

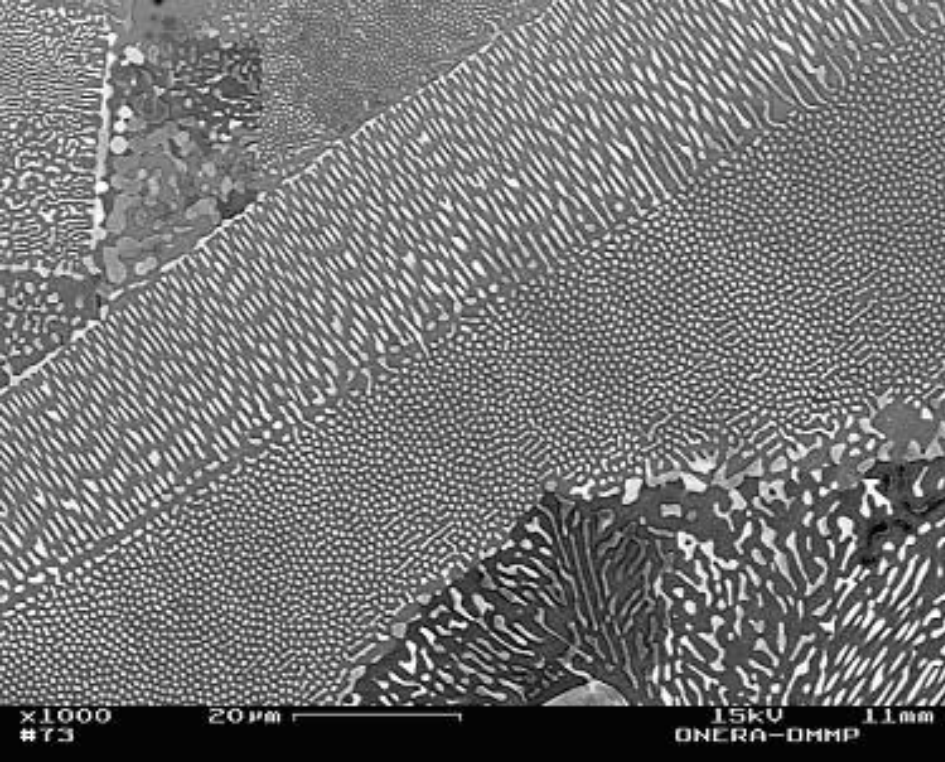
The background of the slide is a photograph of an industrial facility, likely a refinery or chemical plant. It features a complex network of large, silver-colored metal pipes and structures. The pipes are arranged in various directions, some running horizontally and others vertically. The sky is a clear, bright blue with some light, wispy clouds. The overall scene is brightly lit, suggesting a sunny day.

# ΔΙΕΡΓΑΣΙΕΣ ΔΙΑΧΩΡΙΣΜΟΥ

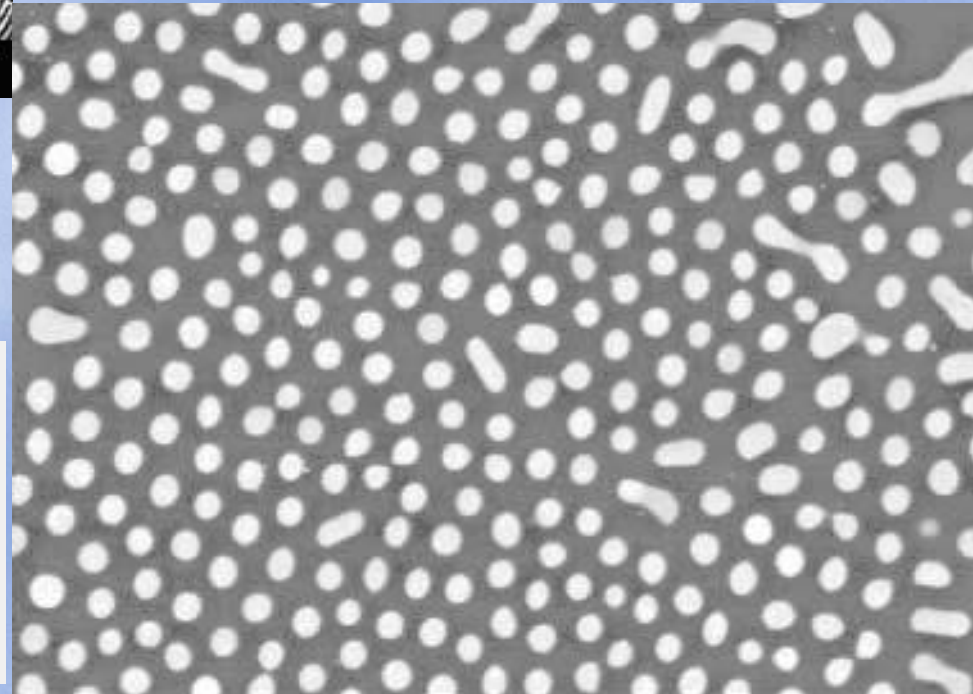
## Μάθημα 4ο

Ακαδημαϊκό έτος 2017-2018

Eutectic microstructure of a Nb (81.8%) - Si (18.2%) (atom percent) alloy: niobium (light phase) dispersed in Nb<sub>3</sub>Si (grey phase).



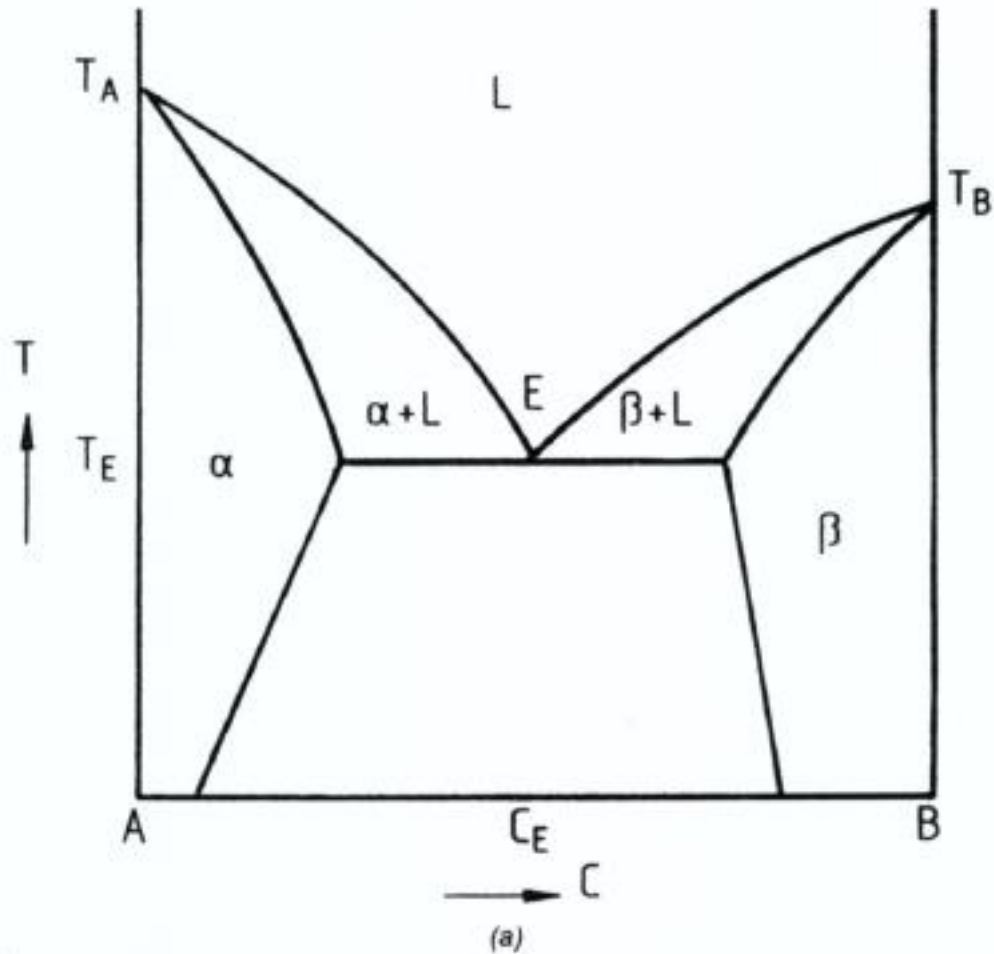
High magnification view of the eutectic microstructure in a Nb (81.8%) - Si (18.2%) alloy (Nb is the light phase, Nb<sub>3</sub>Si is the dark phase).



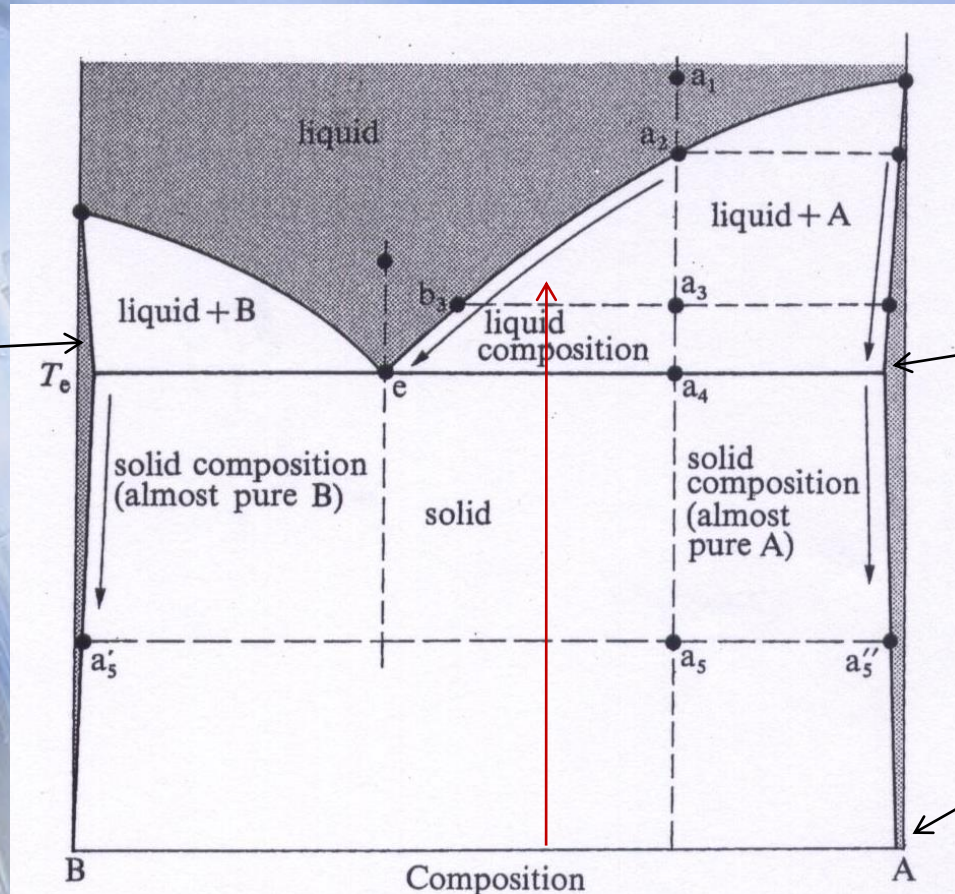
2 μm



# Limited solid solubility



# Phase Diagram For Two Almost Immiscible Solids



region of solubility of A in B

region of solubility of A in B

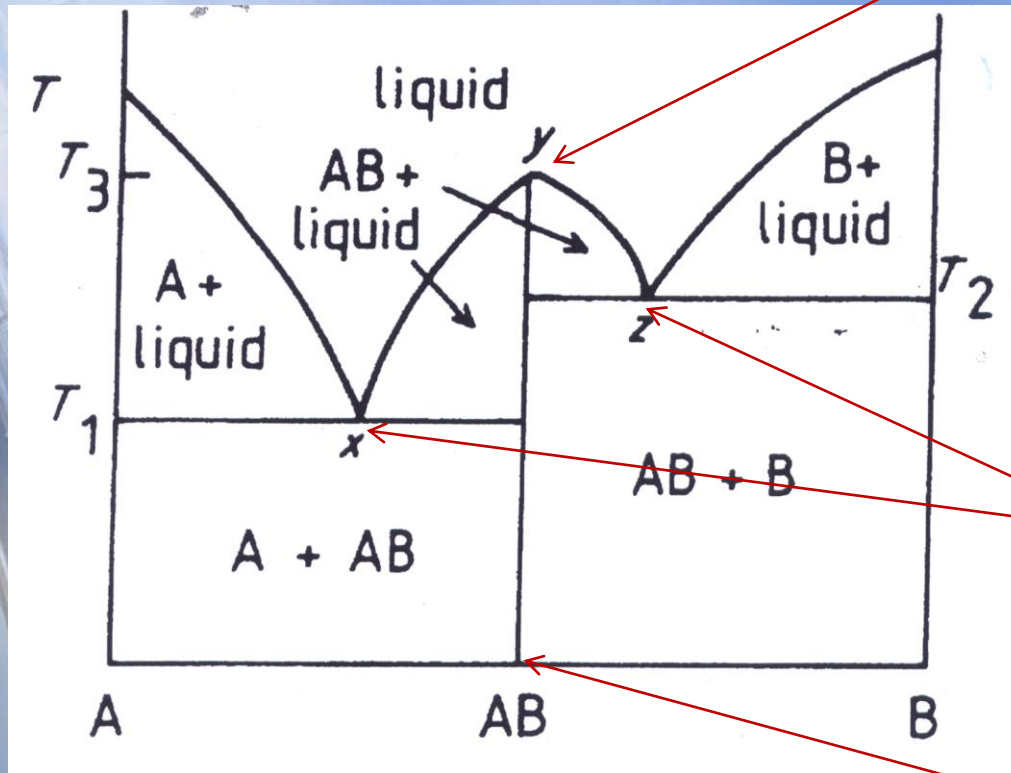
always some width

e.g. most solder is 50:50 Pb/Sn;  
heat to solid/liquid region; get solid particles in slushy solder liquid



# Phase Diagram If Two Components Form 3<sup>rd</sup> Compound

- Looks like two Eutectic Diagrams next to each other.

