Physical Chemistry (Chem 132A)

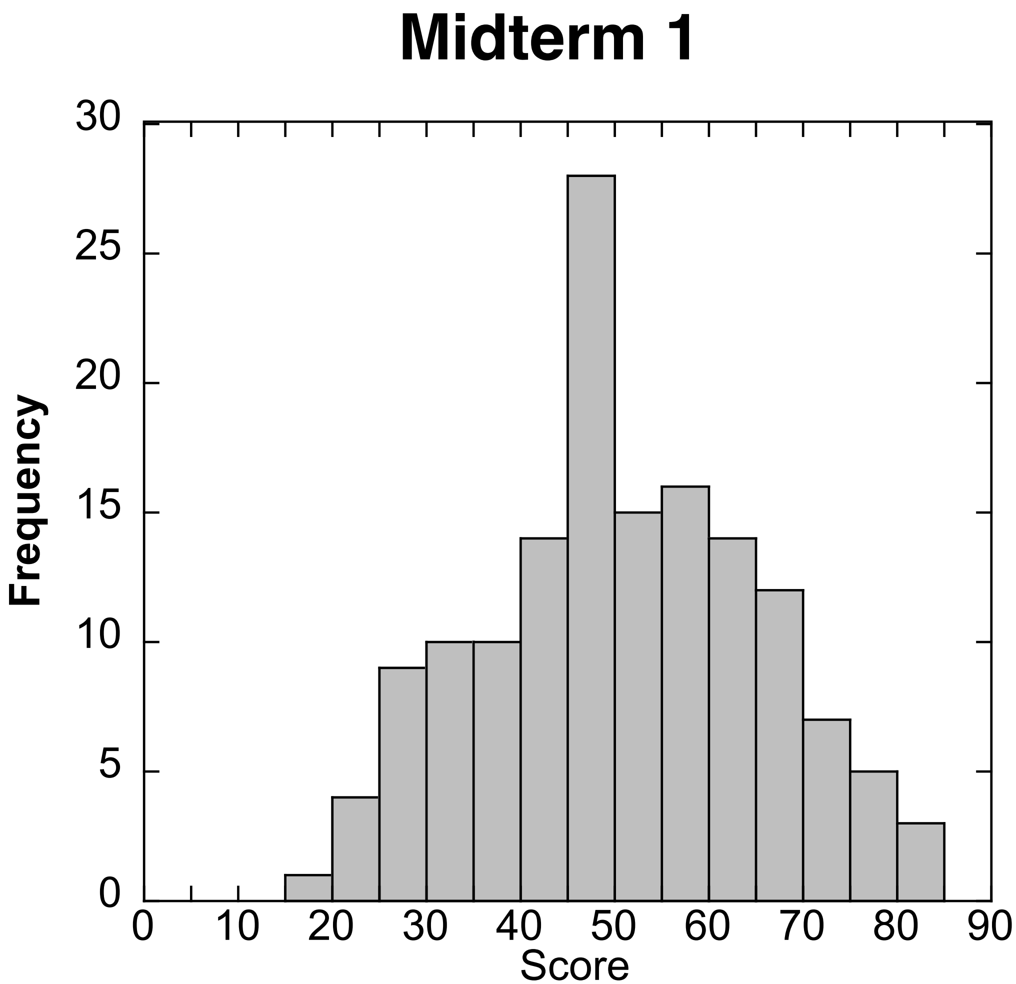
Lecture 14
Wednesday, November 1

Homework #5 will be due November 4

Additional Problems you should look at in the text, from Topic 5C. (not for credit but important for midterm 2 and final.

