Lecture 2
Exploiting vapor-liquid equilibrium for molecular separation

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Intended Learning Outcomes

1. Plot and use x-y, T-x-y and H-x-y diagrams; explain the relationship between these three types of diagrams.

2. To analyze composition, temperature, pressure, enthalpy, etc. upon change in temperature or pressure based on phase diagram.

3. Use flash drum to carry out binary separation by involving mass and energy balances.

4. Explore the limits of flash drum based separation.

5. Apply constant volatility simplification to reduce the mathematical complexity in the flash column problems.

Vapor-liquid equilibrium (2 component)

$Py_1 = \gamma_1 x_1 P_{1,sat}$ where, $\mathrm{P}_{1,\mathrm{sat}} = \mathrm{f(T)}$ $\gamma_1 = g(T, x_1)$

$$k_1 = \frac{\gamma_1 P_{1,sat}}{P}$$

$$\Rightarrow y_1 = k_1 x_1 \qquad \mathbf{y_1 = f(T, P, \gamma_1, x_1)}$$

For ideal solution, $\gamma_1 = 1$

$Py_1 = x_1 P_{1,sat}$ Roult's law

$$k_1 = \frac{P_{1,sat}}{P}$$

$$y_1 = \frac{P_{1,sat}}{P} x_1$$

$\mathscr{F}$ for 2 component, 2 phase = 2

Any of these set of variables can be specified : $(\mathrm{T}, \mathrm{x}_1)$, $(\mathrm{P}, \mathrm{x}_1)$, (T, P), $(\mathrm{x}_1, \mathrm{y}_1)$

Sometime, instead of temperature/pressure, specific enthalpy is specified

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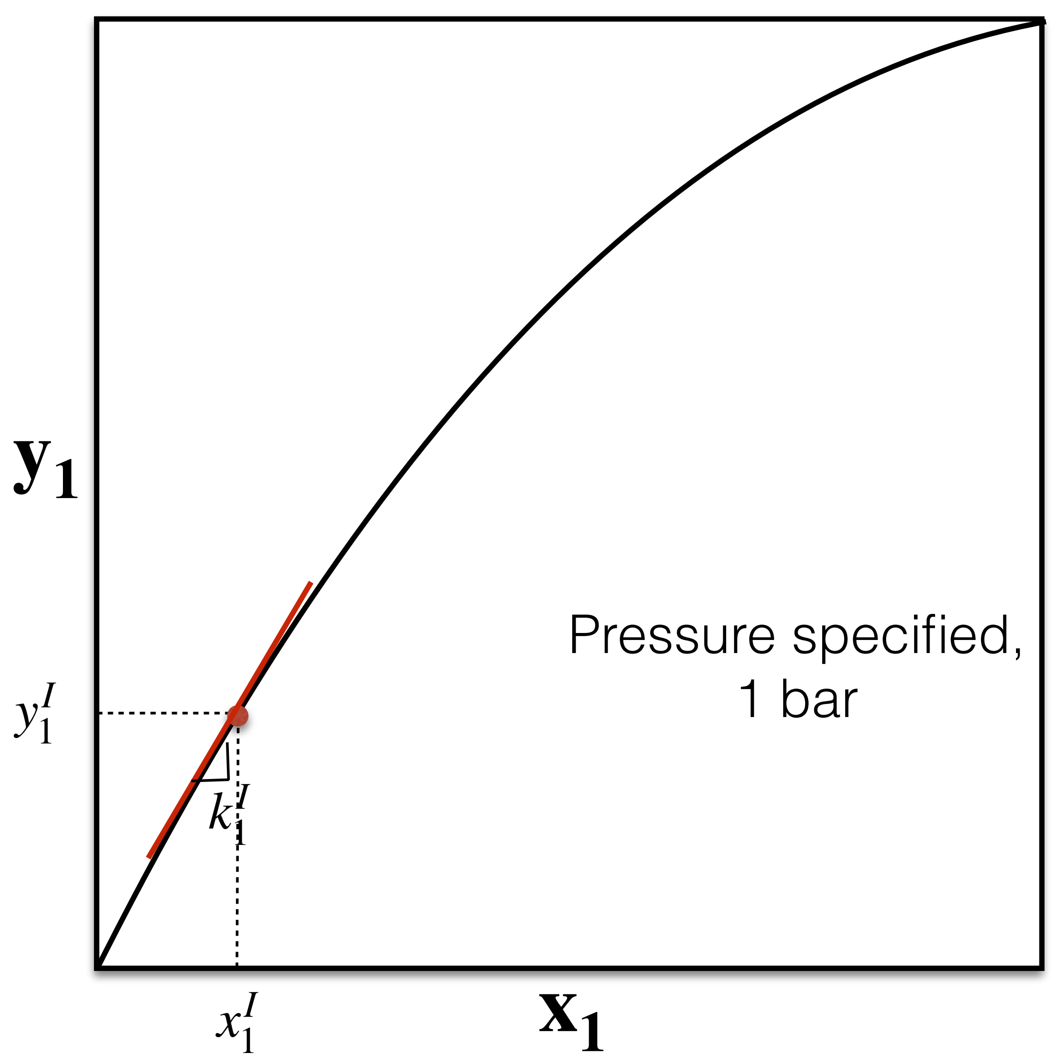
Graphical methods: y-x diagram

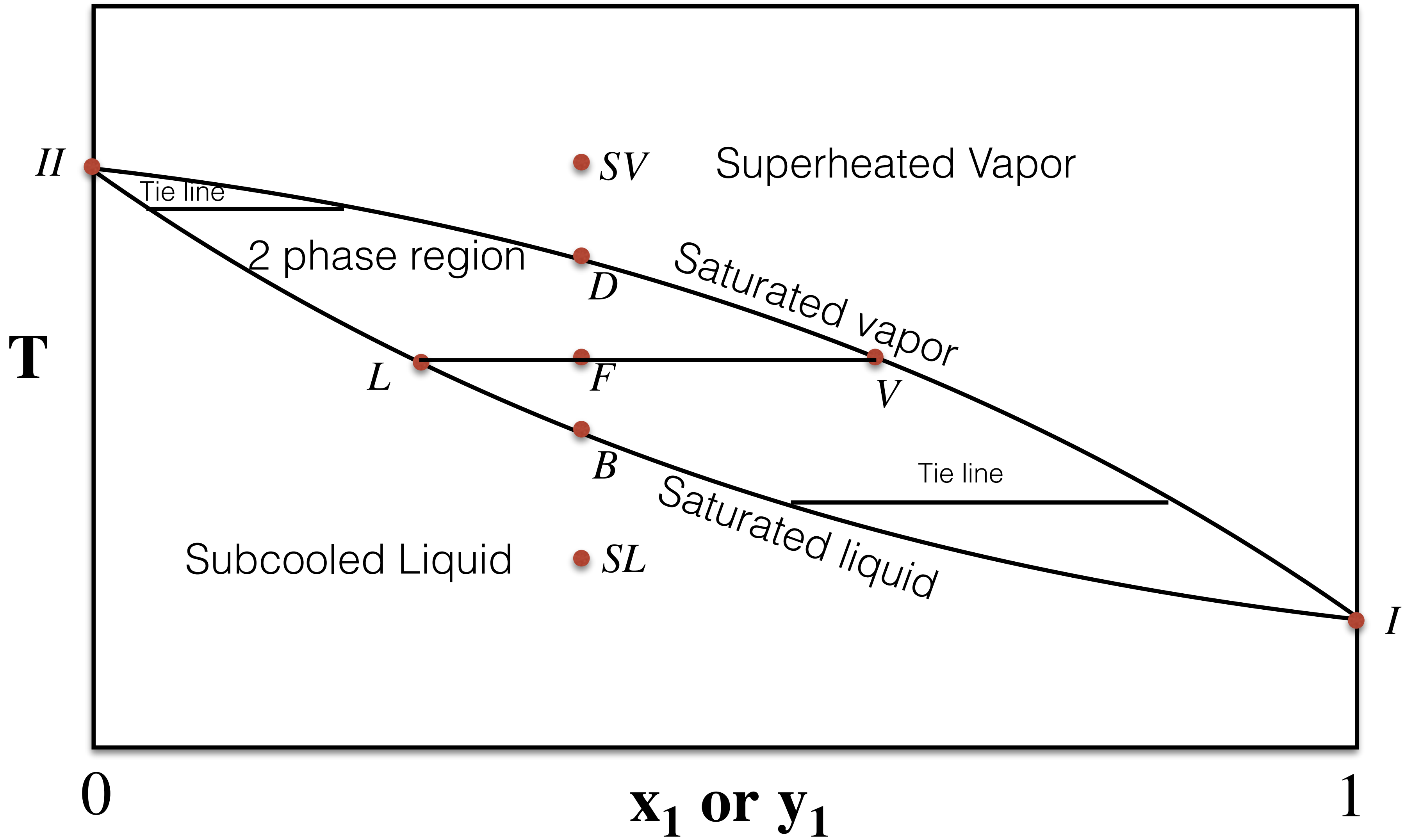


$$P y_1 = \gamma_1 x_1 P_{1,sat}$$

$$k_1 = \frac{\gamma_1 P_{1,sat}}{P}$$

$$y_1^I = k_1^I \, x_1^I$$

Graphical methods: T-x-y diagram for liquid-vapor phase



T_D = Dew point : temperature at which liquid droplets first appear in saturated vapor

T_B = Bubble point : temperature at which vapor bubbles first appear in saturated liquid

