Physical Chemistry (Chem 132A)

Lecture 15
Friday, November 3

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

You should have received your exam pdf file (eee dropbox)

You should:

1. **Check that the scores for each question were properly transferred to the coversheet of the exam**
2. **Check the addition of the scores on the coversheet**
3. **Compare your total on the coversheet with the score you received via eee.**
4. **Look at the posted answers (course site on CANVAS)**
5. **Make sure you understand what we were looking for in the answers.**

I am happy to fix any clerical errors (send email to me with copy to Shane and Moises).

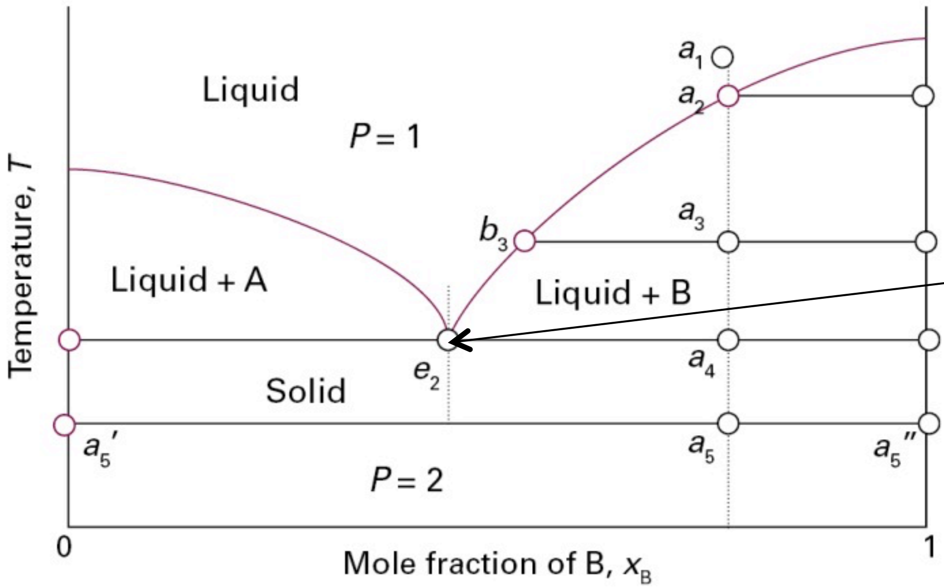
NO Re-grades for changes in partial credit.

Schedule:

Week	Dates	Topics	Readings
0	Before Sept 28	The Properties of Gases	Chapter 1 A, B, C
1	October 1-7	The First Law of Thermodynamics	Chapter 2
2	October 8-14	The First and Second Laws	Chapter 2, 3
3	Oct 15-Oct 21	Third Law; Physical Transformations	Chapter 3, 4
4	October 22-28	Physical Transformations; Mixtures	Chapter 4, 5
Midterm 1 (Chapters 1-4, 5A), Wednesday, October 25			
5	Oct. 29-Nov. 4	Mixtures; Chemical Equilibrium	Chapter 5, 6
6	Nov. 5-11	Chemical Equilibrium	Chapter 6
7	Nov. 12-18	Molecular Motion	Chapter 19
8	Nov. 19-25	Molecular Motion	Chapter 19
Midterm 2 (Chapters 1-6, 19), November 22			
9	Nov. 26-Dec. 2	Chemical Kinetics	Chapter 20
10	Dec. 3-Dec. 9	Chemical Kinetics, Collision Theory	Chapter 20, 21A
Final Exam (Chapters 1-6, 19, 20, 21A), Friday, Dec. 15, 8:00Am-10:00Am			

Immiscible—or partially miscible systems

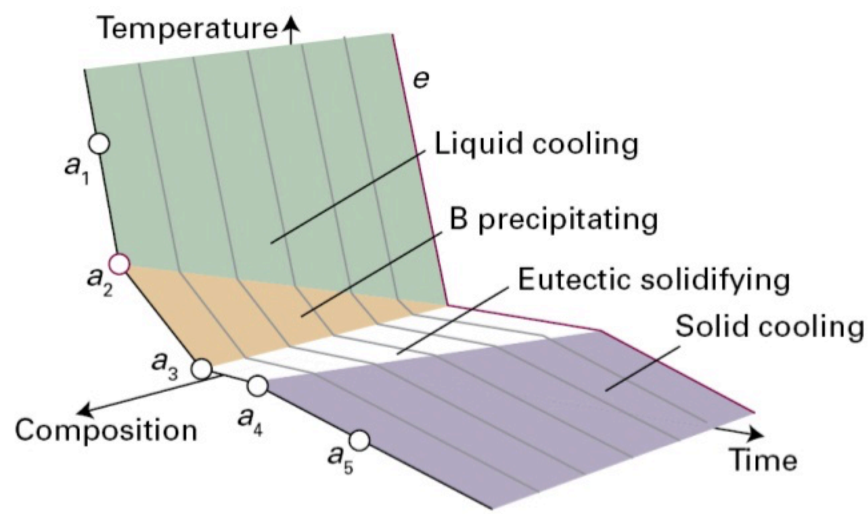
Liquid–Solid Phase Diagrams



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



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

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

$$a_B = \gamma_B x_B$$

Often activities are written in terms of molalities not mole fractions.