Exercises: 5c.3a, 5c.3b, 5c.4a, 5c.7a
Problems: 5c.5, 5c.7

Midterm Exam #1



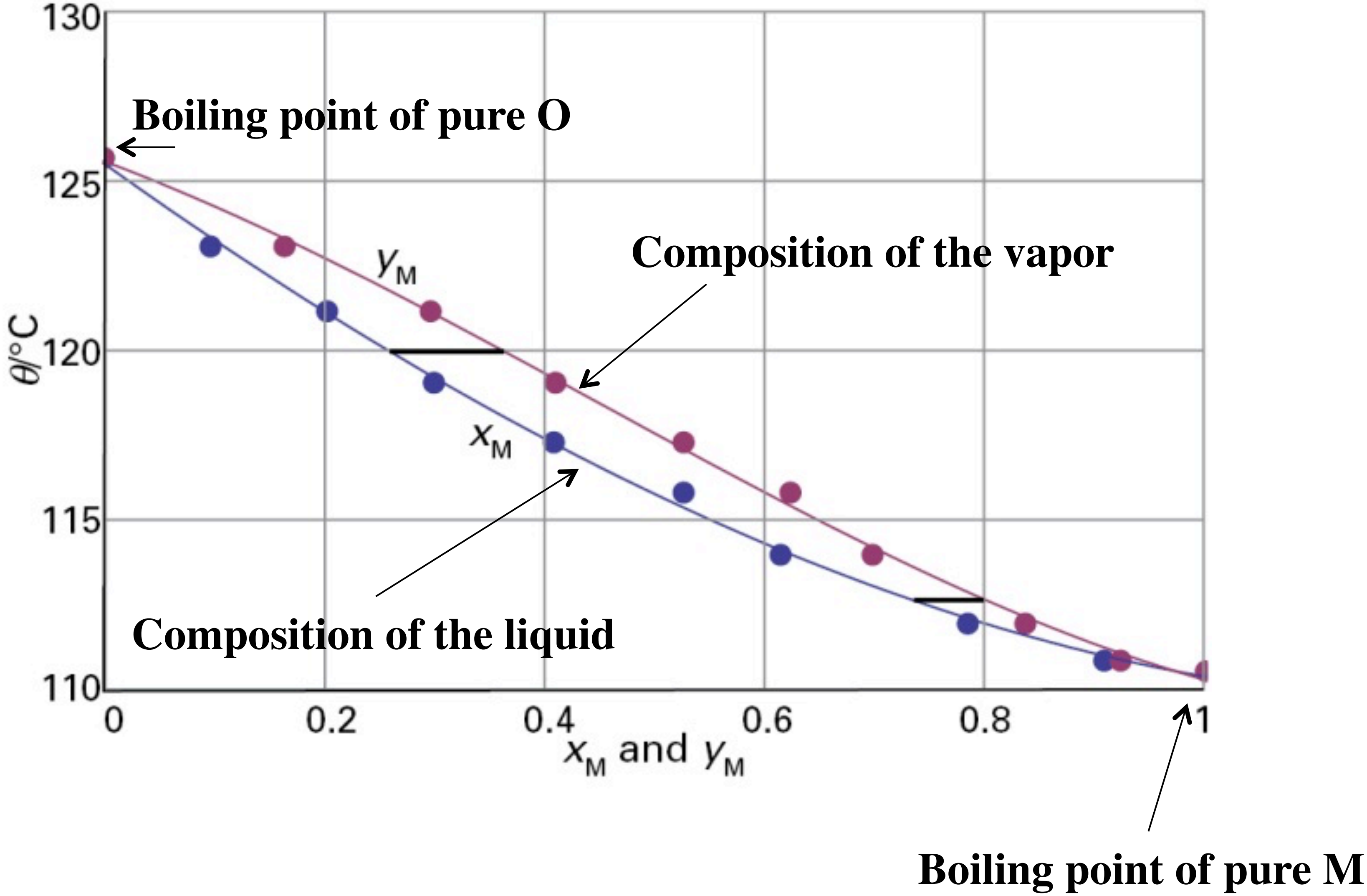
Average = 50.1

Standard deviation = 12

Phase Diagrams for Binary Mixtures

1. Vapor pressure diagrams (pressure / composition)
2. Temperature / composition diagrams
3. Temperature / composition for partially miscible systems
4. Temperature / composition for liquid/solid systems

