

Raoult's law Derivation

We know that for ideal gas system

$$dG_i^g = v_i^g dp - s_i^g dT$$

at const. Temp.

$$dG_i^g = v_i^g dp = \frac{RT}{p} dp$$

$$\Rightarrow G_i^g = RT \ln p + \Gamma(T) \text{ --- constant --- (1)}$$

Similarly for ideal liquid solⁿ.

$$G_i^l = RT \ln f_i^l + \Gamma(T) \text{ --- const --- (2)}$$

① - ② and vapour phase in ideal gas state

$$G_i^v - G_i^l = RT \ln \left(\frac{f_i^v}{f_i^l} \right)$$

at equilibrium. $G_i^v - G_i^l = 0$ or, $G_i^v = G_i^l$

so, $f_i^v = f_i^l = f_i^{\text{sat}}$ (saturated pressure)

$\phi_i^{\text{sat}} = \frac{f_i^{\text{sat}}}{p_i^{\text{sat}}}$ (fugacity coefficient)

\therefore at equilibrium, $\phi_i^{\text{sat}} = \phi_i^{\text{sat}}$

so, $f_i^{\text{sat}} = p_i^{\text{sat}} \cdot \phi_i^{\text{sat}}$

and also $\phi_i^v = \phi_i^l = \phi_i^{\text{sat}}$

Again we know that

$$G_i - G_i^{\text{sat}} = \int_{p_i^{\text{sat}}}^p v_i^l dp \text{ --- (3)}$$

$$G_i - G_i^{\text{sat}} = RT \ln \frac{f_i}{f_i^{\text{sat}}} \text{ --- (4)}$$

Compare eqⁿ (3) & (4)

$$\ln \frac{f_i}{f_i^{\text{sat}}} = \frac{1}{RT} \int_{p_i^{\text{sat}}}^p v_i^l dp$$

$$\frac{f_i}{f_i^{\text{sat}}} = \exp \left(\frac{1}{RT} \times v_i^l (p - p_i^{\text{sat}}) \right)$$

$$\Rightarrow f_i = f_i^{\text{sat}} \exp \left(\frac{v_i^l (p - p_i^{\text{sat}})}{RT} \right)$$

$$\Rightarrow f_i = \phi_i^{\text{sat}} p_i^{\text{sat}} \exp \left[\frac{v_i^l (p - p_i^{\text{sat}})}{RT} \right]$$

$$\text{So, } f_i^l = \phi_i^{\text{sat}} p_i^{\text{sat}} \exp \left[\frac{v_i^l (p - p_i^{\text{sat}})}{RT} \right]$$

at low and moderate pressure,

$$v_i^l \left(\frac{p - p_i^{\text{sat}}}{RT} \right) \rightarrow 0, \exp^0 \approx 1$$

$$\therefore f_i^l = \phi_i^{\text{sat}} \cdot p_i^{\text{sat}}$$

$$\phi_i = \frac{\phi_i^v}{\phi_i^{\text{sat}}}$$

Phase Equilibrium for Ideal Solution

$$\gamma_i = \frac{\hat{f}_i}{\hat{f}_i^{\text{id}}} = \frac{\hat{f}_i}{f_i \cdot x_i}$$

For liquid system

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

For gas system

$$\hat{f}_i^v = y_i \Phi_i^v P$$

Now vapour phase is assume to be ideal gas state and liquid phase is an ideal solution

$$\gamma_i = \Phi_i = 1$$

And if the system is in equilibrium and the pressure of the liquid system will be saturated pressure (P_i^{sat})

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

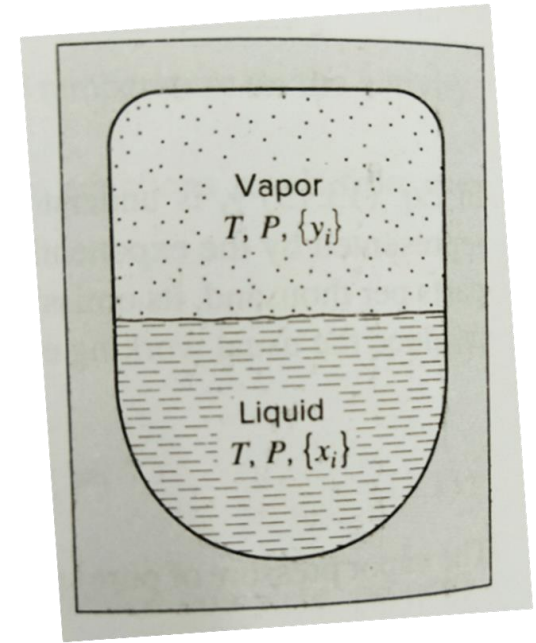
$$x_i \gamma_i^l f_i^l = y_i \Phi_i^v P$$

$$x_i \gamma_i^l \Phi_i^{\text{sat}} P_i^{\text{sat}} = y_i \Phi_i^v P$$

$$x_i \gamma_i^l P_i^{\text{sat}} = y_i \frac{\Phi_i^v}{\Phi_i^{\text{sat}}} P$$

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

$$\hat{f}_i^{\text{id}} = f_i \cdot x_i \quad \text{Lewis and Randall Rule}$$



Limitation:

- Ideal solution
- Low to moderate pressure

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

Modified Raoult's Law

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

..... Raoult's law

Vapour Liquid Equilibrium (VLE)

- Vapour pressure depends on the temperature and quantity of liquid and vapour

Vapour pressure can be calculated from Clausius-Clapeyron equation or Antoine equation

Clausius-Clapeyron equation:

$$\ln\left(\frac{p^v}{p_1^v}\right) = \frac{\lambda}{R} \left(\frac{1}{T_1} - \frac{1}{T} \right)$$

λ = molar latent heat

p^v, p_1^v = vapour pressure in pascal

Antoine equation:

$$\ln p^v = A - \frac{B}{T+C}$$

Parameterisation for T in °C and P in mmHg

	A	B	C	T min. (°C)	T max. (°C)
Water	8.07131	1730.63	233.426	1	100
Water	8.14019	1810.94	244.485	99	374
Ethanol	8.20417	1642.89	230.300	-57	80
Ethanol	7.68117	1332.04	199.200	77	243

T-x-y diagram at Constant Pressure:

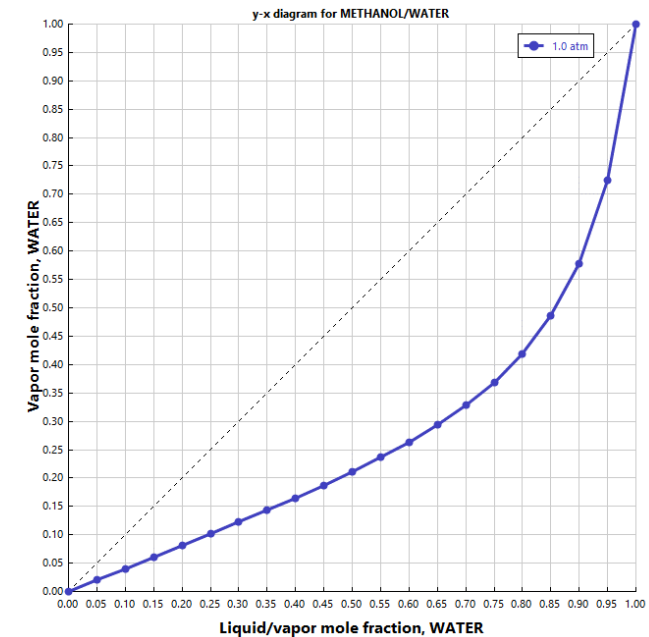
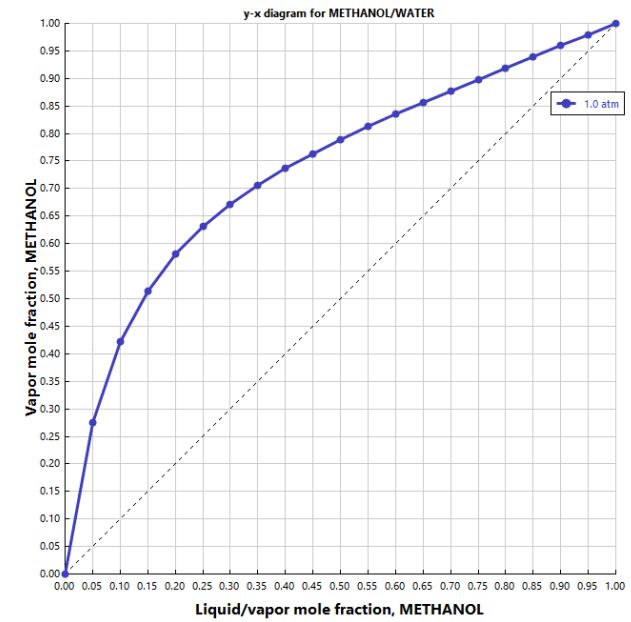
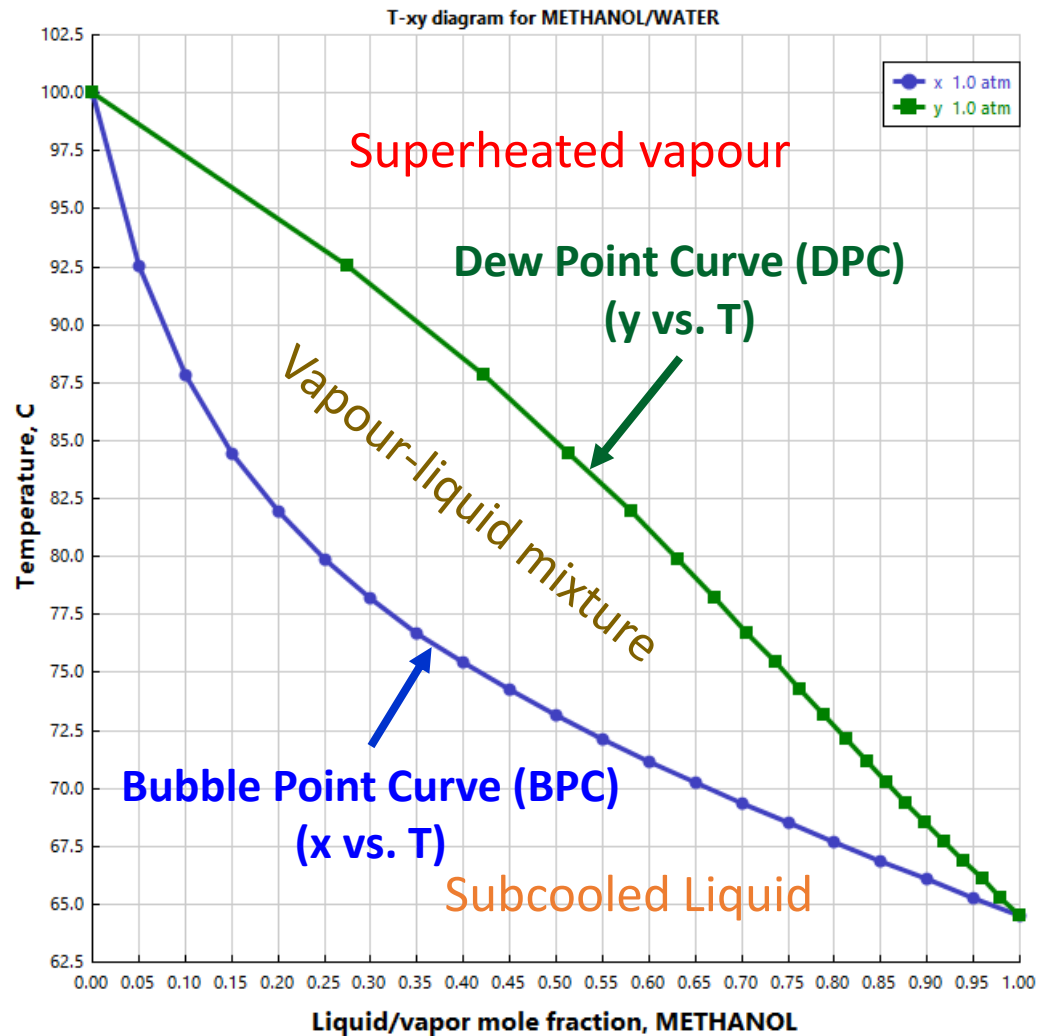
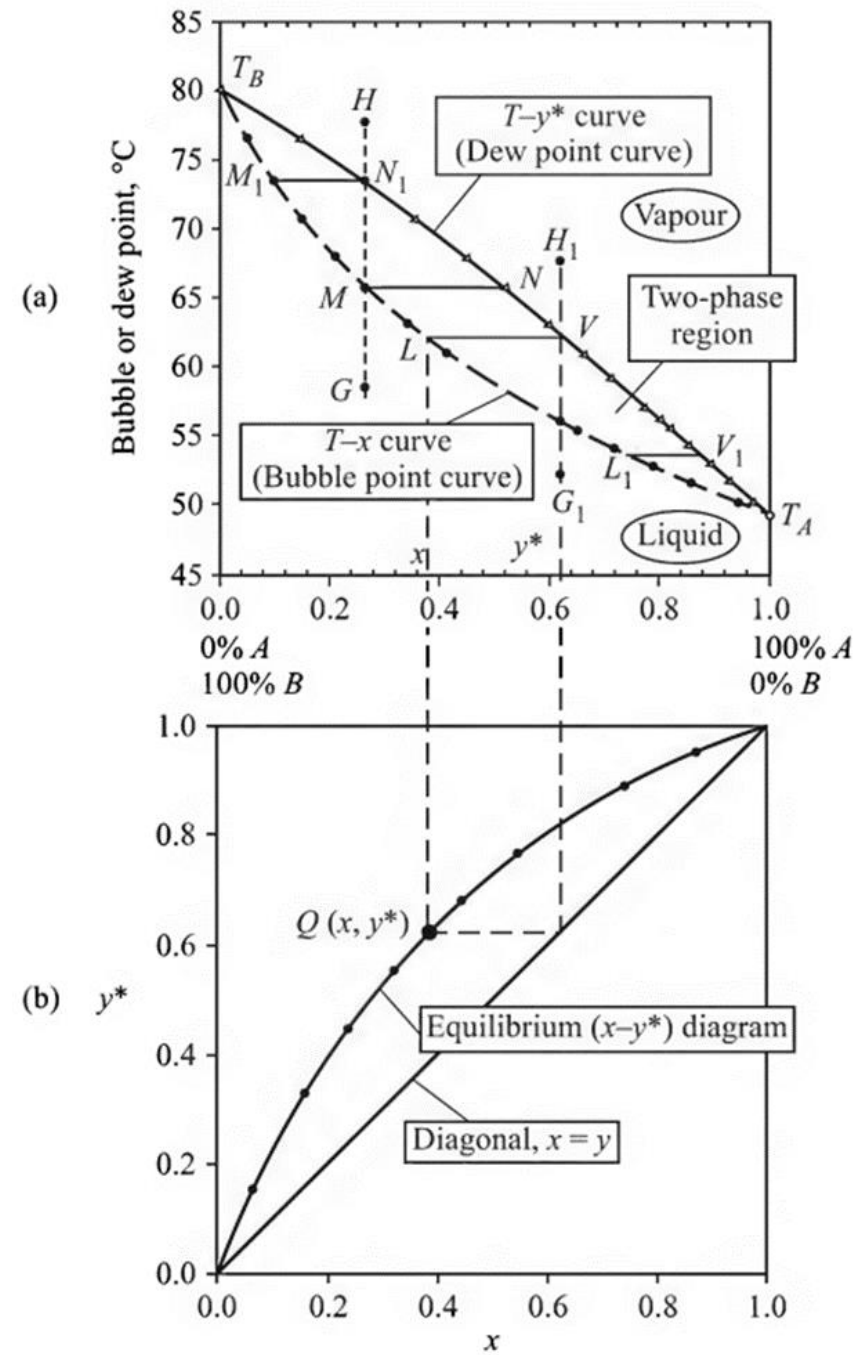