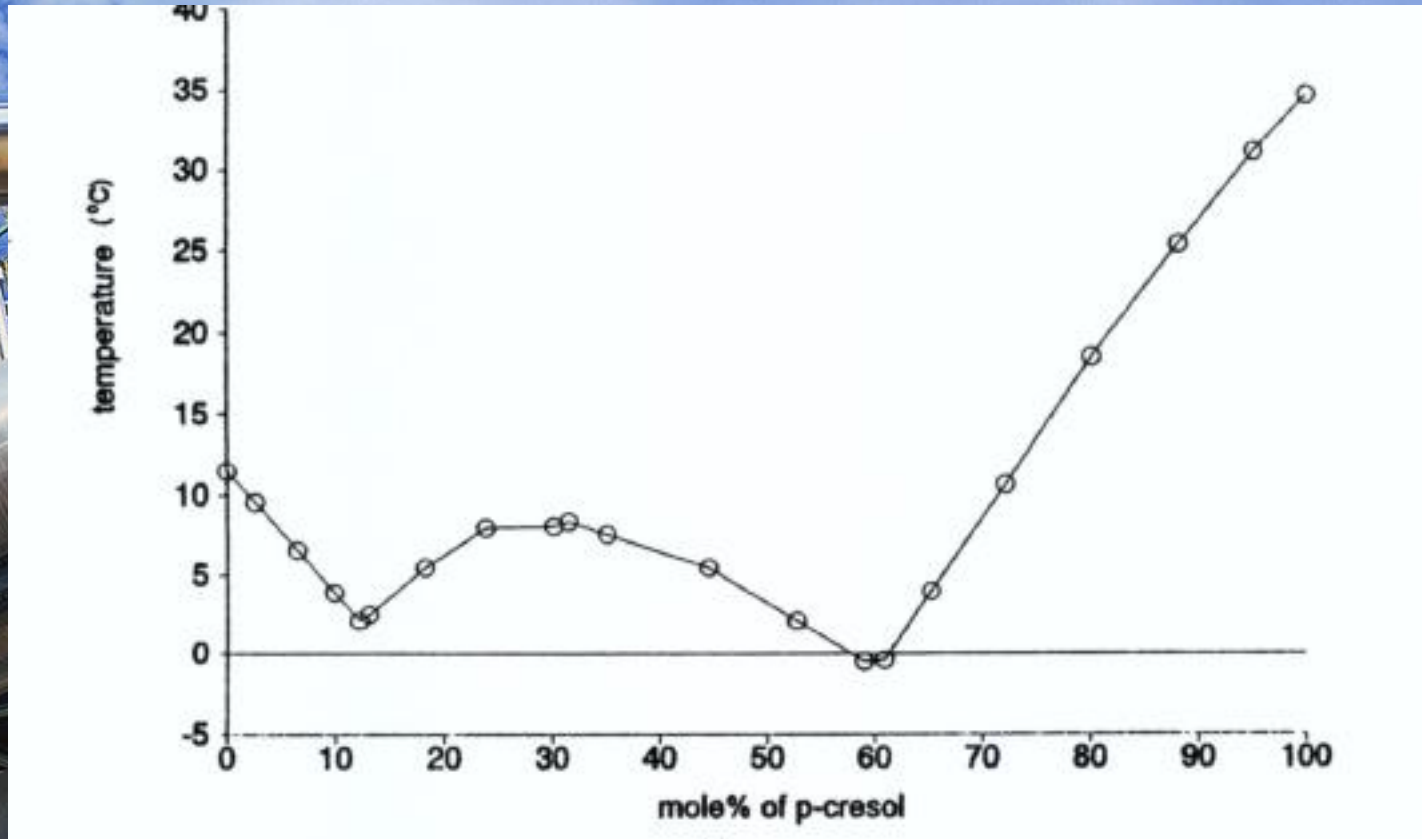


new compound  
melts  
congruently

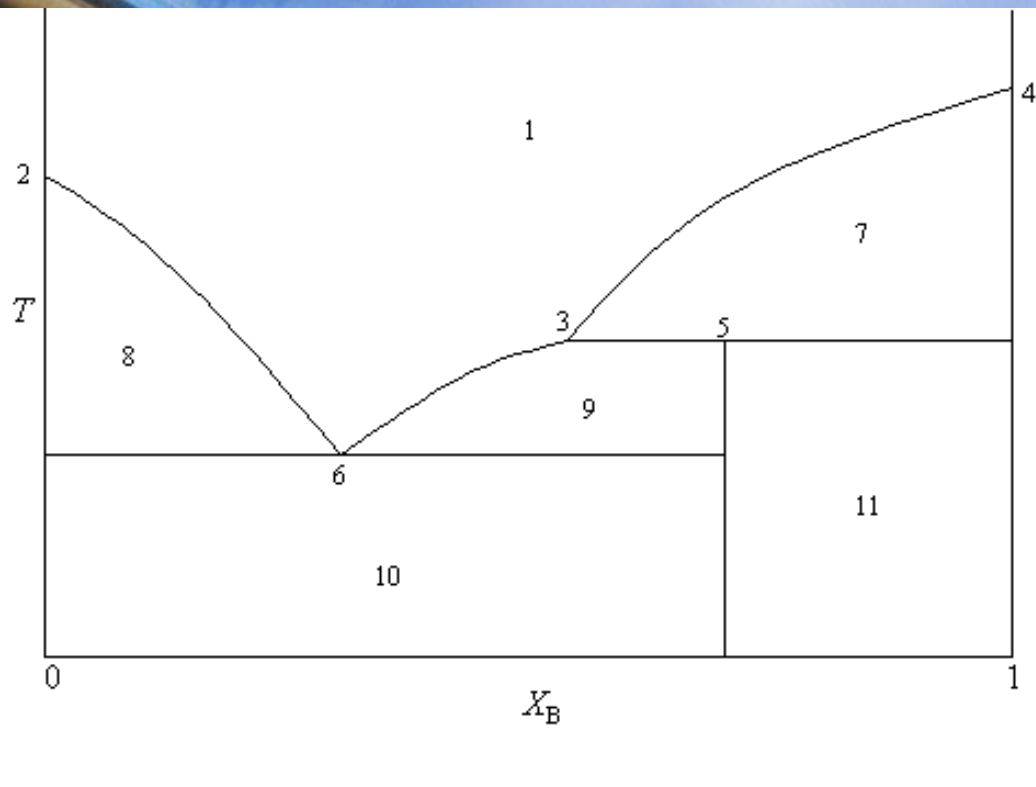
Two  
Eutectic  
Points

Compound Forms;  
called line  
compound

# Formation of a molecular compound (meta and p-cresol system)



Diagrams with two eutectic points



This phase diagram shows an incongruent melting point. The vertical line at point 5 represents formation of a compound. It looks like the composition of the compound is  $X_B = 2/3$ , from which we conclude,

$$X_B = \frac{2}{3} = \frac{n_B}{n_A + n_B} = \frac{2}{1 + 2},$$

so that the compound is  $AB_2$ . Point 5 is the melting point of  $AB_2$ , but notice that melting  $AB_2$  does not give liquid of the same composition. Rather, melting of  $AB_2$  gives liquid with the composition at point 3 and pure B(s). So the compound,  $AB_2$ , melts and decomposes at the same time. An analysis of the points and regions is:

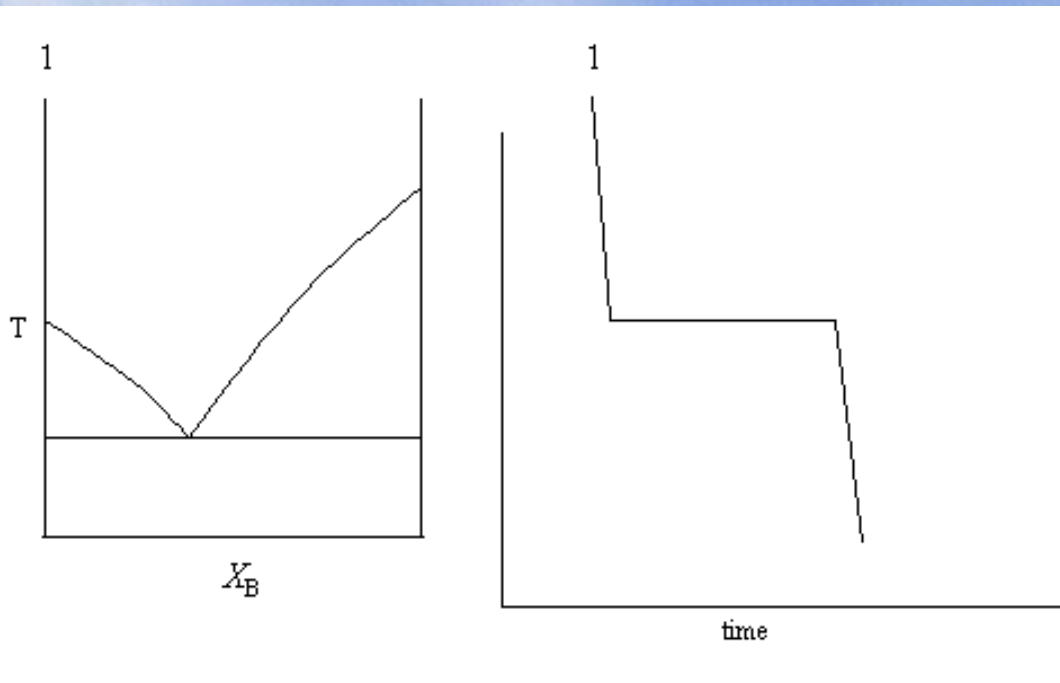
1 = liquid    2 = MP of A    3 = the peritectic point (we don't get a eutectic of  $AB_2$  and B)    4 = MP of B    5 = the incongruent melting point of  $AB_2$     6 = eutectic of A and  $AB_2$     7 = liquid + B(s)    8 = A(s) and liquid    9 = liquid and  $AB_2$ (s)    10 = A(s) +  $AB_2$ (s)    11 =  $AB_2$ (s) + B(s)



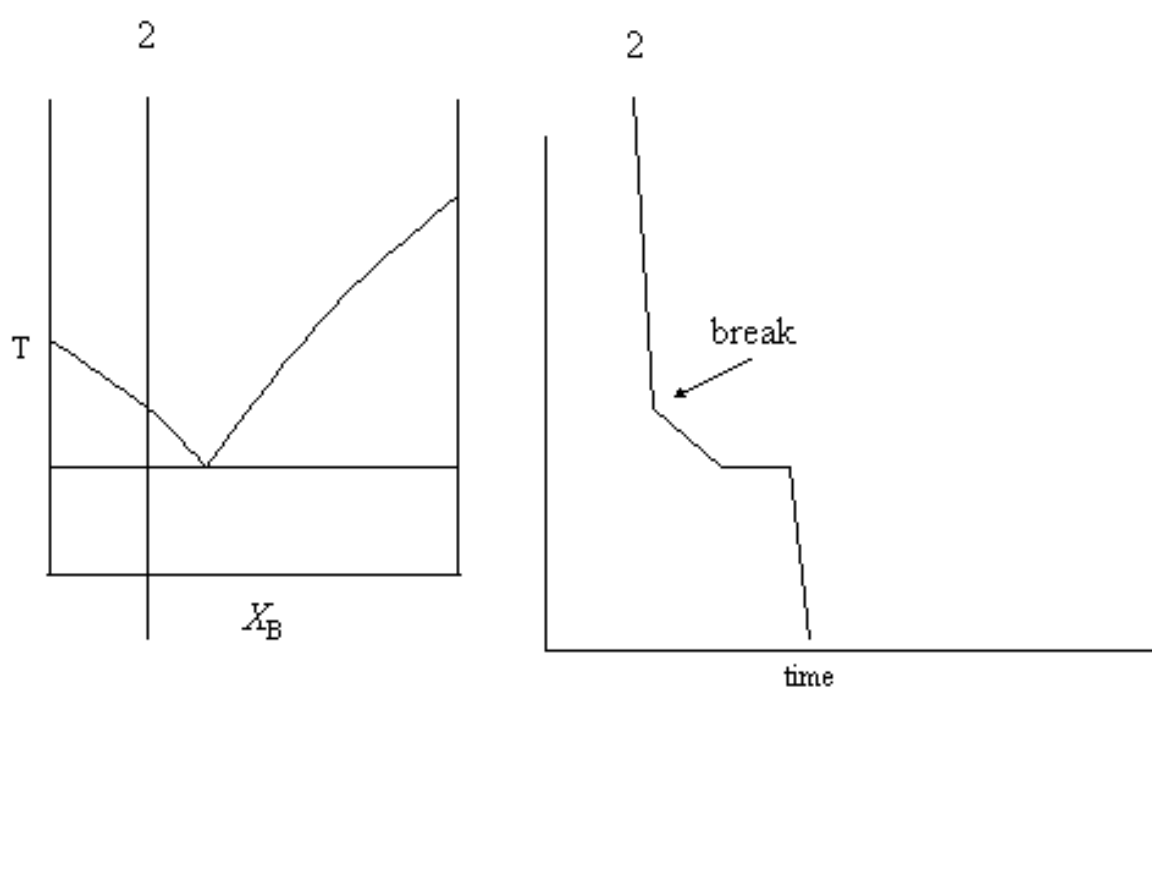
what kind of experimental data it takes to determine the phase diagram of a two-component system.

