Chapter 6. Multiphase Systems

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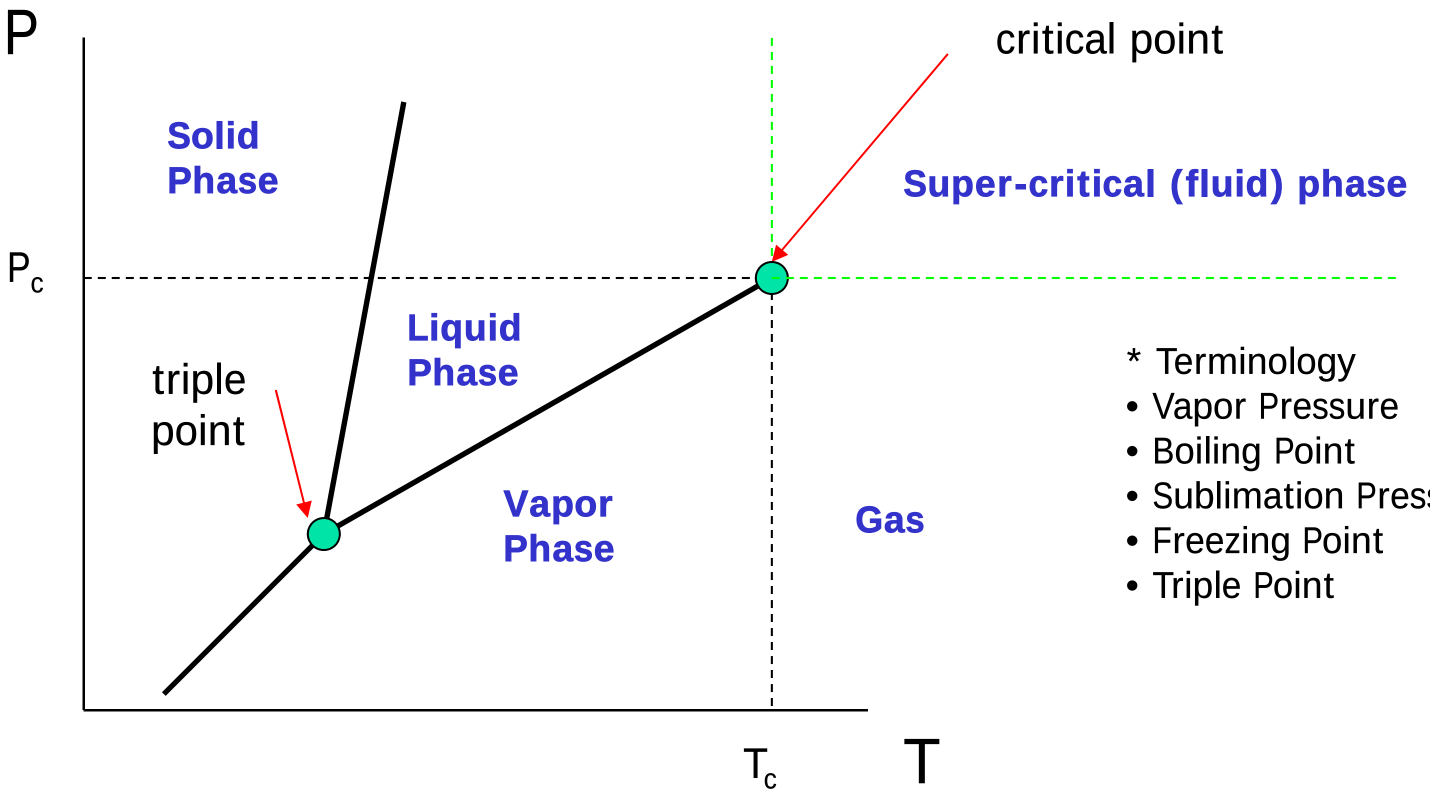
Introduction

- Multiphase systems – Mainly involved in separation process
  - Distillation (증류) : vapor-liquid
    - Driving force of separation : Vapor pressure
  - Crystallization (결정화) : liquid – solid
    - Driving force of separation : solubility
  - Extraction (추출) : liquid – liquid
    - Driving force of separation : distribution coeff.