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"

Ionic Strength

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

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

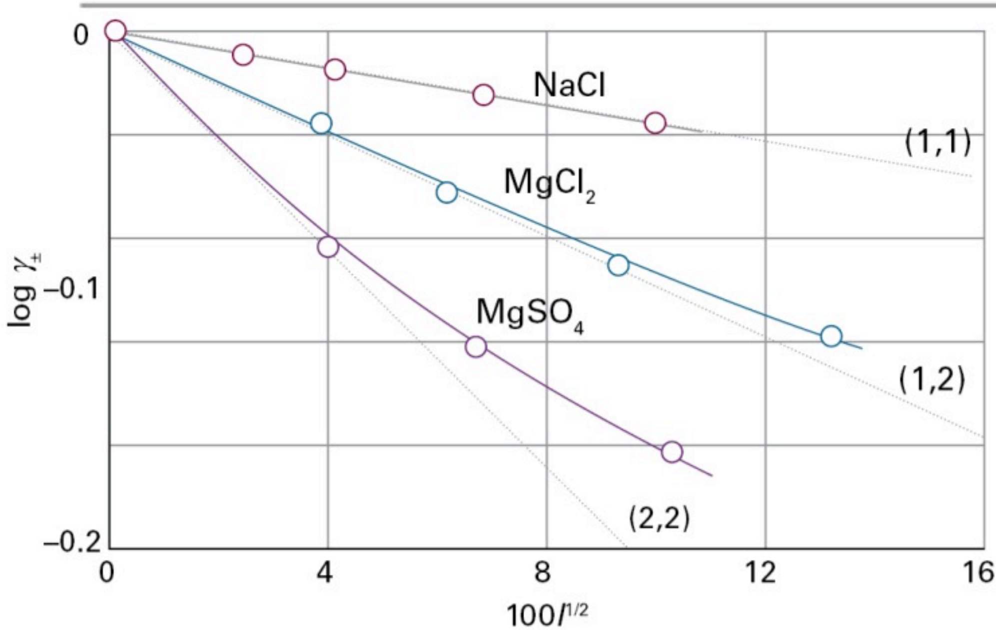
$$\log \gamma_{\pm} = -0.509 |z_+ z_-| I^{1/2}$$

$$I = \frac{1}{2} \left(b_+ z_+^2 + b_- z_-^2 \right) / b^0$$ **For solution with 2 types of ions**

How big is the effect of the ion interactions

Table 5F.2* Mean activity coefficients in water at 298 K

$b/b^{\ominus}$	KCl	$CaCl_2$
0.001	0.966	0.888
0.01	0.902	0.732
0.1	0.770	0.524
1.0	0.607	0.725



