Topic 5C - Phase Equilibria in Two-Component Systems

Binary Liquid Mixtures

Vapor Pressure

for an ideal binary mixture of two volatile liquids, A and B:

$$P_A = x_{A,\,liquid}\,P_{A,\,pure} \quad \text{and} \quad P_B = x_{B,\,liquid}\,P_{B,\,pure}$$

From Dalton's Law:

$$P_T = P_A + P_B = x_{A,\,liquid}\,P_{A,\,pure} + x_{B,\,liquid}\,P_{B,\,pure}$$

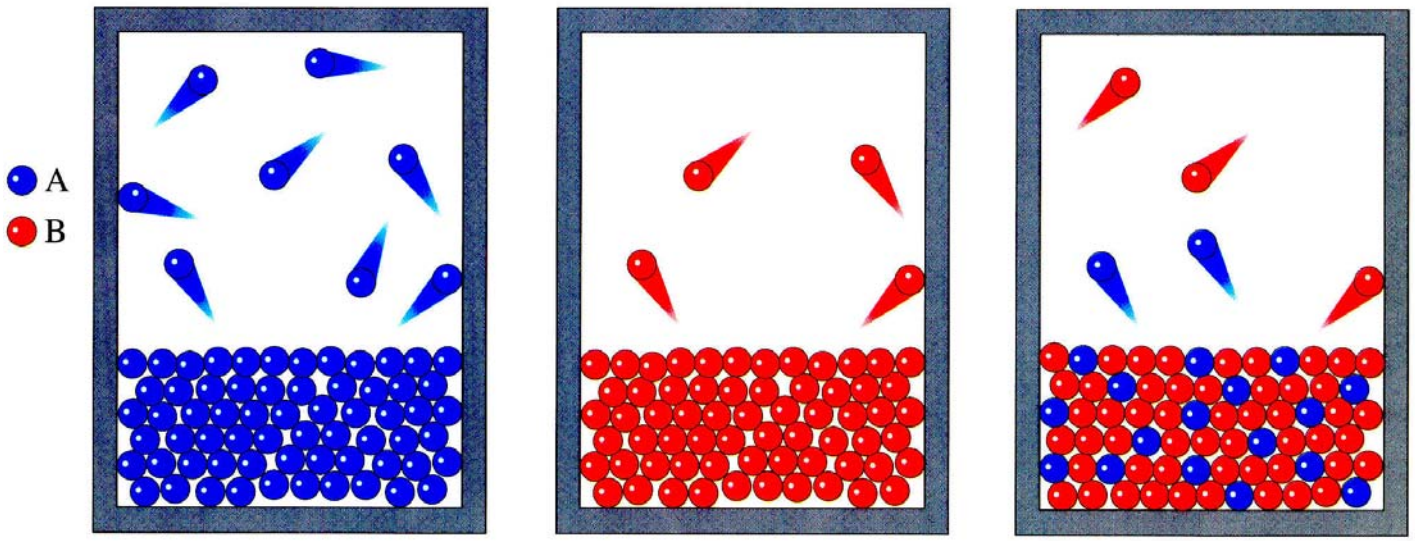
Thus, the vapor that is in equilibrium with the liquid mixture will be richer in the component having the higher vapor pressure.

$$x_{A,\,vapor} = \frac{P_A}{P_T} = \frac{P_A}{P_A + P_B} = \frac{x_{A,\,liquid}\,P_{A,\,pure}}{x_{A,\,liquid}\,P_{A,\,pure} + x_{B,\,liquid}\,P_{B,\,pure}}$$