6.1 Single-Component Phase Equilibrium

- Phase Diagram



* Terminology
- Vapor Pressure
- Boiling Point
- Sublimation Pressure
- Freezing Point
- Triple Point

Vapor Pressure

- Source of Vapor Pressure Data
  - Experimental Data from Litearture
    - Perry's Handbook
    - Journals (J.Chem.Eng.Data, Fluid Phase Equilibria, ...)
  - Equations and Coefficients : Antoine,...
    - Perry's Handbook
    - Data Books, Databases , ...
  - From Cox chart (Fig. 6.1-4)
  - Estimation from Clauisus – Clapeyron Equation

Clauisus-Clapeyron Equation

- Estimation of Vapor Pressure

$$\frac{dP}{dT} = \frac{\Delta H_v}{T\Delta \hat{V}}$$

→ **Enthalpy of Vaporization**

→ **Volume change of Vaporization (V(gas)-V(liquid))**

$$\frac{d\ln P^*}{d(1/T)} = -\frac{\Delta H_v}{R}$$

↓ **Integration**

$$\ln P^* = -\frac{\Delta H_v}{RT} + B$$

→ **This equation can be used as fitting equation for Vapor pressure data.**

Vapor Pressure Equations

- Antoine equation (Table 6.1-1)

$$\log_{10} = A - \frac{B}{T + C}$$

- Wagner equation
  - "Properties of Gases and Liquids"

$$\ln P_{vpr} = (A\tau + B\tau^{1.5} + C\tau^{3} + D\tau^{6}) / T_r$$

$$\tau = 1 - T_r$$

6.2 Gibbs Phase Rule

- Types of Process Variables
  - Extensive Variables – depend on the size of the system (N, V,…)
  - Intensive Variables – do not depend on the size of the system (T,P,…)
- Gibbs Phase Rule
  - Degree of freedom for intensive variables

$$F = 2 + m - \Pi$$

- Π → **The number of phases**
- m → **The number of chemical species**
- F → **The number of degree of freedom**

Gibbs Phase Rule – Examples

$$F = 2 + m - \Pi$$

- Pure Water
  - F = 2 + 1 – 1 = 2
- Mixture of Ice and Water
  - F = 2 + 1 – 2 = 1
- VLE of acetone + nitrogen
  - F = 2 + 2 –2 = 2

(example)
T and P

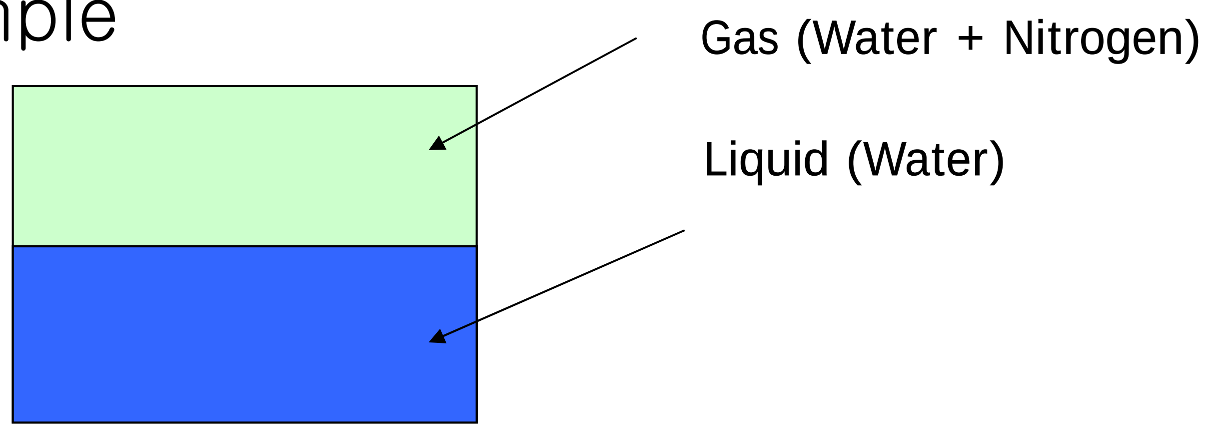
(example)
T or P

(example)
T and x
P and x
T and P
:

Other intensive variables can be calculated using thermodynamic relations

6.3 Gas-Liquid Systems

- Processes involving gas-liquid systems
  - Evaporation, drying, humidification
  - Condensation, dehumidification
- Example



The gas in GLE is called "noncondensable" .
The gas phase is "saturated" with water.

