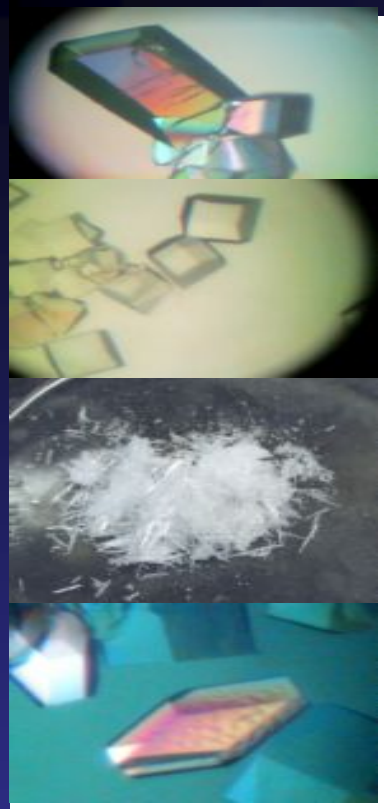
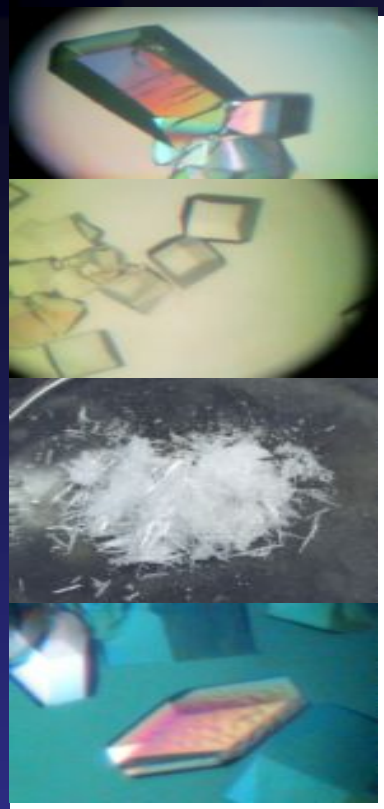


결정화 공정의 상평형의 원리와 이해

2007년 8월 20일

결정화 분리기술 사업단

고려대학교 화공생명공학과 강정원



3. 용해도 계산과 상도

Simple Solubility Correlation for Solutions

- Influence of temperature on solubility

$$c = A + Bt + Ct^2 + ...$$

$$\log x = A + BT$$

$$\log x = A + BT + CT^2$$

$$\log x = A + BT^{-1}$$

$$\log x = A + BT^{-1} + CT^{-2}$$

$$\log x = A + BT^{-1} + C \log T$$

Solubility expression for inorganic salts (Electrolytes)

- Ionic equilibrium relation (Or Reaction Equilibrium)

a **A** + b **B** → c **C** + d **D**

Example) NaCl (s) → $Na^+ + Cl^-$

- Condition for Equilibrium

Chemical Potential

$$a\mu_A + b\mu_B = c\mu_C + d\mu_D$$

$$\mu_i(T) = \mu_i^0(T) + RT \ln \gamma_i x_i$$

$$\mu_i(T) = \mu_{im}^0(T) + RT \ln \gamma_i m_i$$

Can be expressed in composition Or molarity

Solubility expression for inorganic salts (Electrolytes)

$$a\mu_A + b\mu_B = c\mu_C + d\mu_D \qquad \mu_i(T) = \mu_{im}^0(T) + RT\ln\gamma_i m_i$$

$$a\mu_A^0 + b\mu_B^0 - c\mu_C^0 - d\mu_D^0 = RT\ln\frac{(\gamma_C m_C)^c(\gamma_D m_D)^d}{(\gamma_A m_A)^a(\gamma_B m_B)^b}$$

$$K_T = \exp\left(\frac{a\Delta G_{fA}^0 + b\Delta G_{fB}^0 - c\Delta G_{fC}^0 - d\Delta G_{fD}^0}{RT}\right)$$

Standard free energy Change of reaction

$$K_T = \frac{(\gamma_C m_C)^c(\gamma_D m_D)^d}{(\gamma_A m_A)^a(\gamma_B m_B)^b}$$

Solubility expression for inorganic salts (Electrolytes)

- For the case of salt in solution,

$$M(s) \rightarrow a\ A\ (aq) + b\ B\ (aq)$$

$$K_{sp} = \frac{(\gamma_C m_C)^c (\gamma_D m_D)^d}{(\gamma_M x_M)}$$

This value becomes 1 (Pure solid)

$$K_{sp} = \exp\left(\frac{a\Delta G^0_{fA} + b\Delta G^0_{fB} - \Delta G^0_{fM}}{RT}\right)$$

Basis : formation of hypothetical Ideal solution of 1 molarity at standard condition

Basis : formation of 1 mol of solid at standard condition

Solubility expression for inorganic salts (Electrolytes)

- Solubility Product

$$M(s) \rightarrow a\ A\ (aq) + b\ B\ (aq)$$

$$K_{sp} = (\gamma_C m_C)^c (\gamma_D m_D)^d$$

$$K_{sp} = \exp\left(\frac{a\Delta G^0_{fA} + b\Delta G^0_{fB} - \Delta G^0_{fM}}{RT}\right)$$

Example) $Al(OH)_3 \rightarrow Al^{3+} + 3OH^-$ $\quad K_{sp}$ = 1.1E-15

$$K_{sp} = (m_{Al^{3+}})(m_{OH^-})^3 = 1.1\times10^{-15}$$

$$3m_{Al^{3+}} = m_{OH^-}$$

$$m_{Al(OH)_3} = m_{Al^{3+}} = 8\times10^{-5}\ g/mol$$

Advanced Topics in Electrolyte Solutions

- Effect of K_{sp}
  - Temperature
  - Pressure
- Activity Coefficients
  - From thermodynamic models
    - Debye-Huckel Model
    - Guggenheim Model
    - Pitzer Model
    - Bromley Model
    - Meissner Model

Difficulties in Electrolyte Solution

- Existing activity model only applies to limited range
  - Applicable only for dilute solution
  - No model can effectively explain the behavior of dilute and highly concentrated solution
- For practical purposes, simple empirical correlations are normally used ….

$$\log x = A + BT$$

$$\log x = A + BT + CT^2$$

$$\log x = A + BT^{-1}$$

$$\log x = A + BT^{-1} + CT^{-2}$$

$$\log x = A + BT^{-1} + C\log T$$

Data Source

- Solubility of Electrolytes and Nonelectrolytes
  - J. M. Mullin, “Crystallization” , Butterworth-Heinemann (1993)
- Method for Electrolyte Solutions
  - J. F. Zemaitis, Jr., D. M. Clark, M. Rafal and N. C. Scrivner , “Handbook of Aqueous Electrolyte Solution”, AIChE (1986)

Solubility Expression for Organic Compounds in Organic Solvents

- Ideal Solubility
  - Solution (liquid phase) exhibit "ideal behavior"
    - Fugacity of mixture is proportional to mole fraction (solubility)

$$f_{2,liquid}(T,P,x) = x_2 f_{2,liquid}^{pure}(T,P)$$

- Nonideal solubility
  - Solution exhibit non-ideal behavior

$$f_{2,liquid}(T,P,x) = \gamma_2 x_2 f_{2,liquid}^{pure}(T,P)$$

Solubility Expression for Organic Compounds in Organic Solvents

- Ideal Solubility Calculation Method
  - Solution (liquid phase) exhibit "ideal behavior"
  - Solid (crystal) is in a pure state