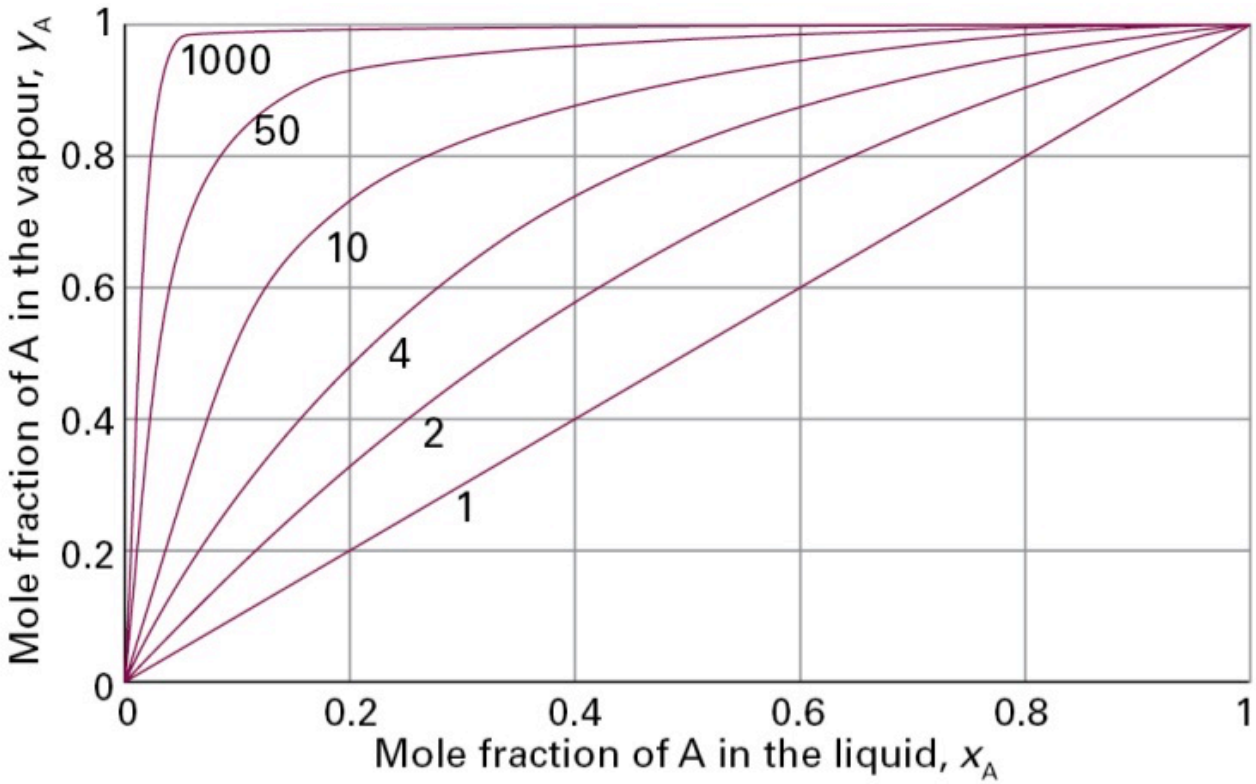
Example of a Vapor Pressure Diagram



Vapor Mole Fraction as a function of Liquid Mole Fraction