GLE-Calculations

- For 2- component GLE
  - Saturation condition, single condensable species

    $$p_v = y_v P = p_v^*(T)$$

  - Gibbs Phase Rule $F = 2 + m - \Pi$
    - F = 2 + 2 – 2 = 2
    - Intensive Variables : y, T, P

Important characteristics of GLE systems

- GLE → gas must be saturated with liquid
- The partial pressure cannot exceed the vapor pressure of the liquid

$$p_v \le p_v^*(T) \longrightarrow \text{if } p_v > p_v^*(T) \text{ then condensation starts.}$$

- Superheated vapor (과열증기)

$$p_v = y_v P < p_v^*(T)$$

- Dew Point (이슬점)

$$p_v = y_v P = p_v^*(T_{dp})$$

- Degree of Superheat (과열도)

$$= (T - T_{dp})$$

Quantities for GLE systems

- Special case of air+water systems → humidity
- Terminology
  - Relative Saturation (Relative Humidity)

$$s_r(h_r) = \frac{p_v}{p_v^*(T)} \times 100\%$$

  - Molar Saturation (Molar Humidity)

$$s_m(h_m) = \frac{p_v}{P - p_v} = \frac{\text{moles of vapor}}{\text{moles of vapor} - \text{free(dry) gas}}$$

  - Absolute Saturation (Absolute Humidity)

$$s_a(h_a) = \frac{p_v M_v}{(P - p_v) M_{dry}} = \frac{\text{mass of vapor}}{\text{mass of vapor} - \text{free(dry) gas}}$$

  - Percentage Saturation (Percentage Humidity)

$$s_p(h_p) = 100 \frac{s_m}{(s_m)^*} = 100 \frac{p_v / (P - p_v)}{p_v^* / (P - p_v^*)}$$

6.4 Multicomponent Gas-Liquid Systems

- Transfer process
  - Gas → Liquid : absorption (흡수)
  - Liquid → Gas : stripping (탈기)
- VLE information
  - From tabulated VLE data
  - Raoult's Law and Henry's Law
  - VLE calculation assuming ideal solution
  - Rigorous VLE calculation using model equations

Raoult's Law and Henry's Law

- Distribution of component between vapor and liquid phase

→ <u>Phase equilibrium thermodynamics</u>

- Simplifications
  - Raoult's Law $p_a \equiv y_a P = x_a p_a^*(T) \quad , \quad x_a \to 1$
    - Valid for almost pure component. Similar components
  - Henry's Law $p_a \equiv y_a P = x_a H_a^*(T) \quad , \quad x_a \to 0$
    - Valid for almost dilute component.
- Distribution coefficient $K \equiv y_a / x_a$

VLE calculations for ideal solutions

- Bubble Point temperature calculation
  - Given P,x → calculate T,y

$$P = x_a p_a^*(T_{bp}) + x_a p_a^*(T_{bp}) + \ldots$$

$$\mathrm{y_i} = \frac{x_i p_i^*(T_{bp})}{P}$$

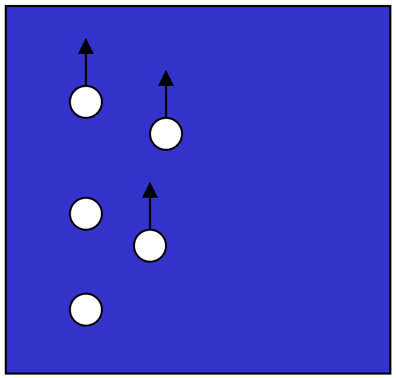
- Dew point temperature calculation
  - Given P,y→ calculate T,x

$$x_i = \frac{y_i P}{p_i^*(T_{dp})}$$

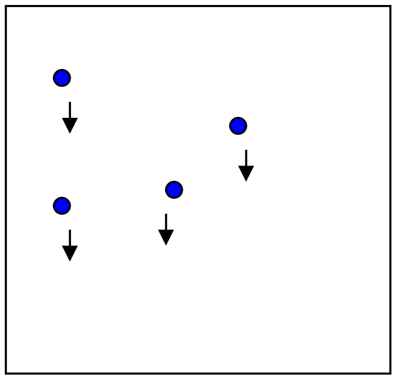
$$\sum_i x_i = \sum_i \frac{y_i P}{p_i^*(T_{dp})} = 1$$

VLE calculations

- Bubble T : P,x → T,y
- Bubble P : T,x → P,y
- Dew T : P,y → T,x
- Dew P : T,y → P,x