Fig. Constant pressure vapor liquid equilibria

Constant pressure Binary T-x-y and x-y diagram



➤ Vapor-liquid equilibria at increased pressures

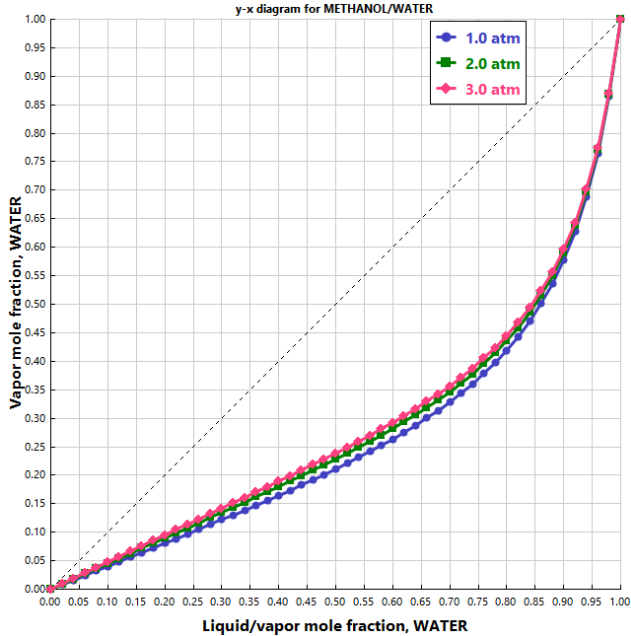
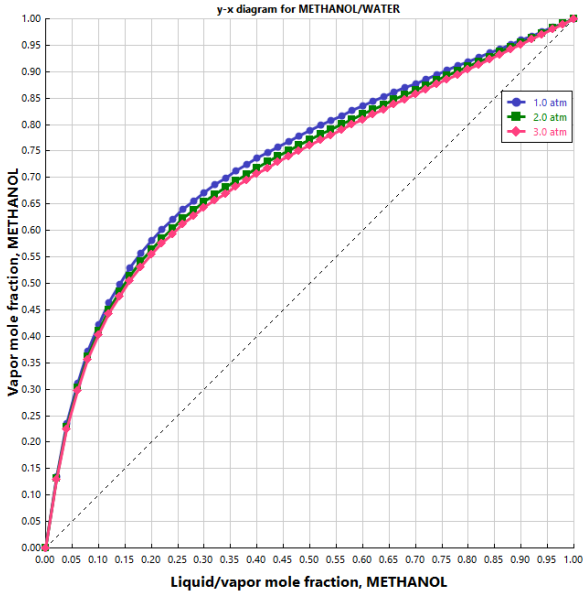
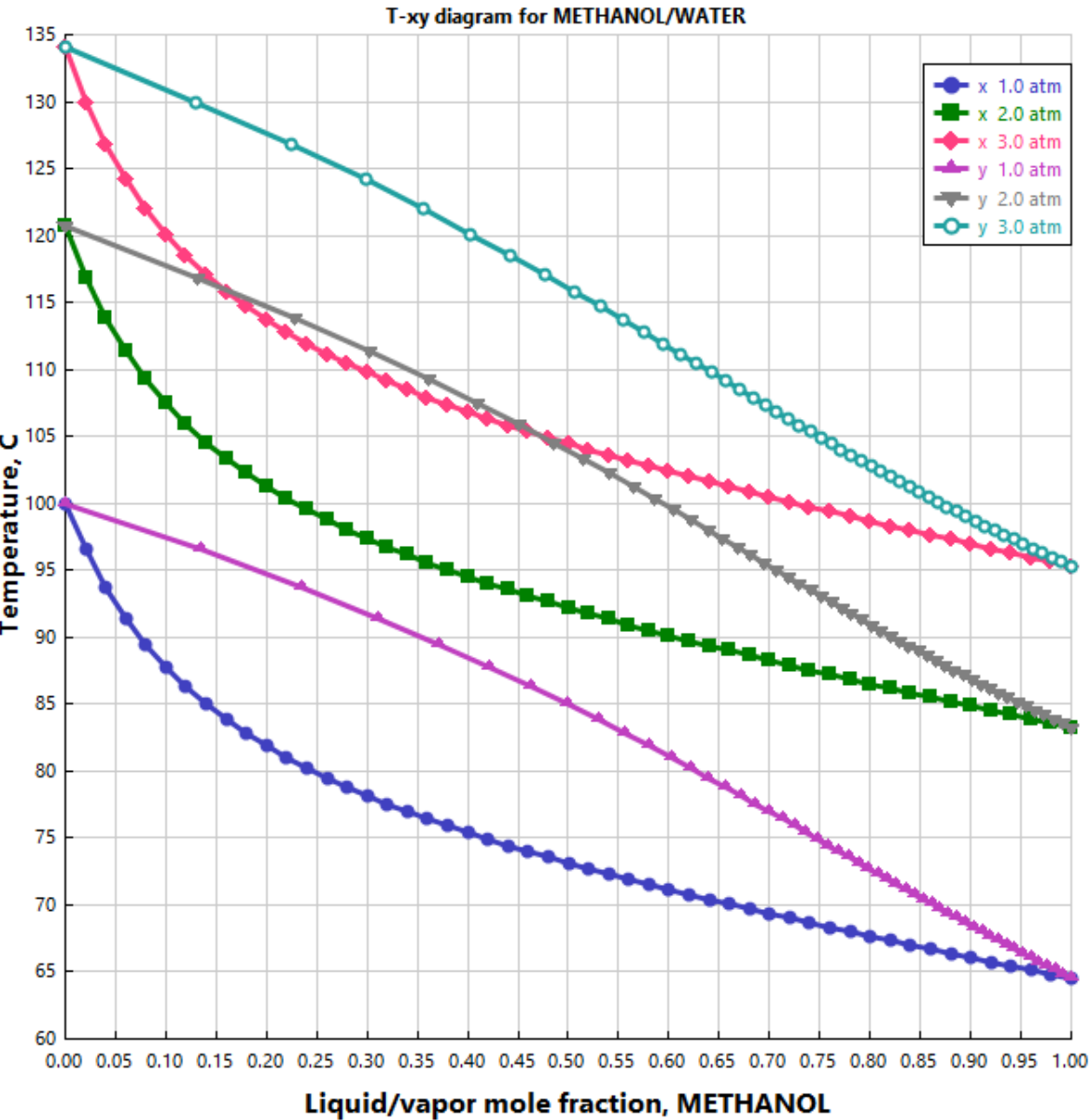