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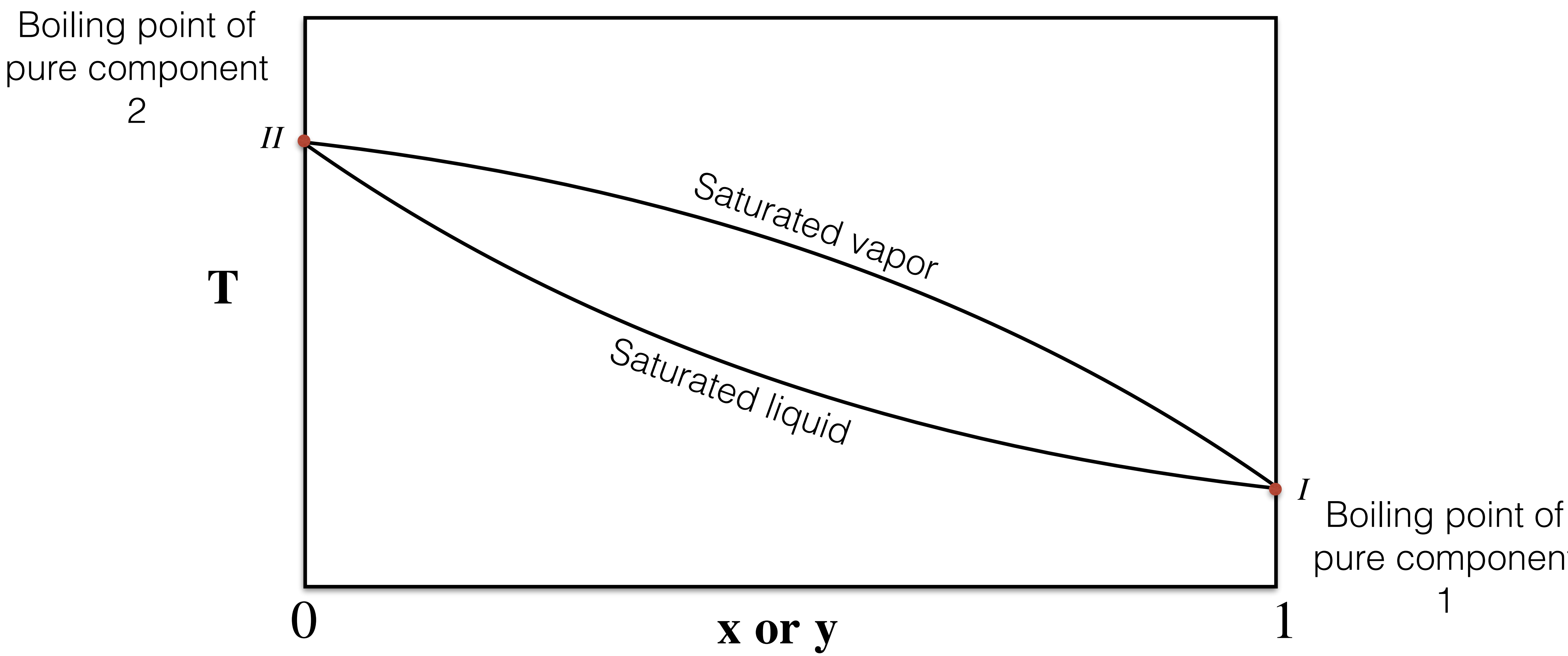
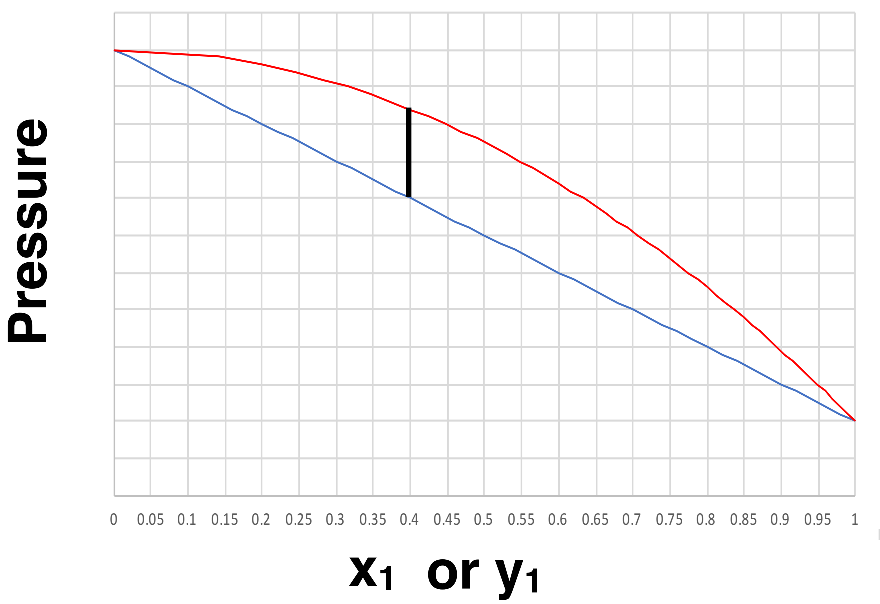
Graphical methods: T-x-y diagram for liquid-vapor phase

What is special about points I and II ?

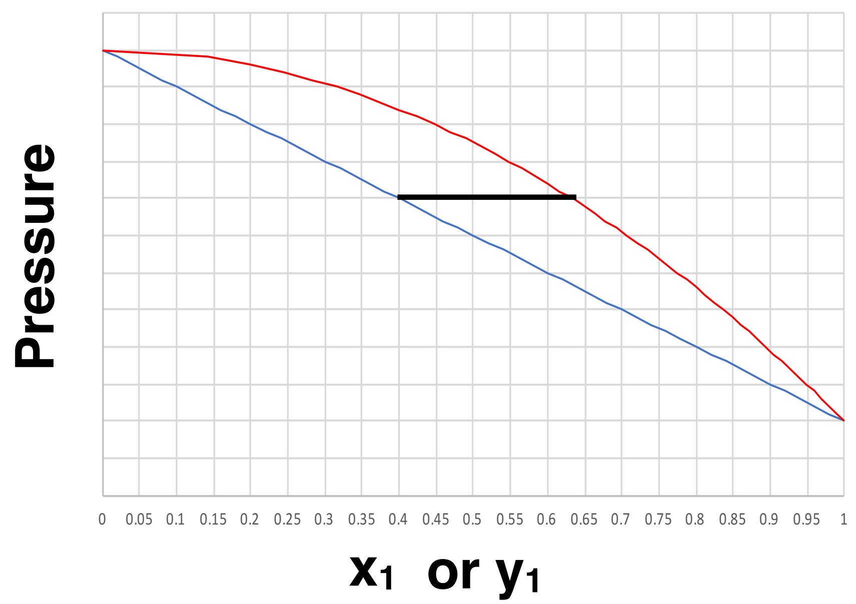


Which of the following represents the correct relationship between a liquid and a vapor phase which are at equilibrium at a given temperature.

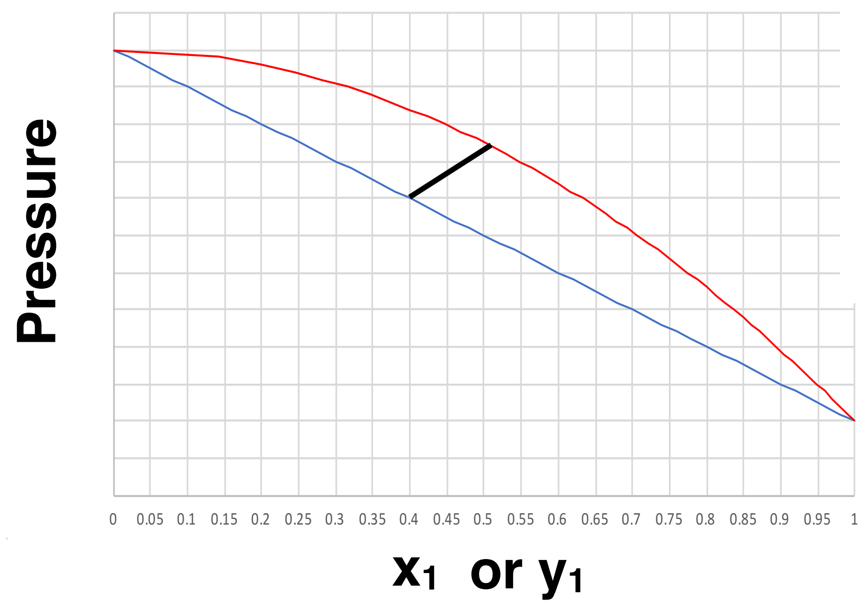
A



B



C



D None of the above

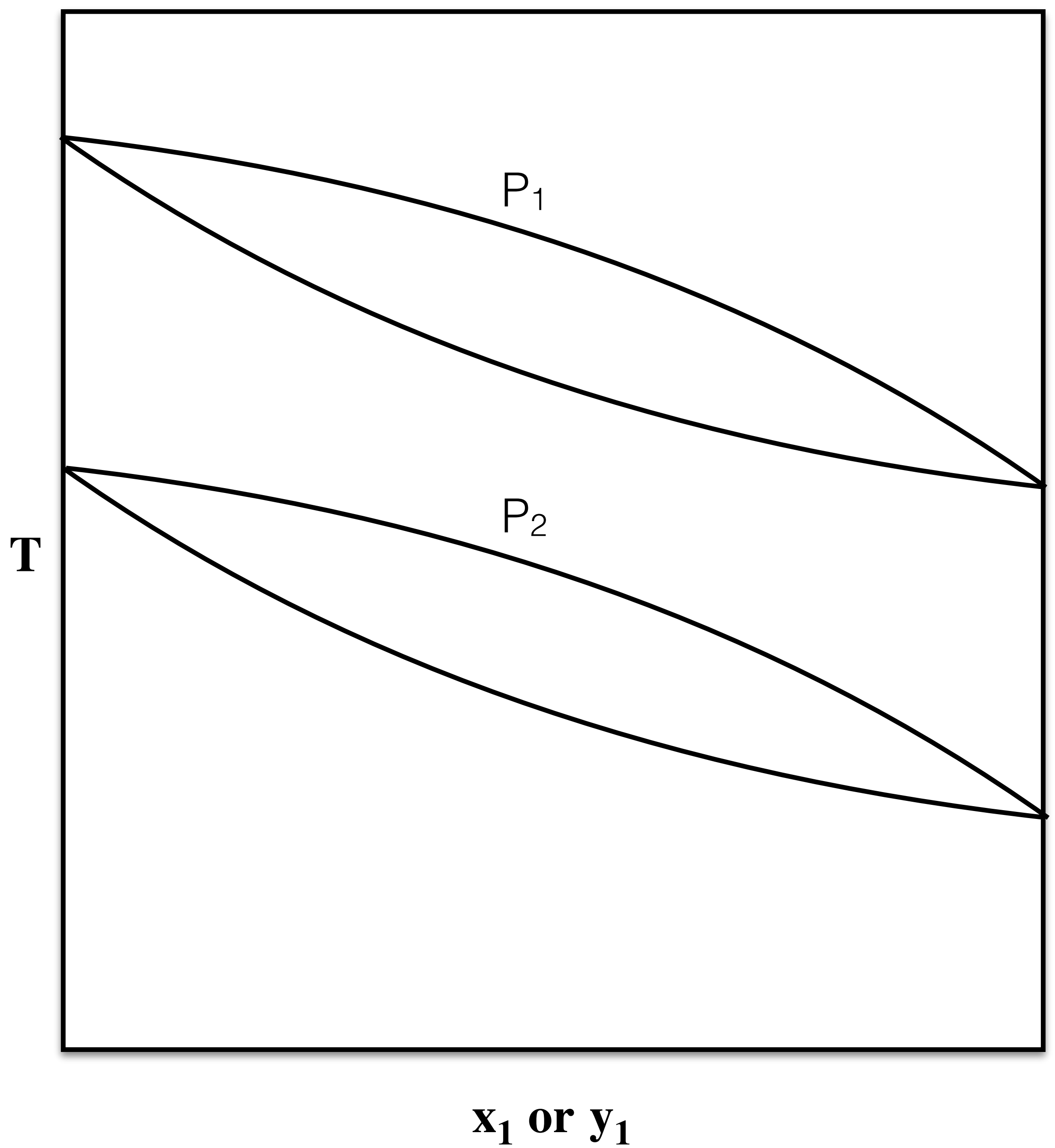
What is the relationship between P_1 and P_2 in this T-x-y diagram representing liquid vapor equilibrium.