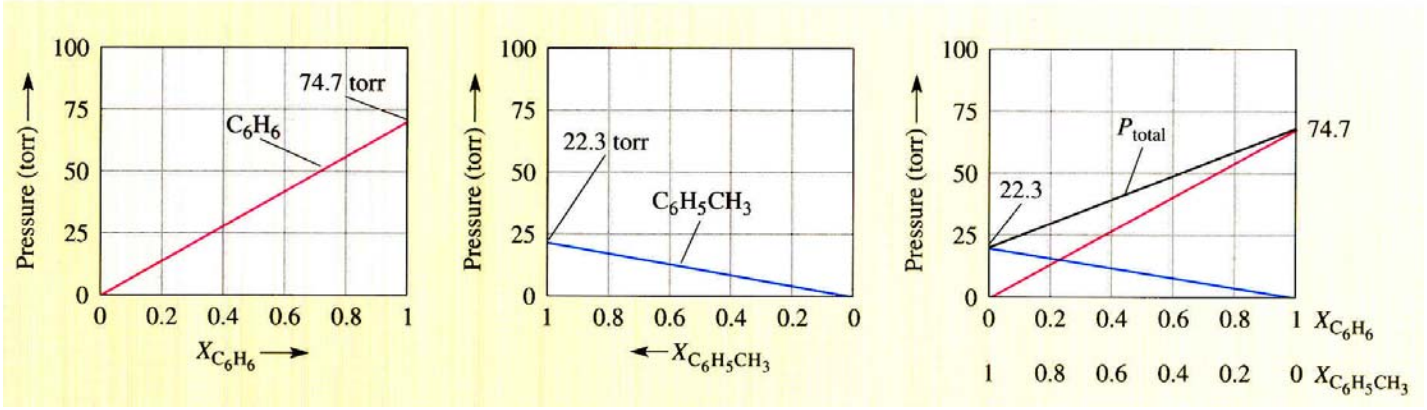
Distillation

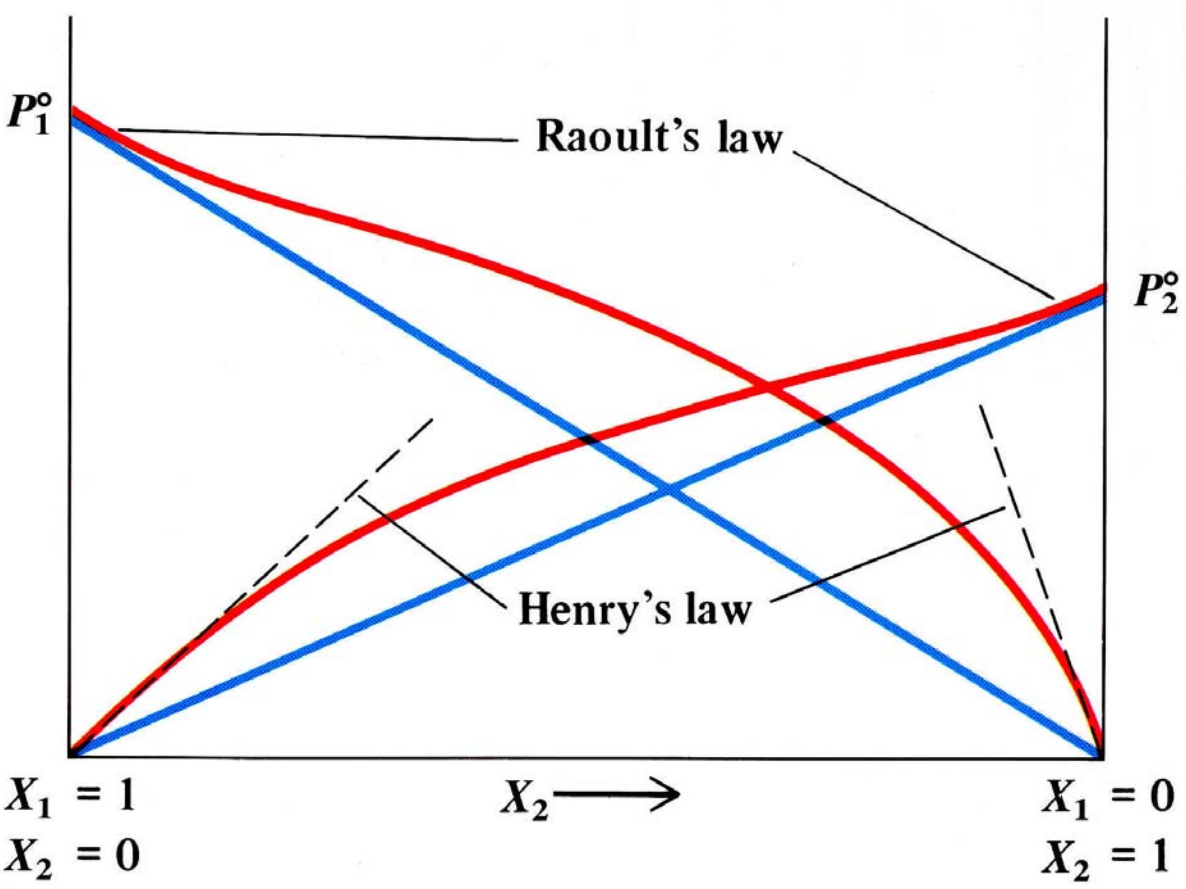
Boiling point of binary mixture is intermediate between B.P.'s of the two pure components.