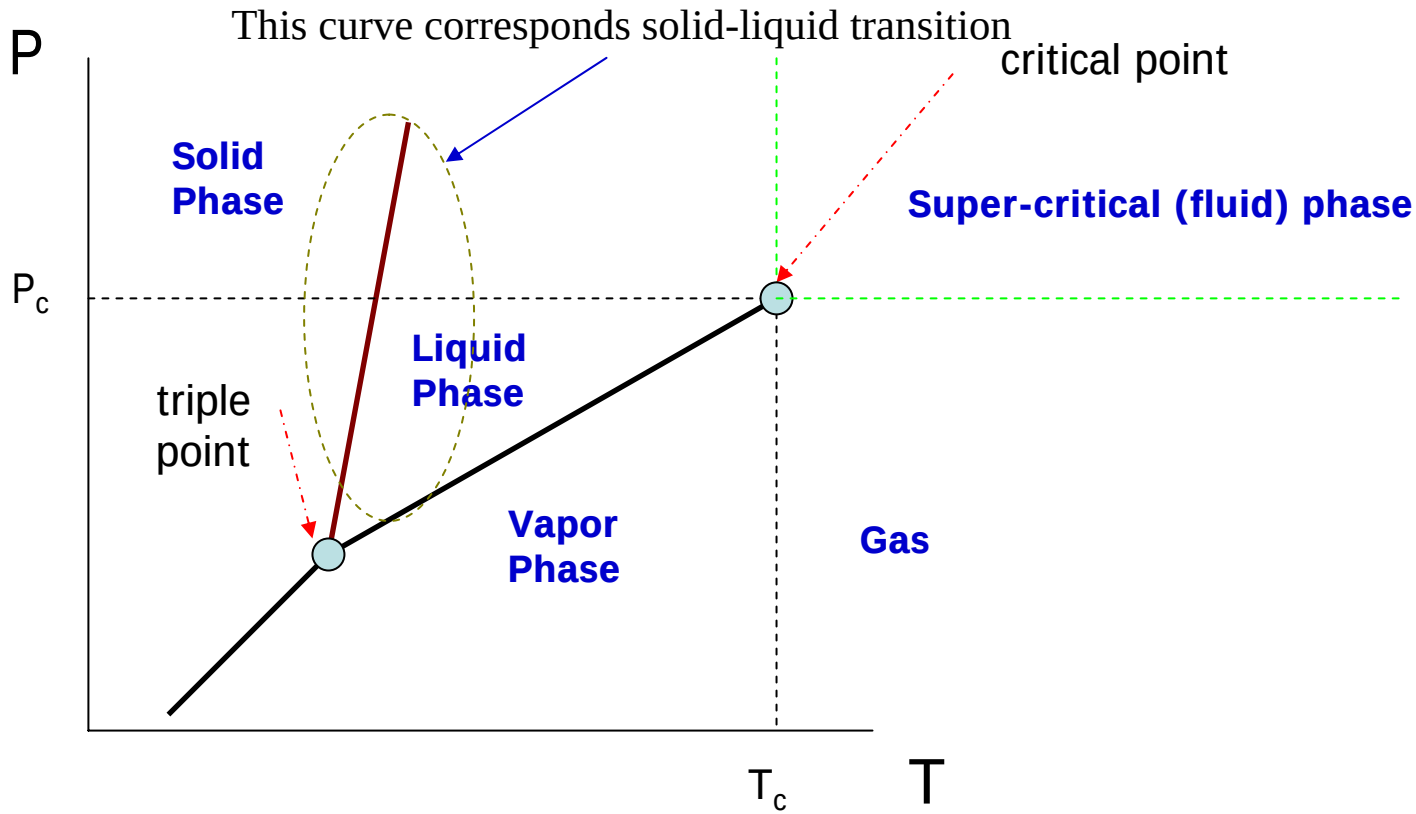
$$f_{2,\,pure\ solid}(T,P) = x_2\, f^{\,pure}_{2,liquid}(T,P)$$

$$x_2 = \frac{f_{2,\,pure\ solid}(T,P)}{f_{2,\,pure\ subcooled\ liquid}(T,P)}$$

Solid → Liquid transition properties are important
Solid→ Liquid Transition can occur in any temperature

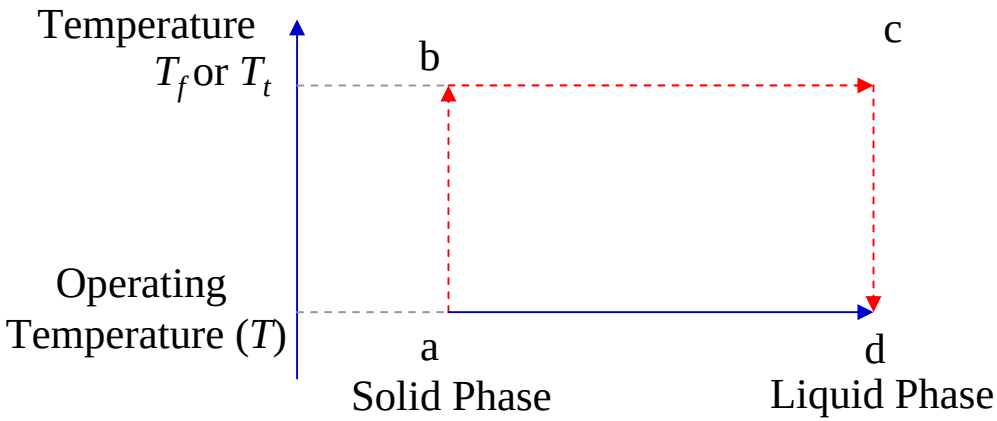
Solubility Expression for Organic Compounds in Organic Solvents

- Solid-Liquid transition

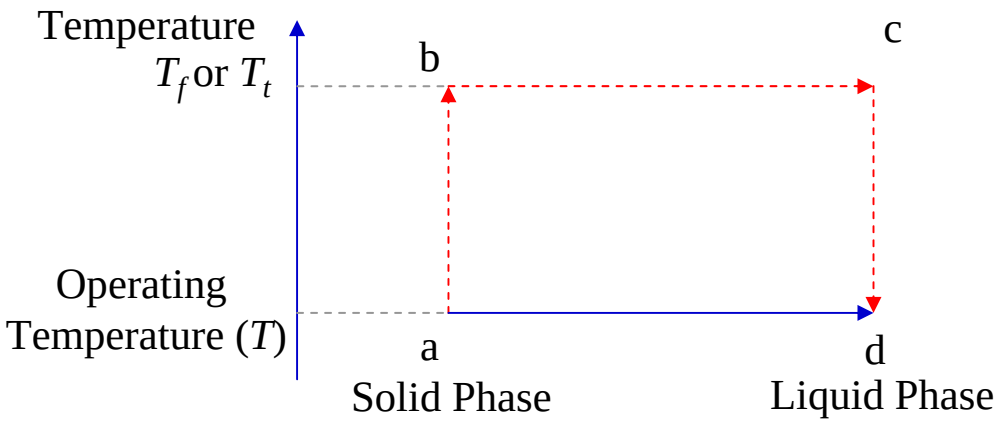


Solubility Expression for Organic Compounds in Organic Solvents

- Solid-Liquid transition
  - To calculate fugacity ratio of solid and liquid phase, two reference states are normally used
    - Triple point : T_t
    - Normal Melting Point : T_m
  - Because heat of fusion (H_f) data are reported at those temperatures
- Thermodynamic Cycles for calculating fugacity ratio (or chemical potential changes)



Solubility Expression for Organic Compounds in Organic Solvents



$$RT \ln \frac{f_L}{f_S} = \Delta G_{a\to d} = \Delta H_{a\to d} - T\Delta S_{a\to d} = \Delta H_{a\to b\to c\to d} - T\Delta S_{a\to b\to c\to d}$$

$$\Delta H_{a\to b\to c\to b} = \Delta H_{a\to b} + \Delta H_{b\to c} + \Delta H_{c\to d} = \int_T^{T_f} C_p^s dT + \Delta H_f(T_f) + \int_{T_f}^T C_p^L dT$$

$$\Delta S_{a\to b\to c\to b} = \Delta S_{a\to b} + \Delta S_{b\to c} + \Delta S_{c\to d} = \int_T^{T_f} \frac{C_p^s}{T} dT + \frac{\Delta H_f}{T_f} + \int_{T_f}^T \frac{C_p^L}{T} dT$$

Solubility Expression for Organic Compounds in Organic Solvents

- Ideal Solubility equation

$$f_{2,solid} = x_2 f_{2,liquid}$$

$$x_2 = \frac{f_{2,solid}}{f_{2,liquid}} \qquad RT \ln \frac{f_2}{f_1} = \Delta G_{1\to 2} = \Delta H_{1\to 2} - T\Delta S_{1\to 2}$$

$$RT \ln \frac{1}{x_2} = \frac{\Delta H_f}{RT_f}\left(\frac{T_f}{T} - 1\right) - \frac{\Delta C_P}{R}\left(\frac{T_f}{T} - 1\right) + \frac{\Delta C_P}{R} \ln \frac{T_f}{T}$$