A $P_1 = P_2$

B $P_1 < P_2$

C $P_1 > P_2$

D Insufficient information



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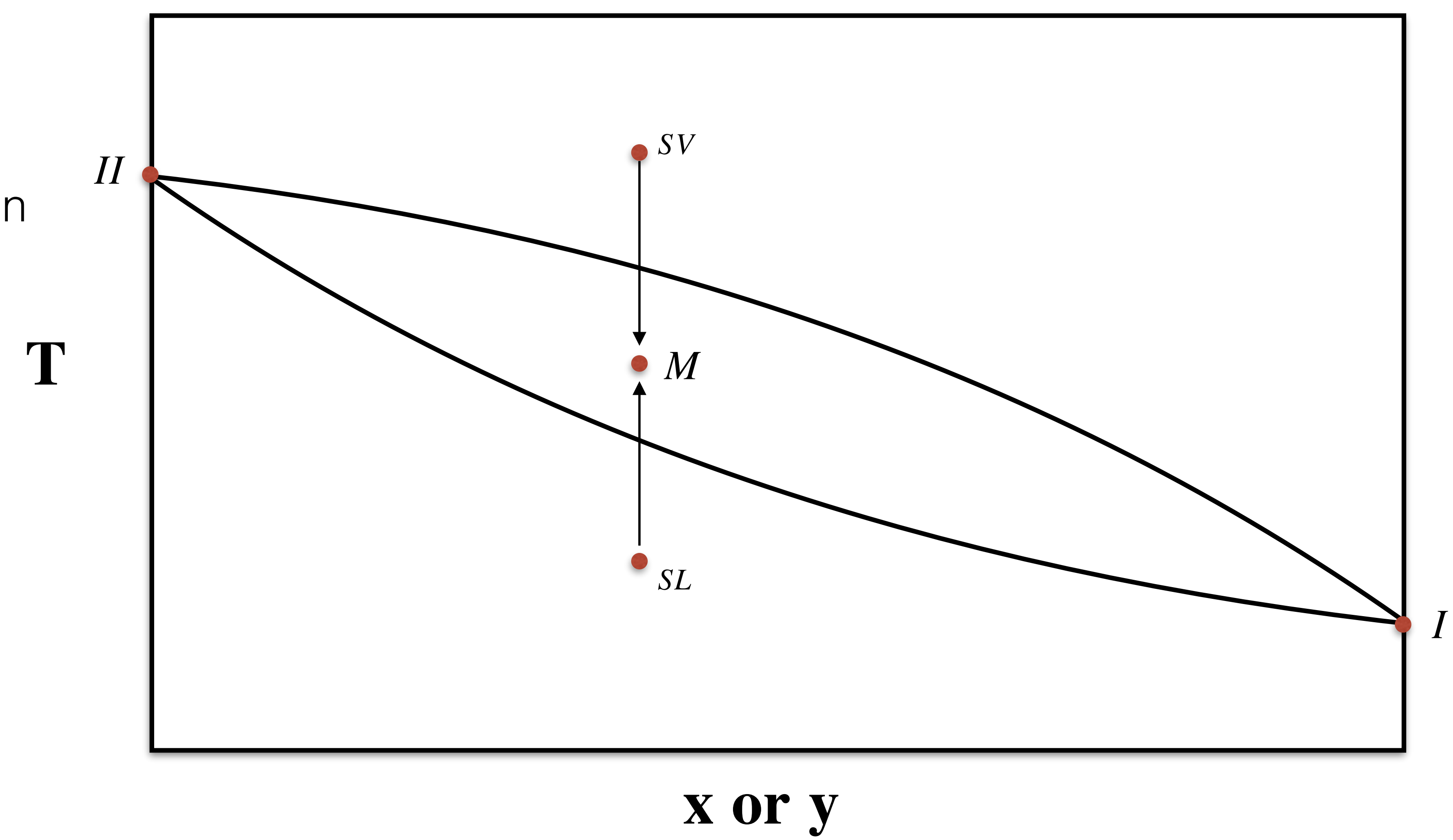
Graphical methods: T-x-y diagram

In the following scenario, as shown in the figure below:
Path 1 : a subcooled liquid mixture at point SL is heated to point M
Path 2: a superheated vapor mixture at point SV is cooled to point M

Which of the following is correct ?

a. Path 1 leads to more vapor than path 2
b. Path 1 leads to more liquid than path 2
c. Path 1 is not possible.
d. Path 1 and 2 leads to same composition



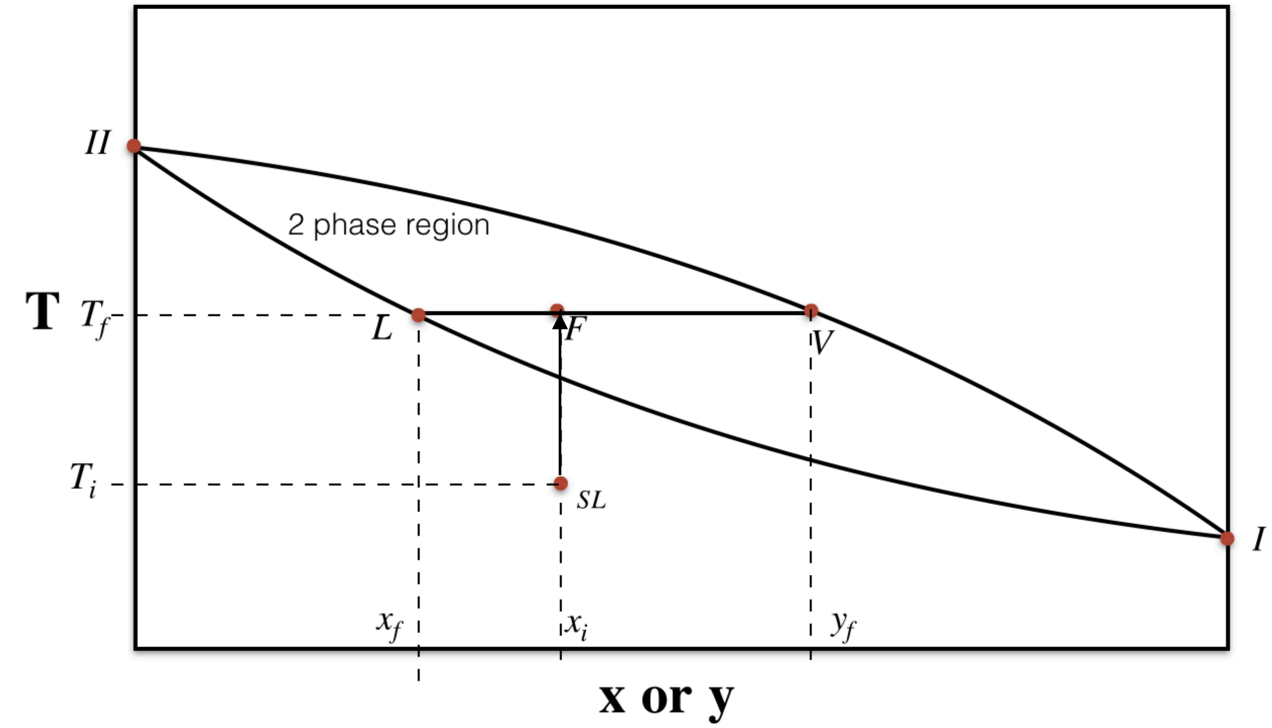
Graphical methods: T-x-y diagram

100 moles of subcooled liquid mixture, initially at temperature T_i and liquid phase composition x_i (point SL in the plot) is heated to T_f (point F in the plot) as shown in the figure below. This brings the mixture in the two-phase region forming saturated liquid and saturated vapor phases in equilibrium. How would you estimate the quantity of the two phases?

Amount of material in liquid and vapor phase under equilibrium can be determined by the lever rule.

$$\frac{\text{amount of liquid}}{\text{total amount}} = \frac{\text{FV}}{\text{LV}}$$

$$\frac{\text{amount of vapor}}{\text{total amount}} = \frac{\text{LF}}{\text{LV}}$$

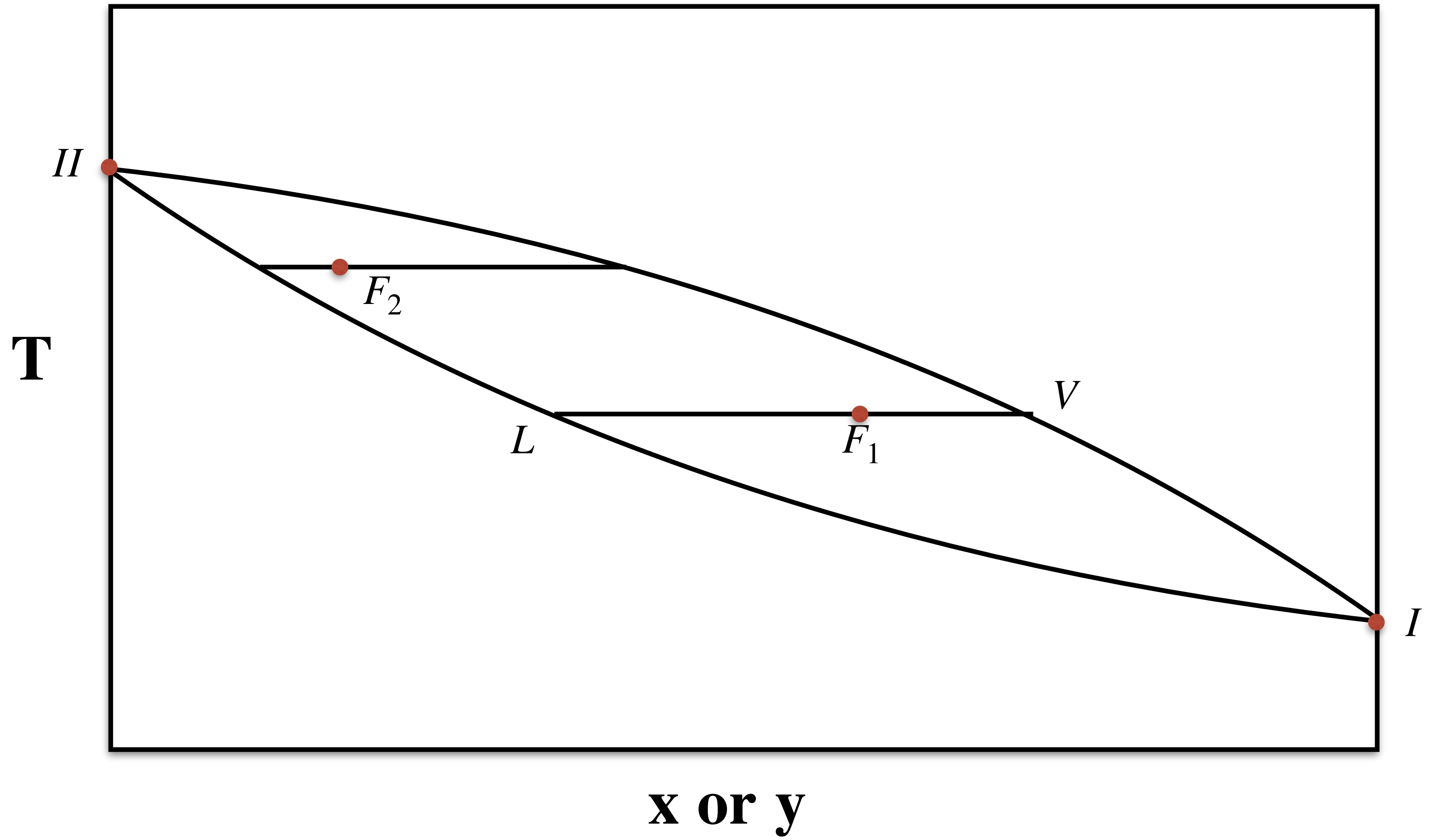


Graphical methods: T-x-y diagram

Study the scenario below.