Shown for a range of values of the ratio of the pure liquid vapor pressures

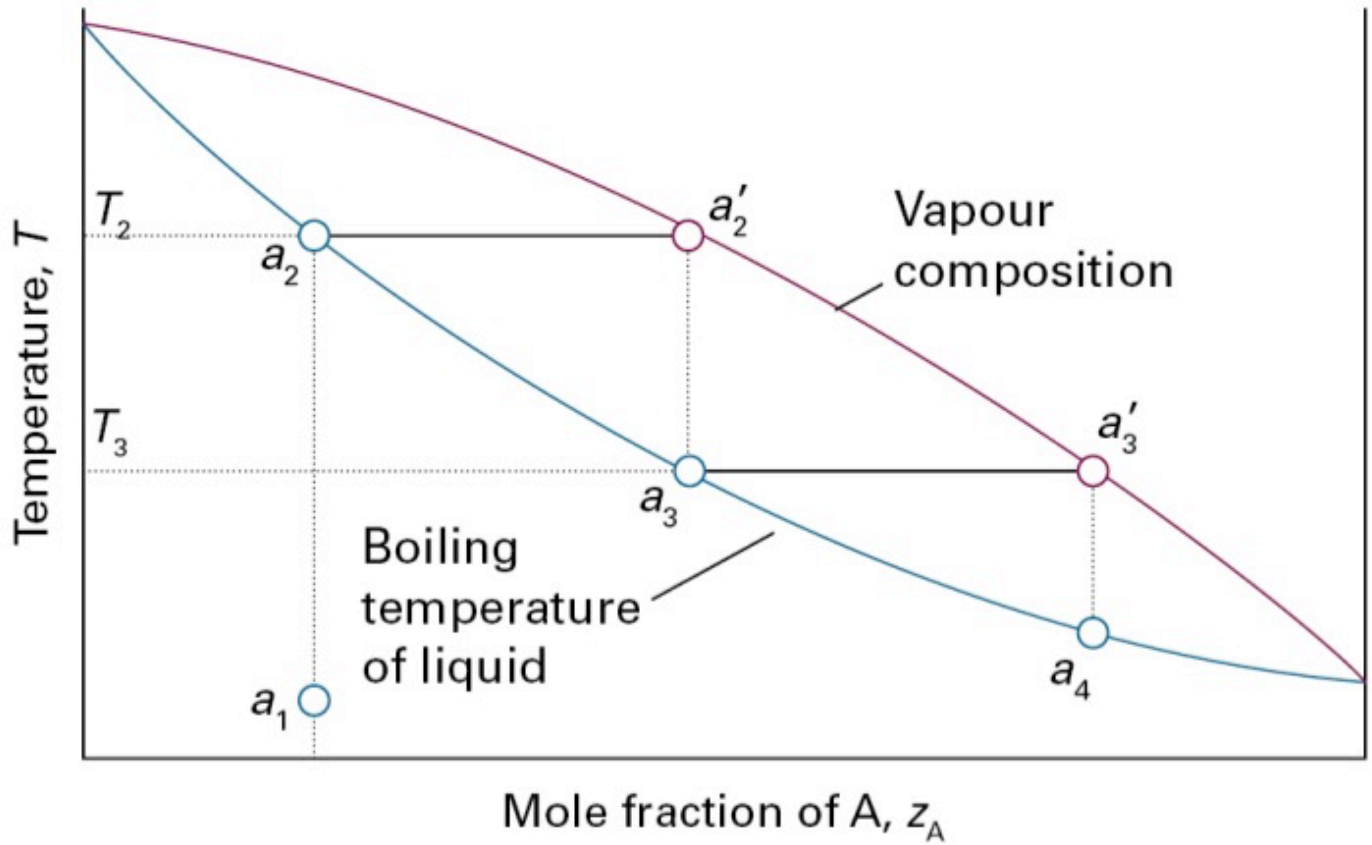
MESSAGE: Liquid and Vapor have different compositions



