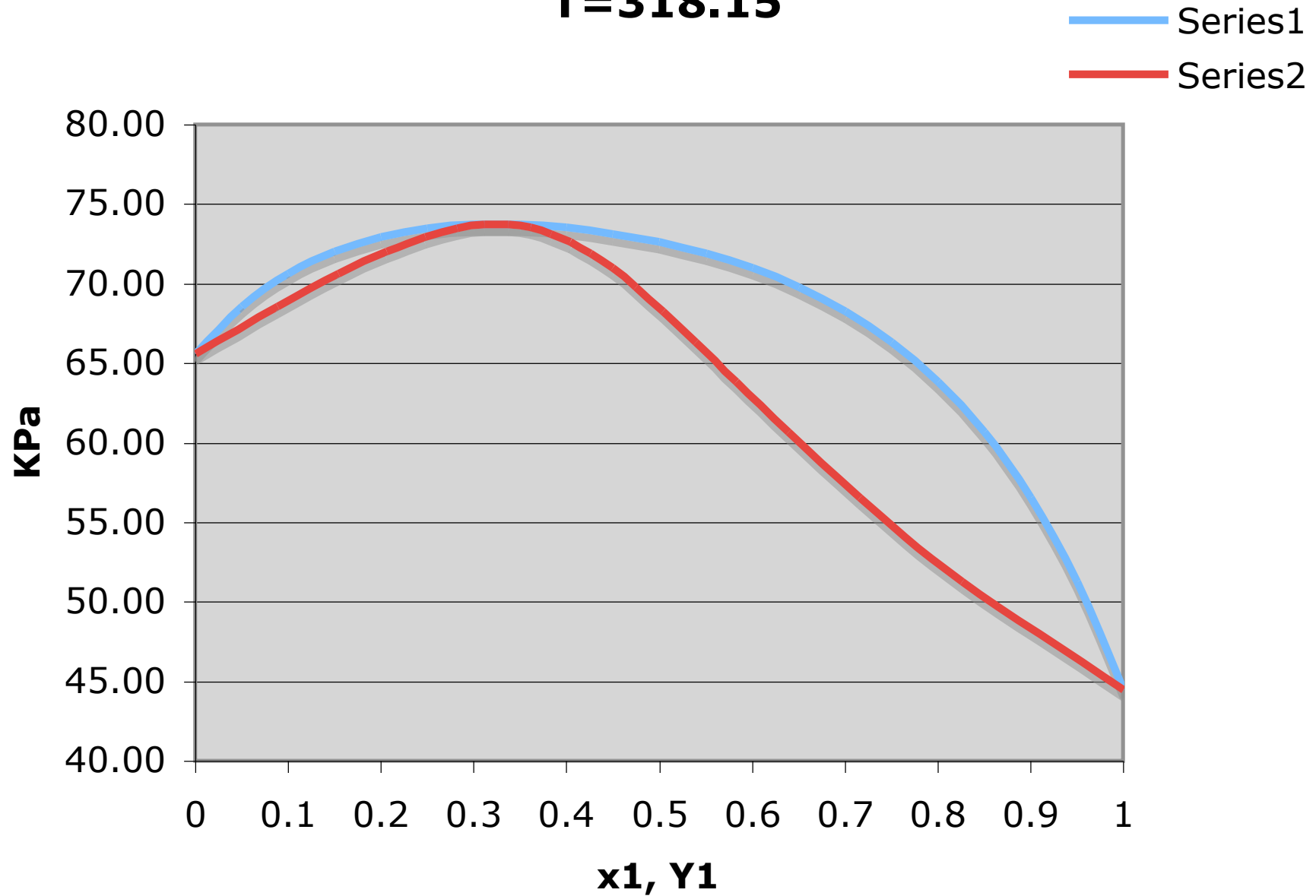
Calculate P_b

Calculate y_1

| x1 | G1 | G2 | P | y1 |
|------|------|------|-------|------|
| 0.00 | 3.03 | 1.00 | 65.64 | 0.00 |
| 0.05 | 2.72 | 1.00 | 68.57 | 0.09 |
| 0.10 | 2.45 | 1.01 | 70.64 | 0.15 |
| 0.15 | 2.23 | 1.03 | 72.06 | 0.21 |
| 0.20 | 2.03 | 1.05 | 72.97 | 0.25 |
| 0.25 | 1.86 | 1.07 | 73.50 | 0.28 |
| 0.30 | 1.72 | 1.10 | 73.73 | 0.31 |
| 0.35 | 1.60 | 1.15 | 73.73 | 0.34 |
| 0.40 | 1.49 | 1.19 | 73.54 | 0.36 |
| 0.45 | 1.40 | 1.25 | 73.17 | 0.38 |
| 0.50 | 1.32 | 1.32 | 72.63 | 0.40 |
| 0.55 | 1.25 | 1.40 | 71.92 | 0.43 |
| 0.60 | 1.19 | 1.49 | 70.99 | 0.45 |
| 0.65 | 1.15 | 1.60 | 69.81 | 0.47 |
| 0.70 | 1.10 | 1.72 | 68.29 | 0.50 |
| 0.75 | 1.07 | 1.86 | 66.36 | 0.54 |
| 0.80 | 1.05 | 2.03 | 63.88 | 0.58 |
| 0.85 | 1.03 | 2.23 | 60.70 | 0.64 |
| 0.90 | 1.01 | 2.45 | 56.60 | 0.72 |
| 0.95 | 1.00 | 2.72 | 51.31 | 0.83 |
| 1.00 | 1.00 | 3.03 | 44.51 | 1.00 |