Fig. Vapor liquid equilibria at increased pressures

Relative volatility (α)

- This is the ratio of the concentration ratio of A and B in one phase to that in the other and is a measure of the separability.

$$\alpha = \frac{\frac{y^*}{(1-y^*)}}{\frac{x}{(1-x)}} = \frac{y^* (1-x)}{x (1-y^*)} \quad (1)$$

$$y^* = \frac{\alpha x}{1 + (\alpha - 1)x}$$

x – mole fraction of the more volatile substance in the liquid

y^* – mole fraction of the more volatile substance in the vapor

- The value of α will ordinarily change as x varies from 0 to 1.
- If $y^* = x$ (except at $x = 0$ or 1), $\alpha=1$ and no separation is possible.
- The larger the value of α above unity, the greater the degree of separability.

➤ P-x-y diagram for methanol-water

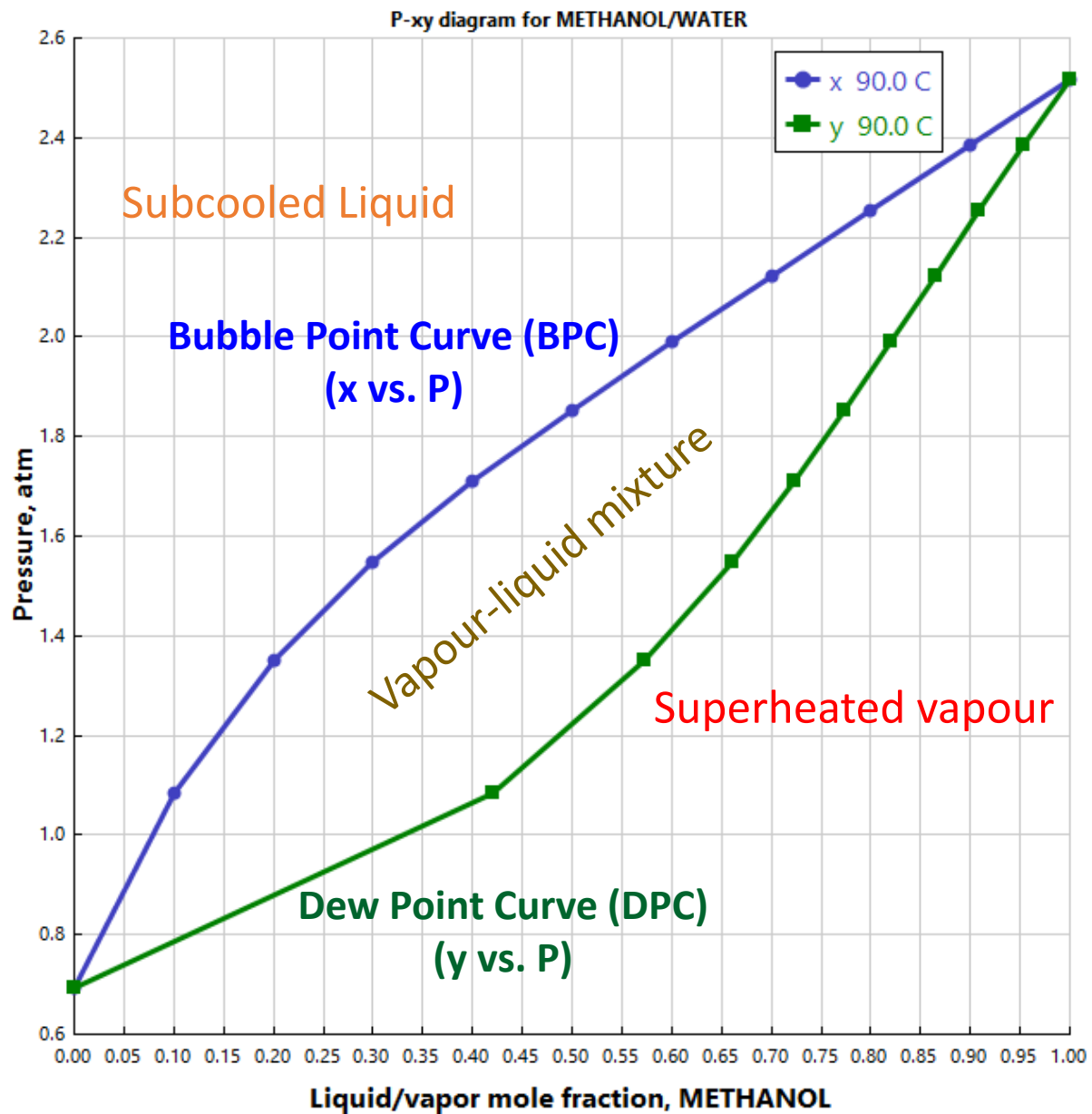
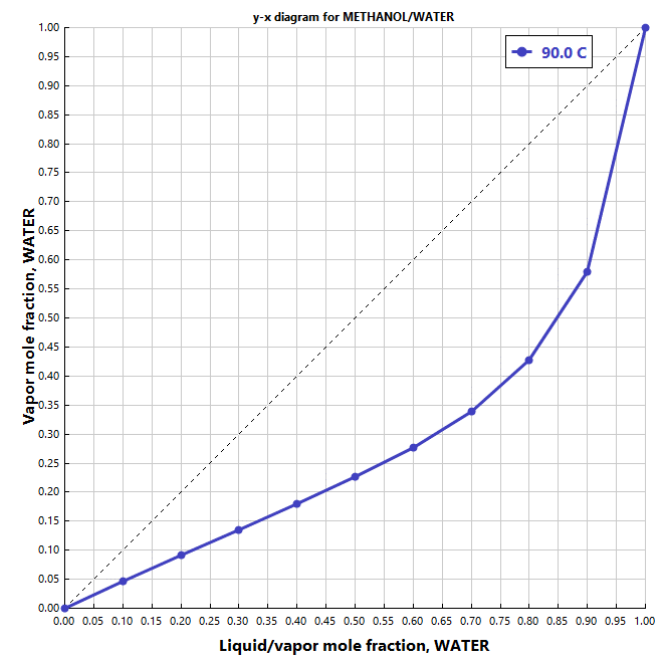
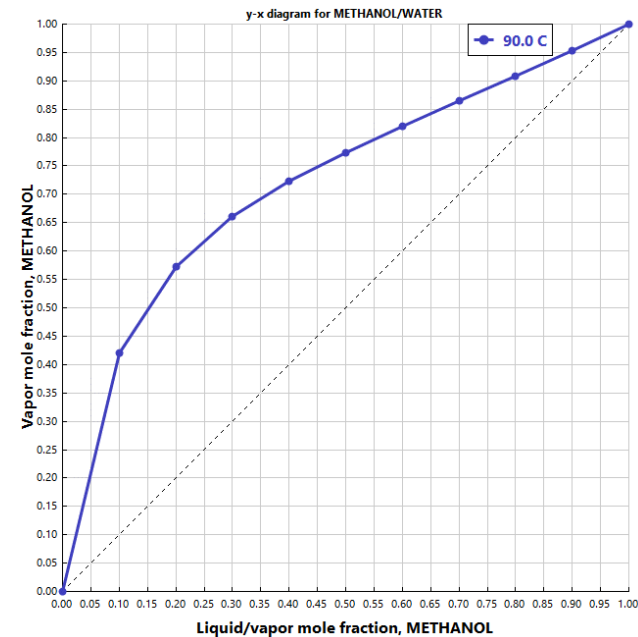