TEMPERATURE / COMPOSITION

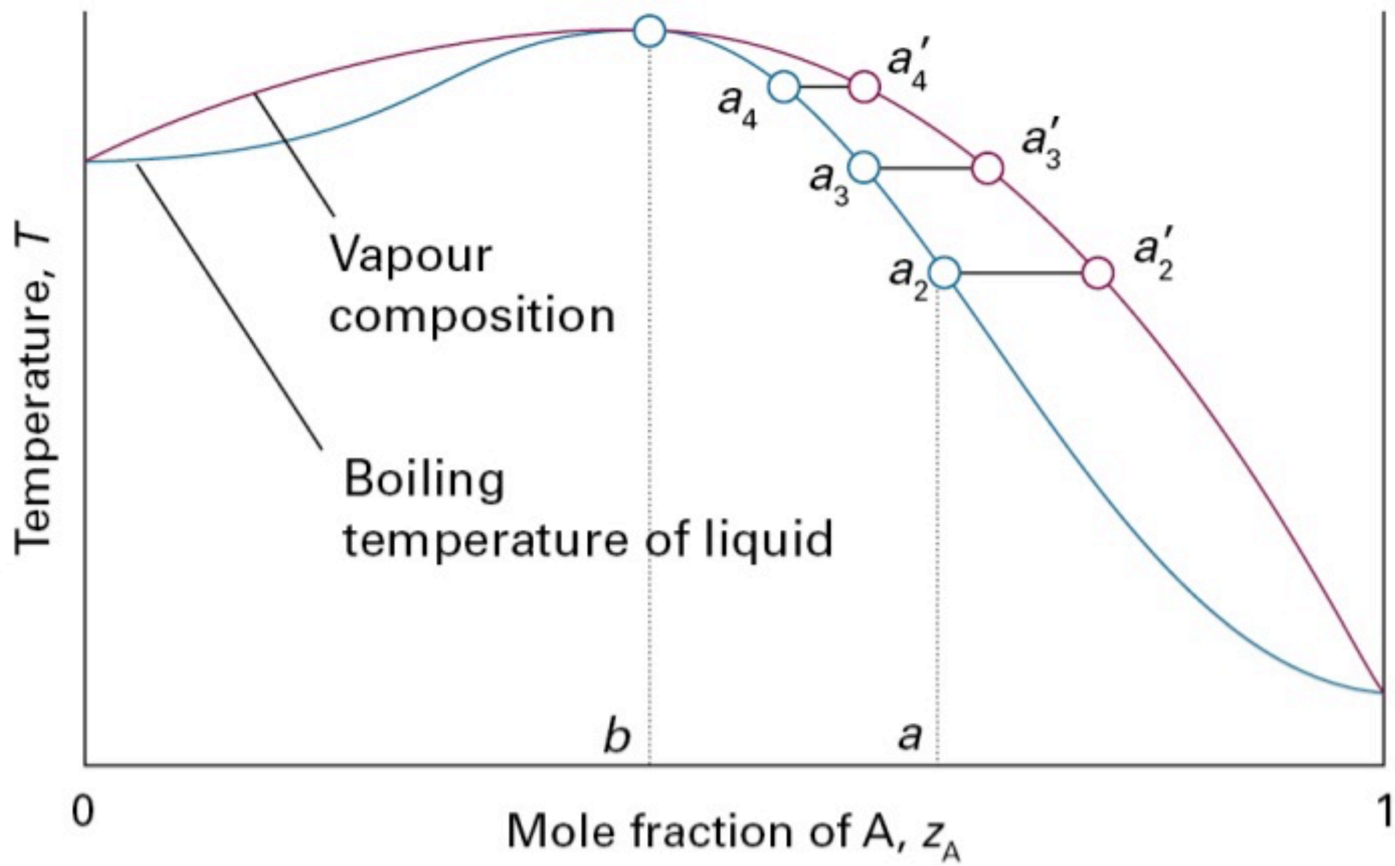
DISTILLATION

IDEAL SOLUTION

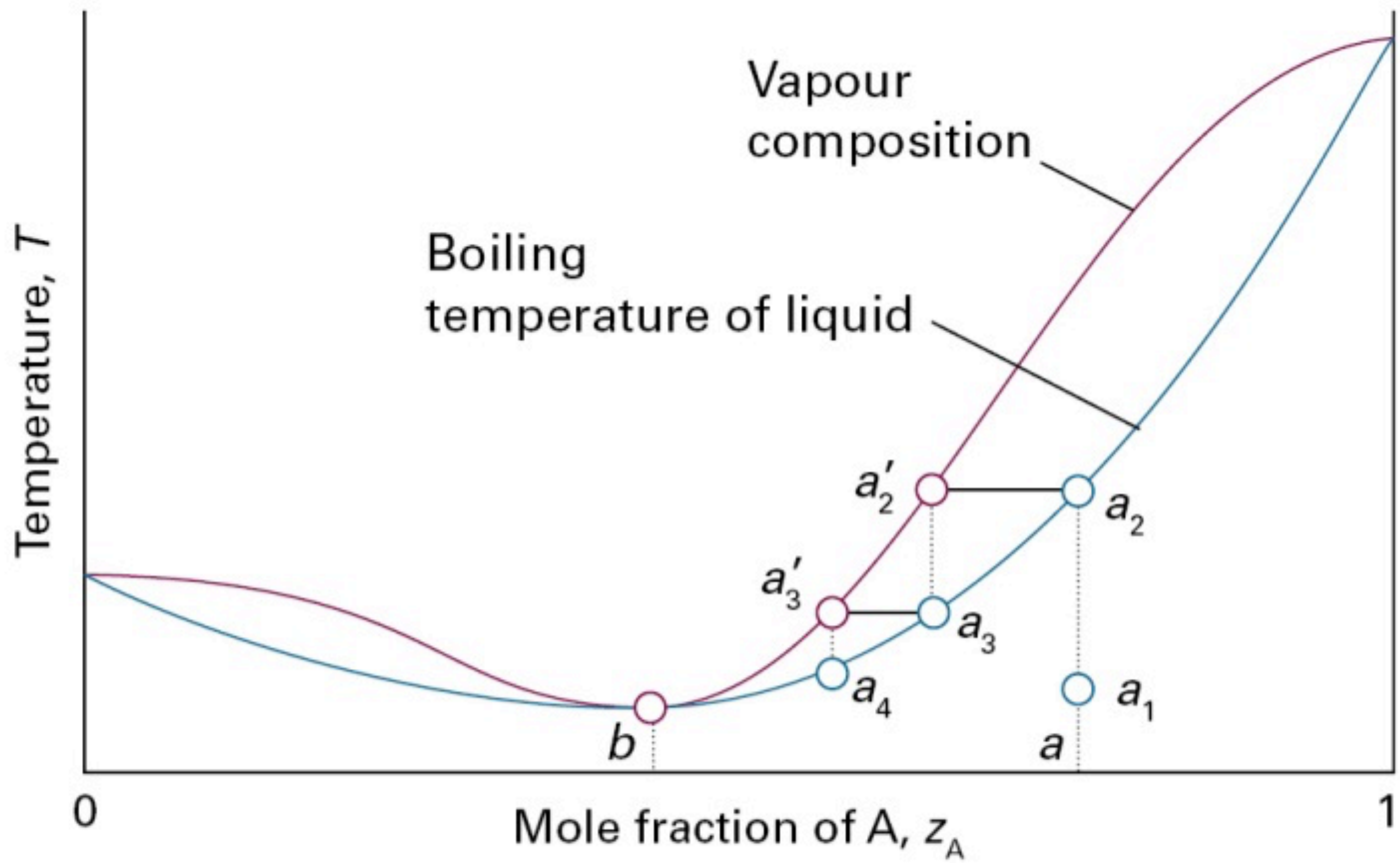


AZEOTROPE

Favorable interactions between A and B Lead to reduced vapor pressure compared to ideal solution behavior