Bubble point



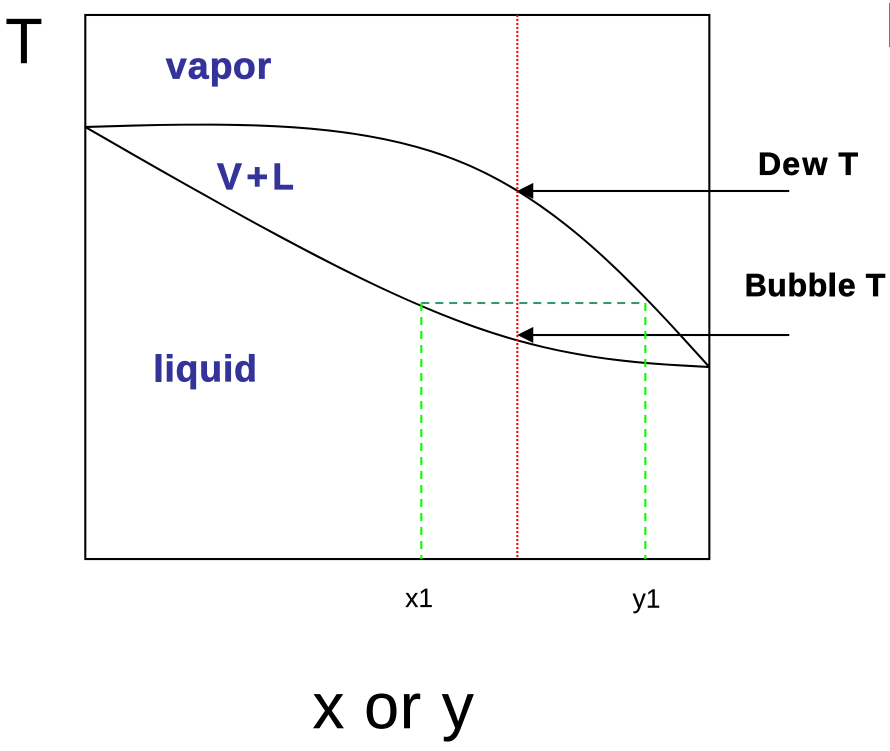
Dew point

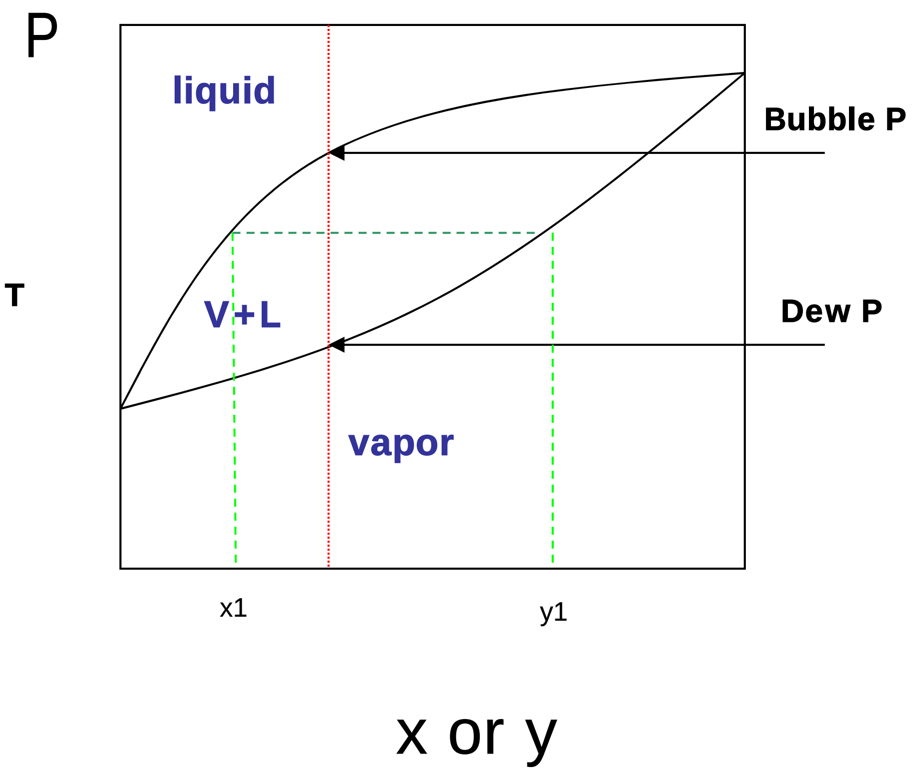
Numerical Methods for the VLE calculations

- Newton – Raphson Method
- Secant Method
- …
- ←Student presentation

Phase diagrams for binary VLE

- Txy diagram
- Pxy diagram





Solutions of Solids in Liquids

- Solubility
  - Limits on the amount of solids that can be dissolved
  - Solubility of a solid depends strongly on T
  - Ex)
    - 222 g $AgNO_3$ / 100 g H_2O at 20 ^{o} C
    - 0.003 g $AgCO_3$ / 100 g H_2O at 20 ^{o} C
    - 0.00002 g AgBr / 100 g H_2O at 20 ^{o} C
- Crystallization
  - Separation of solids and liquids
  - Driving force = solubility difference
  - A solute in equilibrium with a crystal must be saturated.