Fig. Constant temperature vapor liquid equilibria



Raoult's Law: (Ideal gas-liquid system)

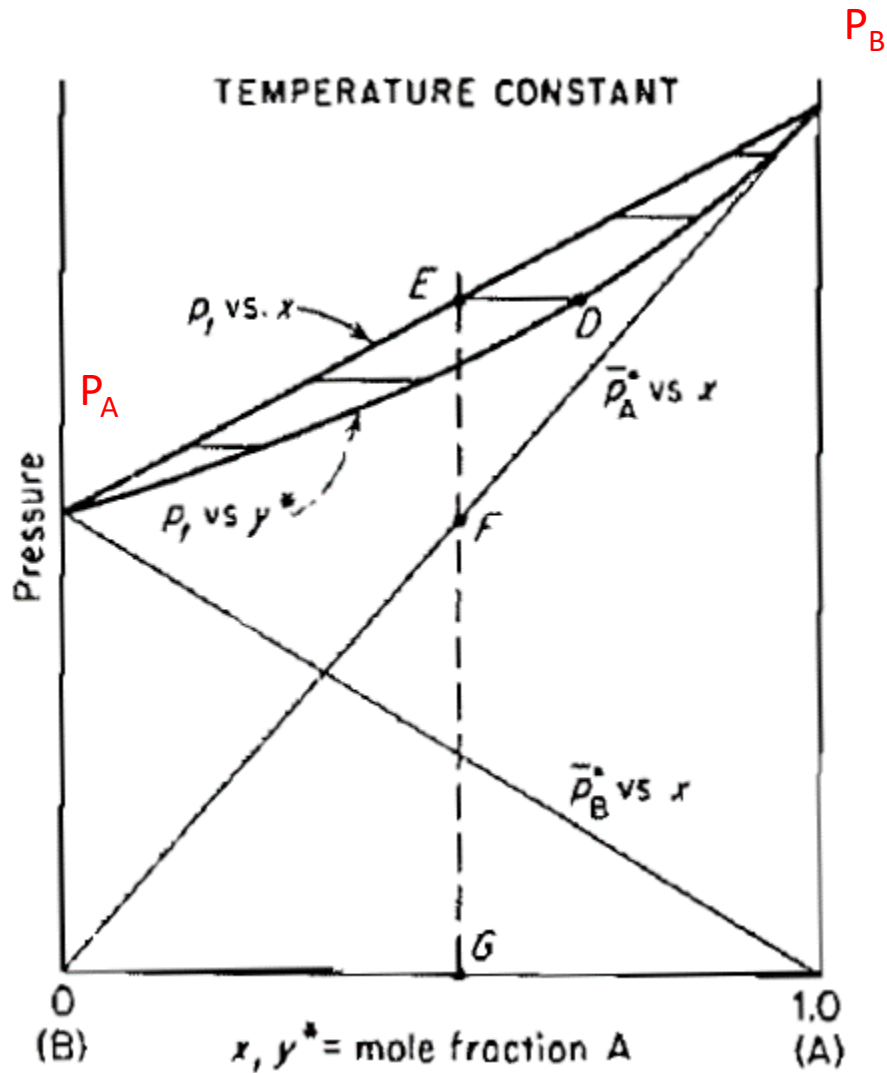


Fig. Ideal solutions

$$y^* = \frac{\text{distance FG}}{\text{distance EG}} = \frac{\bar{P}_A^*}{P_t} = \frac{P_A x}{P_t} \quad (5)$$