One such data set comes from cooling curves.

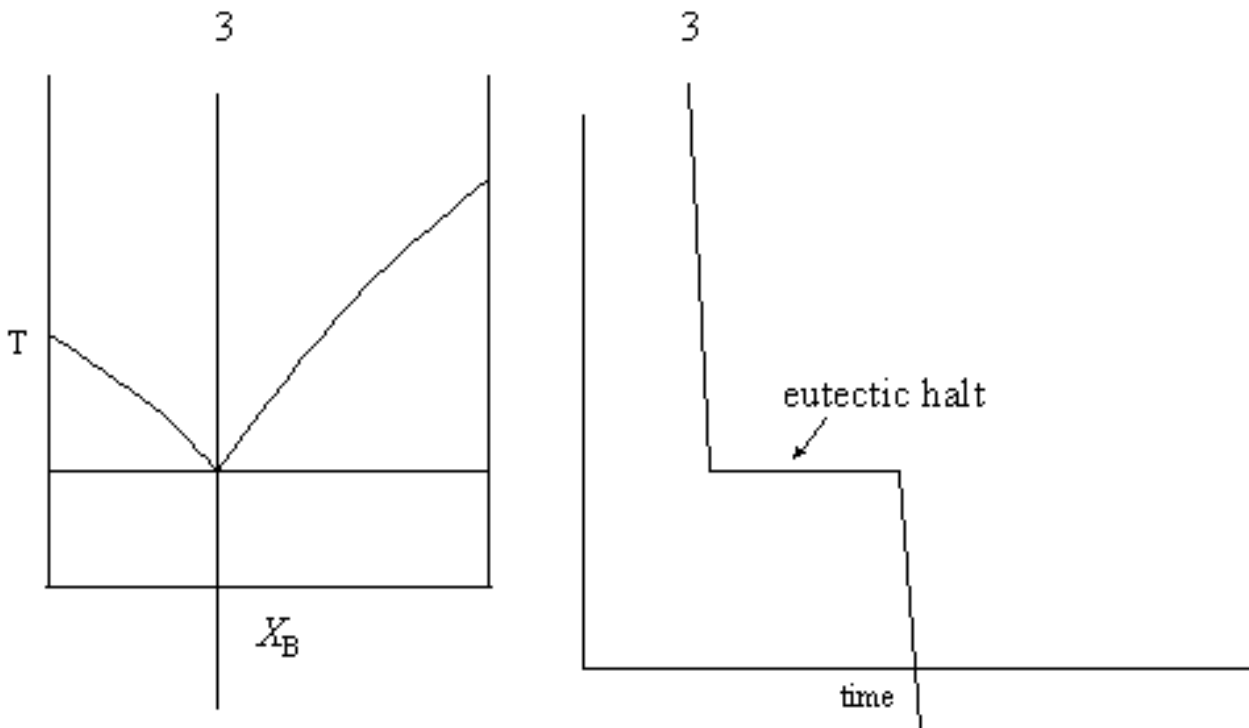
To make a cooling curve you start with liquid at some composition. Then you allow it to cool slowly and measure the temperature as a function of time. (You want it to cool slowly so that the system has time to establish equilibrium at each temperature. This may be hard to do because physical and chemical processes involving solids can be very slow. Nevertheless, you would like to be as close to equilibrium as you can be.)







On this cooling curve we have a break (change in slope) at the point where  $A(s)$  begins to precipitate out. The system cools slower at the break because  $A(s)$  is crystalizing (freezing) out and the heat of fusion being released in this process must be dissipated in addition to the heat removed in simply lowering the temperature.



The next cooling curve will be at the composition of the eutectic. Nothing happens until we reach the melting point of the eutectic, at which point the temperature remains constant until all of the material has solidified



A photograph of an industrial facility, likely a refinery or chemical plant, featuring large, shiny metal pipes and structures against a clear blue sky with some light clouds. The pipes are arranged in a complex network, with some curving upwards and others running horizontally. The overall scene is bright and clear.

# Solid solutions

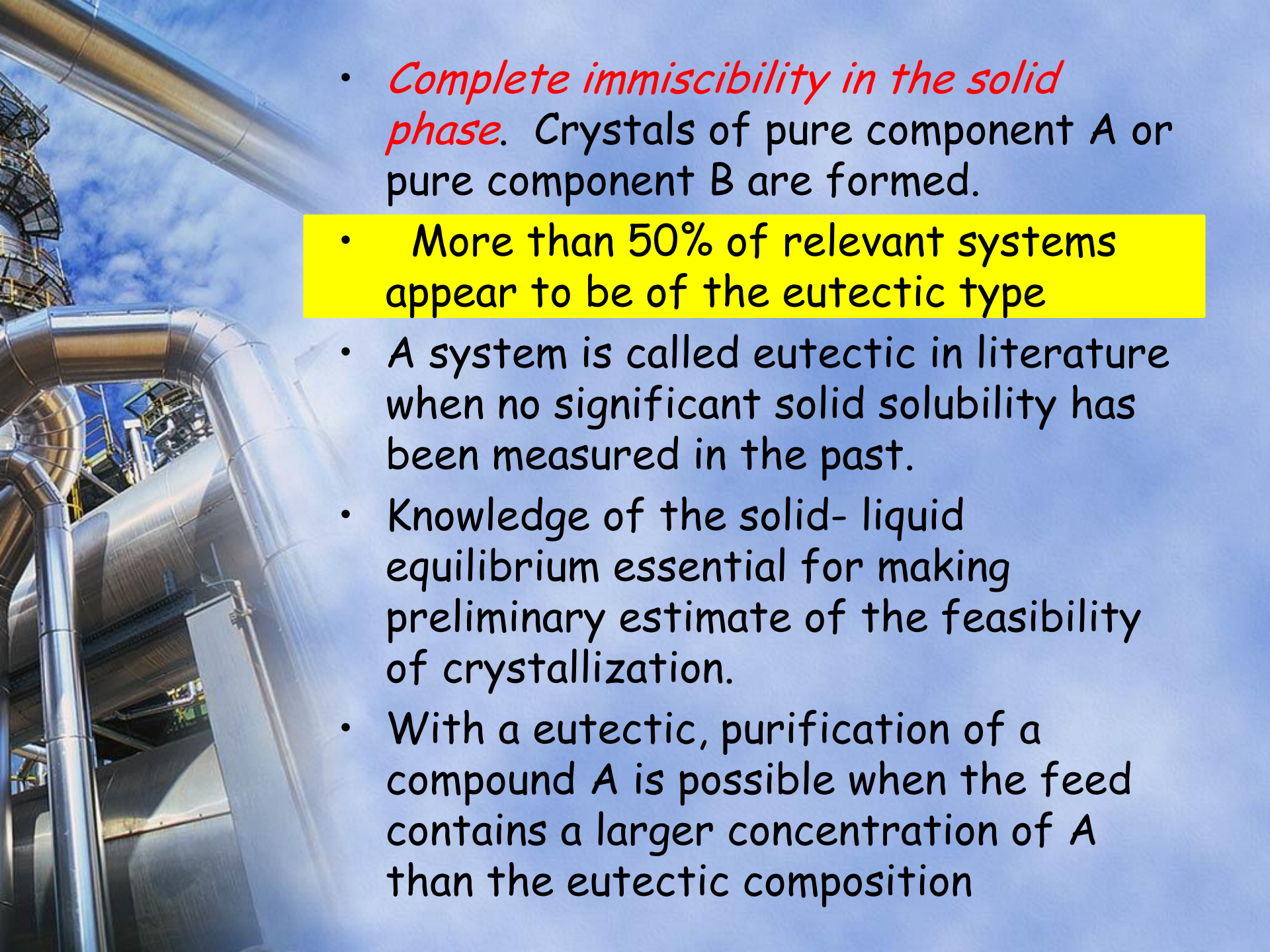
- Due to isomorphous substitution of host molecules by molecules of impurities
- Similarity in size and shape between host and guest molecules essential for the formation of solid solutions
- Host molecules are usually replaced more easily by smaller than from larger molecules
- *Solid solution continuous series when the structure of the components has identical space groups, the same number of molecules per unit cell and similar molecular packing*

A photograph of an industrial facility with large, shiny metal pipes and structures against a blue sky with light clouds. The pipes are arranged in a complex network, with some curving upwards and others running horizontally. The background shows more industrial equipment and a clear sky.

# Three groups of phase diagrams

- *Complete miscibility of the solid phase, termed as solid solution.* Besides practically ideal solid and liquid solutions, systems showing melting temperatures higher or lower than the highest or lowest melting temperatures of the pure compounds
- *Limited miscibilities in the solid phase.* Appearance of eutectic. Impurities in general have a limited solubility, even when quite different in nature and shape from crystals. Difficult to have purities > 99.999% in a single step.



- 
- The background of the slide is a photograph of an industrial facility, likely a refinery or chemical plant. It features a complex network of large, silver-colored metal pipes and structures. The pipes are arranged in various directions, some running horizontally and others vertically. The sky is a clear, bright blue with a few wispy white clouds. The overall scene is brightly lit, suggesting a sunny day.
- *Complete immiscibility in the solid phase.* Crystals of pure component A or pure component B are formed.
  - More than 50% of relevant systems appear to be of the eutectic type
  - A system is called eutectic in literature when no significant solid solubility has been measured in the past.
  - Knowledge of the solid- liquid equilibrium essential for making preliminary estimate of the feasibility of crystallization.
  - With a eutectic, purification of a compound A is possible when the feed contains a larger concentration of A than the eutectic composition



- High purity may be obtained in a single crystallization **when no solid solution formation is encountered**
- The purification potential of melt crystallization is usually indicated by the ratio of the impurity contents of the crystal phase and the liquid phase.
- The ratio is called: **Distribution Coefficient**



# Solution thermodynamics.1

- Saturation is the state in which solution is in equilibrium with solid solute.
- From the thermodynamics point of view equilibrium is characterized by the equality between the chemical potentials of the solute in the solution and the solid.

$$\mu_{\text{solid}} = \mu_{\text{solution}}$$

$$\mu_{\text{solid}} = v_c \mu_c + v_\alpha \mu_\alpha$$

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

$$\gamma_i = \frac{\alpha_i}{m_i}$$

# Solution Thermodynamics 2

$$m_{\pm} = (m_c^{v_c} m_{\alpha}^{v_{\alpha}})^{1/v_{\alpha}+v_c}$$

$$\alpha_m = m\gamma_m$$

$$\gamma_{\pm} = (\gamma_c^{v_c} \gamma_{\alpha}^{v_{\alpha}})^{1/v_{\alpha}+v_c}$$