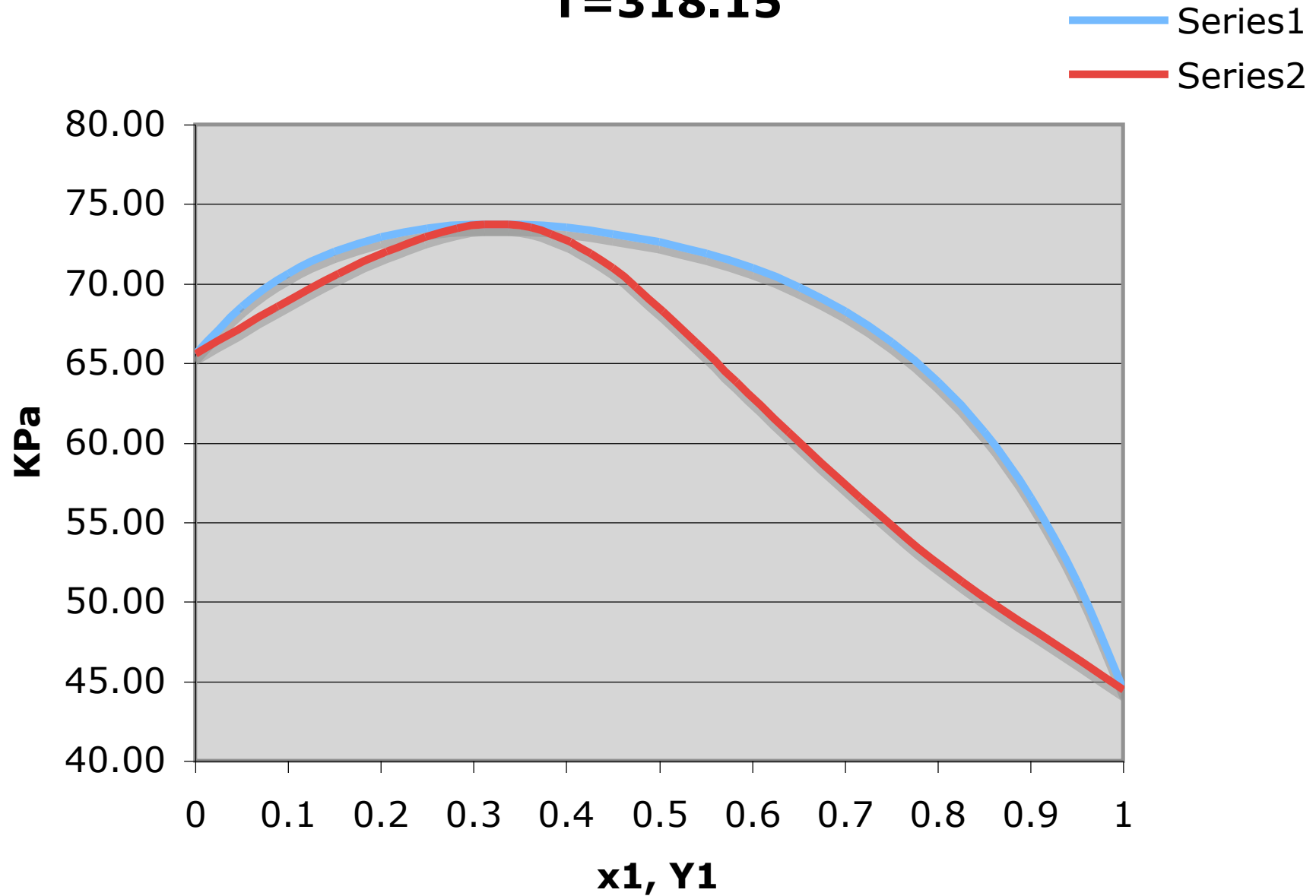
G1 is gamma1

T=318.15