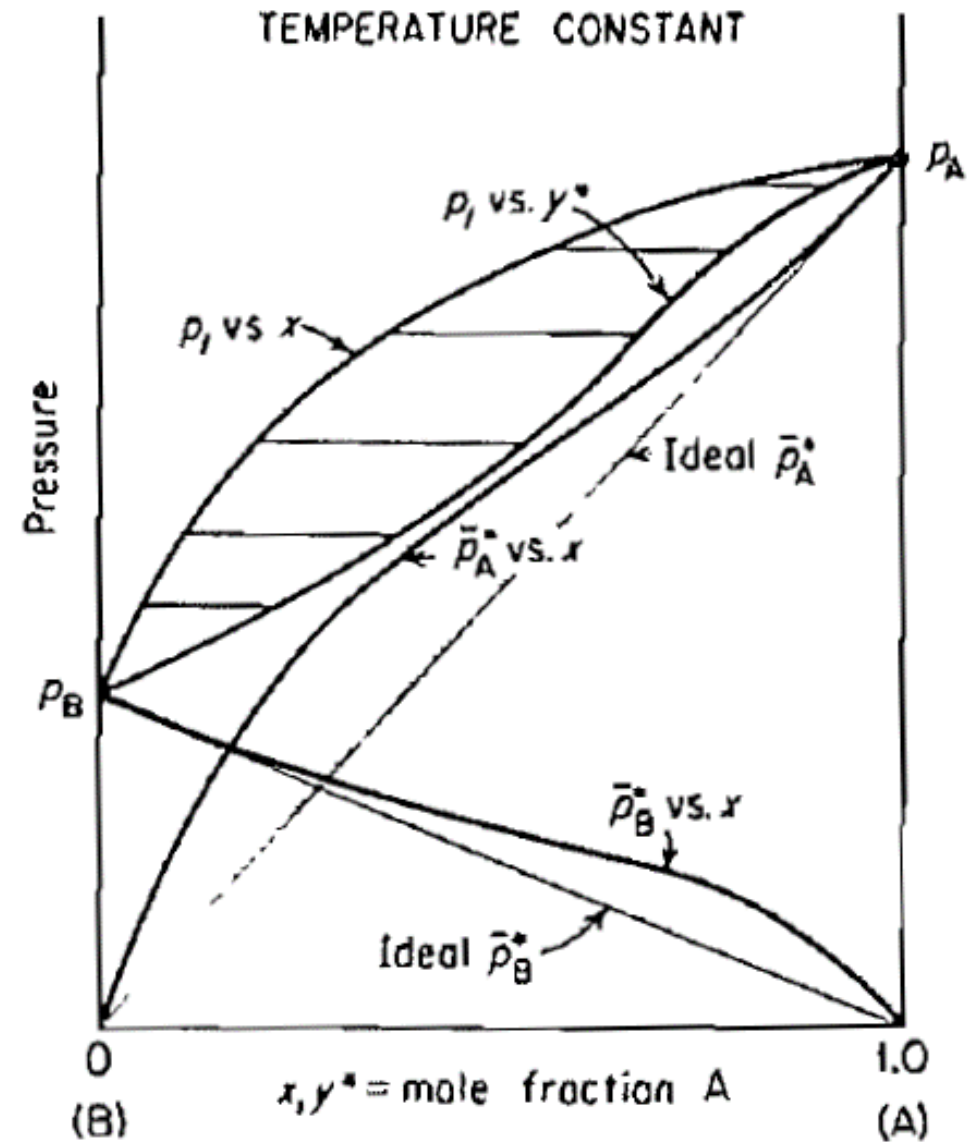
$$1 - y^* = \frac{\bar{P}_B^*}{P_t} = \frac{P_B (1 - x)}{P_t} \quad (6)$$

The relative volatility α is, by substitution in equation (1)

$$\alpha = \frac{P_A}{P_B} \quad (7)$$

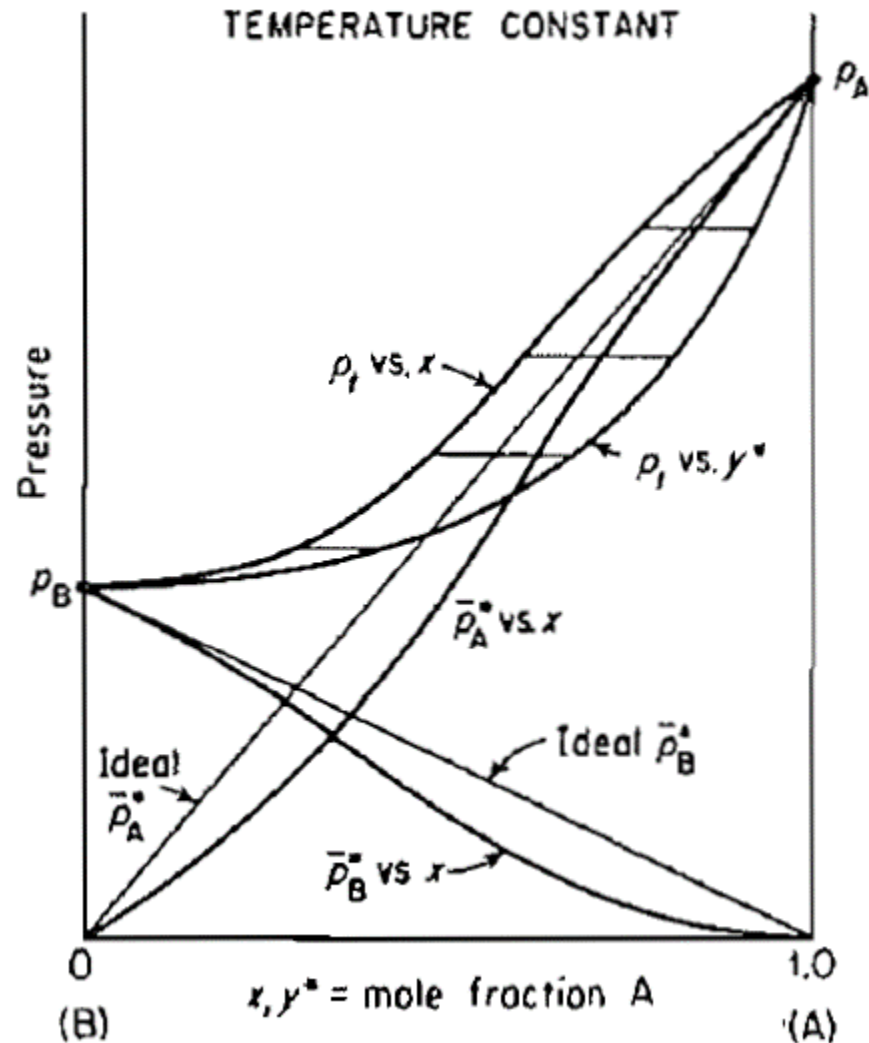
➤ Positive deviations from ideality

- A mixture whose total pressure is greater than that computed for ideality (eq. 4) is said to show positive deviations from Raoult's law.