Για διαλύματα ηλεκτρολυτών

$$\alpha_m = \alpha_{\pm,m}^v = (Qm\gamma_{\pm,m})^v$$

$$Q = (v_{v^+}^{v^+} v_{v^-}^{v^-})^{1/v}$$

$$v = v_+ + v_-$$

$$\gamma_{\pm} = (\gamma_+^{v^+} \gamma_-^{v^-})^{1/v}$$

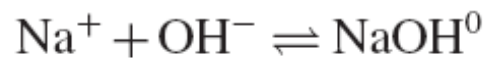
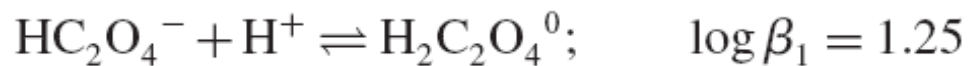
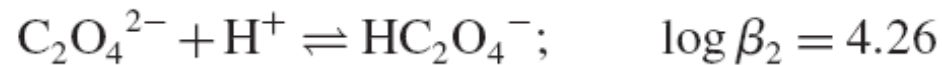
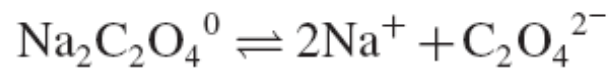
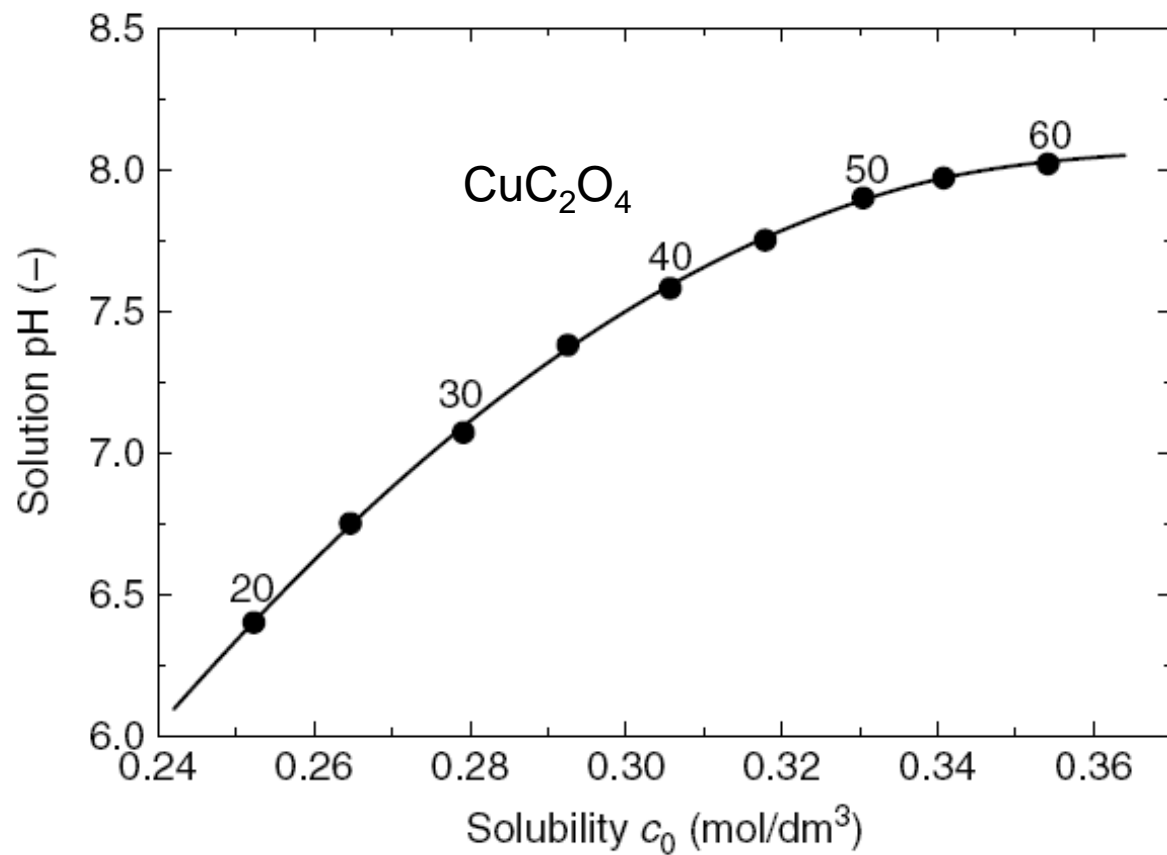
$$\alpha_{\pm} = (\alpha_+^{v^+} \alpha_-^{v^-})^{1/v}$$

$$\mu_{i,m} = \mu_{i,m}^0 + vRT \ln(Qm\gamma_{\pm,m})$$



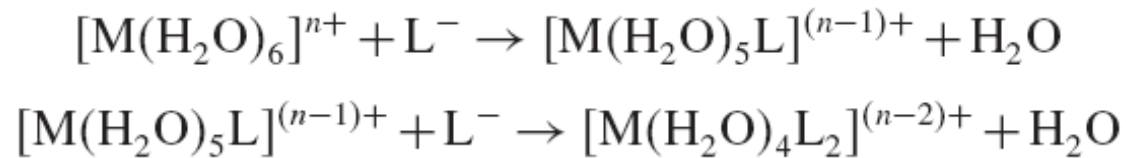
# Electrolyte solutions

- ❖ In dilute solutions there are only hydrated ions (surrounded by an ionic cloud of oppositely charged ions)
- ❖ In more concentrated solutions ion pairs are forming, because of the interpenetration of the ionic spheres of the ions
- ❖ Ion pairs are dipoles with zero net charge
- ❖ Further increase of electrolyte concentration leads to the formation of additional species because of the interaction of ions (ion pairs) and with the solvent molecules
- ❖ Increase of the electrolyte concentration decreases the dielectric constant of water and thus it affects the value of the activity coefficients





# Formation of hydroxo and other complexes

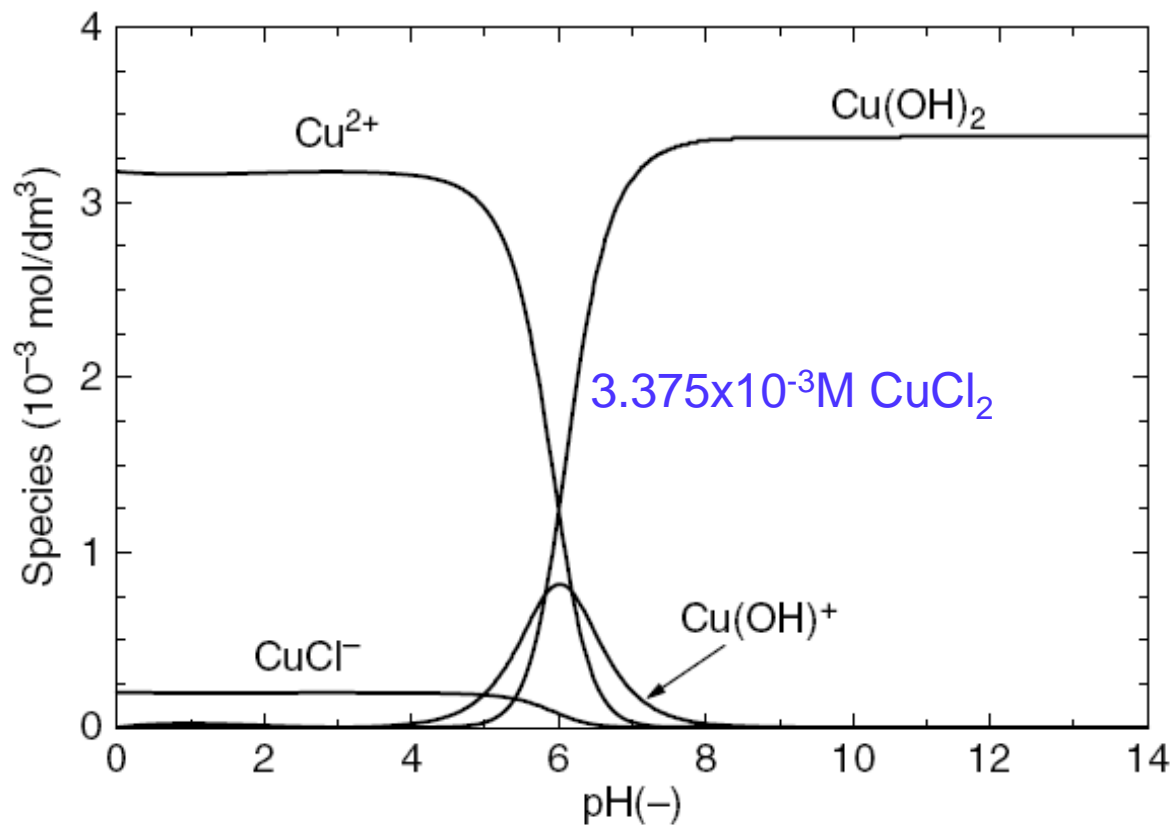


$$\beta_n = \frac{[\text{ML}_n]}{[\text{ML}_{n-1}][\text{L}]}$$



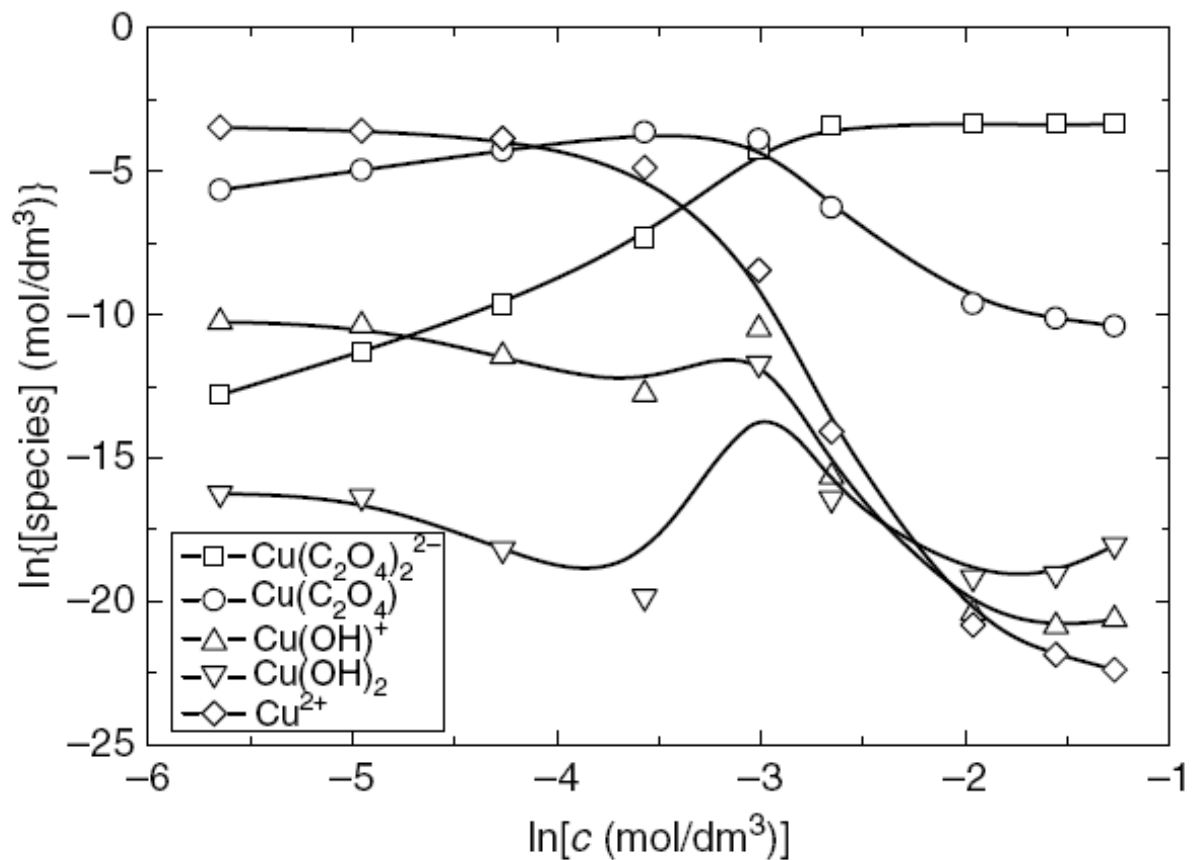
$$K_s = [\text{M}^{n+}][\text{L}]^n$$

$$\beta_1 > \beta_2 > \cdots > \beta_{n-1} > \beta_n$$





Cu :  $1,173 \times 10^{-2} \text{M}$  +  $(\text{NH}_4)_2\text{C}_2\text{O}_4$



- Electrolytes not fully dissociated

$$(Qm\gamma_{\pm})^{\nu} = (Qm\gamma'_{\pm}\alpha')^{\nu} = \gamma' m K_m (1 - \alpha')$$

$\gamma_{\pm}$  mean ionic coefficient taking into account dissociation

$\gamma'$  activity coefficient of non dissociated molecules

$m$ : overall molality of the solution

$K_m$  equilibrium dissociation constant



# Considering the solvent

- Osmotic coefficient

$$\varphi = -\frac{1000}{vmM_1} \ln a_1$$

The relationship between osmotic coefficient of the solution and the activity coefficient of the dissolved substance, from the Gibbs-Duhem equation is

$$(1000/M_1)d \ln a_1 + vmd \ln (Qm\gamma_{\pm,m}) = 0$$



$$\ln \gamma_{\pm,m} = \varphi - 1 + \int_0^m (\varphi - 1) d \ln m$$

or

$$\varphi = 1 + \frac{1}{m} \int_0^m m d \ln \gamma_{\pm,m}$$

# Temperature dependence of the activity coefficients

Differentiate wrt temperature:  $\mu_{i,m} = \mu_{i,m}^0 + vRT \ln(Qm\gamma_{\pm,m})$

$$\left(\frac{\partial \ln \gamma_{\pm,m}}{\partial T}\right)_{P, m_{j \neq i}} = -\frac{\bar{H}_i - \bar{H}_i^\infty}{RT^2}$$