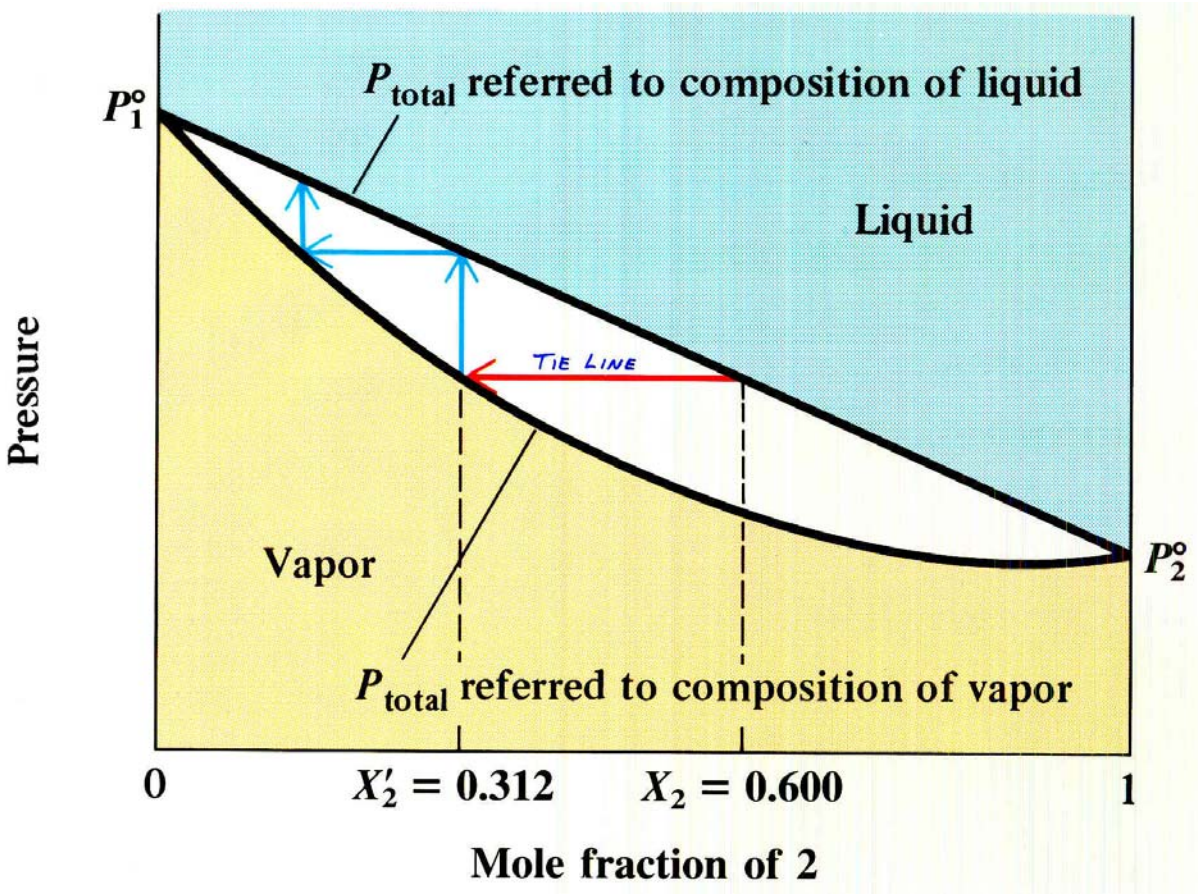
Temperature-Composition diagrams
- Tie Lines
- Vapor-Liquid Compositions