- You can use T_t or T_f depending on H_f data available

Solubility Expression for Organic Compounds in Organic Solvents

- Non-Ideal Solubility equation

$$f_{2,solid} = x_2 \gamma_2 f_{2,liquid}$$

$$\gamma_2 x_2 = \frac{f_{2,solid}}{f_{2,liquid}}$$

$$RT \ln \frac{1}{\gamma_2 x_2} = \frac{\Delta H_f}{RT_f}\left(\frac{T_f}{T} - 1\right) - \frac{\Delta C_P}{R}\left(\frac{T_f}{T} - 1\right) + \frac{\Delta C_P}{R} \ln \frac{T_f}{T}$$

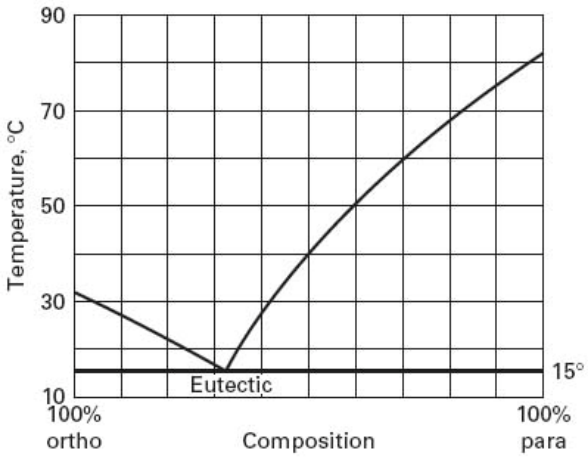
- How to calculate activity coefficient ?
  - Solution models in molecular thermodynamics
    - Magules
    - Wilson
    - NRTL
    - UNIQUAC

Table 2.9 Empirical and Semitheoretical Equations for Correlating Liquid-Phase Activity Coefficients of Binary Pairs

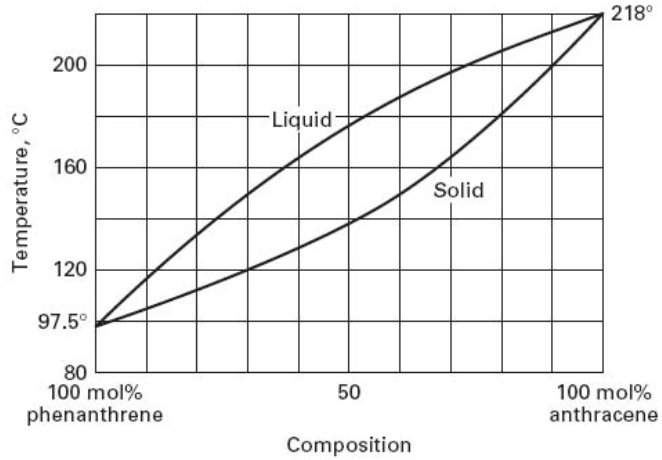
Name	Equation for Species 1	Equation for Species 2
(1) Margules	$\log \gamma_1 = Ax_2^2$	$\log \gamma_2 = Ax_1^2$
(2) Margules (two-constant)	$\log \gamma_1 = x_2^2[\overline{A}_{12} + 2x_1(\overline{A}_{21} - \overline{A}_{12})]$	$\log \gamma_2 = x_1^2[\overline{A}_{21} + 2x_2(\overline{A}_{12} - \overline{A}_{21})]$
(3) van Laar (two-constant)	$\ln \gamma_1 = \dfrac{A_{12}}{[1 + (x_1A_{12})/(x_2A_{21})]^2}$	$\ln \gamma_2 = \dfrac{A_{21}}{[1 + (x_2A_{21})/(x_1A_{12})]^2}$
(4) Wilson (two-constant)	$\ln \gamma_1 = -\ln(x_1 + \Lambda_{12}x_2) + x_2\left(\dfrac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \dfrac{\Lambda_{21}}{x_2 + \Lambda_{21}x_1}\right)$	$\ln \gamma_2 = -\ln(x_2 + \Lambda_{21}x_1) - x_1\left(\dfrac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \dfrac{\Lambda_{21}}{x_2 + \Lambda_{21}x_1}\right)$
(5) NRTL (three-constant)	$\ln \gamma_1 = \dfrac{x_2^2\tau_{21}G_{21}^2}{(x_1 + x_2G_{21})^2} + \dfrac{x_1^2\tau_{12}G_{12}}{(x_2 + x_1G_{12})^2}$ $G_{ij} = \exp(-\alpha_{ij}\tau_{ij})$	$\ln \gamma_2 = \dfrac{x_1^2\tau_{12}G_{12}^2}{(x_2 + x_1G_{12})^2} + \dfrac{x_2^2\tau_{21}G_{21}}{(x_1 + x_2G_{21})^2}$ $G_{ij} = \exp(-\alpha_{ij}\tau_{ij})$
(6) UNIQUAC (two-constant)	$\ln \gamma_1 = \ln\dfrac{\Psi_1}{x_1} + \dfrac{\overline{Z}}{2}q_1 \ln\dfrac{\theta_1}{\Psi_1} + \Psi_2\left(l_1 - \dfrac{r_1}{r_2}l_2\right) - q_1\ln(\theta_1 + \theta_2T_{21}) + \theta_2q_1\left(\dfrac{T_{21}}{\theta_1 + \theta_2T_{21}} - \dfrac{T_{12}}{\theta_2 + \theta_1T_{12}}\right)$	$\ln \gamma_2 = \ln\dfrac{\Psi_2}{x_2} + \dfrac{\overline{Z}}{2}q_2 \ln\dfrac{\theta_2}{\Psi_2} + \Psi_1\left(l_2 - \dfrac{r_2}{r_1}l_1\right) - q_2\ln(\theta_2 + \theta_1T_{12}) + \theta_1q_2\left(\dfrac{T_{12}}{\theta_2 + \theta_1T_{12}} - \dfrac{T_{21}}{\theta_1 + \theta_2T_{21}}\right)$

SLE for Solid Solution

- Two Types of Phase Behavior



(b) Eutectic-forming system of ortho- and parachloro-nitrobenzene system suitable for melt crystallization



(c) Solid-solution system suitable for fractional melt crystallization

Molecular structures are different

Molecular structures are similar

SLE for Solid Solution

- Basic Thermodynamic Framework

$$f_i^l = f_i^s$$

$$x_i \gamma_i^l f_i^l = z_i \gamma_i^s f_i^s$$

$$x_i \gamma_i^l = z_i \gamma_i^s \psi_i \longrightarrow \psi_i \equiv \frac{f_i^s}{f_i^l}$$

Similar technique in 2.2 can be used

⇨ Required information
- Melting points
- Heat of fusion/melting
- Heat capacity of solid and liquid

SLE for Solid Solution – Rigorous Derivation

$$\psi_i = \exp \int_{T_{m_i}}^{T} \frac{H_i^l - H_i^s}{RT^2} dT$$

$$\int_{T_{m_i}}^{T} \frac{H_i^l - H_i^s}{RT^2} dT = \frac{\Delta H_i^{sl}}{RT_{m_i}} \left(\frac{T - T_{m_i}}{T} \right) + \frac{\Delta C_{P_i}^{sl}}{R} \left[\ln \frac{T}{T_{m_i}} - \left(\frac{T - T_{m_i}}{T} \right) \right] + I$$

$$I \equiv \int_{T_{m_i}}^{T} \frac{1}{RT^2} \int_{T_{m_i}}^{T} \int_{T_{m_i}}^{T} \left[\frac{\partial (C_{P_i}^l - C_{P_i}^s)}{\partial T} \right]_P dT\, dT\, dT$$