Similarly, for the solvent

$$\left(\frac{\partial \ln a_1}{\partial T}\right)_{P, m_1} = -\frac{\bar{H}_1 - H_1^0}{RT^2}$$

For the osmotic coefficient

$$\left(\frac{\partial \varphi}{\partial T}\right)_{P, m_1} = \frac{\bar{H}_1 - H_1^0}{RT^2} \frac{1000}{vmM_1}$$



The chemical potential is independent on concentration or activity scale selected

$$\mu = \mu_c^0 + RT \ln a_c = \mu_x^0 + RT \ln a_x = \mu_m^0 + RT \ln a_m$$

$$\begin{aligned} a_c &= (Qc\gamma_{\pm,c})^{\nu} = a_{\pm,c}^{\nu} \\ a_x &= (Qx\gamma_{\pm,x})^{\nu} = a_{\pm,x}^{\nu} \\ a_m &= (Qm\gamma_{\pm,m})^{\nu} = a_{\pm,m}^{\nu} \end{aligned}$$

substitution

And assuming infinitely dilute solutions, i.e.  $\gamma \rightarrow 1$

$$\begin{aligned} \mu_c^0 &= \mu_m^0 - RT \ln \rho_w \\ \mu_x^0 &= \mu_m^0 + RT \ln 55.51 \end{aligned}$$

and

$$\begin{aligned} \gamma_{\pm,c} &= \gamma_{\pm,m} (1 + 0.001mM)(\rho_w/\rho_t) \\ \gamma_{\pm,x} &= \gamma_{\pm,m} (1 + mv/55.51) \end{aligned}$$

# Activity and osmotic coefficients in supersaturated solutions

- These solutions are thermodynamically unstable, we have to rely on theoretical estimates
- Ionic strength:  $I=0.5\sum c_i z_i^2$
- For a binary solution:  $I=0.5 |z_+ z_-| \nu c$
- For low ionic strength theoretical evaluations



## Güntelberg equation

$$\log \gamma_{\pm} = -A|z_+z_-|\sqrt{I}/(1 + \sqrt{I})$$

the expanded Debye-Hückel relationship

$$\log \gamma_{\pm} = -A|z_+z_-|\sqrt{I}/(1 + \bar{a}B\sqrt{I})$$

where  $\bar{a}$  represents an effective ionic radius

$$I \leq 0.1 \text{ M}$$

## Jones equation

$$\log \gamma_{\pm} = -A|z_+z_-|\left[\frac{\sqrt{I}}{1 + a\sqrt{I}} + bl\right]$$

$$I \leq 1 \text{ M}$$

$\theta/^\circ\text{C}$	$A$	$B$	$\theta/^\circ\text{C}$	$A$	$B$
0	0.4884	3.241	40	0.5242	3.318
10	0.4961	3.258	50	0.5352	3.341
18	0.5029	3.273	60	0.5472	3.366
20	0.5047	3.277	70	0.5599	3.392
25	0.5092	3.287	80	0.5740	3.420
30	0.5141	3.297	90	0.5892	3.450

# The Bromley Equation, 25°C

$$\frac{1}{|z_+ z_-|} \log \gamma_{\pm} = -0.511 \frac{\sqrt{I}}{1 + \sqrt{I}} + \frac{(0.06 + 0.6B_1)I}{(1 + 1.5I/|z_+ z_-|)^2} + \frac{B_1 I}{|z_+ z_-|}$$

Cation	$B_+$	$\delta_+$	Anion	$B_-$	$\delta_-$
H <sup>+</sup>	0.0875	0.103	F <sup>-</sup>	0.0295	-0.093
Li <sup>+</sup>	0.0691	0.138	Cl <sup>-</sup>	0.0643	-0.067
Na <sup>+</sup>	0	0.028	Br <sup>-</sup>	0.0741	0.064
K <sup>+</sup>	-0.0452	-0.079	I <sup>-</sup>	0.089	0.196
Rb <sup>+</sup>	-0.0537	-0.10	ClO <sub>3</sub> <sup>-</sup>	0.005	0.45
NH <sub>4</sub> <sup>+</sup>	-0.042	-0.02	ClO <sub>4</sub> <sup>-</sup>	0.002	0.79
Tl <sup>+</sup>	-0.135	-0.02	BrO <sub>3</sub> <sup>-</sup>	-0.032	0.14
Ag <sup>+</sup>	0.058	0	IO <sub>3</sub> <sup>-</sup>	-0.04	0
Be <sup>2+</sup>	0.10	0.20	NO <sub>3</sub> <sup>-</sup>	-0.025	0.27
Mg <sup>2+</sup>	0.057	0.157	H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>	-0.052	0.20
Ca <sup>2+</sup>	0.0374	0.119	H <sub>2</sub> AsO <sub>4</sub> <sup>-</sup>	-0.03	0.05
Str <sup>2+</sup>	0.0245	0.11	CNS <sup>-</sup>	0.071	0.16
Ba <sup>2+</sup>	0.0022	0.098	OH <sup>-</sup>	0.076	-1.0
Mn <sup>2+</sup>	0.037	0.21	CrO <sub>4</sub> <sup>2-</sup>	0.019	-0.33
Fe <sup>2+</sup>	0.046	0.21	SO <sub>4</sub> <sup>2-</sup>	0	-0.40
Co <sup>2+</sup>	0.049	0.21	S <sub>2</sub> O <sub>3</sub> <sup>2-</sup>	0.019	-0.70
Ni <sup>2+</sup>	0.054	0.21	HPO <sub>4</sub> <sup>2-</sup>	-0.01	-0.57
Cu <sup>2+</sup>	0.022	0.30	HAsO <sub>4</sub> <sup>2-</sup>	0.021	-0.67
Zn <sup>2+</sup>	0.101	0.09	CO <sub>3</sub> <sup>2-</sup>	0.028	-0.67
Cd <sup>2+</sup>	0.072	0.09	PO <sub>4</sub> <sup>3-</sup>	0.024	-0.07
Pb <sup>2+</sup>	-0.104	0.25	AsO <sub>4</sub> <sup>3-</sup>	0.038	-0.78
Cr <sup>3+</sup>	0.066	0.15	Fe(CN) <sub>6</sub> <sup>2-</sup>	0.065	0
Al <sup>3+</sup>	0.052	0.12	Fe(CN) <sub>6</sub> <sup>3-</sup>	0.054	0
Th <sup>4+</sup>	0.062	0.19	Mo(CN) <sub>8</sub> <sup>3-</sup>	0.056	0

$$B_1 = B_+ + B_- + \delta_+ \delta_-$$



Relationship between molal osmotic coefficient and solution ionic strength is according to Bromley:

$$\begin{aligned} \varphi - 1 = & -2.303 \times 0.511 |z_+ z_-| [1 + \sqrt{I} - 1/(1 + \sqrt{I}) - 2 \ln(1 + \sqrt{I})]/I \\ & + 2.303(0.06 + 0.6B_1) |z_+ z_-| [(1 + 2rI)/(1 + rI)^2 - \ln(1 + rI)/rI]/r \\ & + 2.303B_1 I/2 \end{aligned} \quad (2.54)$$

where  $r = 1.5 |z_+ z_-|$  and  $B_1$  is again determined by eq.  $B_1 = B_+ + B_- + \delta_+ \delta_-$

# Multicomponent systems

1. **The Lietzke-Stoughton (LS) Method:** For the calculation of activity coefficients of a compound in electrolyte mixtures containing a common ion (the system may be asymmetric as well e.g.  $\text{BaCl}_2$ -  $\text{NaCl}$ )

$$\frac{1}{|z_{+,i}z_{-,i}|} \log \gamma_{\pm,i} = \frac{1}{|z_{+,i}z_{-,i}|} \log \gamma_{\pm,i}^0 + \sum_{\substack{j=1 \\ j \neq i}}^n \frac{Y_j}{2} \left[ \frac{1}{|z_{+,j}z_{-,j}|} \log \gamma_{\pm,j}^0 - \frac{1}{|z_{+,i}z_{-,i}|} \log \gamma_{\pm,i}^0 \right]$$

$\gamma_{\pm,i}$ : mean activity coefficient of the  $i$ th component of the mixture

$\gamma_{\pm,i}^0, \gamma_{\pm,j}^0$ : mean activity coefficient of the  $i$ th and  $j$ th components in a binary solution in which the ionic strength is equal to the ionic strength of the mixture and  $Y_j = I_j/I$  where  $I_j$  is the ionic strength due to the presence of compound  $j$  and  $I$  the overall ionic strength of the medium.



The osmotic coefficient of the solution containing  $n$  electrolytes is:

$$\varphi = \frac{\sum_{j=1}^n v_j m_j \varphi_j^0}{\sum_{j=1}^n v_j m_j}$$

$\varphi_j^0$  the osmotic coefficient of the binary system containing the  $j$ th electrolyte whose ionic strength equals that of the mixture

$m_j$  the molal concentration of the  $j$ th electrolyte in the mixture

A photograph of an industrial facility, likely a refinery or chemical plant, featuring large, shiny metal pipes and structures against a clear blue sky. The pipes are arranged in a complex network, with some curving upwards and others running horizontally. The background shows a bright blue sky with a few wispy clouds.

## 2. The Reilly-Wood-Robinson Method

- Binary solutions for all possible combinations that may arise due to combinations of the ions present in the system and an ionic strength equal to that of the multicomponent system
- For concentrated solutions it is necessary to know the parameters describing interactions among the components within the solution
- For systems in which a component is present in trace concentrations relations are simplified



1. The MX-NY-H<sub>2</sub>O system

$$\begin{aligned} \frac{z_M - z_X}{z_M z_X} \ln \gamma_{\pm, MX} &= \frac{z_M - z_Y}{z_M z_Y} (1 - \varphi_{MY}^0 + \ln \gamma_{\pm, MY}^0) \\ &+ \frac{z_N - z_X}{z_N z_X} (1 - \varphi_{NX}^0 + \ln \gamma_{\pm, NX}^0) \\ &- \frac{z_N - z_Y}{z_N z_Y} (1 - \varphi_{NY}^0 + \ln \gamma_{\pm, NY}^0) - \frac{z_M - z_X}{z_N z_Y} (1 - \varphi_{NY}^0) \end{aligned}$$

2. The MX-NX-H<sub>2</sub>O system

$$\ln \gamma_{\pm, MX} = \ln \gamma_{\pm, MX}^0 + \left[ 1 - \varphi_{MX}^0 - \frac{z_M}{z_N} (1 - \varphi_{NX}^0) \right]$$

and

$$\ln \gamma_{\pm, NX} = \ln \gamma_{\pm, NX}^0 + \left[ 1 - \varphi_{NX}^0 - \frac{z_N}{z_M} (1 - \varphi_{MX}^0) \right]$$

z: charges of  
the respective  
ions



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$$+ \frac{z_N - z_X}{z_N z_X} (1 - \varphi_{NX}^0 + \ln \gamma_{\pm, NX}^0)$$
$$- \frac{z_N - z_Y}{z_N z_Y} (1 - \varphi_{NY}^0 + \ln \gamma_{\pm, NY}^0) - \frac{z_M - z_X}{z_N z_Y} (1 - \varphi_{NY}^0)$$

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and

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z: charges of  
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ions

### 3. The Bromley method

The activity coefficient of a compound  $M_1X_1$  in a multicomponent system

$$\log \gamma_{\pm, m, M_1X_1} = -\frac{0.511 |z_{M_1} z_{X_1}| \sqrt{I}}{1 + \sqrt{I}} + \frac{|z_{M_1} z_{X_1}|}{|z_{M_1}| + |z_{X_1}|} \left[ \frac{F_1}{|z_{M_1}|} + \frac{F_2}{|z_{X_1}|} \right]$$

where

$$F_1 = \sum_{m=1}^j \dot{B}_{M_1X_m} (\bar{Z}_{M_1X_m})^2 m_{X_m}$$

$$F_2 = \sum_{l=1}^i \dot{B}_{M_lX_1} (\bar{Z}_{M_lX_1})^2 m_{M_l}$$

$$\bar{Z}_{M_lX_m} = [ |z_{M_l}| + |z_{X_m}| ] / 2$$

$$\dot{B}_{M_lX_m} = \frac{(0.06 + 0.6 B_{l, M_lX_m}) |z_{M_l} z_{X_m}|}{\left( 1 + \frac{1.51}{|z_{M_l} z_{X_m}|} \right)^2} + B_{l, M_lX_m}$$

$$B_l = B_+ + B_- + \delta_+ \delta_-$$



1. The MX-NY-H<sub>2</sub>O system

$$\begin{aligned} \frac{z_M - z_X}{z_M z_X} \ln \gamma_{\pm, MX} &= \frac{z_M - z_Y}{z_M z_Y} (1 - \varphi_{MY}^0 + \ln \gamma_{\pm, MY}^0) \\ &+ \frac{z_N - z_X}{z_N z_X} (1 - \varphi_{NX}^0 + \ln \gamma_{\pm, NX}^0) \\ &- \frac{z_N - z_Y}{z_N z_Y} (1 - \varphi_{NY}^0 + \ln \gamma_{\pm, NY}^0) - \frac{z_M - z_X}{z_N z_Y} (1 - \varphi_{NY}^0) \end{aligned}$$