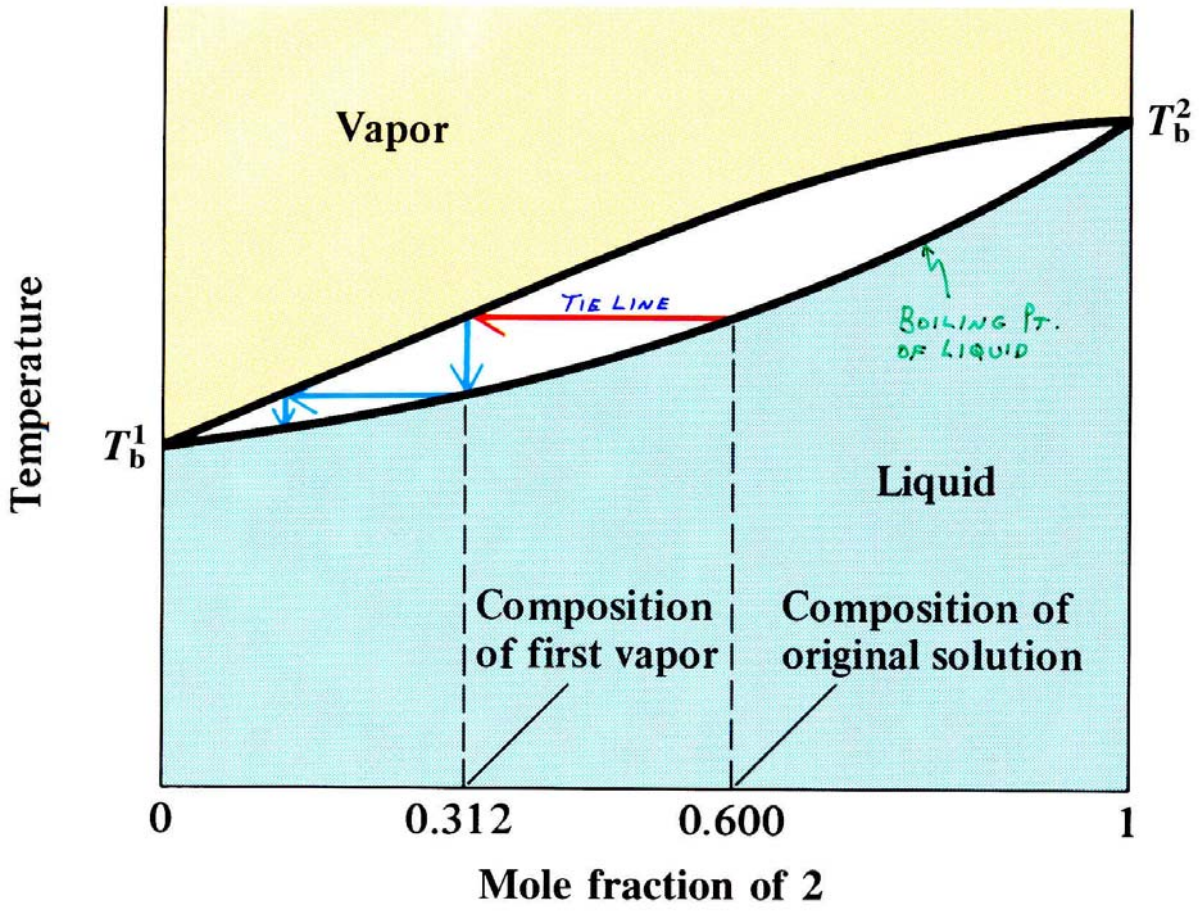


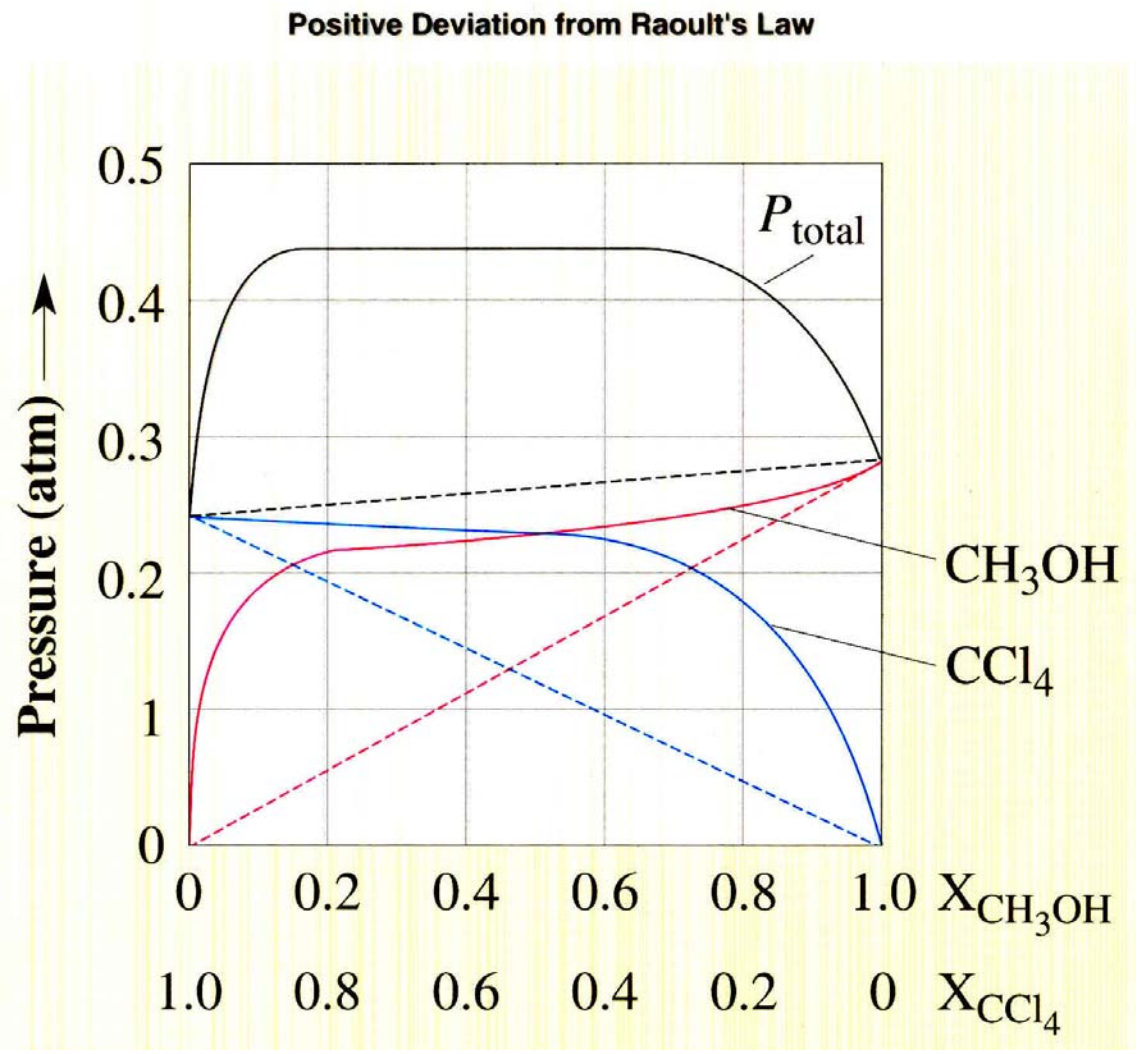
Vapor Pressure vs Composition for Solutions of Benzene and Toluene