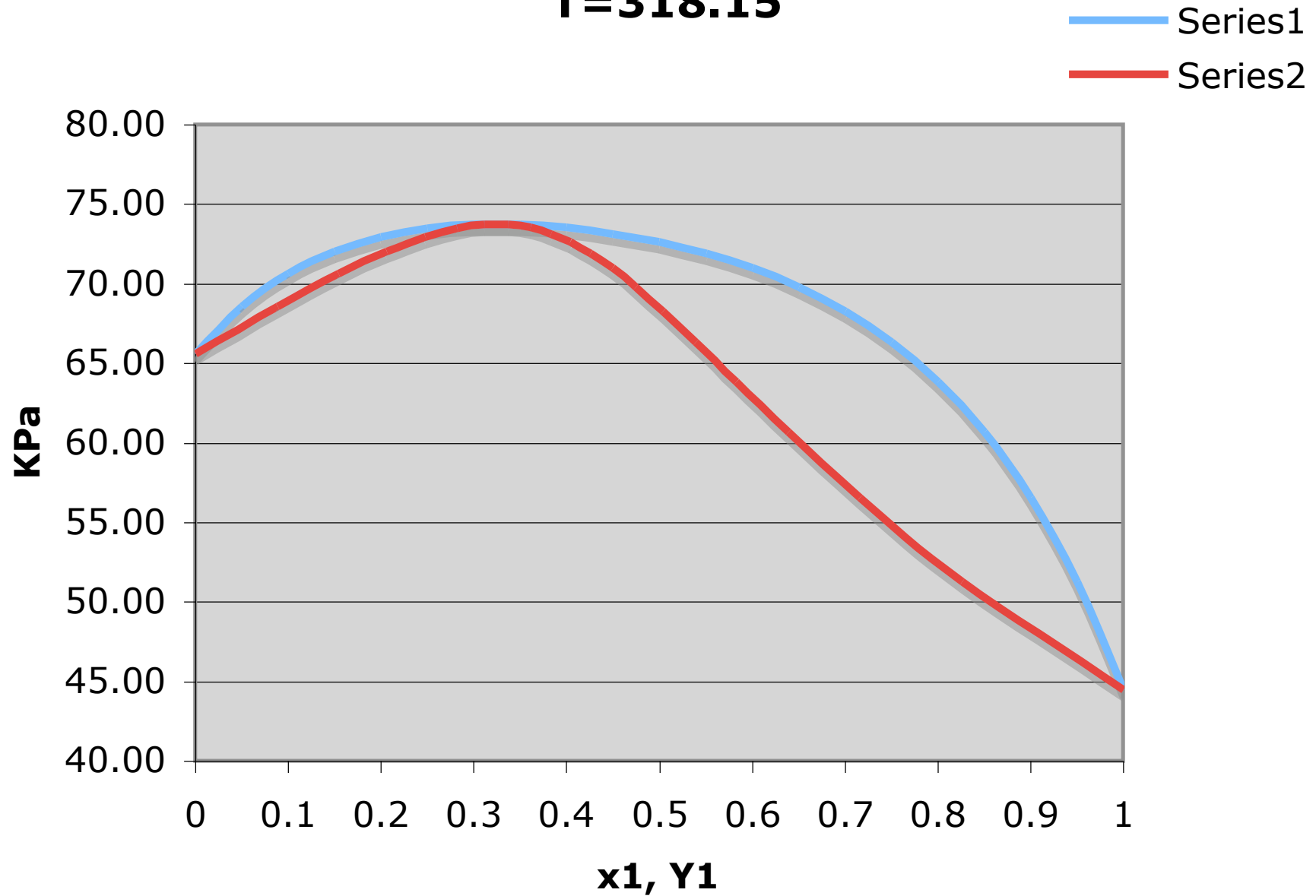
Locate azeotropic pressure at T=318.15K
and its composition