2. The MX-NX-H<sub>2</sub>O system

$$\ln \gamma_{\pm, MX} = \ln \gamma_{\pm, MX}^0 + \left[ 1 - \varphi_{MX}^0 - \frac{z_M}{z_N} (1 - \varphi_{NX}^0) \right]$$

and

$$\ln \gamma_{\pm, NX} = \ln \gamma_{\pm, NX}^0 + \left[ 1 - \varphi_{NX}^0 - \frac{z_N}{z_M} (1 - \varphi_{MX}^0) \right]$$

z: charges of  
the respective  
ions

### 3. The Bromley method

The activity coefficient of a compound  $M_1X_1$  in a multicomponent system

$$\log \gamma_{\pm, m, M_1X_1} = -\frac{0.511 |z_{M_1} z_{X_1}| \sqrt{I}}{1 + \sqrt{I}} + \frac{|z_{M_1} z_{X_1}|}{|z_{M_1}| + |z_{X_1}|} \left[ \frac{F_1}{|z_{M_1}|} + \frac{F_2}{|z_{M_2}|} \right]$$

where

$$F_1 = \sum_{m=1}^j \dot{B}_{M_1X_m} (\bar{Z}_{M_1X_m})^2 m_{X_m}$$

$$F_2 = \sum_{l=1}^i \dot{B}_{M_lX_1} (\bar{Z}_{M_lX_1})^2 m_{M_l}$$

$$\bar{Z}_{M_lX_m} = [ |z_{M_l}| + |z_{X_m}| ] / 2$$

$$\dot{B}_{M_lX_m} = \frac{(0.06 + 0.6 B_{l, M_lX_m}) |z_{M_l} z_{X_m}|}{\left( 1 + \frac{1.51}{|z_{M_l} z_{X_m}|} \right)^2} + B_{l, M_lX_m}$$

$$B_l = B_+ + B_- + \delta_+ \delta_-$$



# Otto Lehmann

first heatable  
microscope (1875)



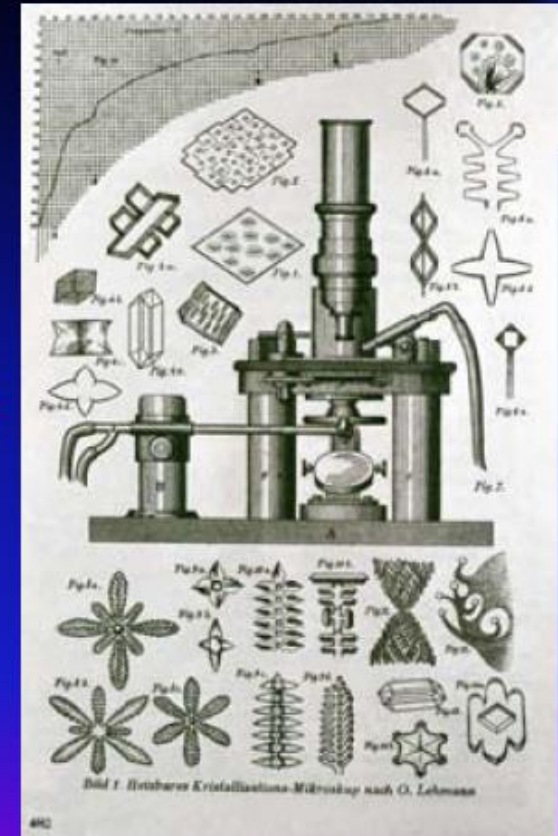
1855-1922

Prof. in Karlsruhe

Physicist, Crystallographer

## Achievements

- Applications and methods
- Crystallization from the melt**
- Monotropism and enantiotropism
- Liquid crystals
- Plastic crystals
- Phase diagrams



O. Lehmann. *Molekularphysik*, W.Engelmann, Leipzig, 1888.

O. Lehmann. *Die Kristallanalyse*, W.Engelmann, Leipzig, 1891

O. Lehmann. *Das Kristallisationsmikroskop*, Viehweg, Brunswick 1910

# Κρυστάλλωση από τήγματα

## Melt crystallization

- *Melt Crystallization is the common term applied to the controlled cooling crystallization and separation of systems with the objective of producing one or more of the components in relatively pure form.*

Mullin 2001

- *Separation of components of a binary mixture without addition of solvent*

Chemical Engineers Handbook - Perry and Green (1999)



# MELT

Liquid above the  $T_{\text{fus}}$  ( $< T_{\text{vap}}$ )

## MELTING POINT ( $T_{\text{fus}}$ )

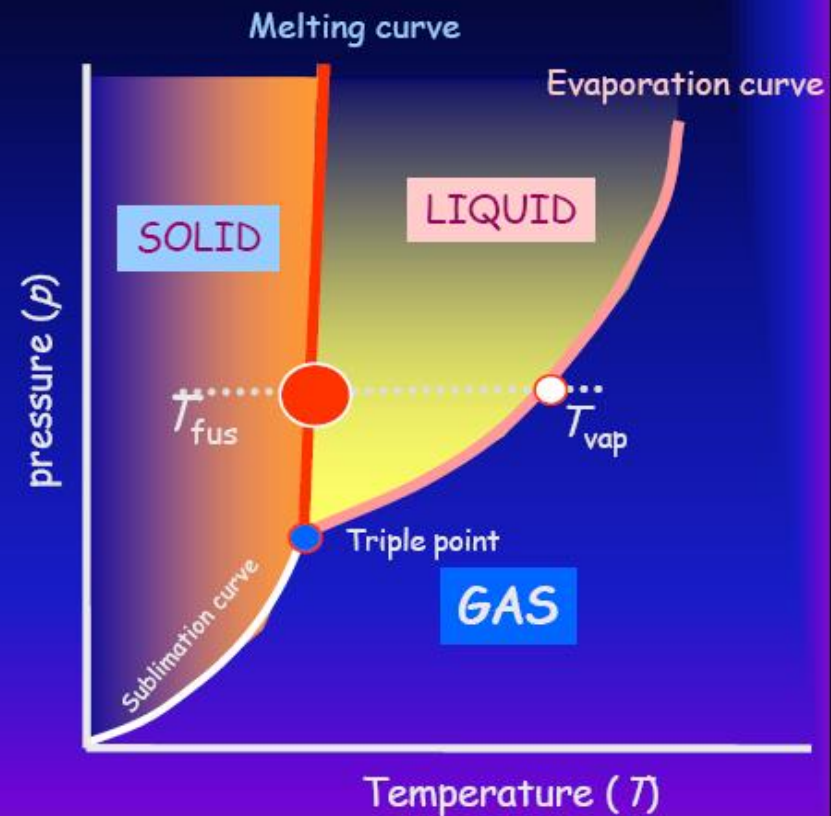
Temperature where a solid substance passes into the liquid state

Equilibrium between the solid and the liquid phase

Melting temperature  
Melting range

## SUPERCOOLED MELT

Liquid below the  $T_{\text{fus}}$  but above the glass transition Temperature ( $T_g$ )



# Why melt crystallization??

## Industrial perspective (purification, separation)

- No solvent used (solvent recovery, costs, energy)
- Produces high degree of purity (> 99.9%)
- Total energy requirement low compared to other separation techniques
- Small volume compared to solution
- No gas phase, closed vessels, higher safety

- Operational problems - equipment
- Refrigeration

## Scientific perspective

- Generation of polymorphs /access to new metastable forms
- Co-crystallization
- Single crystals

## Educational aspects (microscope)



## Examples

- Acrylic acid
- Phenol
- Acetic acid
- Benzene
- P-Xylene
- p-Dichlorobenzene
- p-Chloronitrobenzene
- Caprolactam
- Benzoic acid
- Naphtalene
- Pyridine

- If high purity desired
- m.p. range - 50 to 200 (300)°C
- Thermostable compounds
- Low viscosity melt



# Phase equilibria

- Complete solubility- solid solutions
- Partial solubility
- Formation of eutectic mixtures
- Completely immiscible components

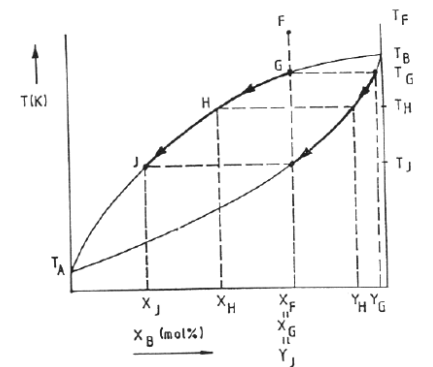
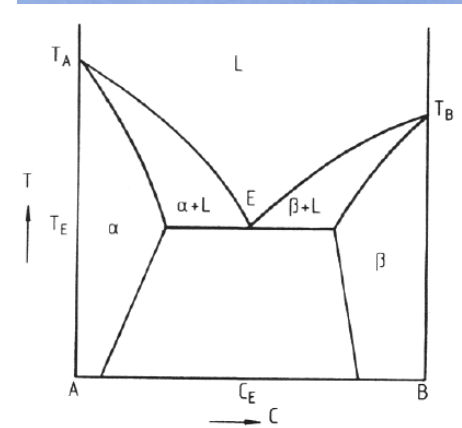
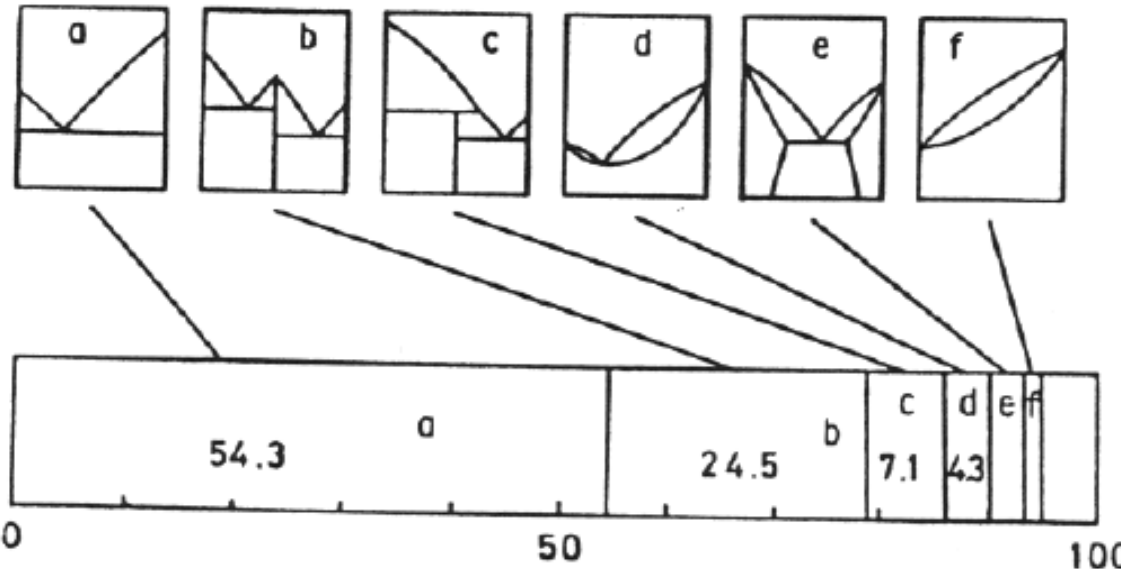


FIGURE 3.2. Complete solid solution system.  $x$  = mole percentage of B.