SLE for Solid Solution

- If ***I*** and Heat capacity changes are negligible,

$$\psi_i \equiv \frac{f_i^s}{f_i^l} = \exp \frac{\Delta H_i^{sl}}{RT_{m,i}} \left(\frac{T - T_{mi}}{T} \right)$$

$$x_i \gamma_i^l = z_i \gamma_i^s \psi_i$$

SLE for Solid Solution

- Case I : Solid Solution

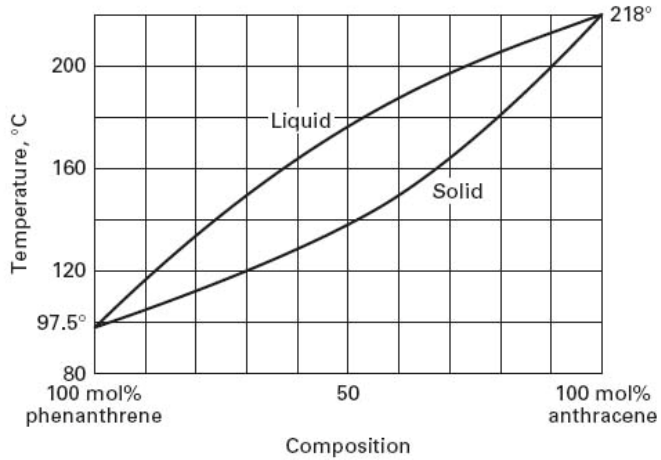
$$x_i \gamma_i^l = z_i \gamma_i^s \psi_i$$

$$x_1 = z_1 \psi_1$$

$$x_2 = z_2 \psi_2$$

$$x_1 + x_2 = 1$$

$$z_1 + z_2 = 1$$



(c) Solid-solution system suitable for fractional melt crystallization

$$x_1 = \frac{\psi_1 (1 - \psi_2)}{\psi_1 - \psi_2}$$

$$x_2 = \frac{(1 - \psi_2)}{\psi_1 - \psi_2}$$

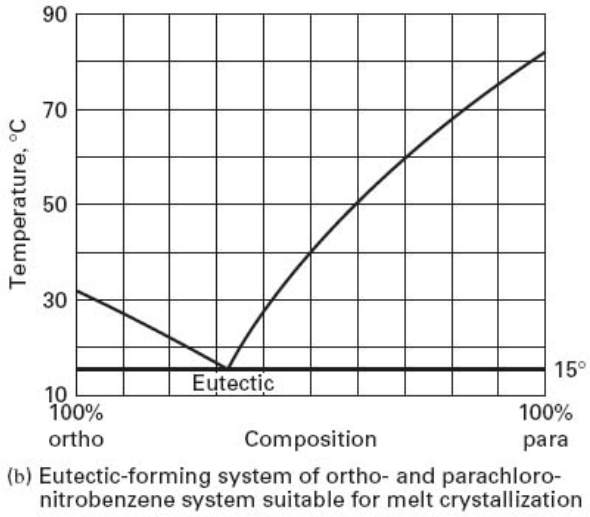
$$\psi_i \equiv \frac{f_i^s}{f_i^l} = \exp \frac{\Delta H_i^{sl}}{R T_{m,i}} \left(\frac{T - T_{mi}}{T} \right)$$

SLE for Solid Solution

- Case II : Immiscible Solid (Eutectic Forming)

$$x_i \gamma_i^l = z_i \gamma_i^s \psi_i$$

$$x_1 = \psi_1$$
$$x_2 = \psi_2$$



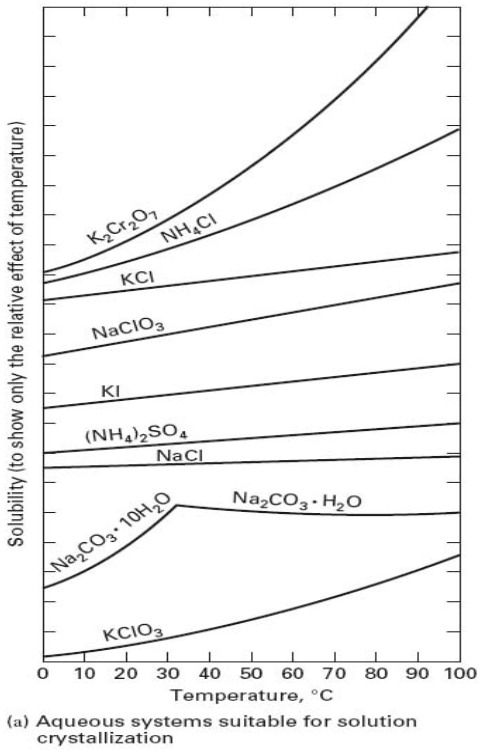
(b) Eutectic-forming system of ortho- and parachloro-nitrobenzene system suitable for melt crystallization

$$x_1 = \psi_1 = \exp \frac{\Delta H_1^{sl}}{RT_{m,1}} \left(\frac{T - T_{m,1}}{T} \right)$$

$$x_2 = \psi_2 = \exp \frac{\Delta H_2^{sl}}{RT_{m,2}} \left(\frac{T - T_{m,2}}{T} \right)$$

Types of Phase Diagram… How to interpret ?

- Two component system



(a) Aqueous systems suitable for solution crystallization

Simple Behavior

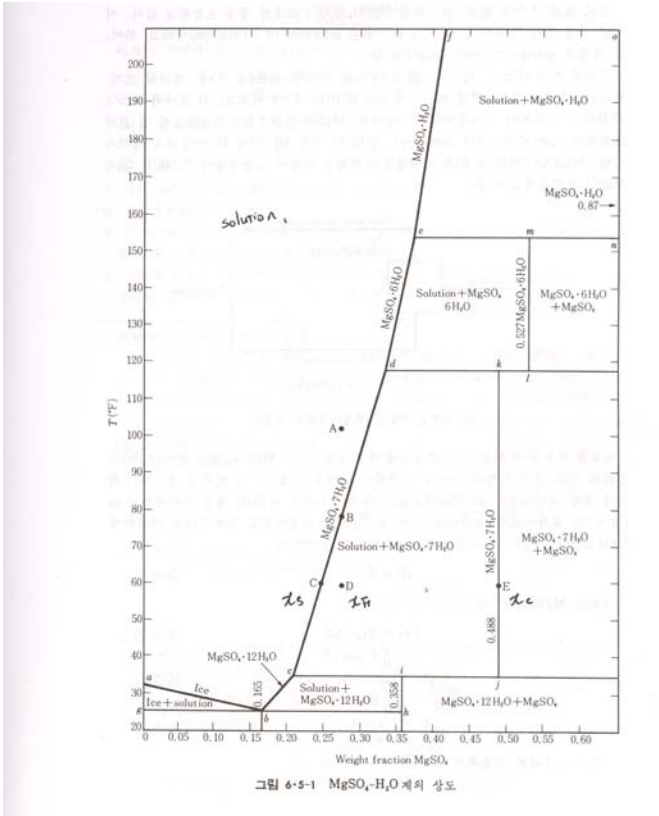


그림 6·5-1 $MgSO_4$-H_2O 계의 상도

Complex Behavior

Types of Phase Diagram… How to interpret ?

- Lever Rule
  - Always applies to any kind of phase diagram
  - Two simple rules
    - Three points those satisfies material balance equation must lie on a same line
    - The amount of splits are proportional to the length of line in opposite direction

Types of Phase Diagram… How to interpret ?

- Example of Lever Rule : MgSO4 System
- Several structures can be produced for water-salt systems.
  - Example) Solid magnesium sulfate

MgSO4	anhydrous magnesium sulfate
MgSO4·H2O	magnesium sulfate monohydrate
MgSO4·6H2O	magnesium sulfate hexahydrate
MgSO4·7H2O	magnesium sulfate heptahydrate
MgSO4·12H2O	magnesium sulfate dodecahydrate