T=318.15

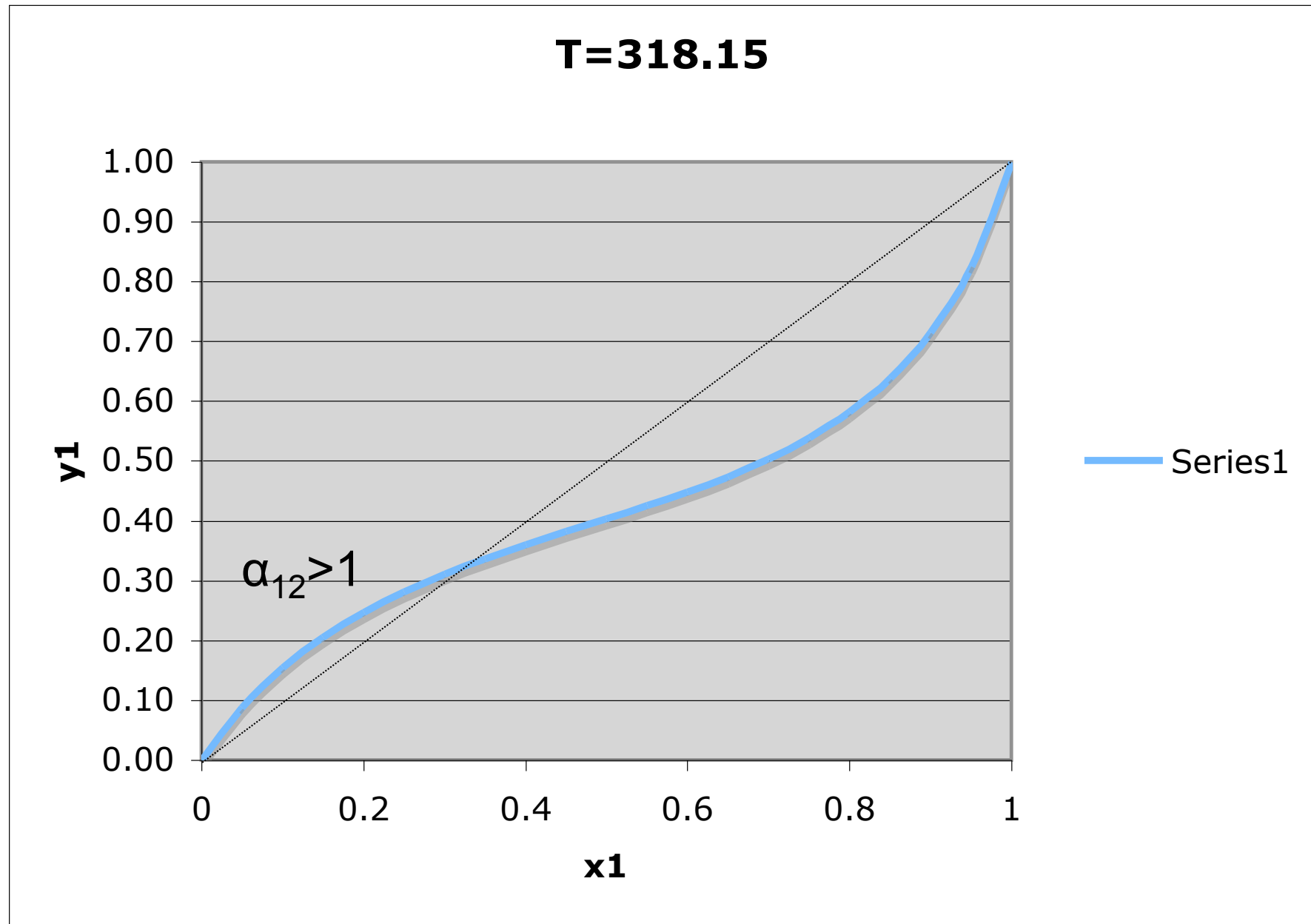


Locate BUBL P at T=318.15K, $x_1=0.25$

T=318.15



Locate DEW P at T=318.15K, $y_1=0.6$



Locate azeotropic composition at 318.15K

A stream of mixture of methanol(1)/methyl acetate(2) is inside a pipeline where the T is 318.15K and P is 66kPa. The stream contains (60 mole percent methanol). What is the phase of the stream?

Let's check bubble pressure and dew pressure.