Which feed is at higher temperature?

a. F1
b. F2
c. They are both equal in temperature
d. Not enough information

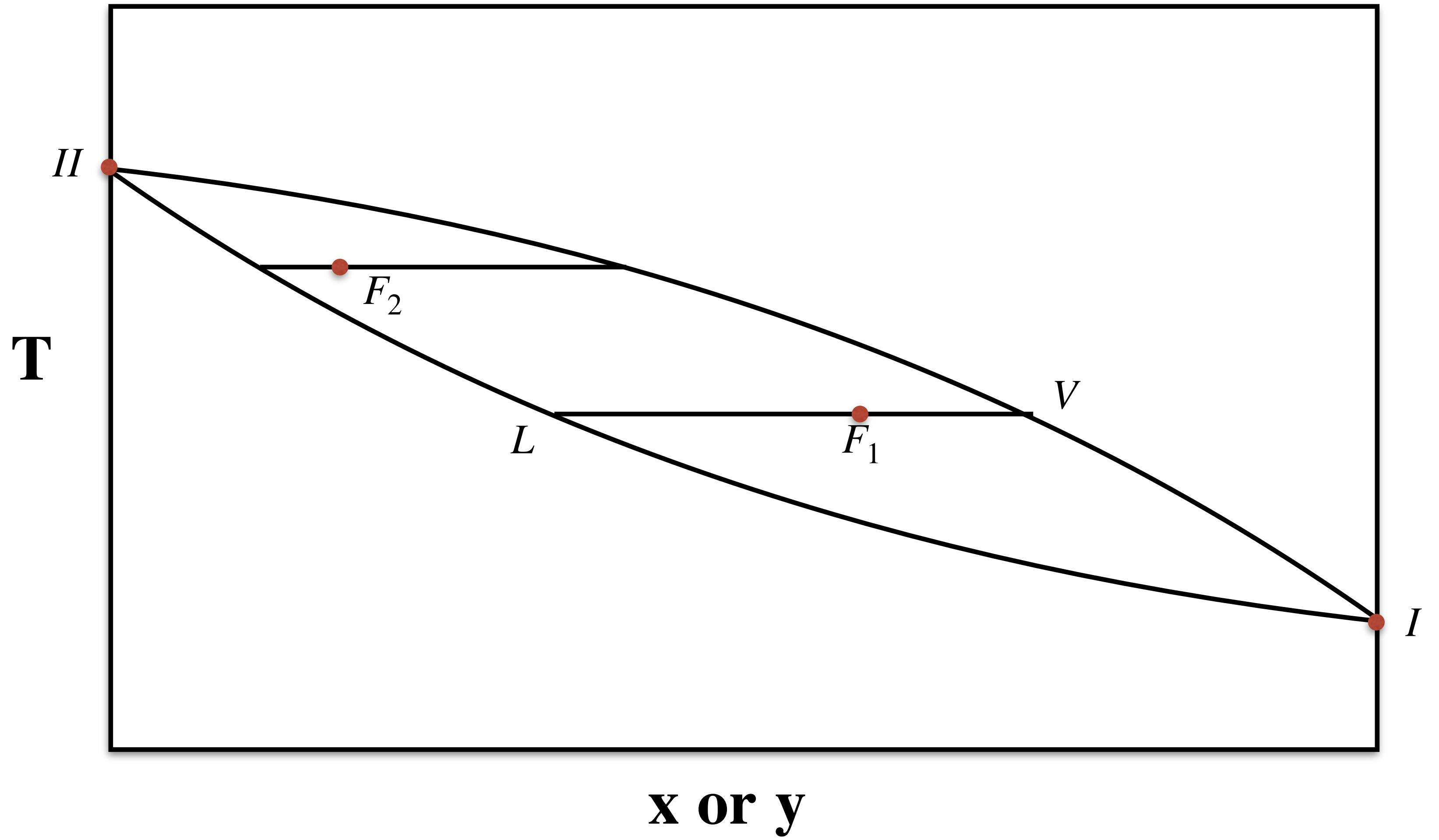


Graphical methods: T-x-y diagram

Study the scenario which is same as previous problem.

Which of the following is true

a. F1 and F2 will lead to same amount of saturated liquid
b. F1 and F2 will lead to same amount of saturated vapor
c. F2 will lead to more saturated liquid than F1
d. F2 will lead to more saturated vapor than F1



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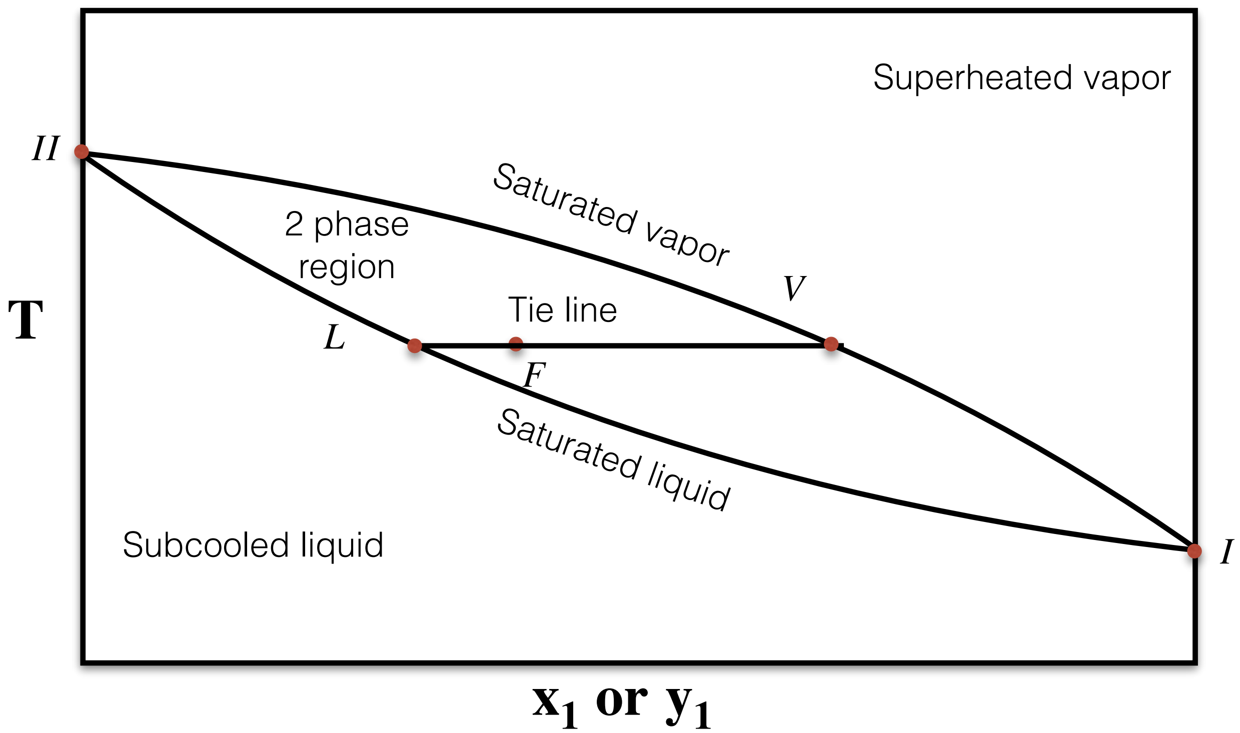
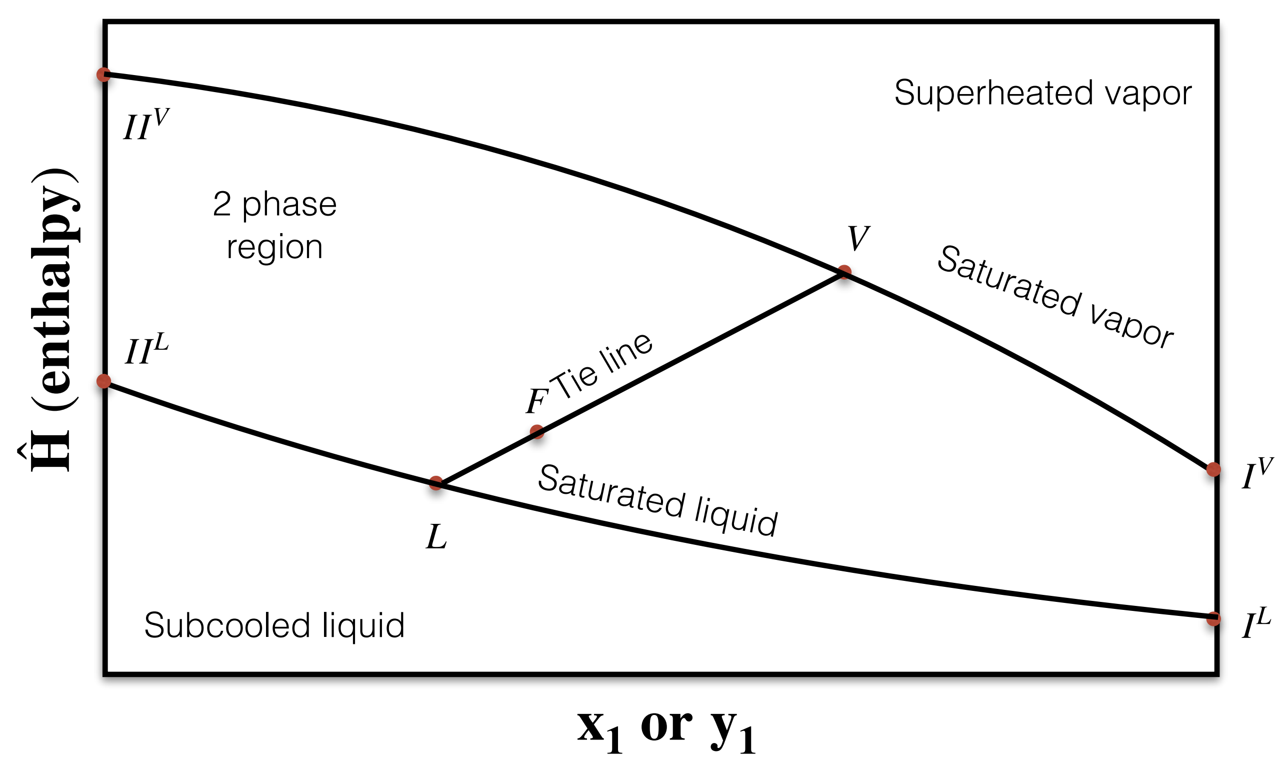
Identify the similarly and differences between T-x-y and H-x-y diagrams





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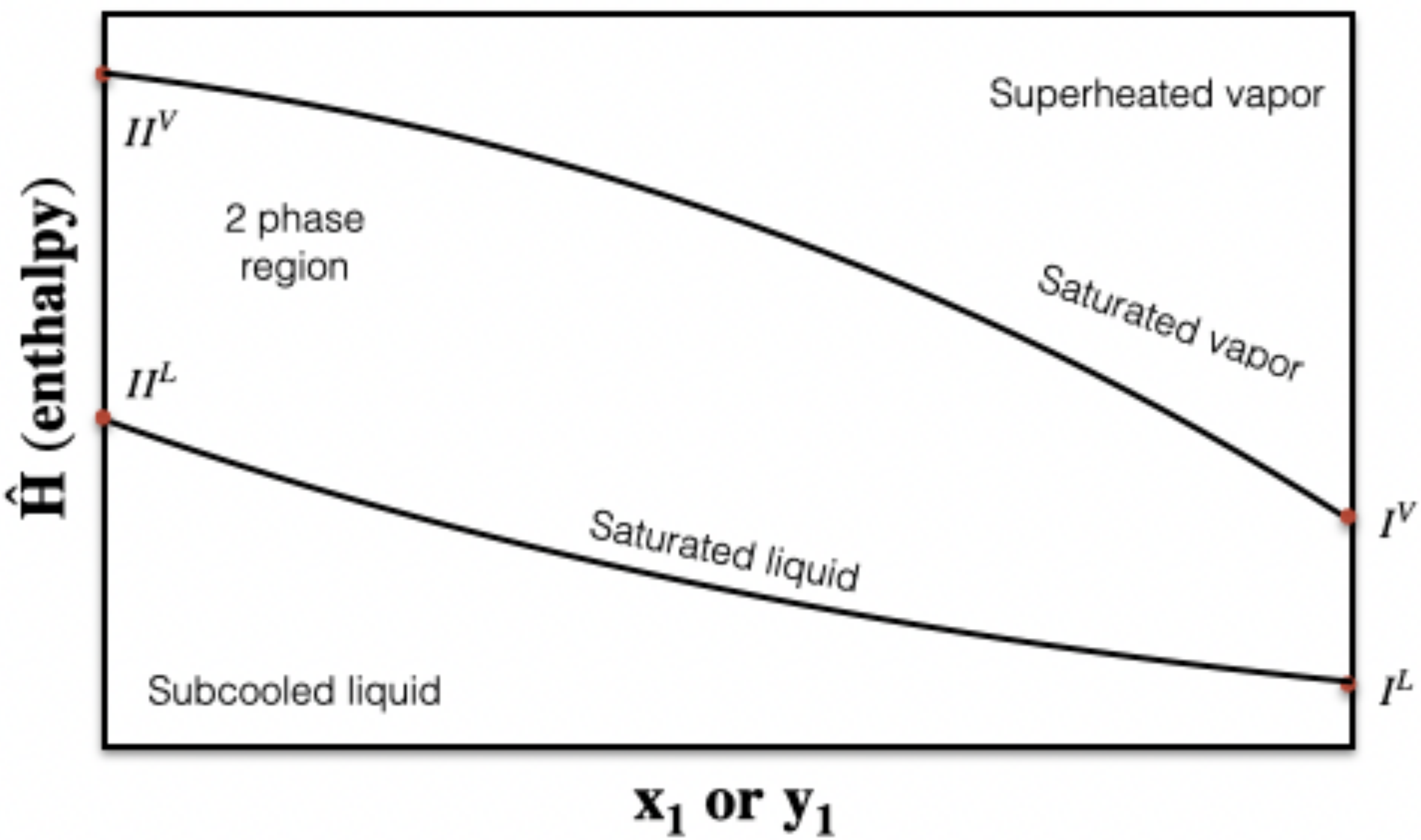
What would tie line look like at x1 = 0 or 1?