Solution State
MgSO4 + H2O

Composition of
Solutions

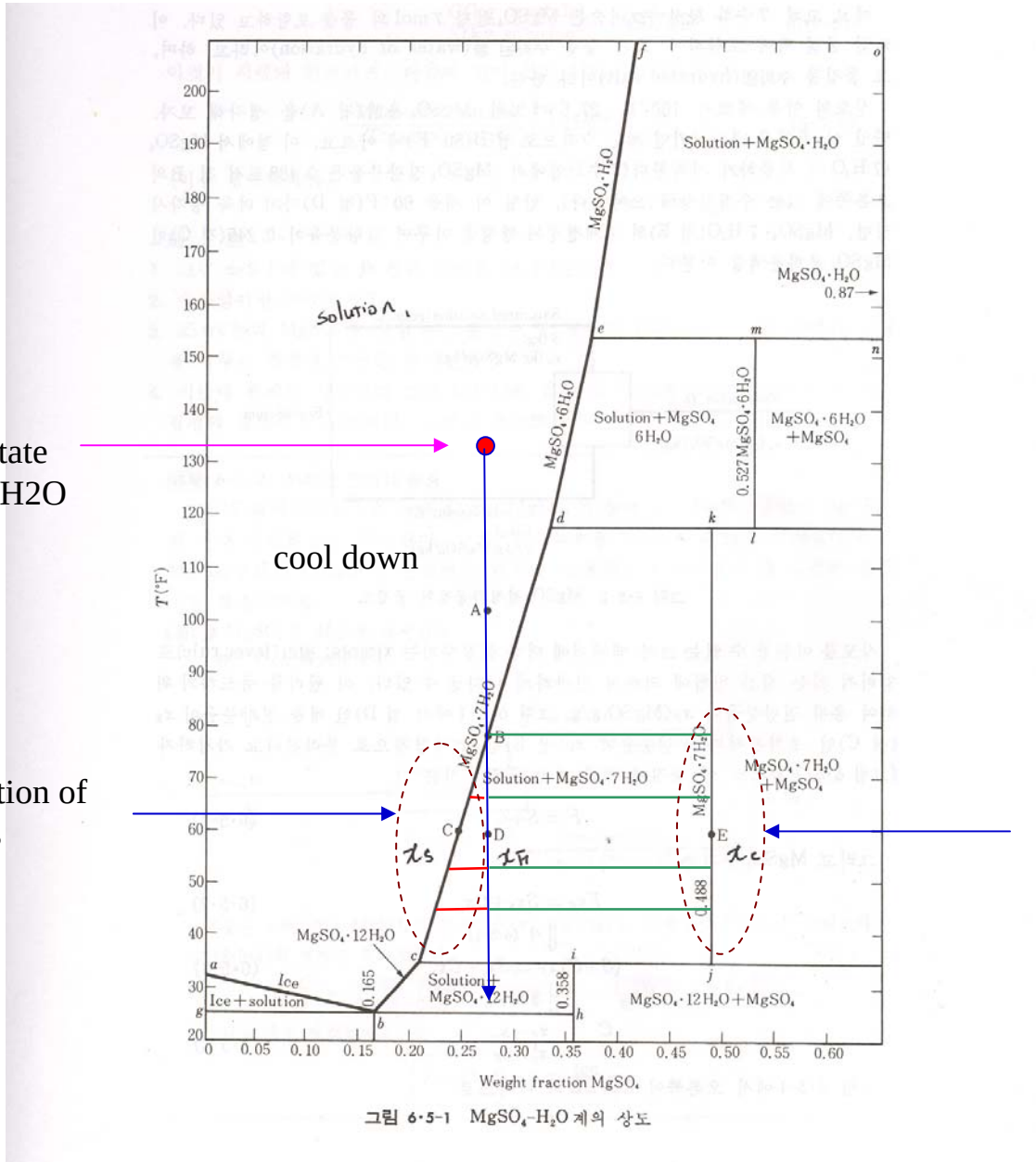


그림 6·5-1 $MgSO_4$-H_2O 계의 상도

Composition of
Solid MgSO4·7H2O

Lever Rule

- Solution → (Cool down) → Solid + Solution
  - **Overall Material Balance Eqn.**

$$F = S + C$$

F : Feed

S : Solution

C : Crystal

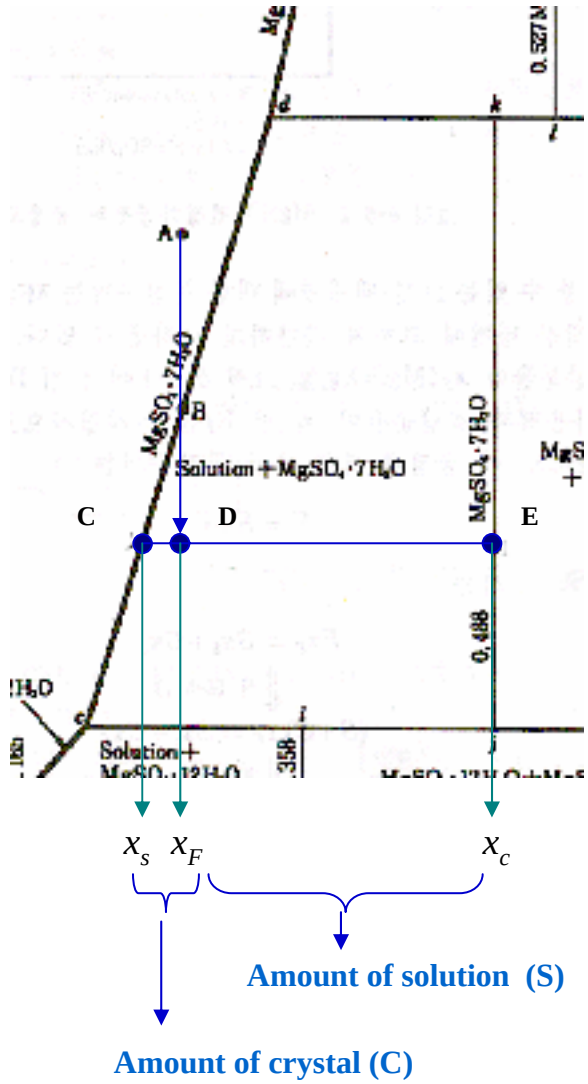
  - **MgSO4 Balance**

$$Fx_F = Sx_s + Cx_c$$

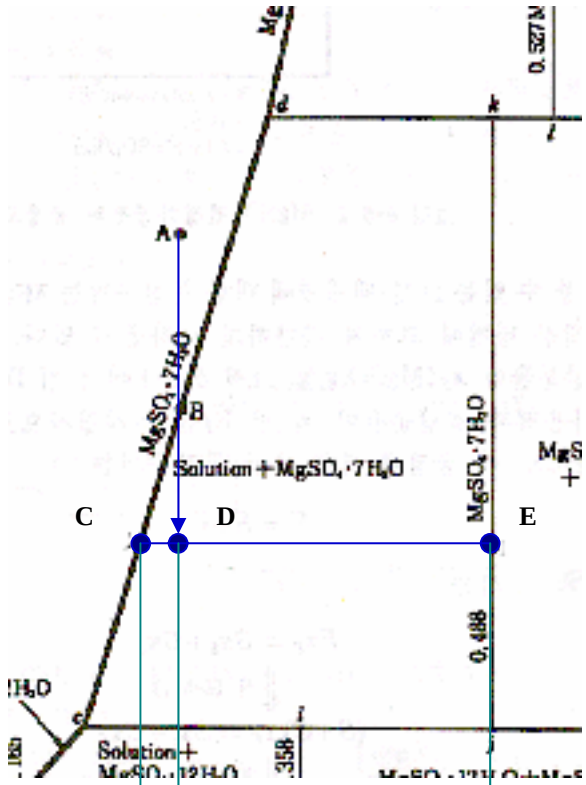
$$(S + C)x_F = Sx_s + Cx_c$$

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

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



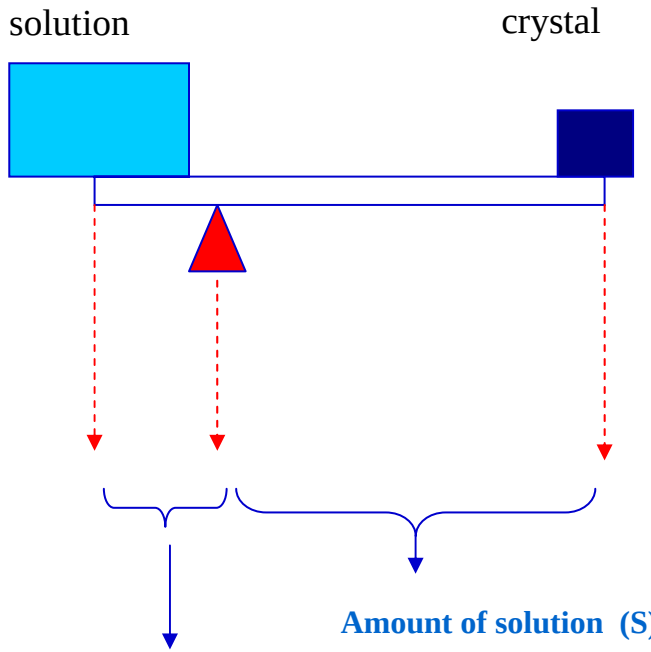
Lever Rule (지렛대원리)



x_s x_F x_c

Amount of solution (S)

Amount of crystal (C)



Amount of solution (S)

Amount of crystal (C)