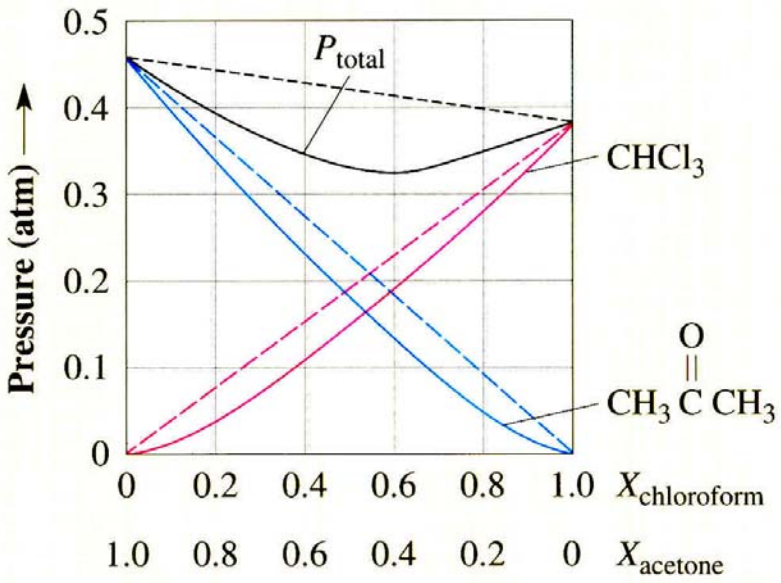

P_1°
Raoult's law
P_2°
Henry's law
$X_1 = 1$
$X_2 = 0$
$X_2 \longrightarrow$
$X_1 = 0$
$X_2 = 1$