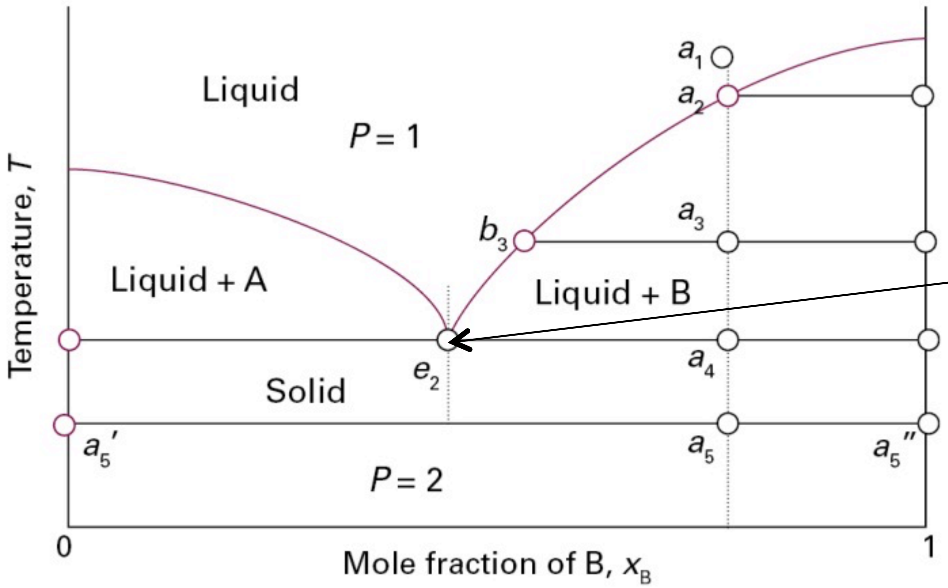


Azeotrope showing unfavorable interactions between A and B



Immiscible—or partially miscible systems

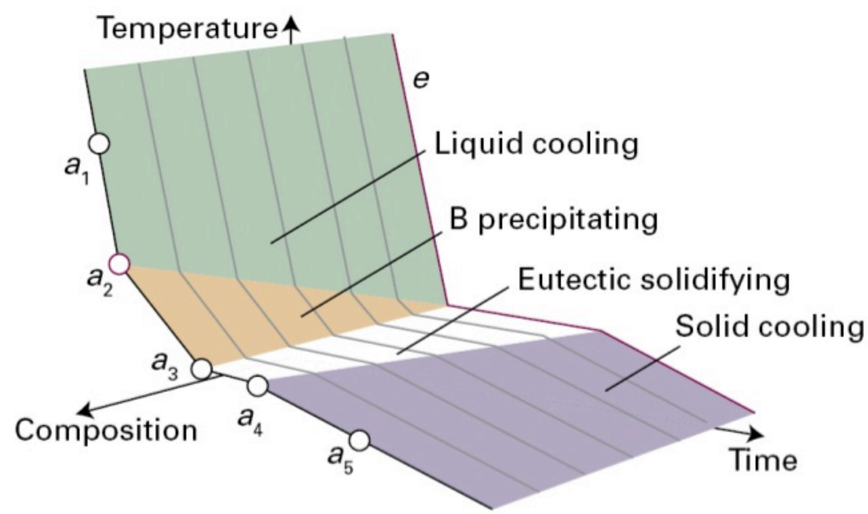
Liquid–Solid Phase Diagrams



Eutectic mixture

Figure 5C.27 The temperature–composition phase diagram for two almost immiscible solids and their completely miscible liquids. Note the similarity to Fig. 5C.25. The isopleth tl

Cooling Curves



$$G_m\left(p_f\right) = G_m\left(p_i\right) + RT\ln\left(\frac{p_f}{p_i}\right)$$

$$G_m^0 = G_m^0\left(p_i\right) + RT\ln\left(\frac{f}{p^0}\right)$$

$$\mathbf{f = \varphi p}$$

ACTIVITIES

Solvent:

$$\mu_A = \mu_A^* + RT\ln\frac{p_A}{p_A^*}$$

Ideal Solution (Raoult's Law:) $p_A = x_A p_A^*$ **and** $\mu_A = \mu_A^* + RT\ln x_A$

Non-ideal solution

$$\mu_A = \mu_A^* + RT\ln a_A$$

$$a_A = \frac{p_A}{p_A^*}$$

a is called the "activity"

Convention is to define "activity coeficient" γ **(gamma)**

$$a_A = \gamma_A x_A$$

$$\mu_A = \mu_A^* + RT\ln x_A + RT\ln\gamma_A$$

Activities (cont.)

Solutes: similar definition but in terms of Henry's Law

$$\mu_B = \mu_B^* + RT \ln \frac{p_B}{p_B^*} = \mu_B^* + RT \ln \frac{K_B}{p_B^*} + RT \ln x_B$$

$$\mu_B = \mu_B^0 + RT \ln a_B$$

$$a_B = \gamma_B x_B$$

Often activities are written in terms of molalities

Ionic Solutions

$$G_m^{ideal} = \mu_+^{ideal} + \mu_-^{ideal}$$

$$G_m = \mu_+^{ideal} + \mu_-^{ideal} + RT\ln\gamma_+ + RT\ln\gamma_-$$

$$G_m = \mu_+^{ideal} + \mu_-^{ideal} + RT\ln\gamma_+\gamma_-$$

Typically re-write this as:

$$\gamma_\pm = \left(\gamma_+\gamma_-\right)^{\frac{1}{2}}$$

$$\mu_i = \mu_i^{ideal} + RT\ln\gamma_\pm$$

Debye-Huckel Law:

$$\log\gamma_\pm = -0.509\left|z_+z_-\right|I^{1/2}$$

$$I = \frac{1}{2}\sum_i z_i^2\left(\frac{b_i}{b^0}\right)$$

I is called the “ionic strength”

THE END

SEE YOU Friday