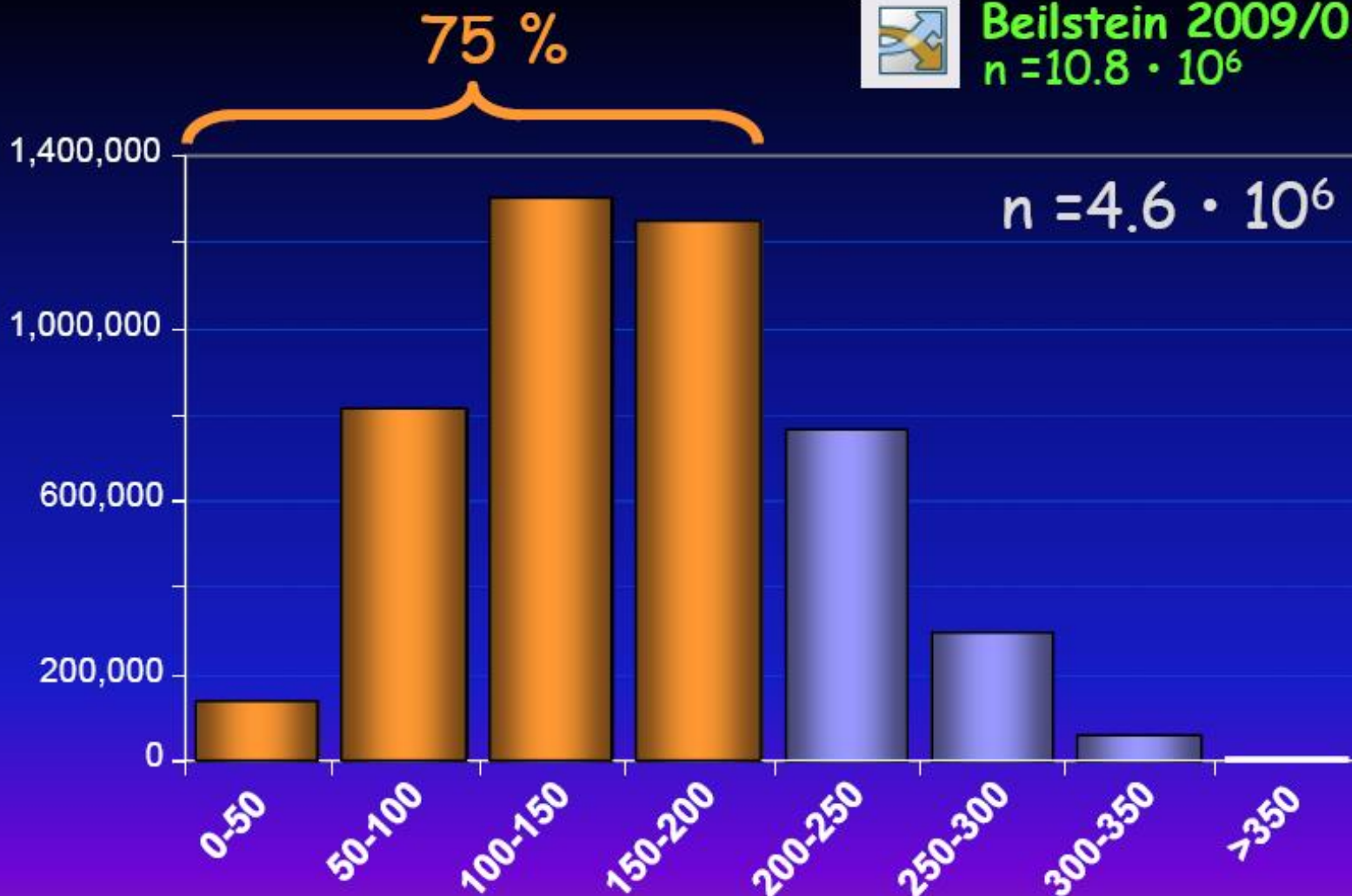




# Melting points of organic compounds

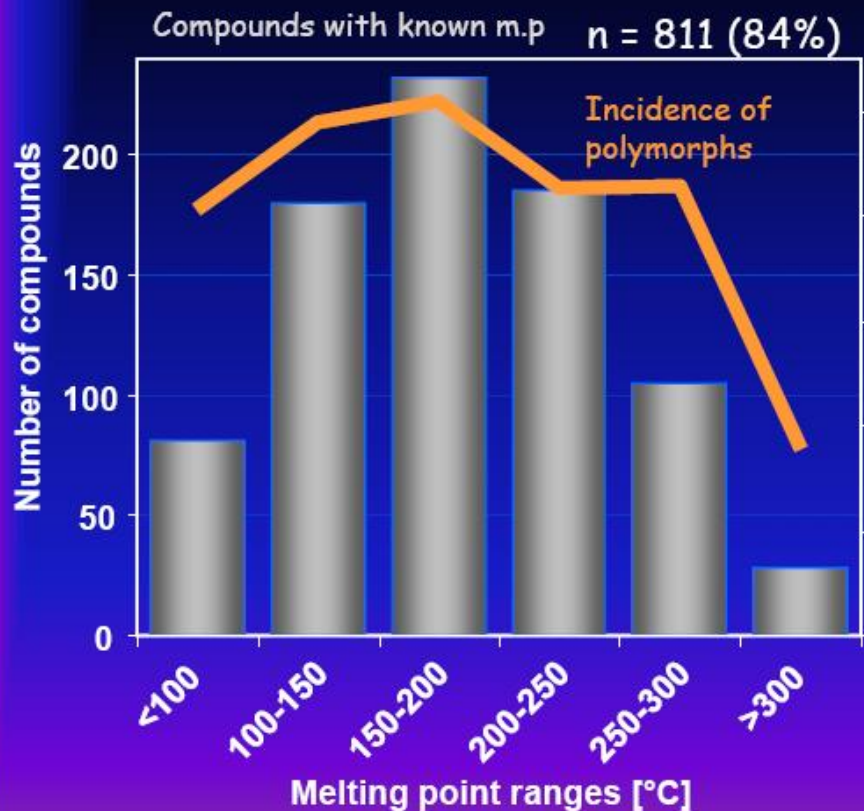


Beilstein 2009/01  
 $n = 10.8 \cdot 10^6$



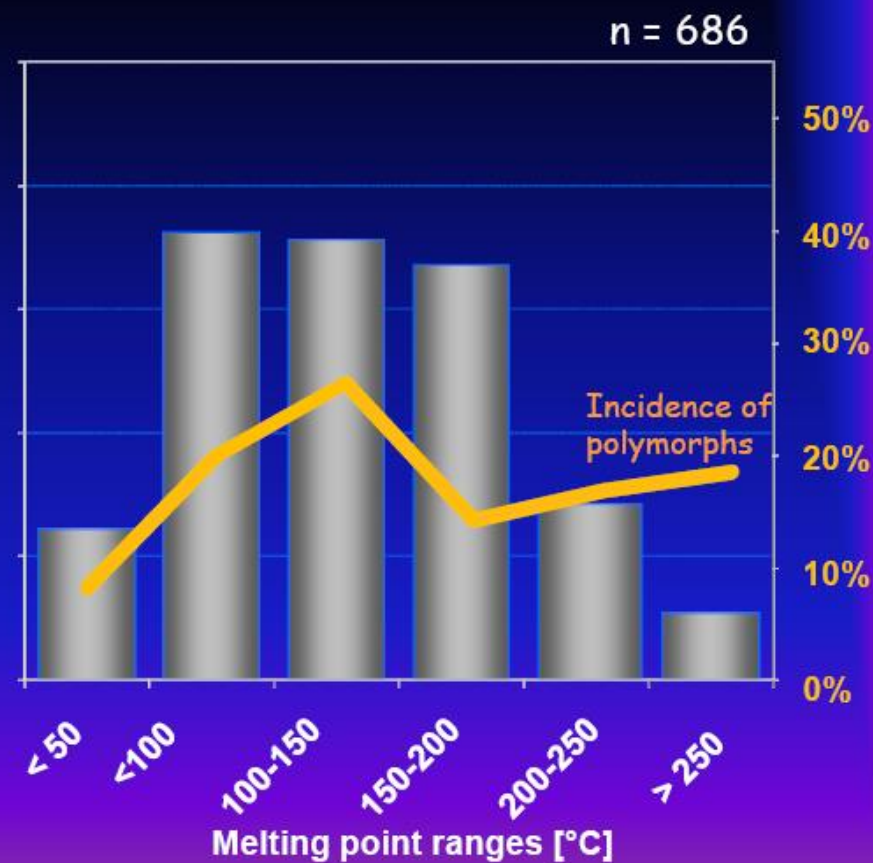
About 3/4 of all compounds melt below 200 °C (-50 -200 °C)

## Drug compounds (PhEur 5, n = 961)



Braun D. & Griesser UJ - unpublished

## Agrochemicals



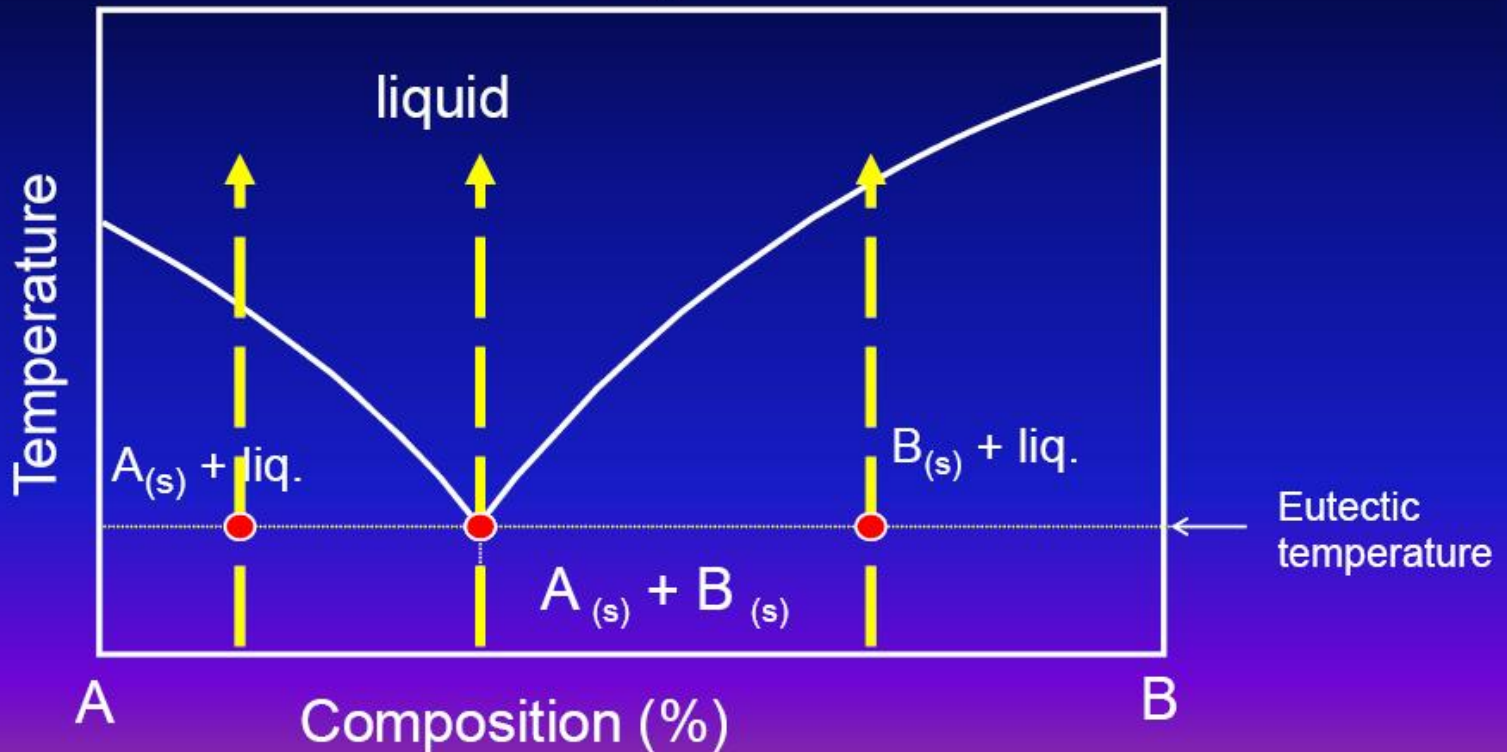
Tischler, M. & Griesser UJ - unpublished