From example 10.3b), Dew P is 62.89kPa

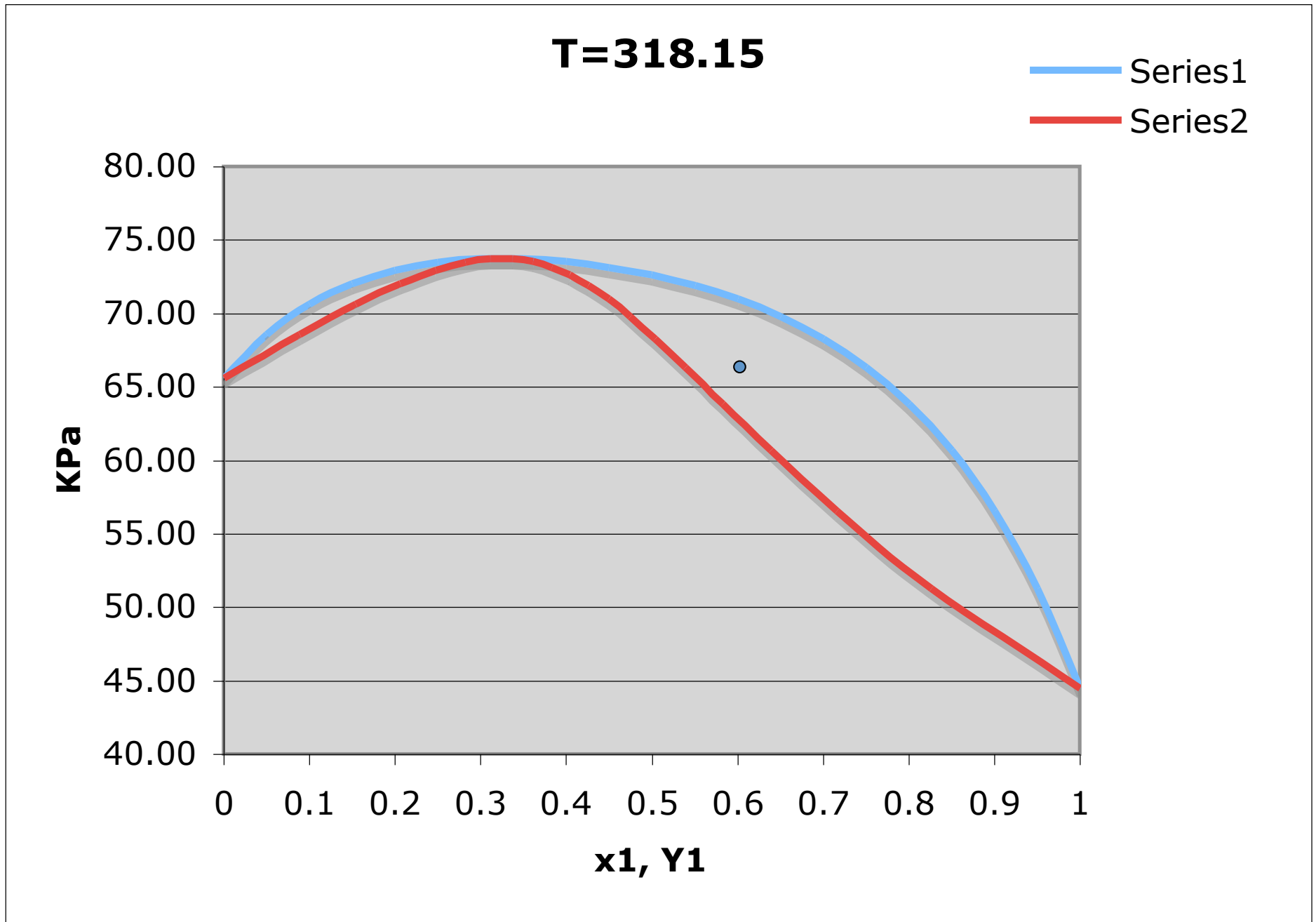
Now calculate bubble P,

$$P_b = x_1 \gamma_1 P_1^{sat} + x_2 \gamma_2 P_2^{sat} = 71kPa$$

$P_d < P < P_b$ hence **two phases!**

Locate the conditions on the following Px_1y_1 diagram.

Determine V, L, $\{x_i\}$ and $\{y_i\}$ using flash calculation.



$$K_1 = \frac{P_1^{sat} \gamma_1}{P} = \frac{P_1^{sat} \exp(A(x_2)^2)}{P}$$

$$K_2 = \frac{P_2^{sat} \exp(A(x_1)^2)}{P}$$

We need x_1 !! Lets us do bubble point calculation at
 $P=66\text{kPa}$, $T=318.15\text{K}$ and x_1

$$P_b = 66\text{kPa} = x_1 \gamma_1 P_1^{sat} + x_2 \gamma_2 P_2^{sat} \quad (\text{a})$$

$$K_1 = \frac{P_1^{sat} \gamma_1}{P} = \frac{P_1^{sat} \exp(A(x_2)^2)}{P}$$

$$K_2 = \frac{P_2^{sat} \exp(A(x_1)^2)}{P}$$

so (a) becomes,

$$66 = x_1 P_1^{sat} \exp(A(1-x_1)^2) + (1-x_1) P_2^{sat} \exp(A(x_1)^2)$$

$$66 = x_1(44.51)\exp(1.107)(1 - x_1)^2 + (1-x_1)(65.64)\exp(1.107(x_1)^2)$$

Guess x_1 ,

$$x_1 = 0.7 \quad P=68.29$$