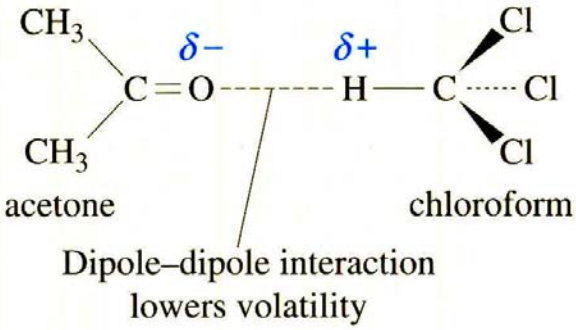

P_1°
P_{total} referred to composition of liquid
Liquid
TIE LINE
Pressure
Vapor
P_2°
P_{total} referred to composition of vapor
0
$X_2' = 0.312$
$X_2 = 0.600$
1
Mole fraction of 2


Vapor
T_b^2
TIE LINE
BOILING PT. OF LIQUID
Temperature
T_b^1
Liquid
Composition of first vapor
Composition of original solution
0
0.312
0.600
1
Mole fraction of 2


Positive Deviation from Raoult's Law
Pressure (atm)
0.5
0.4
0.3
0.2
1
0
P_{total}
CH_3OH
CCl_4
0 0.2 0.4 0.6 0.8 1.0 X_{CH_3OH}
1.0 0.8 0.6 0.4 0.2 0 X_{CCl_4}

Negative Deviation from Raoult's Law



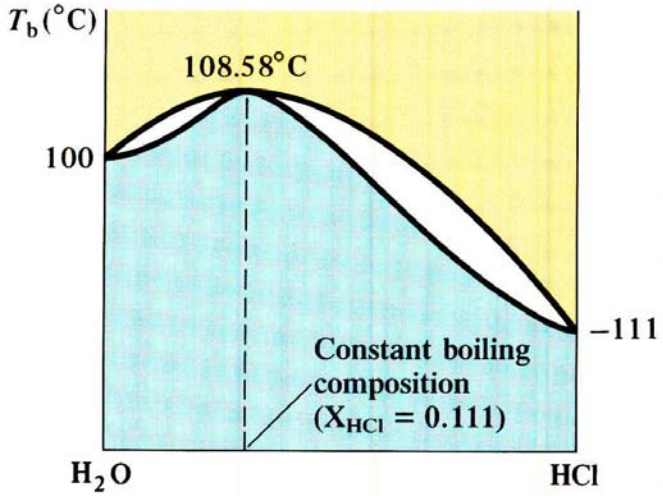


Azeotropes

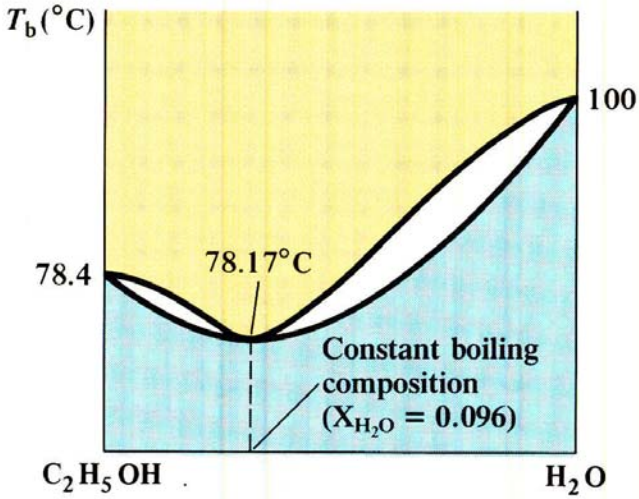
for non-ideal mixtures, the direction of deviation from Raoult's Law is determined by ΔH_{mix}, which is the difference between the enthalpies of the mixture and those of the pure components.

If $\Delta H_{mix} < 0$, then molecules of the two mixture components have attractive interactions, and the V.P. will be lower than that of an ideal mixture.

If $\Delta H_{mix} > 0$, then molecules of the two mixture components have negative interactions, and the V.P. will be higher than that of an ideal mixture.



(*a*) Constant boiling maximum



(*b*) Constant boiling minimum