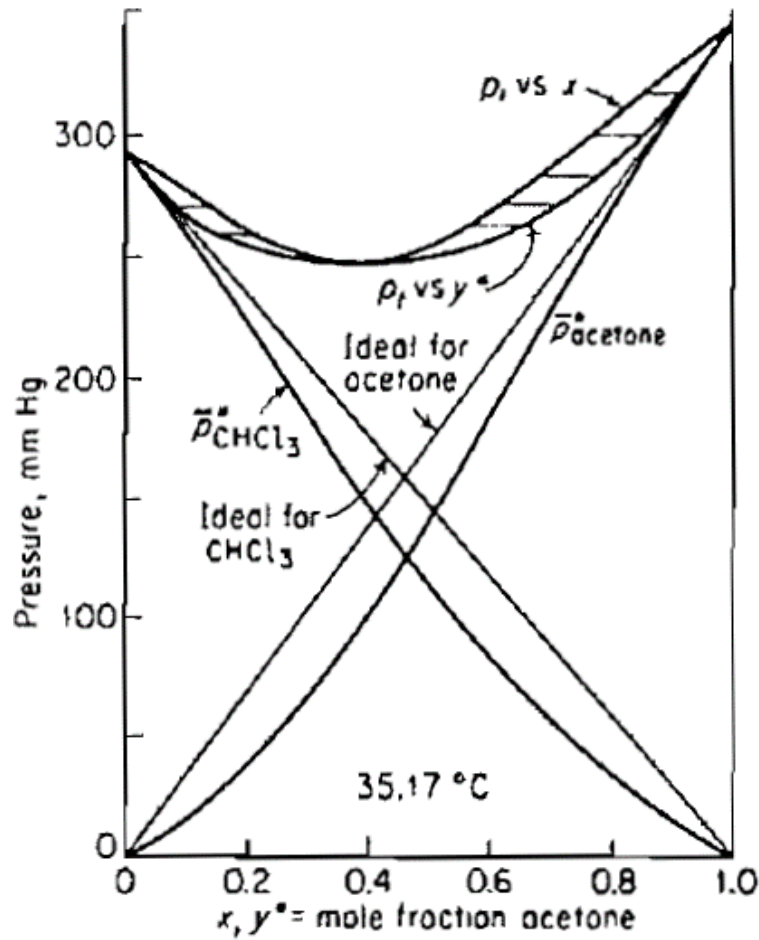


➤ Negative deviations from Ideality

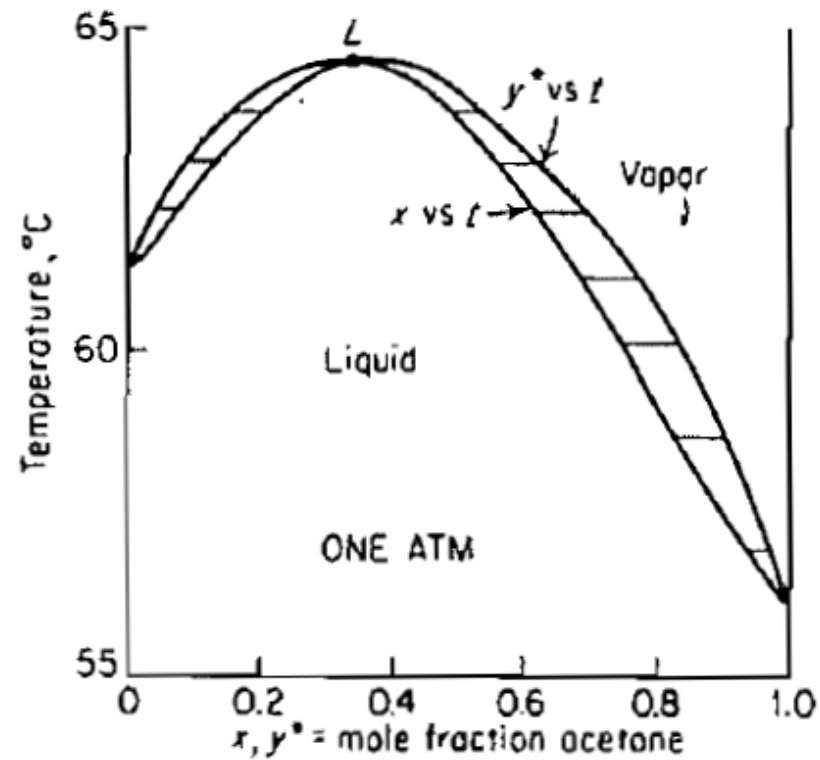
- When the total pressure of a system at equilibrium is less than the ideal value, the system is said to deviate negatively from Raoult's law.



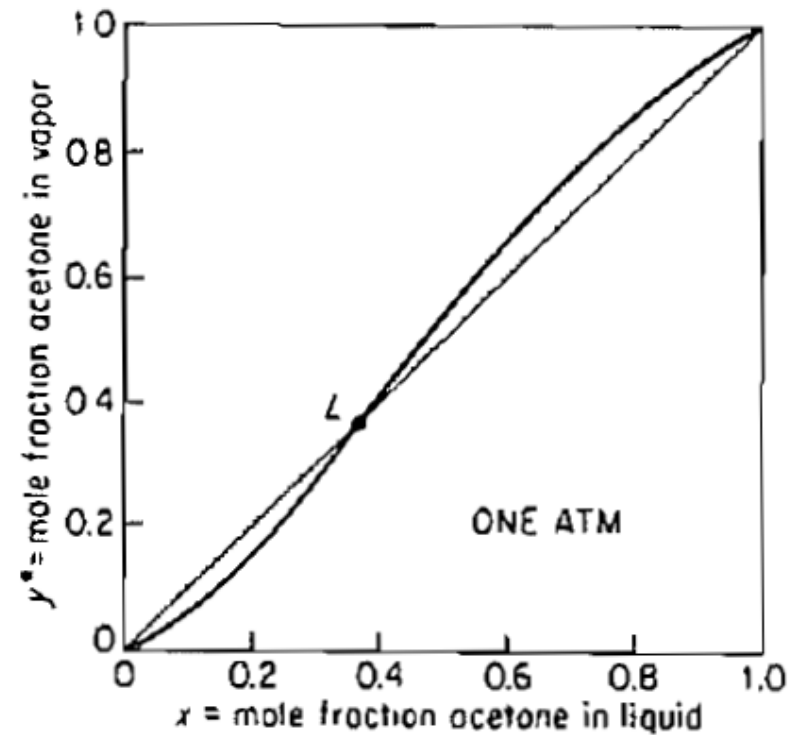
➤ Maximum boiling mixtures - azeotropes



(a)



(b)



(c)

Fig. Maximum-boiling azeotropism in the system acetone-chloroform: (a) at constant temperature; (b) and (c) at constant pressure.