Three Component Systems

- Construction of Ternary Diagram

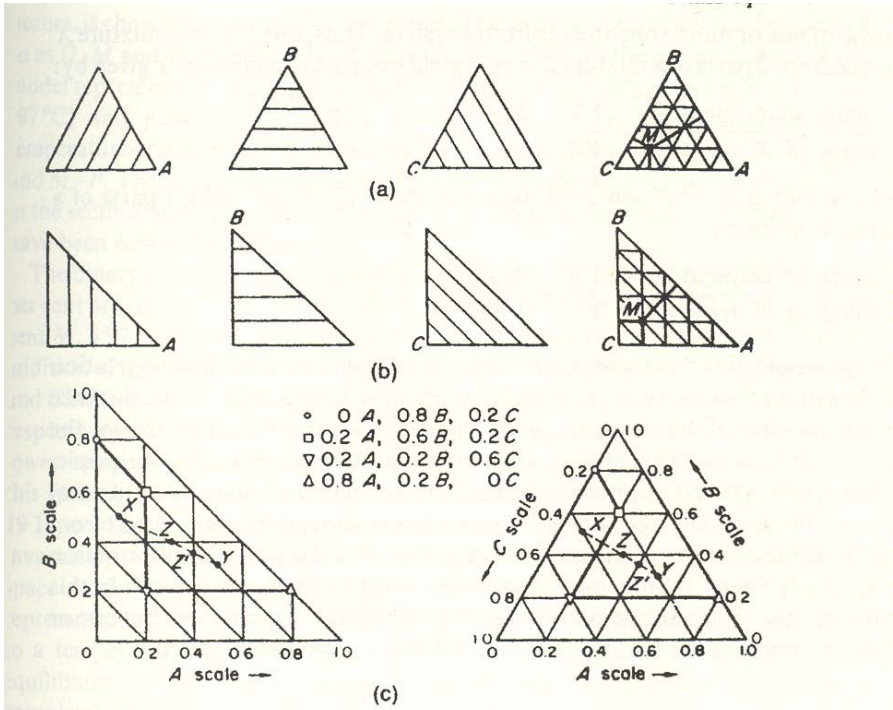
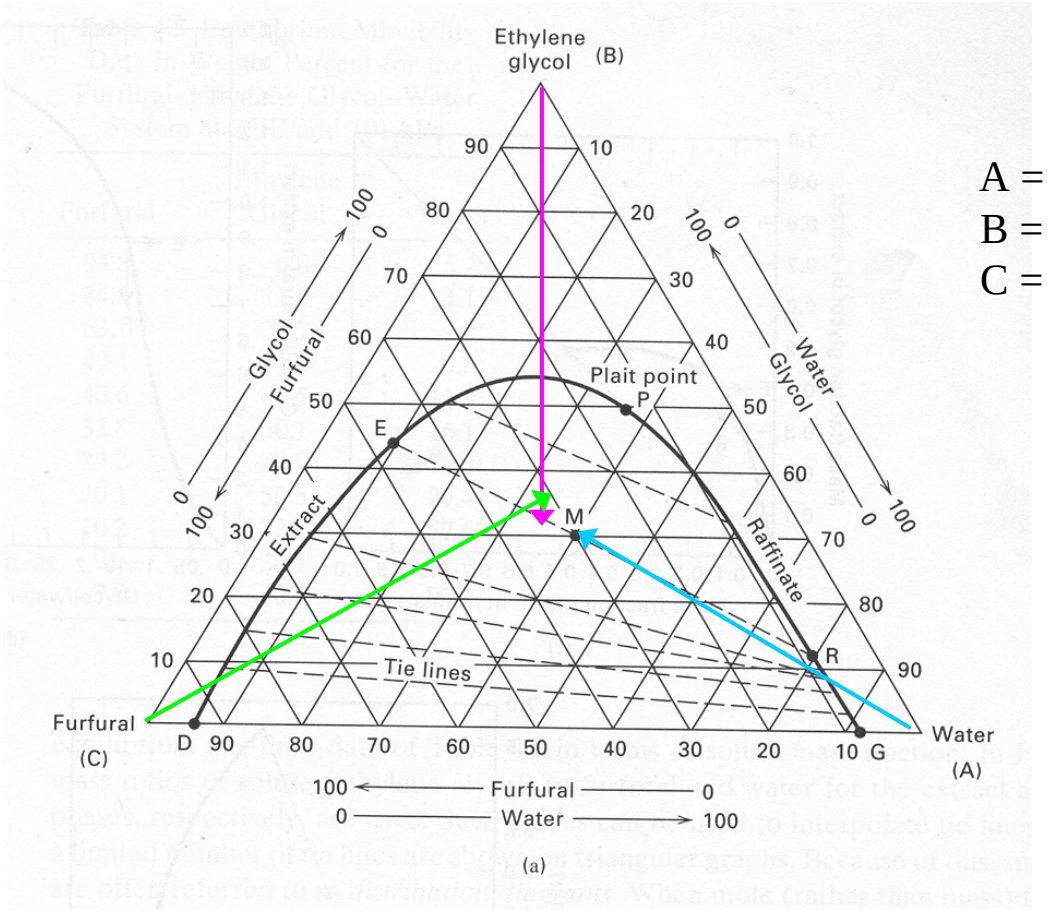


Figure 4.19. *Construction of equilateral triangular diagrams*

Three Component Systems

- How to read composition (M point)