$$x_1 = 0.8 \quad P=63.88$$

$$x_1 = 0.75 \quad P=66.36$$

$$x_1 = 0.76 \quad P=65.91 \dots \text{good enough}$$

Now we can calculate K_1 and K_2 for flash calculation,

$$K_1 = \frac{P_1^{sat} \gamma_1}{P} = \frac{44.51 \exp(1.107(1 - 0.76)^2)}{66} = 0.719$$

$$K_2 = \frac{65.64 \exp(1.107(0.76)^2)}{66} = 1.885$$

Substitute into eqn (10.17),

$$\sum \frac{z_i(K_i)}{1+V(K_i-1)} = 1$$
$$\frac{0.6(0.719)}{1+V(0.719-1)} + \frac{(1-0.6)(1.885)}{1+V(1.885-1)} = 1 \quad (10.17)$$
$$\frac{0.431}{1-0.281V} + \frac{0.754}{1+0.885V} = 1$$

$$\frac{0.431}{1 - 0.281V} + \frac{0.754}{1 + 0.885V} = 1$$

| | |
|--------|--------------|
| Guess, | $\Sigma = 1$ |
| V=0.50 | 1.024 |
| V=0.55 | 1.017 |
| V=0.70 | 1.002 |
| V=0.75 | 0.999 |
| V=0.73 | 1.000 |

So V=0.73 L=1-V=0.27

$$y_i = \frac{z_i K_i}{1 + V(K_i - 1)} \quad (10.16)$$

$$y_1 = \dots\dots\dots$$

$$y_2 = \dots\dots\dots$$

$$x_i = \frac{y_i}{K_i}$$

$$x_1 = \dots\dots\dots$$

$$x_2 = \dots\dots\dots$$