# Eutectic mixture

Two component system (binary) - two substances are mixed

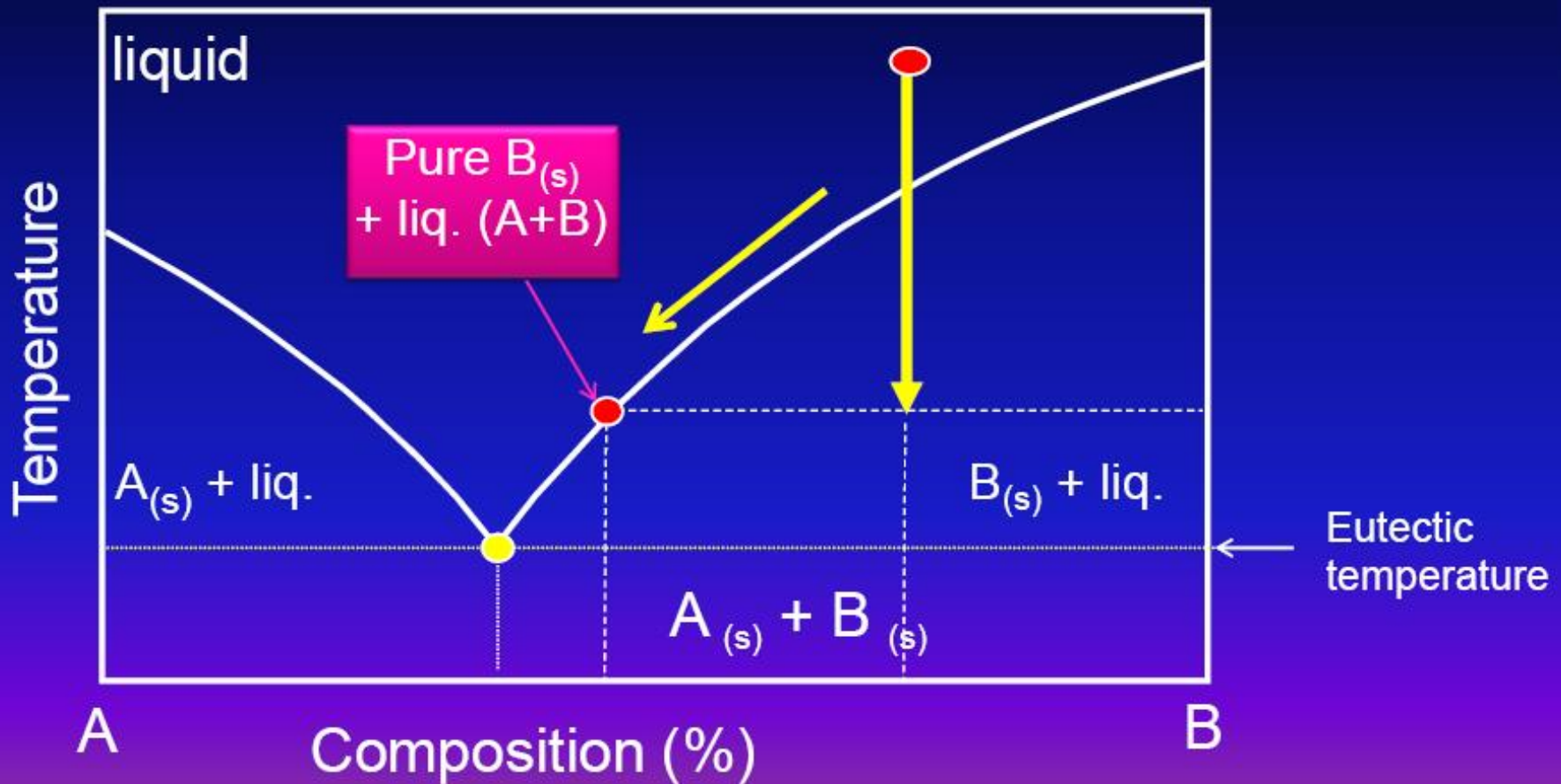
Phase diagram



# Eutectic system

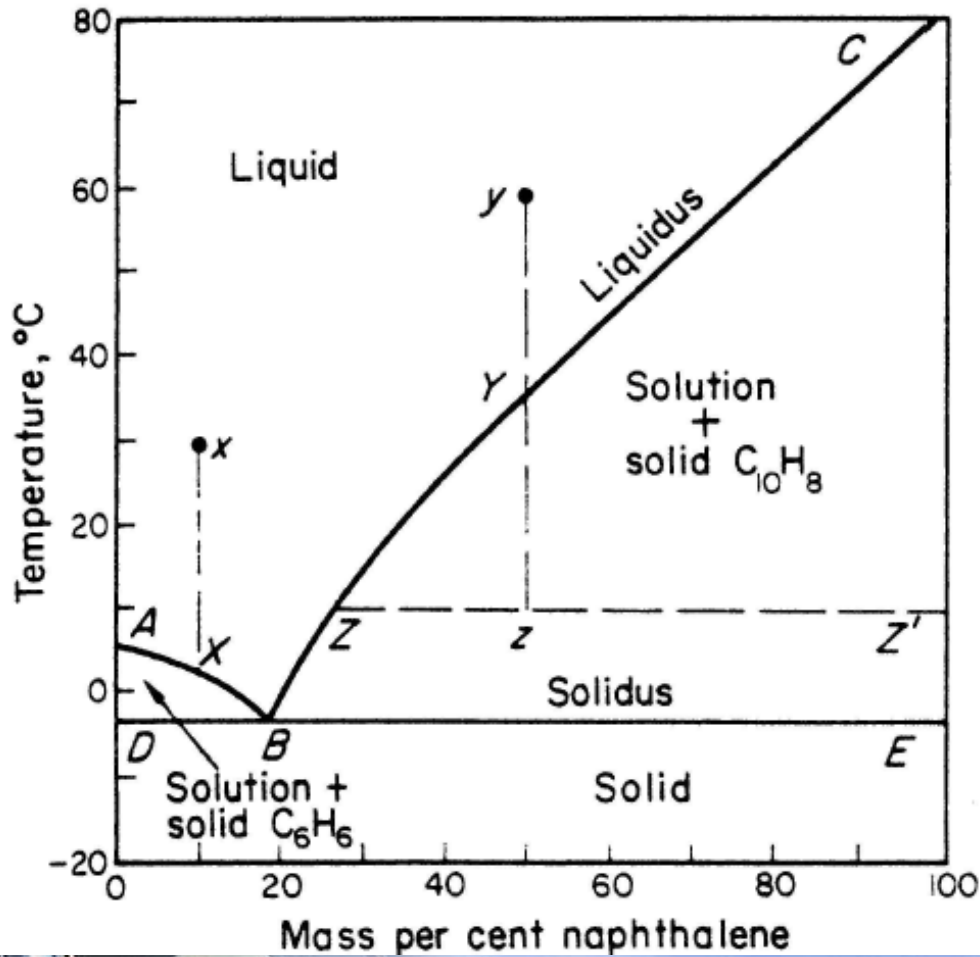
Two component system (binary) - two substances are mixed

Phase diagram





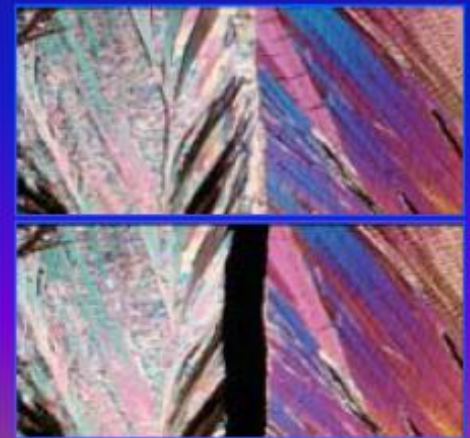
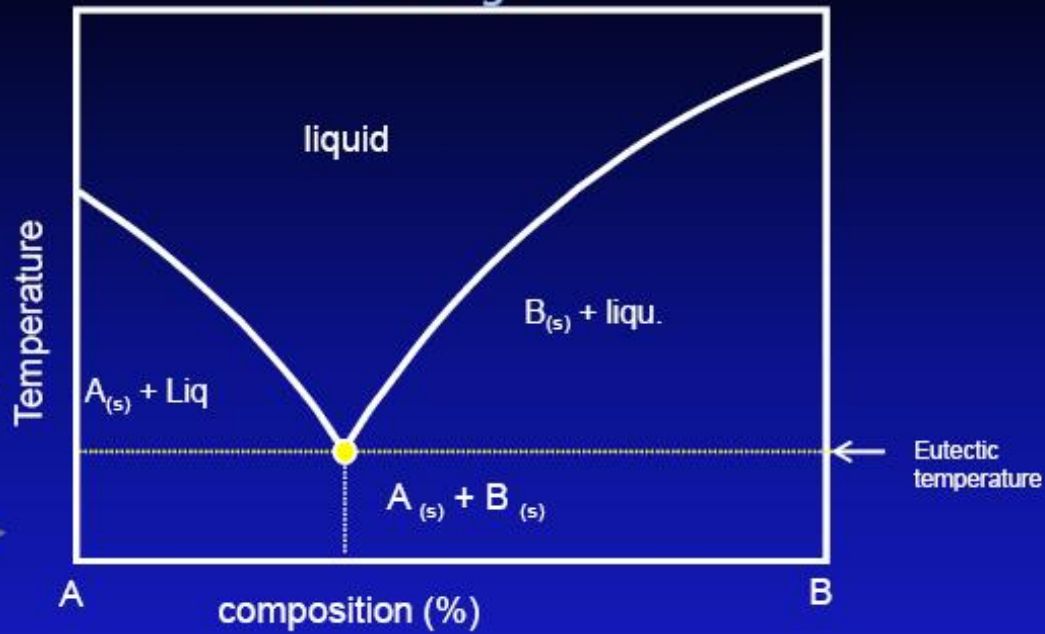
# Naphthalene-Benzene System



$$\frac{\text{mass of solid C}_{10}\text{H}_8}{\text{mass of solution}} = \frac{zZ}{zZ'}$$

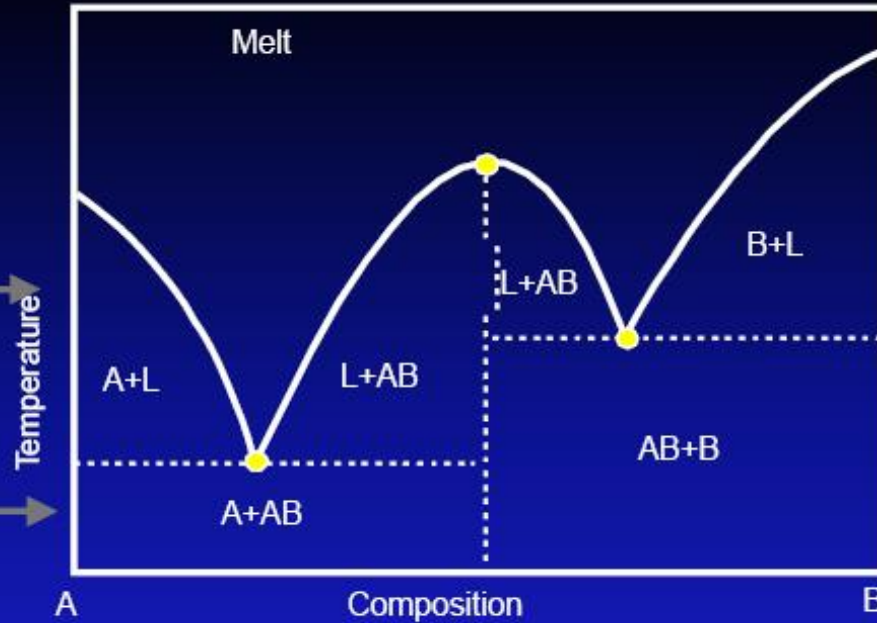
Cooling and evaporation

# Phase diagram





# Molecular compound (complex)



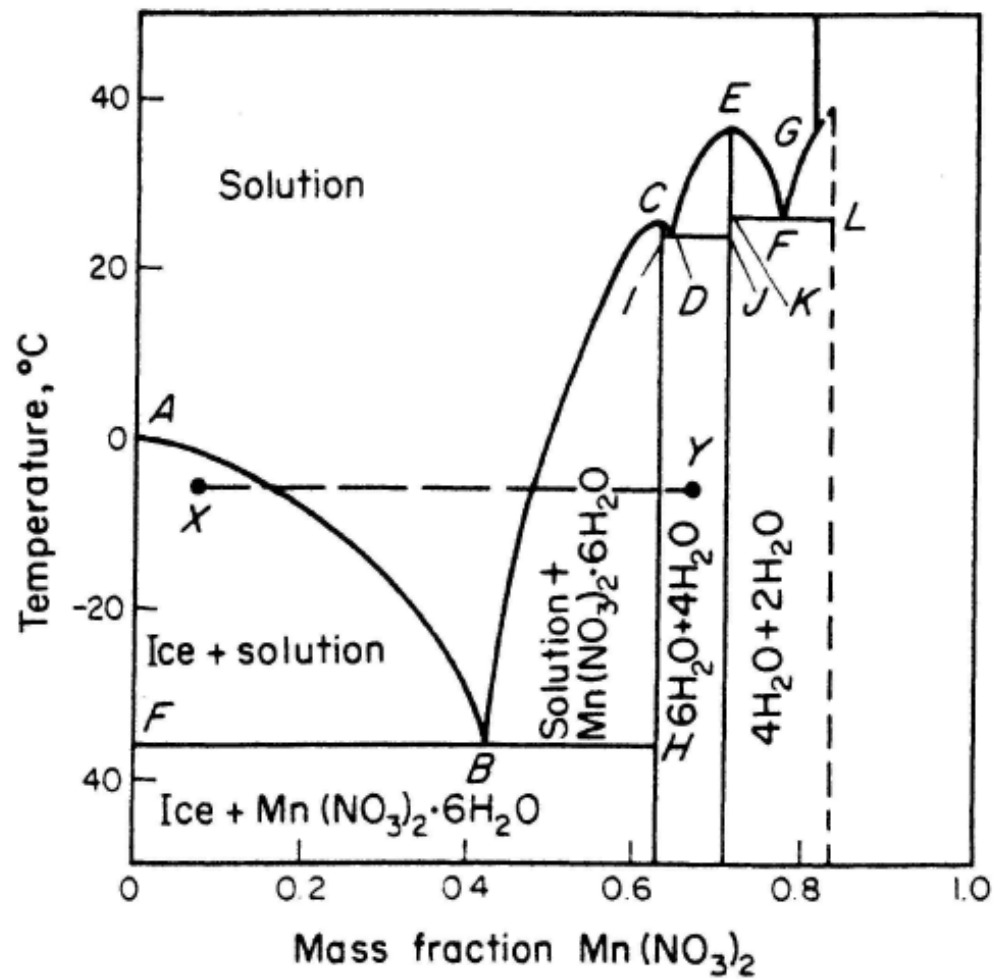


Figure 4.5. Phase diagram for the system  $\text{Mn}(\text{NO}_3)_2\text{-H}_2\text{O}$



# Solid solution (mixed crystal)