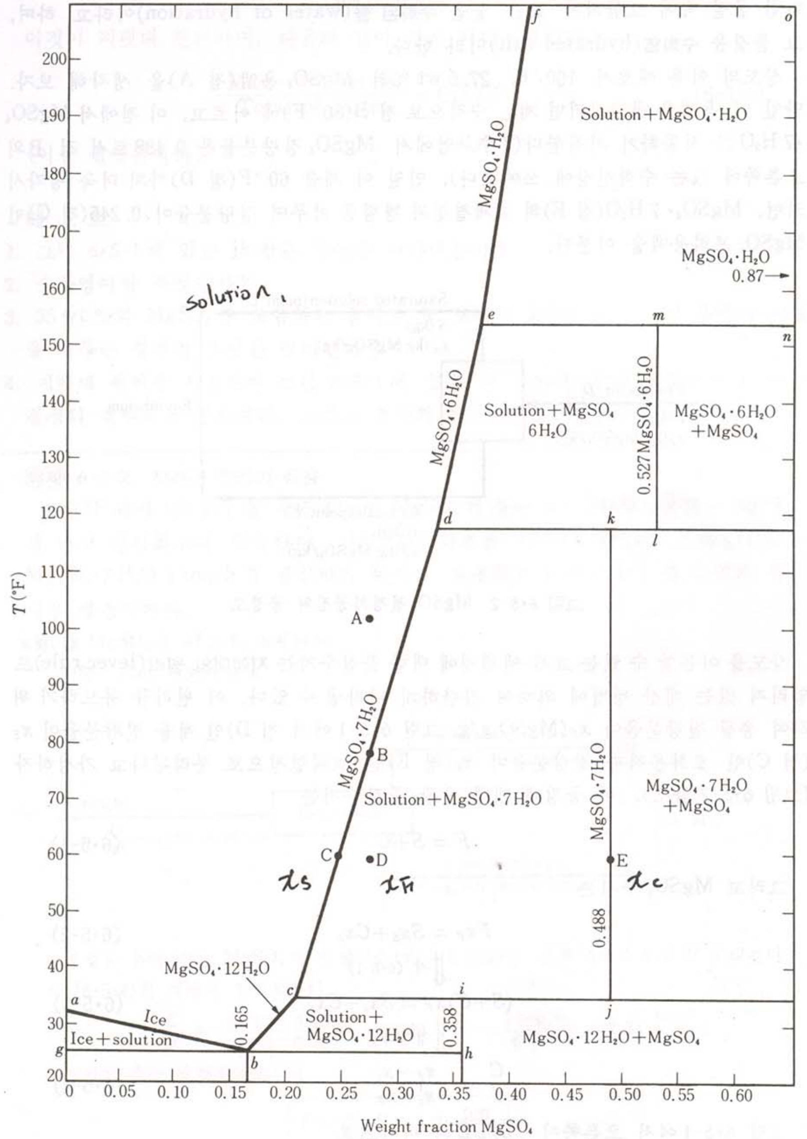


그림 6·5-1 $MgSO_4$-H_2O 계의 상도

A Phase diagram for solid-liquid system

Phase diagrams for solid-liquid systems

- See figure 6.5-1
- Lever rule (지렛대 원리)

$$F(feed) = S(solution) + C(crystal)$$

$$Fx_F = Sx_S + Cx_C$$

$$(S + C)x_F = Sx_S + Cx_C$$

$$\frac{C}{S} = \frac{x_F - x_S}{x_C - x_F} = \frac{\overline{CD}}{\overline{DE}}$$

$$\therefore \frac{C(\text{kg crystal})}{S(\text{kg solution})} = \frac{\overline{CD}}{\overline{DE}}$$