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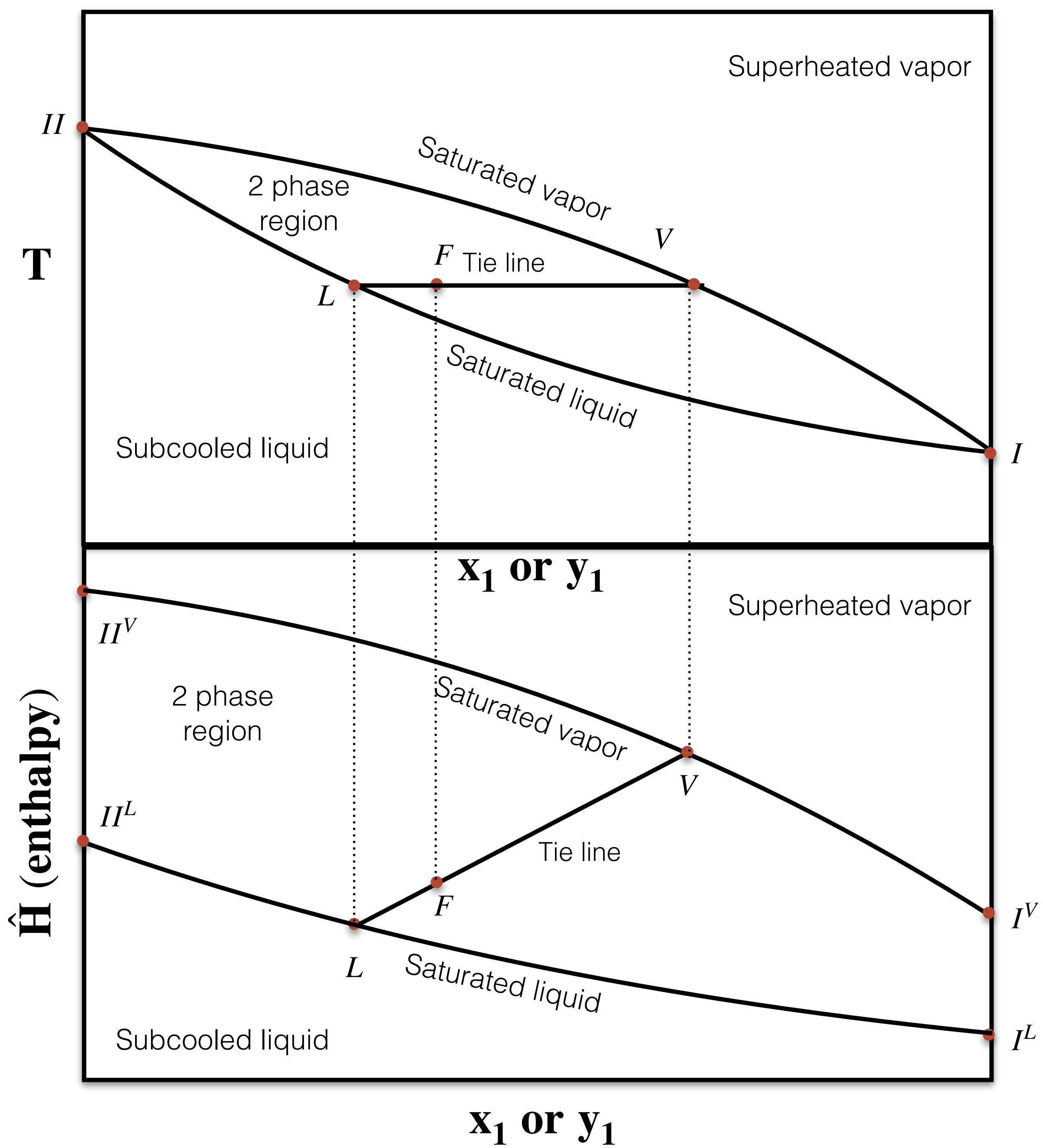
Composite T-x-y and H-x-y diagrams



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H-x-y diagrams that you find in literature

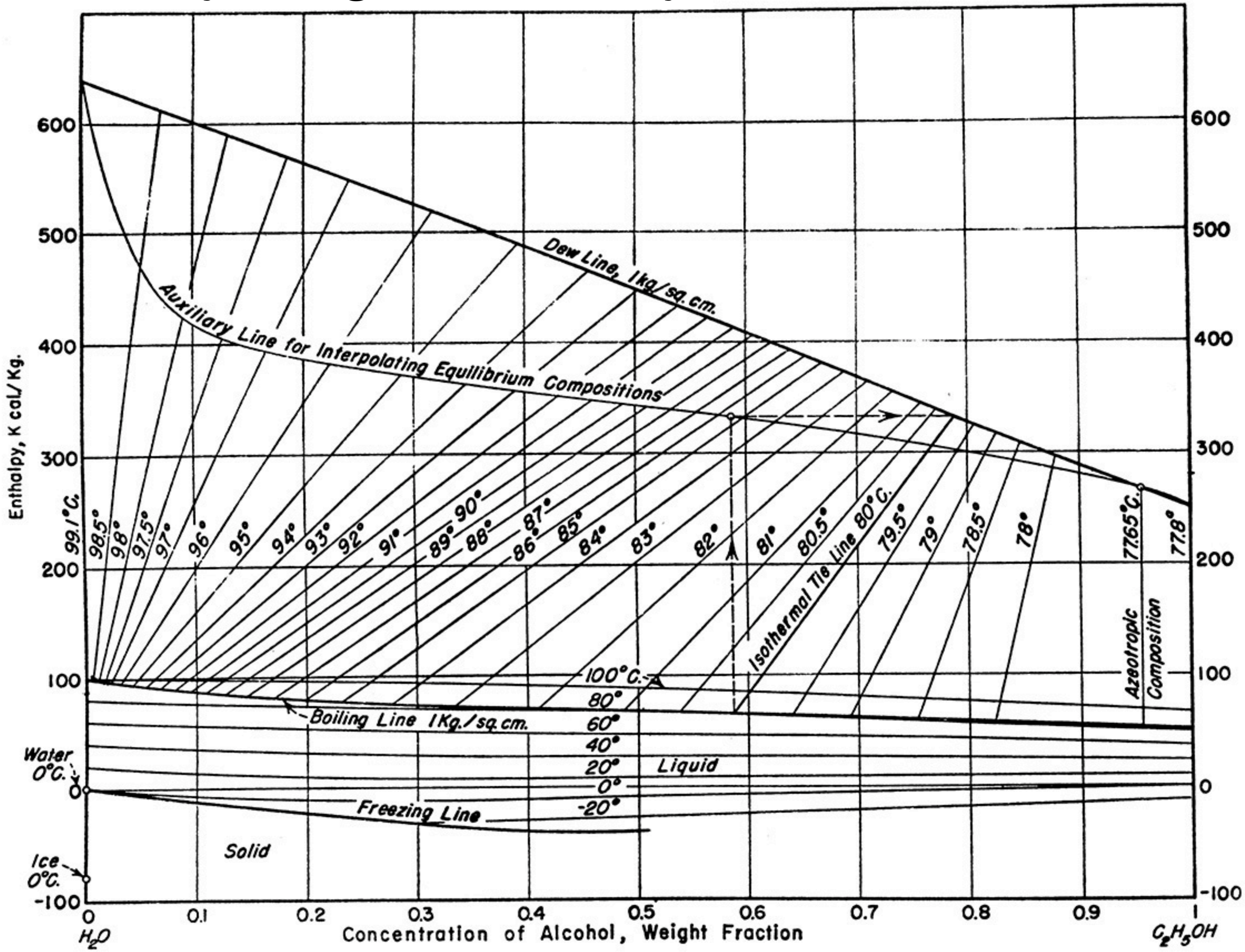

FIGURE 2-4. *Enthalpy-composition diagram for ethanol-water at a pressure of 1 kg/cm*^{2} *(F. Bošnjakovic,* Technische Thermodynamik, *T. Steinkopff, Leipzig, 1935)*