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

Extensions to Debye-Huckel Theory

Book discusses, don’t worry about it for this course

Chemical Equilibrium and Spontaneous Reactions

A simple reaction: A $\rightleftharpoons$ B

$$dn_A = -d\xi$$

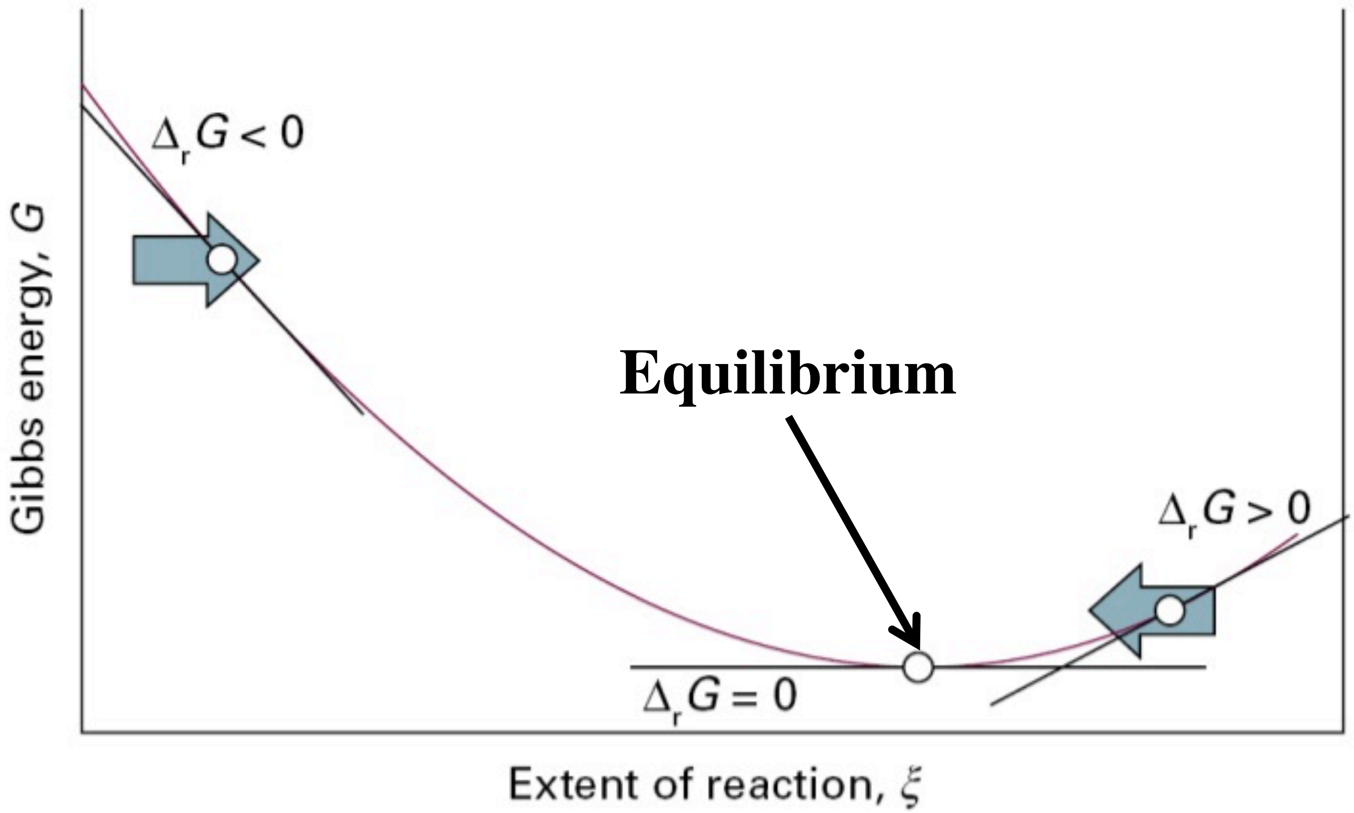
$$dn_B = +d\xi$$

Where ξ is the "extent of reaction"

$$\Delta_r G = \left(\frac{\partial G}{\partial \xi}\right)_{p,T}$$

$$\Delta_r G = \mu_B - \mu_A$$

Free Energy Change as a Function of Extent of Reaction



Simple Case: Ideal Gases

$$\Delta_r G = \mu_B - \mu_A$$

$$\Delta_r G = \left(\mu_B^0 + RT\ln p_B\right) - \left(\mu_A^0 + RT\ln p_A\right)$$

$$\Delta_r G = \Delta_r G^0 + RT\ln\left(\frac{p_B}{p_A}\right)$$

$$\Delta_r G = \Delta_r G^0 + RT\ln(Q)$$

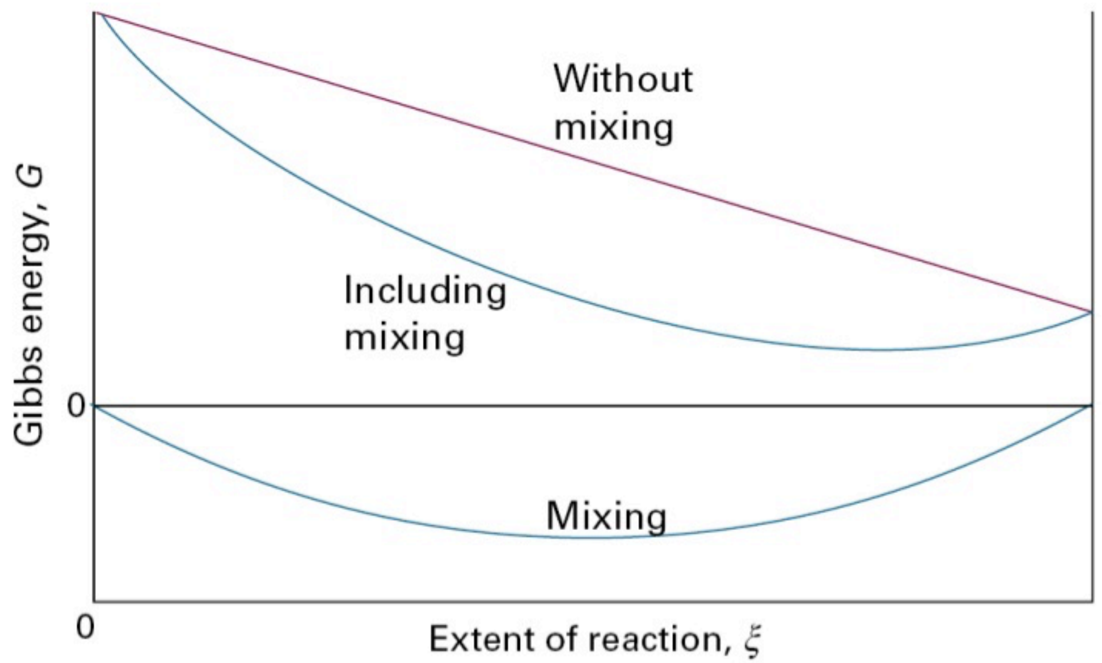
At equilibrium: $\Delta G_r = 0$

So: $\Delta G^0 = -RT\ln Q_{equilibrium}$

$\Delta G^0 = -RT\ln K$

$$K = \left(\frac{p_B}{p_A}\right)_{equilibrium}$$

For A↔B (ideal gases) Mixing is important



THE END

SEE YOU Monday