Enthalpy Concentration Diagram

○ 40 wt% ethanol water mixture at 84 °C

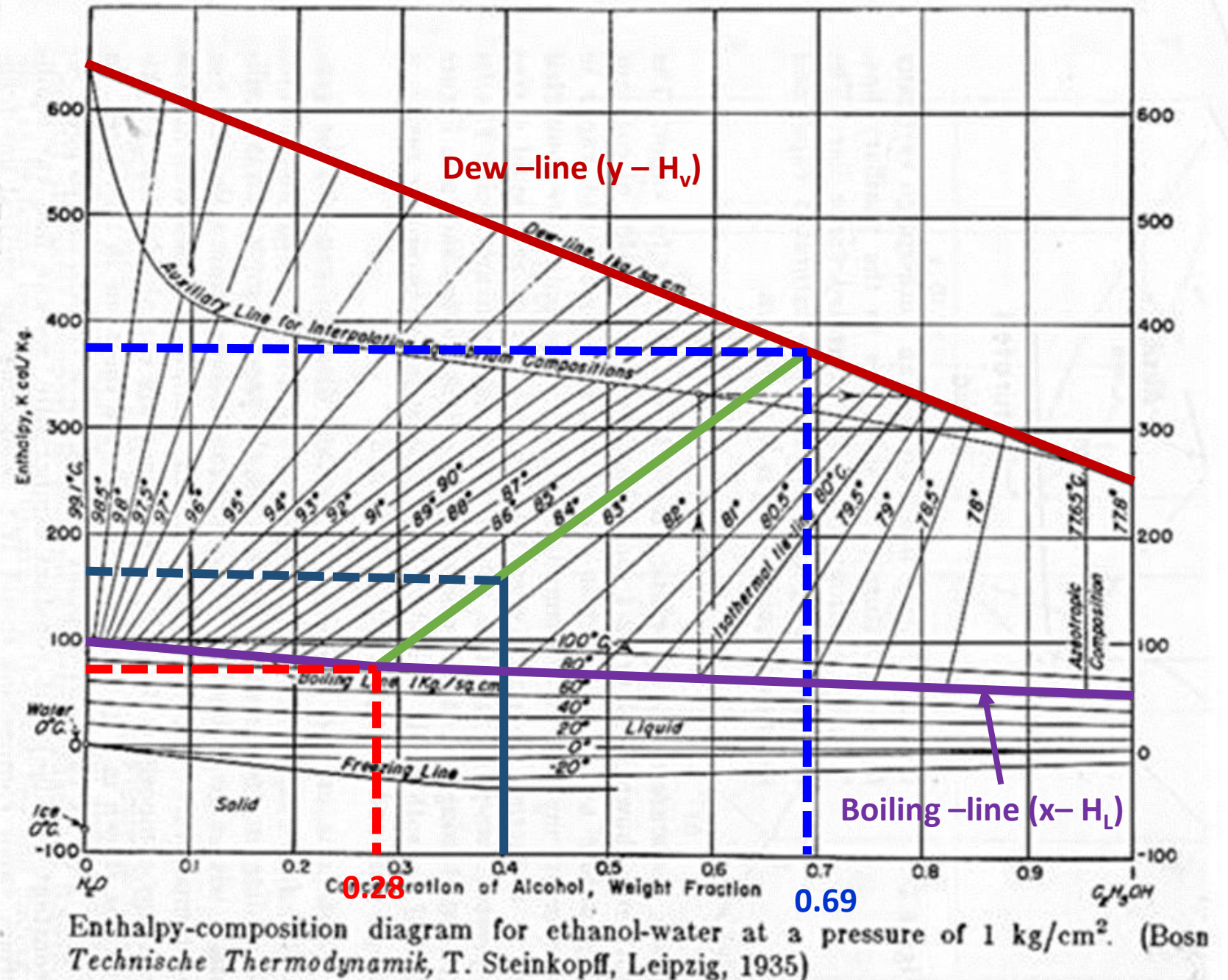
✓ $x_{\text{ethanol}} = 0.28$

✓ $y_{\text{ethanol}} = 0.69$

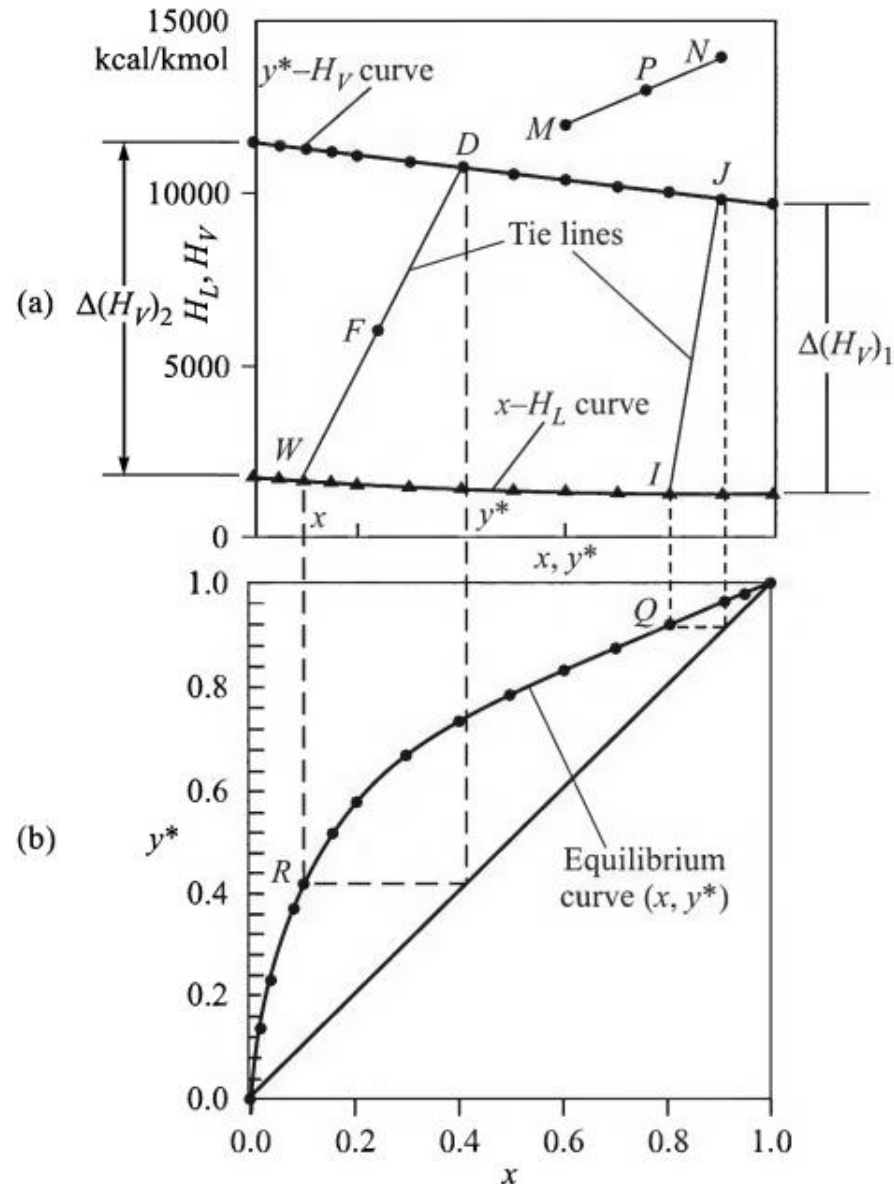
✓ $H_F = 165 \text{ Kcal/kg}$

✓ $H_v = 380 \text{ Kcal/kg}$

✓ $H_L = 70 \text{ Kcal/kg}$



Enthalpy Concentration Diagram to Equilibrium Diagram



Total material balance:

$$M + N = P$$

Component A balance:

$$Mz_M + Nz_N = Pz_P$$

Enthalpy balance:

$$MH_M + NH_N = PH_P$$

$$\frac{M}{N} = \frac{z_N - z_P}{z_P - z_M}$$

$$\frac{M}{N} = \frac{H_N - H_P}{H_P - H_M}$$

$$\frac{H_N - H_P}{z_N - z_P} = \frac{H_P - H_M}{z_P - z_M}$$