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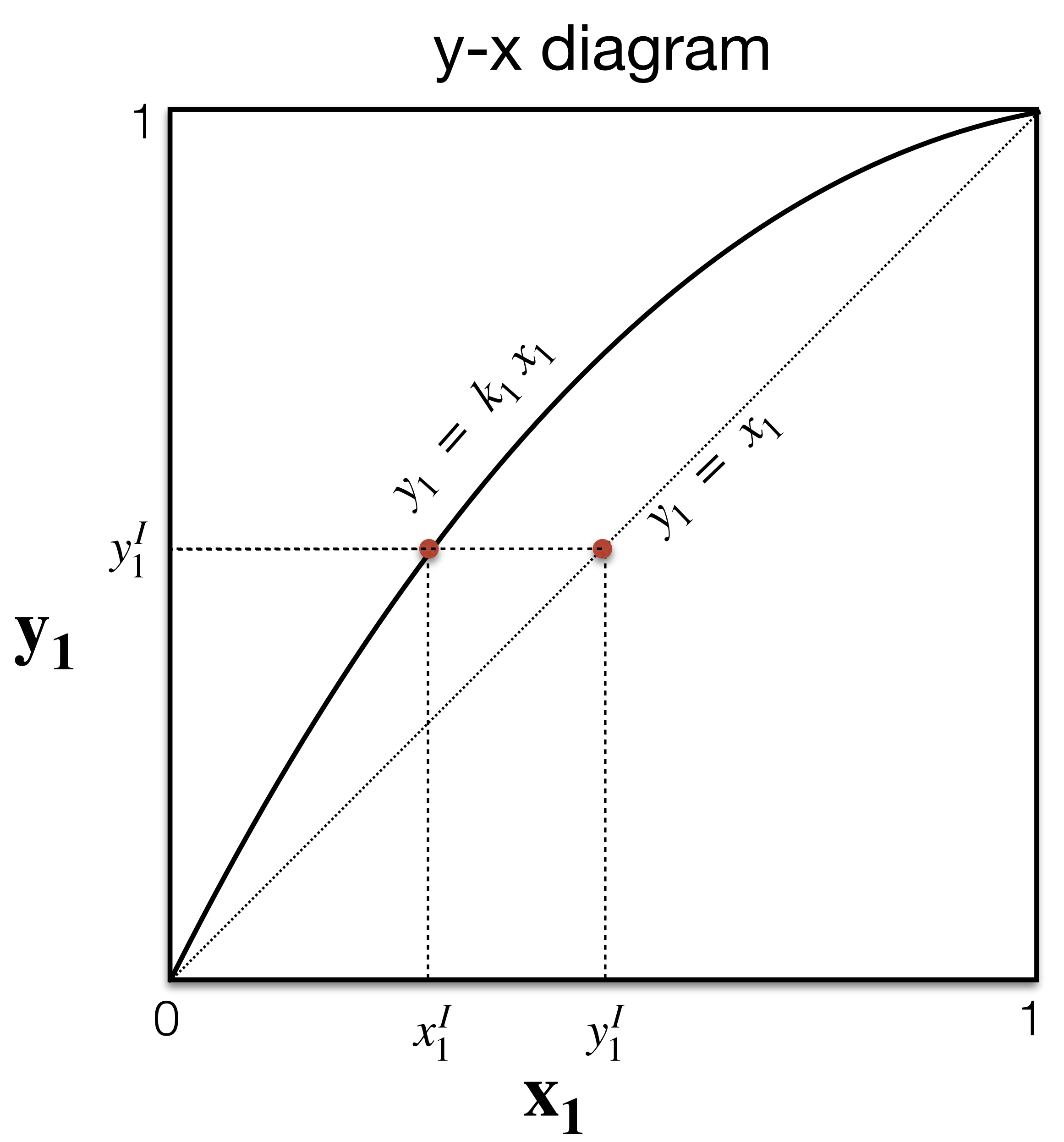
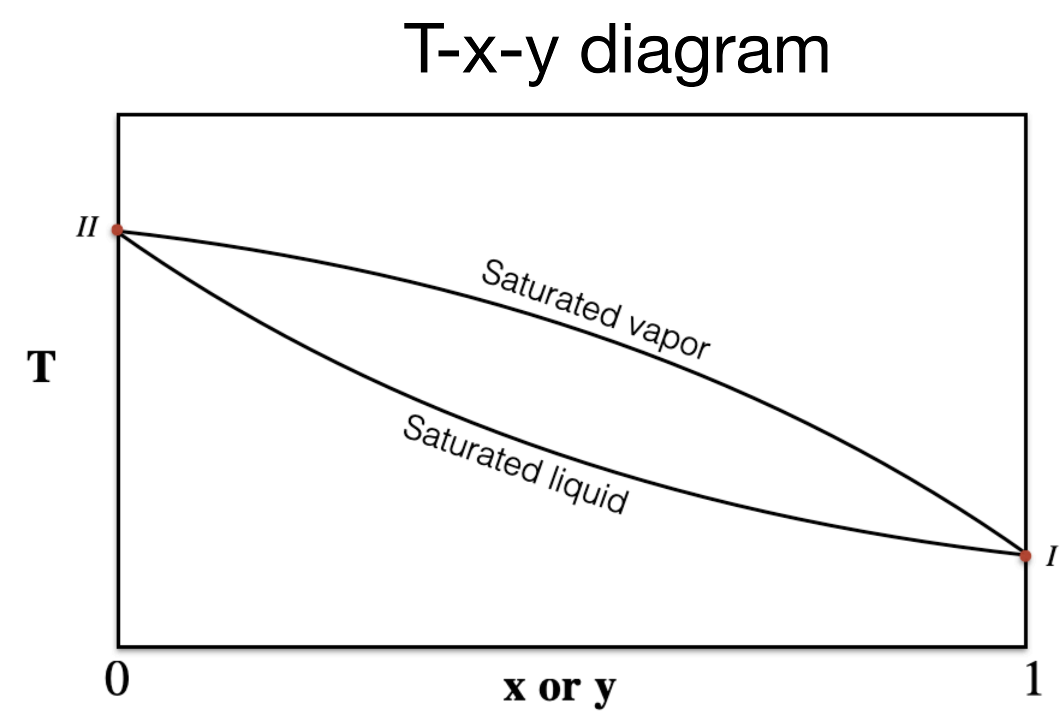
Graphical methods: y-x diagram

How would your read x1 as well as y1 in the x-axis similar to T-x-y plot?





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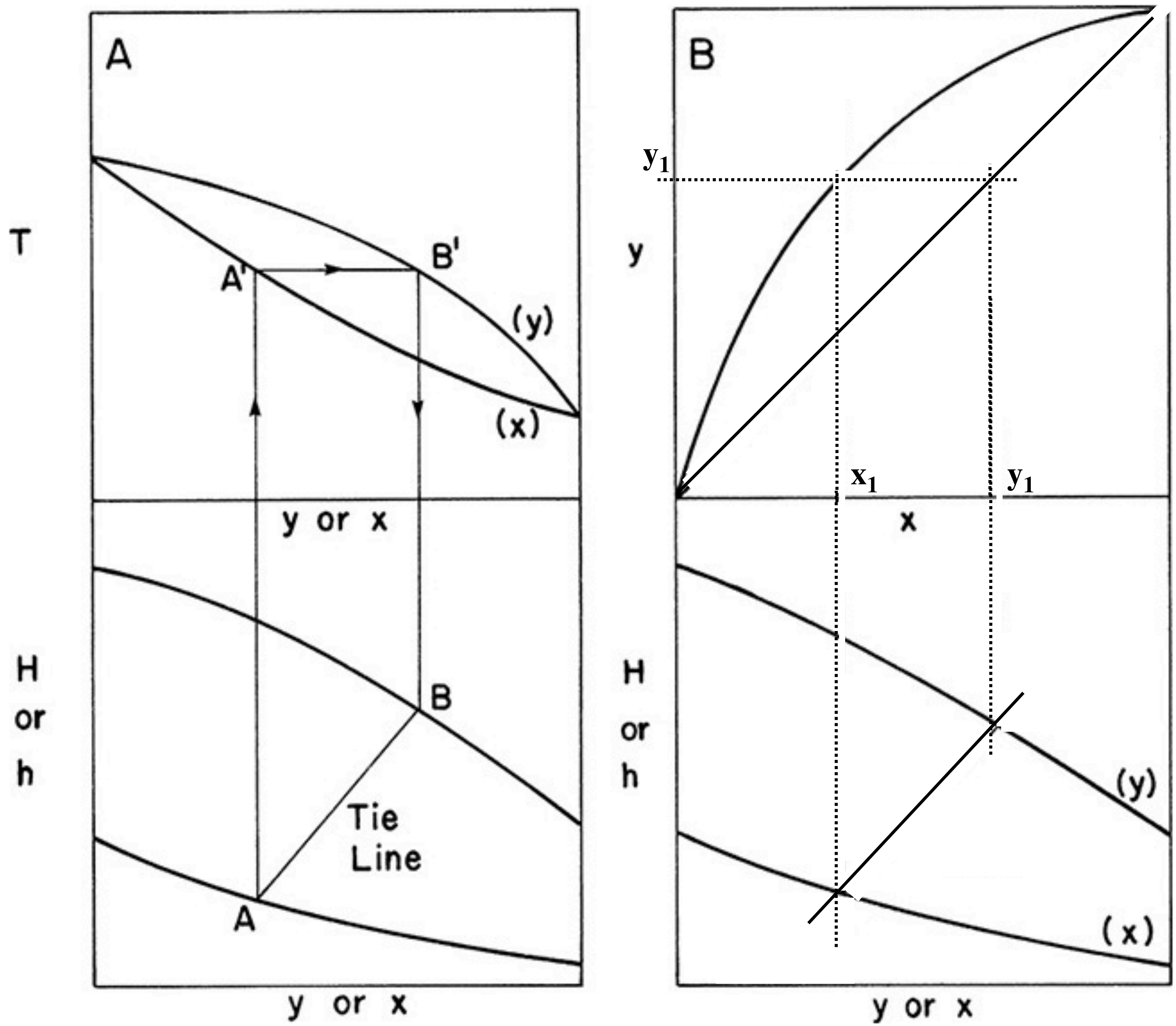
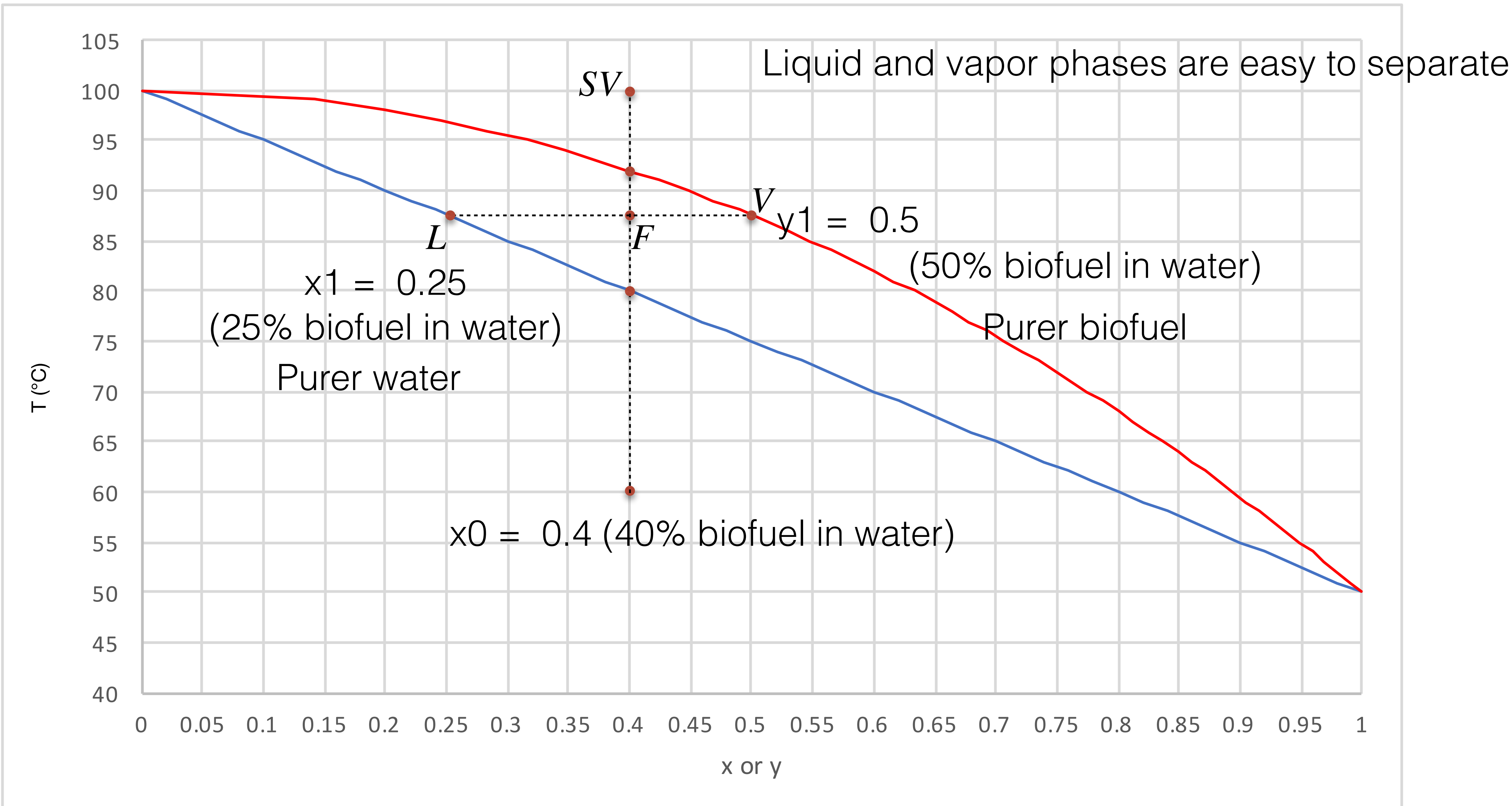
H-x-y diagrams and relating to T-x-y or xy diagram