Colligative Solution Properties

- 용액의 총괄성
  - Properties chage on a solution
    - Vapor pressure lowering
    - Boiling point elevation
    - Melting point depression
    - Osmotic pressure
  - Depend <u>only on molar concentration</u>

    (not on the solute and solvent)

Colligative properties

- Vapor Pressure Lowering

$$p_s(T) = (1 - x)\,p_s^*(T)$$

$$\Delta p_x^* = p_s^* - (p_s^*)_e = x p_s^*$$

- Boiling Point Elevation

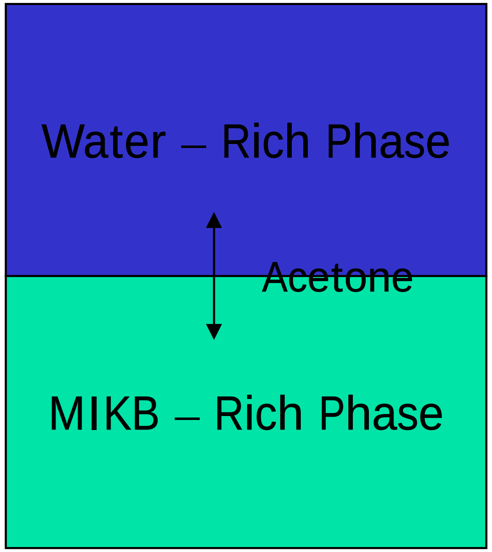
$$\Delta T_b = \frac{RT_{b0}^2}{\Delta \hat{H}_v} x$$

- Melting Point Depression

$$\Delta T_m = \frac{RT_{m0}^2}{\Delta \hat{H}_m} x$$

6.6 Immiscible and Partially Miscible Liquids

- Example) Water + MIBK (Methyl Isobutyl Ketone) + Acetone System



Distribution Coefficient

$$K = \frac{(x)_{MIBK}}{(x)_{WATER}}$$

- Partially miscible liquids
- Immiscible System
- Liquid-Liquid Extraction

Phase diagram for ternary LLE systems

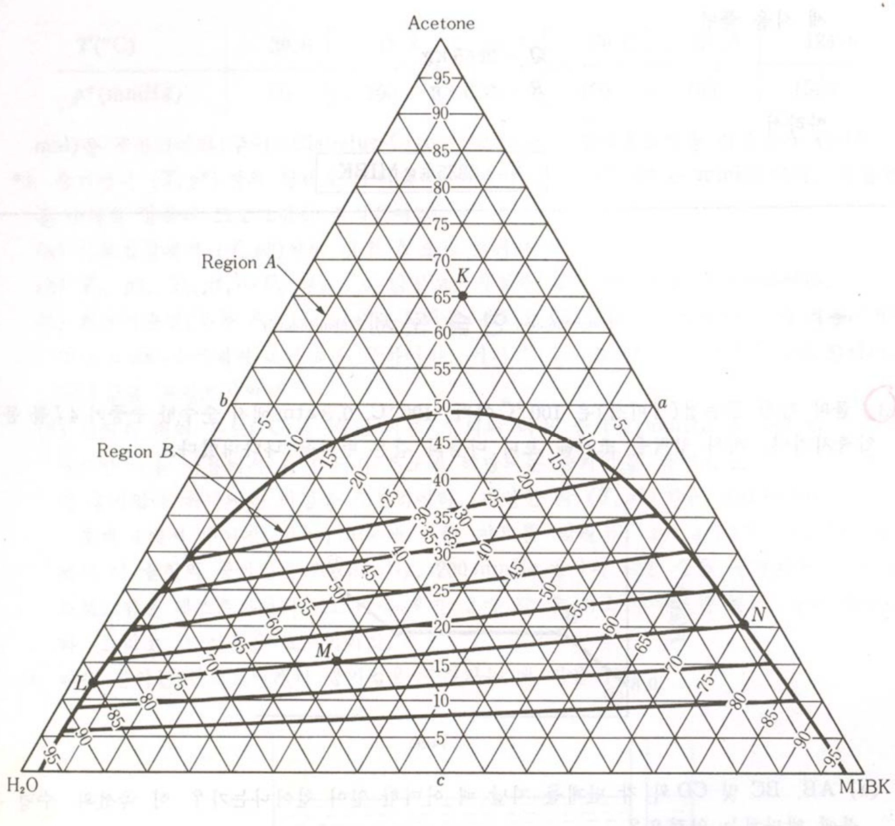


그림 6·6-1 25°C에서 물-아세톤-메틸이소부틸케톤의 삼각상도