A = 40 %
B = 30 %
C = 30 %

Three Component Systems

- Lever Rule

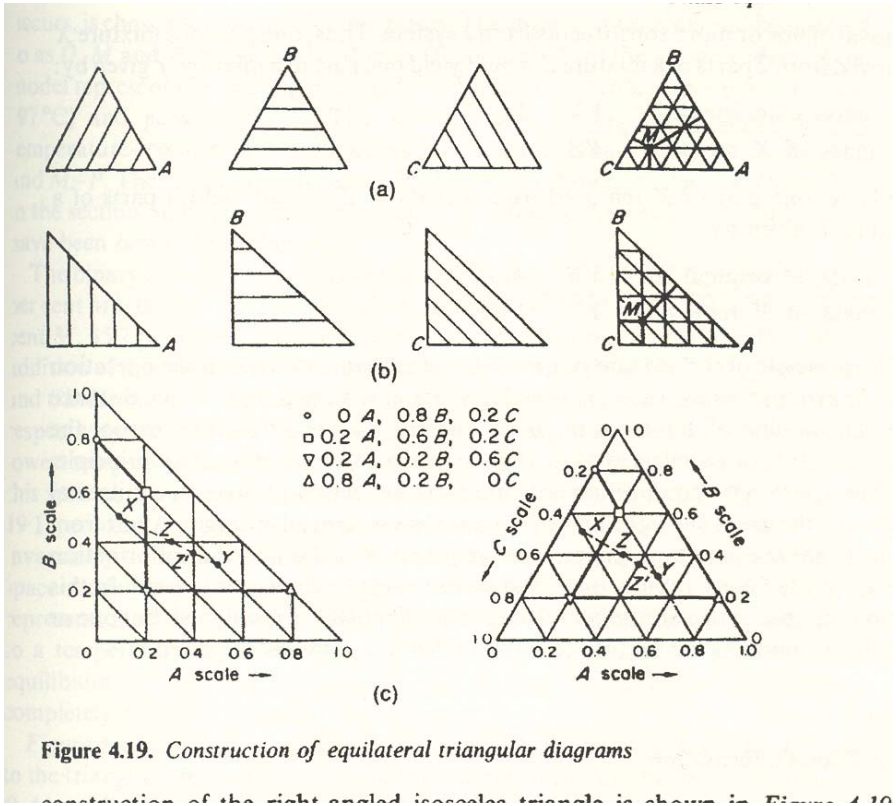


Figure 4.19. *Construction of equilateral triangular diagrams*

$$X + Y = Z$$

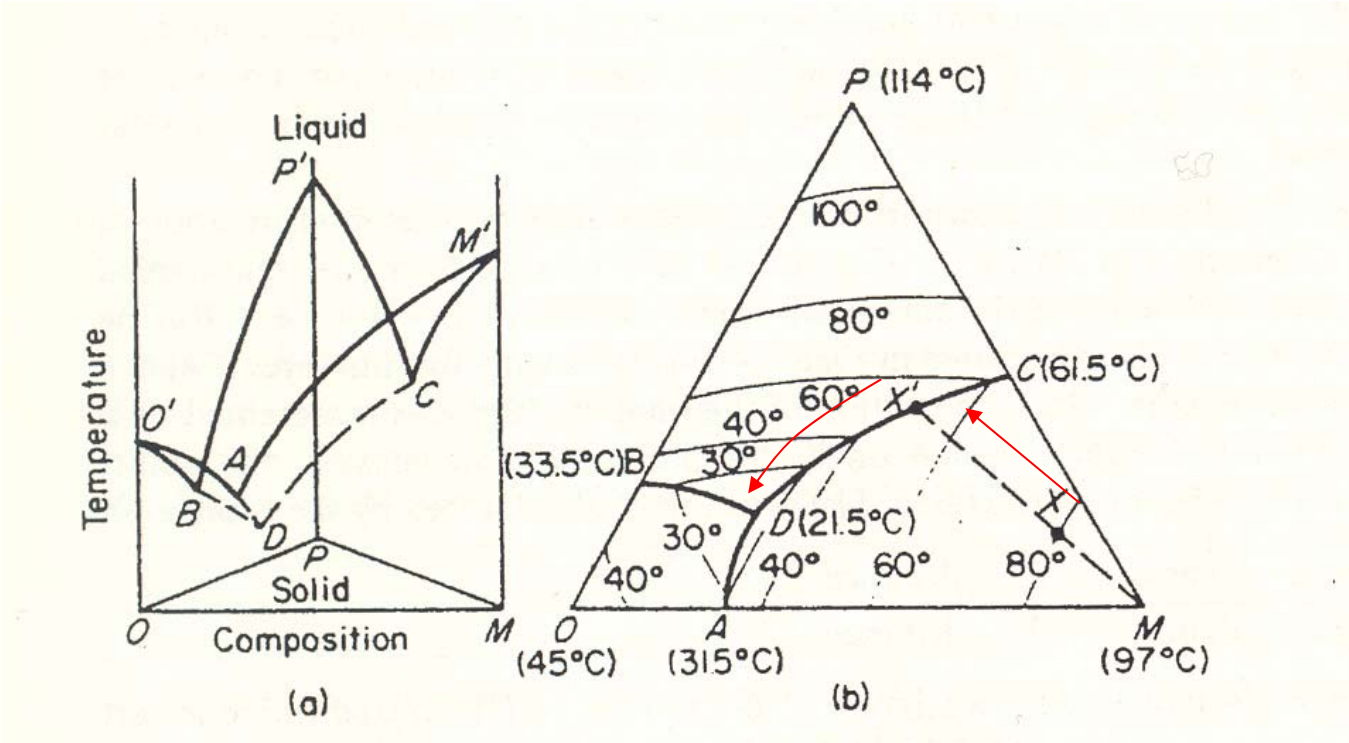
Or

$$Z = X + Y$$

$$\frac{\text{mass of mixture X}}{\text{mass of mixture Y}} = \frac{\text{distance YZ}}{\text{distance XZ}}$$

Three Component System - (1) Solid Solutions

- System : o-, m-, p- nitrophenol
  - A, B, C : Eutectic Points



Three Component System – (2) Two Salts and Water

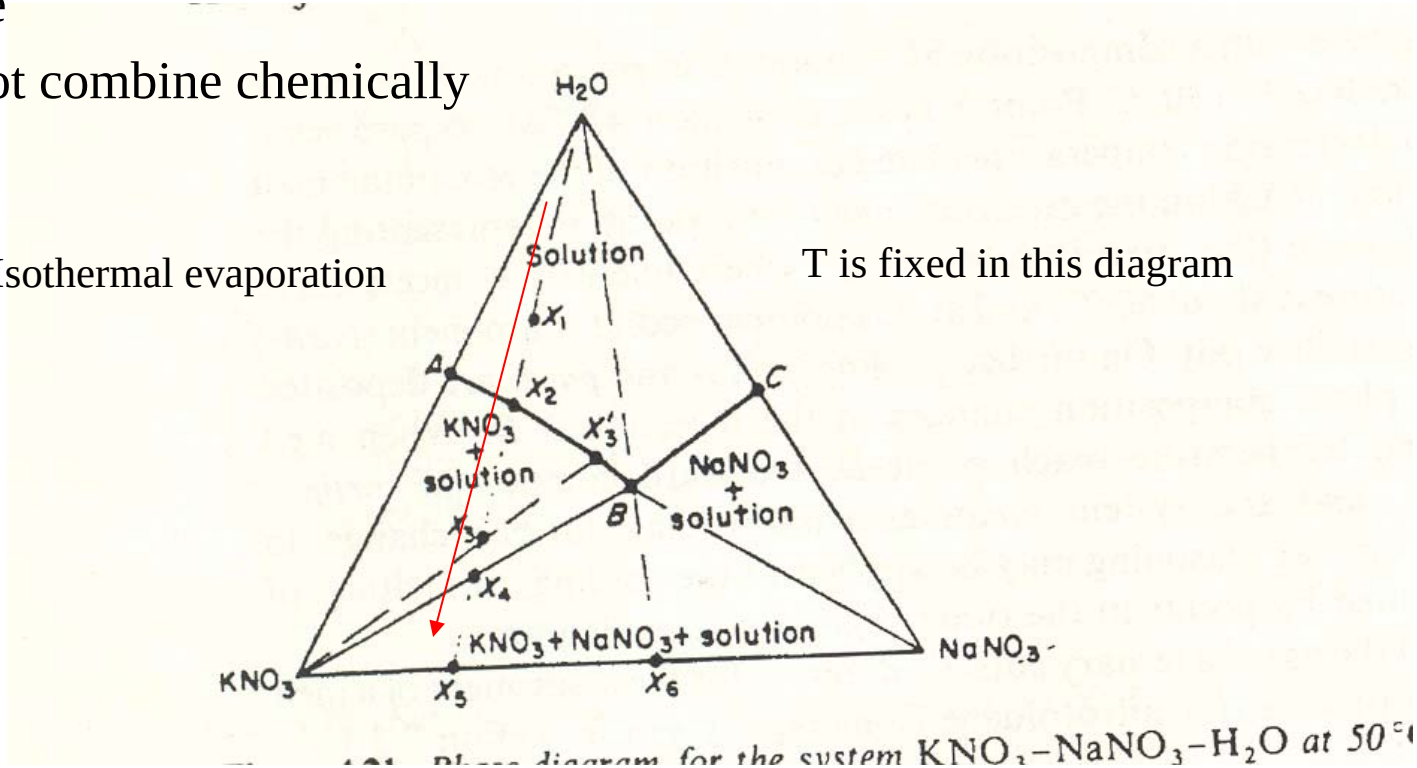
- Different Types of Phase Behavior
  - No chemical reaction
  - Formation of a solvate (hydrate)
  - Formation of double salt
  - Formation of hydrate double salt

Two salt and water – No chemical reaction

- KNO3 + NaNO3 + Water
- No chemical reaction
- No hydrate
- They do not combine chemically