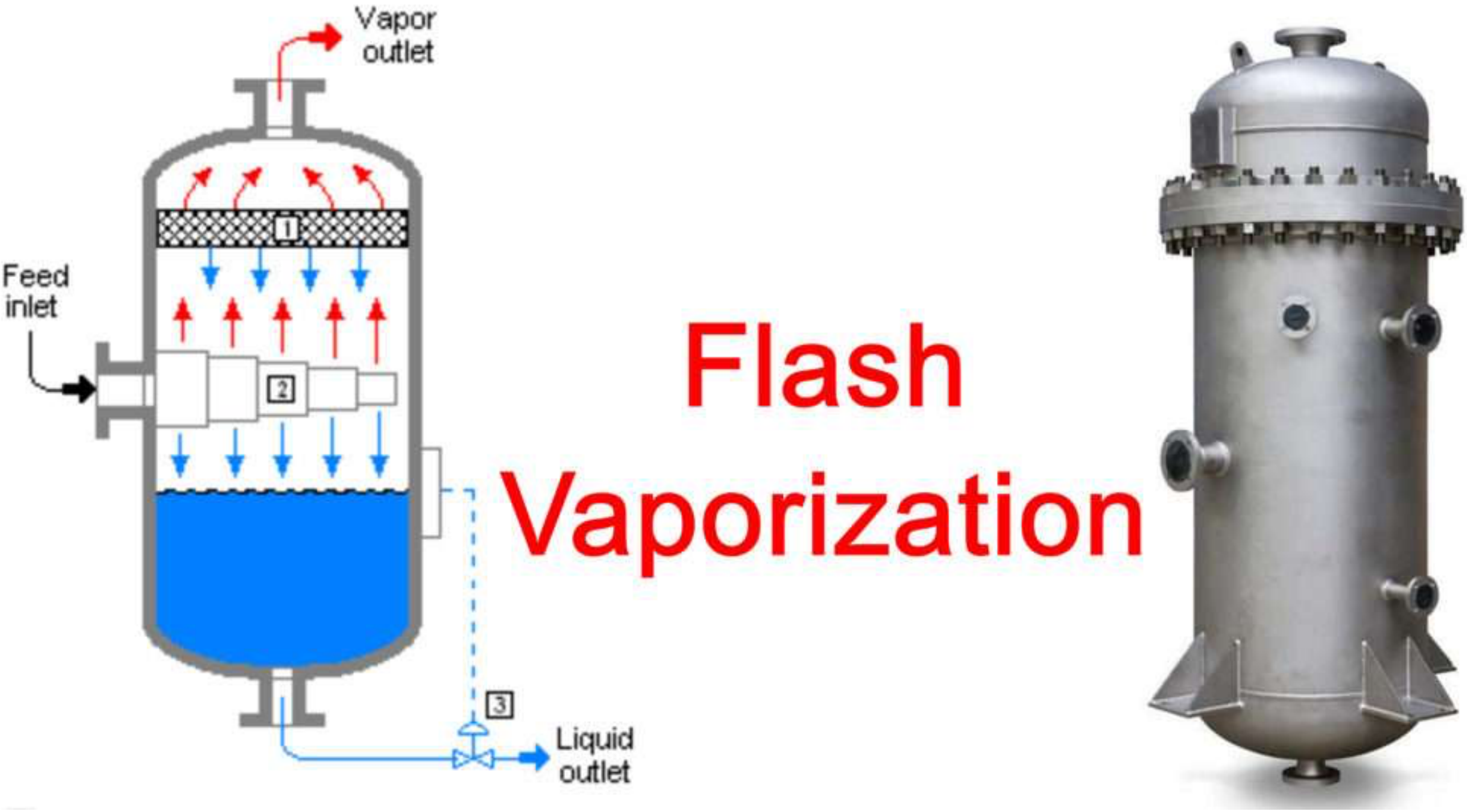


Using phase diagram to design separation

You are an engineer working in a biofuel fermentation plant. Immediately after fermentation and initial processing, you obtain 40% biofuel in water at 60 °C. How would you increase the concentration of biofuel?



The concept of flash drum: separation of liquid and vapor phases



Source: https://chemicalengineeringworld.com/flash-vaporization/#google_vignette

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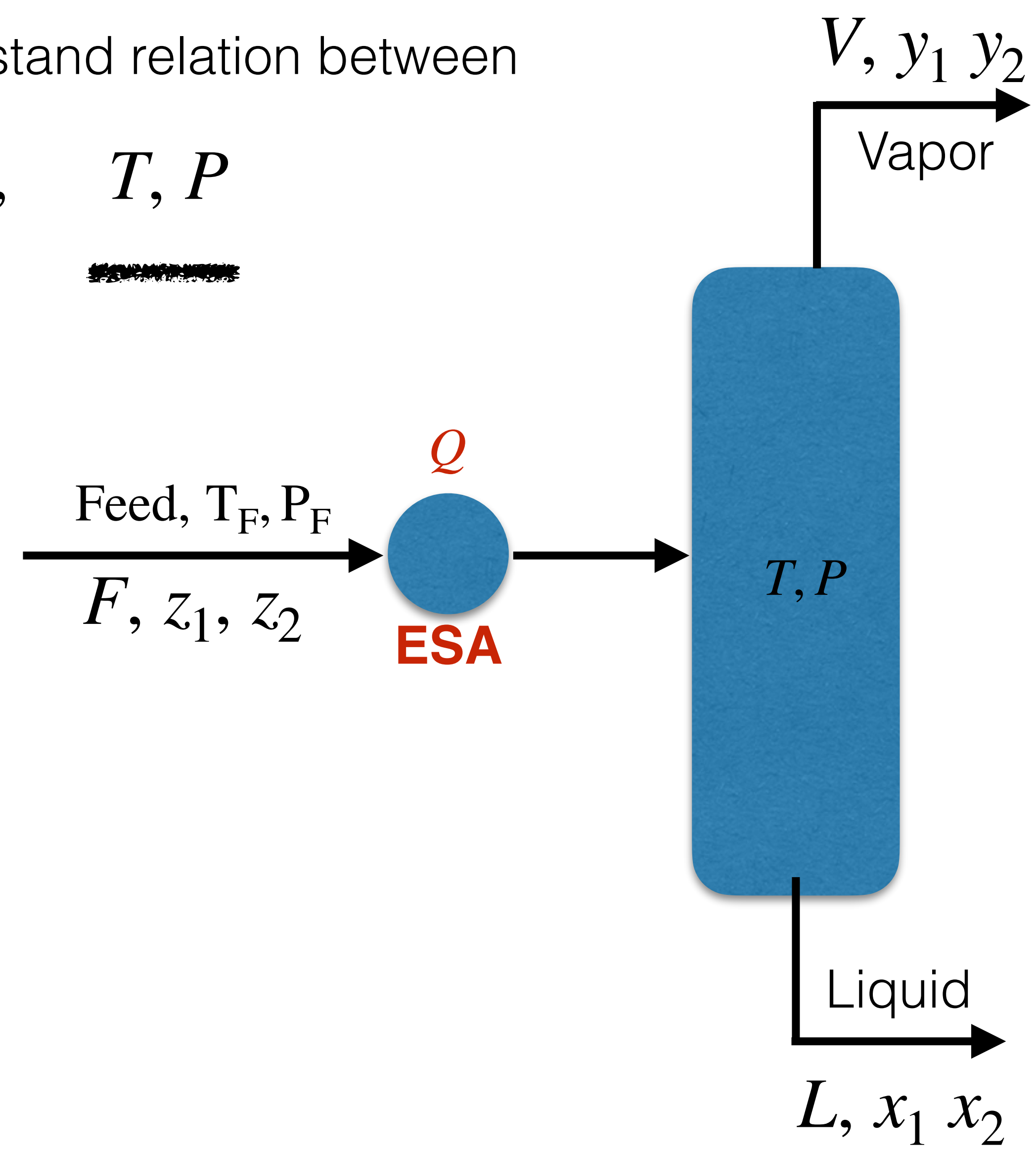
Mass and energy balance in flash drum

What independent equations can we write to understand relation between

$F, z_1, z_2, T_F, P_F, Q,$ $L, x_1, x_2,$ $V, y_1, y_2,$ T, P



Overall mass balance;

Mass balance for components;

Equilibrium relationship;

Overall energy balance;

Neglecting heat of mixing
Ideal solution

If heat is added Q will be positive, otherwise negative

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Flash drum based separation

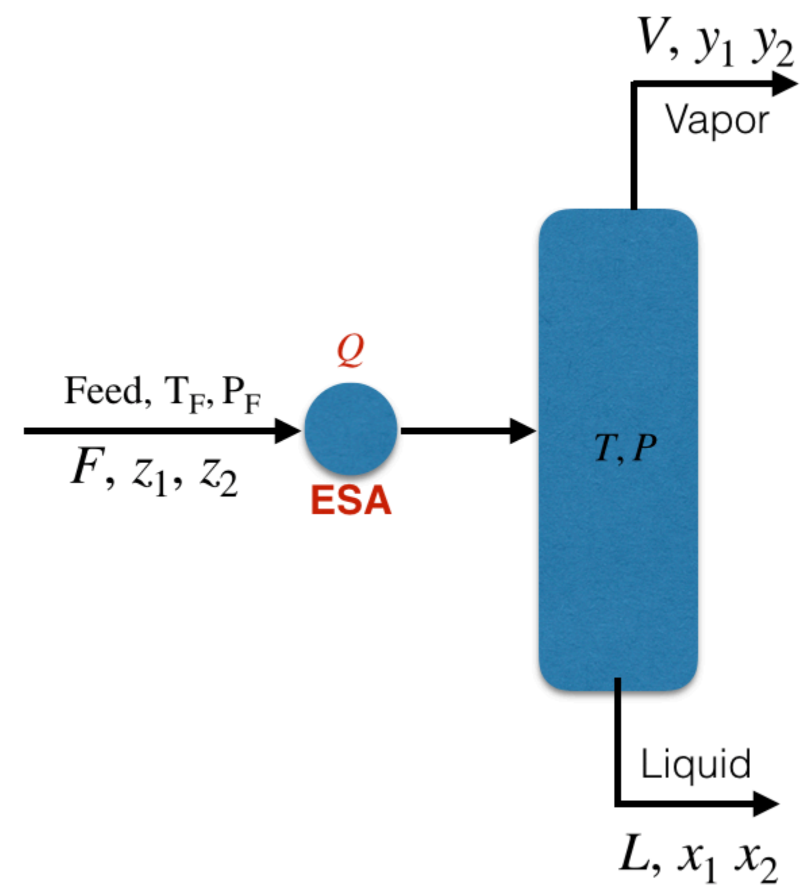
Mass balance

$$F = L + V$$

$$Fz_1 = Lx_1 + Vy_1$$

Equilibrium relationship

$$y_1 = k_1 x_1$$



$$\Rightarrow Fz_1 = Lx_1 + k_1 x_1 V = x_1(L + k_1 V)$$

$$\Rightarrow x_1 = \frac{Fz_1}{L + k_1 V}$$

$$\Rightarrow x_1 = \frac{z_1}{\frac{L}{F} + k_1 \frac{V}{F}}$$

$$\Rightarrow y_1 = k_1 x_1 = \frac{k_1 z_1}{\frac{L}{F} + k_1 \frac{V}{F}}$$

Energy balance

$$Fh_F(@T_F, P_F) + Q = Lh_L(@T, P) + Vh_v(@T, P)$$

$$Q = Lh_L + Vh_v - Fh_F$$

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Simplifying complex calculations

$y_1 = k_1 x_1$ $\quad k_1 = P_1^{sat} / P$ **Roult's law for ideal solution**

k_1 varies with temperature and can lead to complexity if y-x diagram is not available