Isothermal evaporation

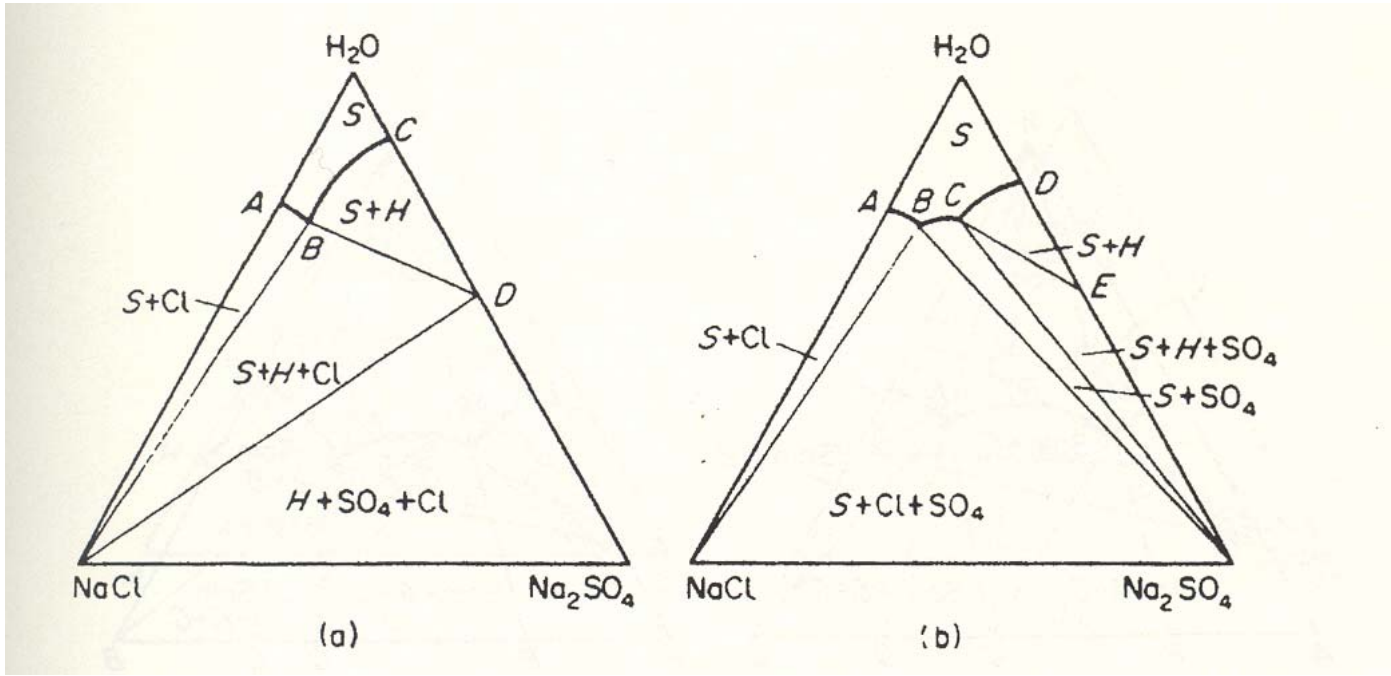
T is fixed in this diagram



Phase diagram for the system KNO_3–$NaNO_3$–H_2O at 50 °C

Two salt and water – Solvate formation

- When one of solutes can form a compound (solvate, hydrate)
- NaCl + NaSO4 + Water System
- Legend : S(solution), H(hydrate, Na2SO4.10H2O), SO4 (Na2SO4), Cl (NaCl)

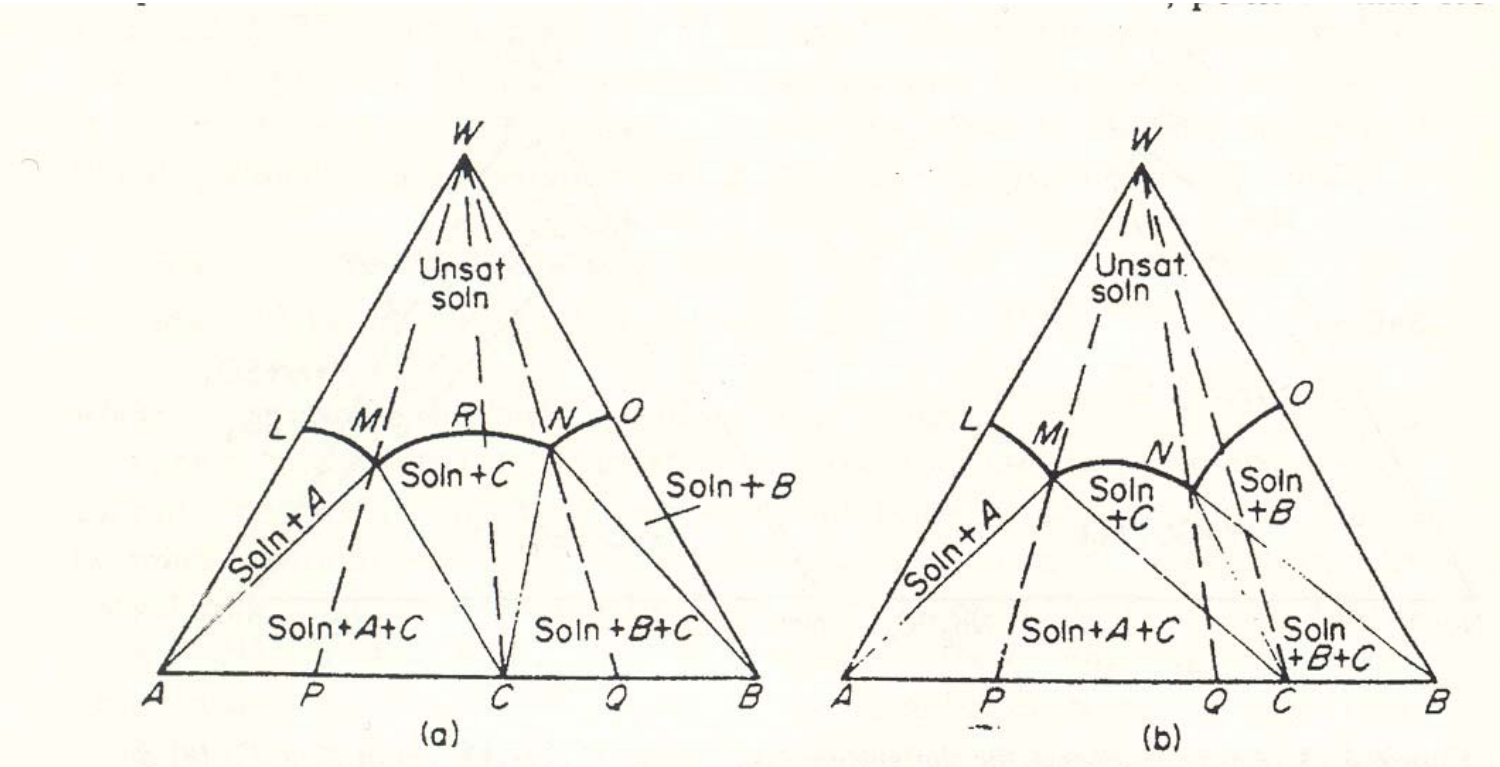


At 17.5 degree C

At 25 degree C

Two salt and water – Double Compound Formation

- When two dissolved solutes form double compound
  - C : double salt

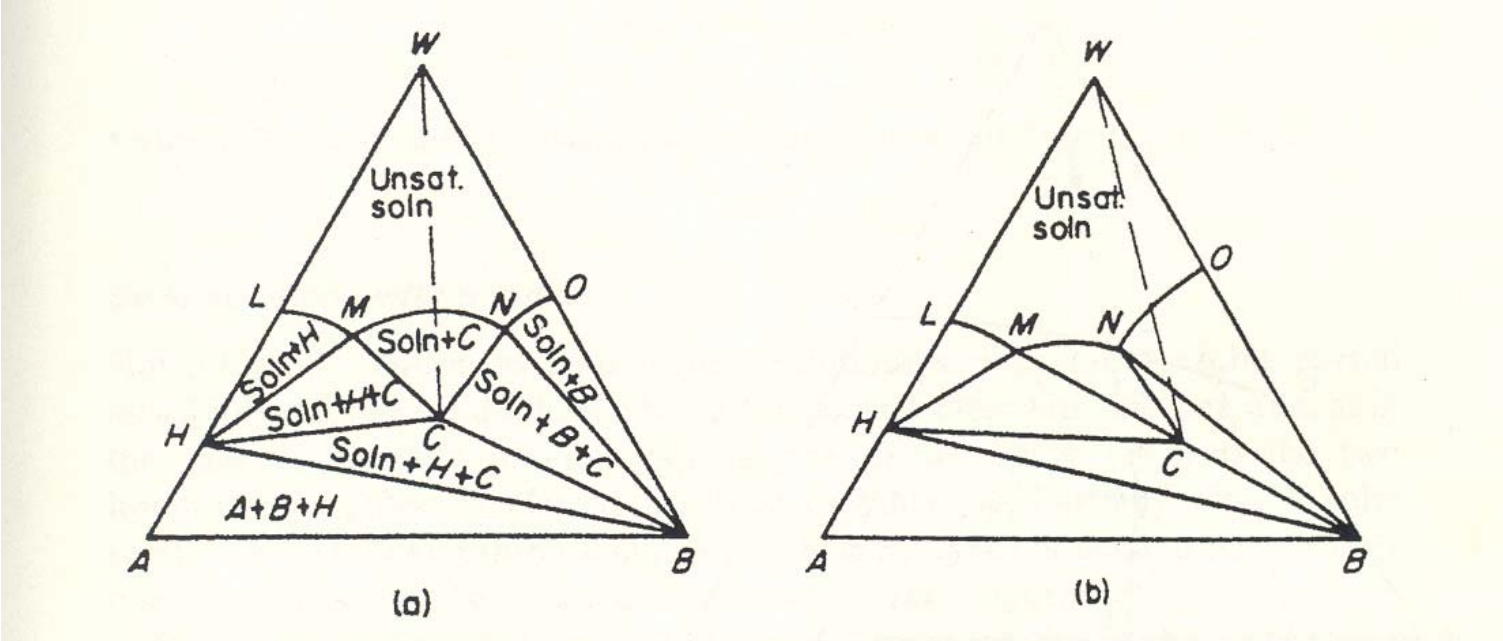


Stable in Water

Decomposed by Water

Hydrated Double Salt

- H : Hydrate
- C : Hydrated Double Salt



Two Salt and Water – Solid Solution Formation

- Water + Two electrolyte with common ion