Alternatively, for ideal solutions, we can use the concept of relative volatility, α_{12}

$$\alpha_{12} = \frac{k_1}{k_2} = \frac{y_1/x_1}{y_2/x_2} = \frac{P_1^{sat}}{P_2^{sat}},$$

and is often constant for ideal solution

$P y_1 = x_1 P_{1,sat}$ **Roult's law**

$$\Rightarrow \alpha_{12} = \frac{y_1 x_2}{y_2 x_1} = \frac{y_1(1 - x_1)}{(1 - y_1)x_1}$$

$$\Rightarrow \alpha_{12}(1 - y_1)x_1 = y_1(1 - x_1)$$

$$\Rightarrow y_1(1 - x_1 + \alpha_{12}x_1) = \alpha_{12}x_1$$

$$\Rightarrow x_1 = \frac{y_1}{\alpha_{12}(1 - y_1) + y_1}$$

$$\Rightarrow y_1 = \frac{\alpha_{12}x_1}{(1 - x_1 + \alpha_{12}x_1)}$$

Equilibrium relationships (thermodynamics)

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Simplifying complex calculations using constant relative volatility

$$y_1 = \frac{\alpha_{12}x_1}{(1 - x_1 + \alpha_{12}x_1)}$$

Equilibrium relationships (thermodynamics)

$$Lx_1 + Vy_1 = Fz_1 \qquad \Rightarrow y_1 = \frac{F}{V}z_1 - \frac{L}{V}x_1$$

Feed line (operator's decision)

Combining equilibrium and feed line, we get

$$\Rightarrow \frac{\alpha_{12}x_1}{(1 - x_1 + \alpha_{12}x_1)} = \frac{F}{V}z_1 - \frac{L}{V}x_1$$

$$\Rightarrow \frac{L}{V}(\alpha_{12} - 1)x_1^2 + \left(\frac{L}{V} - \frac{F}{V}(\alpha_{12} - 1)z_1 + \alpha_{12}\right)x_1 - \frac{F}{V}z_1 = 0$$

Leads to quadratic equation. Usually only 1 solution possible because $0 \leq x_1 \leq 1$

Example, $\alpha_{12} = 2$, L = V, $z_1 = 0.5$

Energy balance

$$Fh_F(@T_F, P_F) + Q = Lh_L(@T, P) + Vh_v(@T, P)$$

$$h_F = \Sigma z_i h_{iF}, \text{ where } h_{i,F} = C_{P,i,L}(T_F - T_{ref})$$ Liquid feed

$$h_{i,F} = h_{i,latent} + C_{P,i,V}(T_F - T_{ref})$$ Vapor feed

$$h_L = \Sigma x_i h_{iL}, \text{ where } h_{i,L} = C_{P,i,L}(T - T_{ref})$$

$$h_V = \Sigma y_i h_{iV}, \text{ where } h_{i,V} = h_{i,latent} + C_{P,i,V}(T - T_{ref})$$

A good choice of T_{ref} is T_F

If you choose so, $h_F = 0$ for liquid feed

Multicomponent flash column

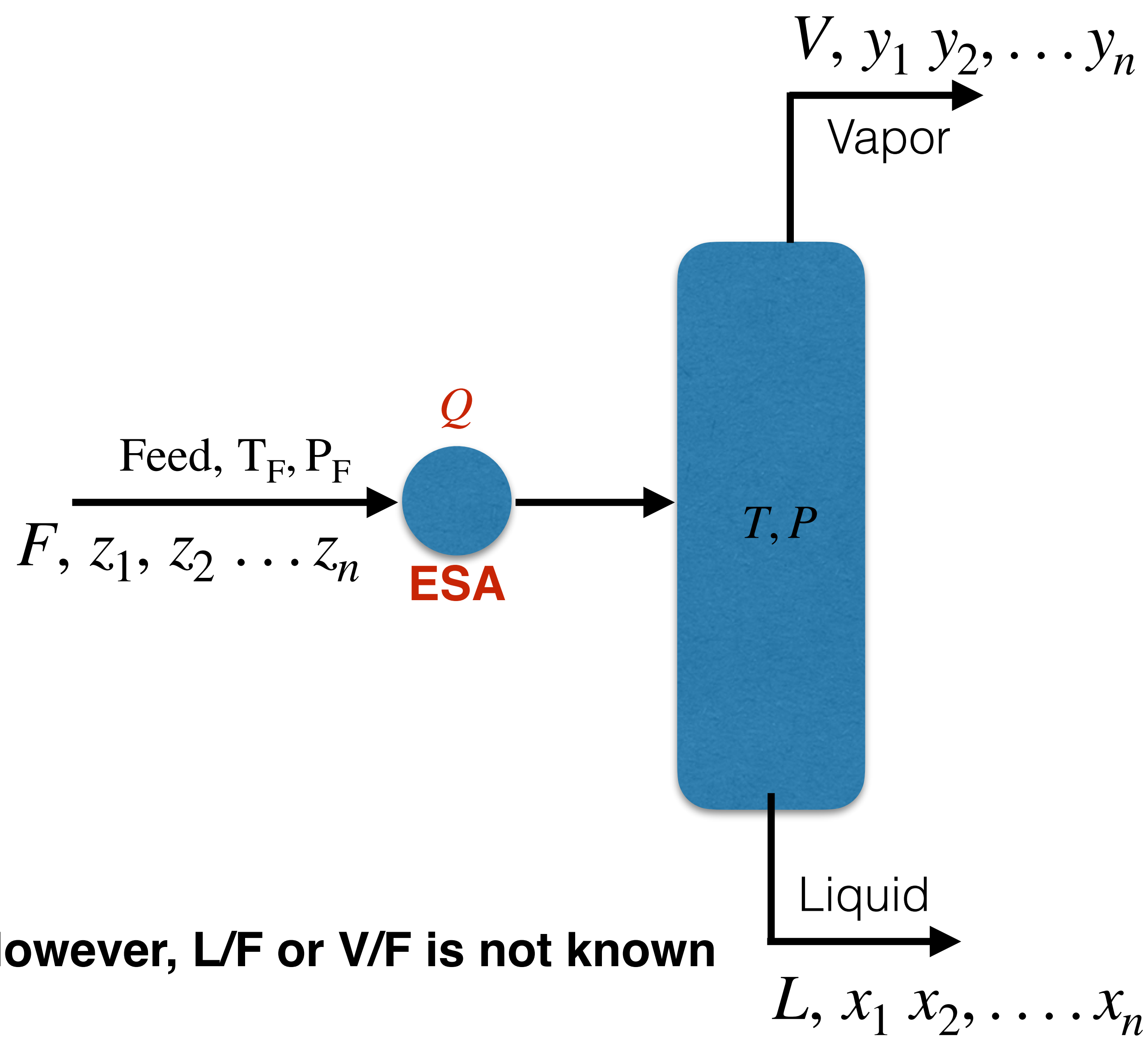
$$F = L + V$$

$$Fz_i = Lx_i + Vy_i \qquad y_i = k_i x_i$$

$$\Rightarrow Fz_i = Lx_i + k_i x_i V = x_i(L + k_i V)$$

$$\Rightarrow x_i = \frac{z_i}{\frac{L}{F} + k_i \frac{V}{F}}$$

$$\Rightarrow y_i = k_i x_i = \frac{k_i z_i}{\frac{L}{F} + k_i \frac{V}{F}}$$



Generally, P and T are known, therefor k_i is known. However, L/F or V/F is not known

$$\Sigma y_i - \Sigma x_i = 0 \qquad \Rightarrow \Sigma \frac{k_i z_i - z_i}{\frac{L}{F} + k_i \frac{V}{F}} = 0 \qquad \frac{L}{F} = 1 - \frac{V}{F}$$

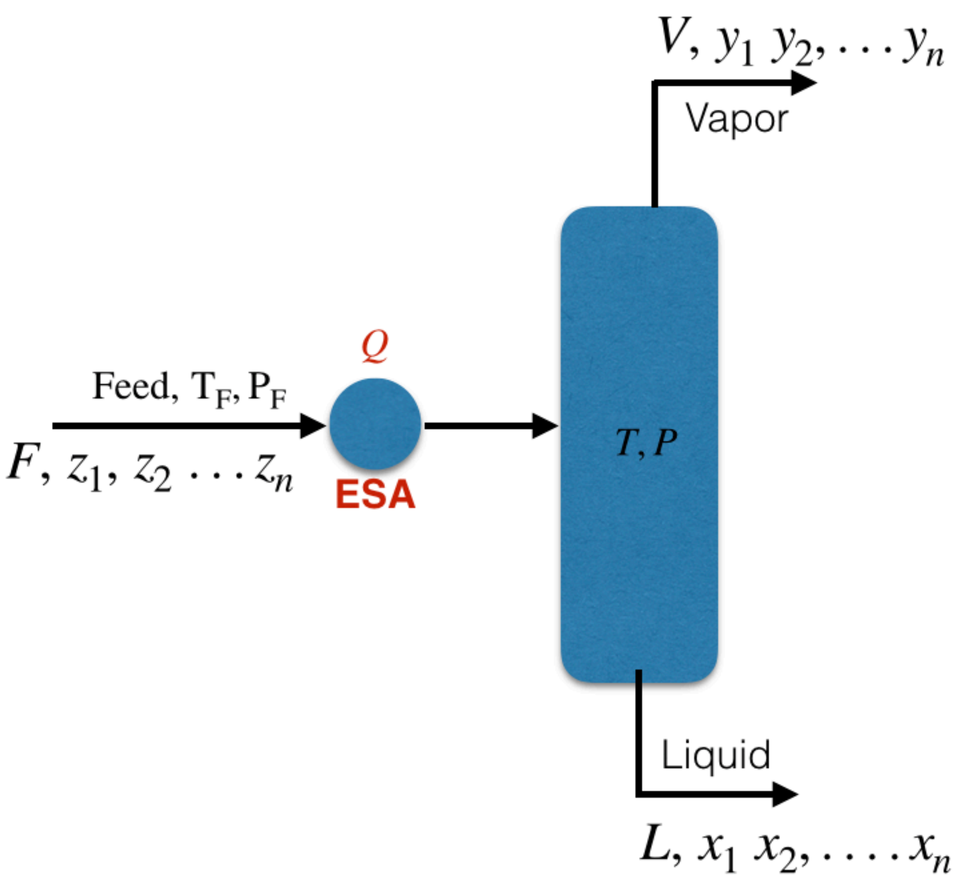
$$\Rightarrow \Sigma \frac{k_i z_i - z_i}{\frac{L}{F} + k_i \frac{V}{F}} = \Sigma \frac{z_i(k_i - 1)}{1 - \frac{V}{F} + k_i \frac{V}{F}} = \Sigma \frac{z_i(k_i - 1)}{1 + \frac{V}{F}(k_i - 1)} = 0$$

Rachford-Rice equation

Multicomponent flash column

$$\Sigma \frac{z_i(k_i - 1)}{1 + \frac{V}{F}(k_i - 1)} = 0$$

Rachford-Rice equation



Can be solved numerically using iterative techniques.

Newton-Raphson conversion technique can be used.

$$G = F(r) = 0$$

$$r_{n+1} = r_n - \frac{F(r_n)}{F'(r_n)}$$

$$\left(\frac{V}{F}\right)_{n+1} = \left(\frac{V}{F}\right)_n + \frac{\Sigma \frac{z_i(k_i - 1)}{1+\left(\frac{V}{F}\right)_n(k_i - 1)}}{\Sigma \frac{z_i(k_i - 1)^2}{\left(1+\left(\frac{V}{F}\right)_n(k_i - 1)\right)^2}}$$

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