Physical Chemistry (Chem 132A)

Lecture 16
Monday, November 6

Homework #6 is due November 11

Midterm Exam #1

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

It is your responsibility to:

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 and on Shane's github site)**
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 Moisesa—attach exam pdf).

NO Re-grades for changes in partial credit.

Schedule

1. **This Friday (November 10) is a campus holiday so no lecture.**

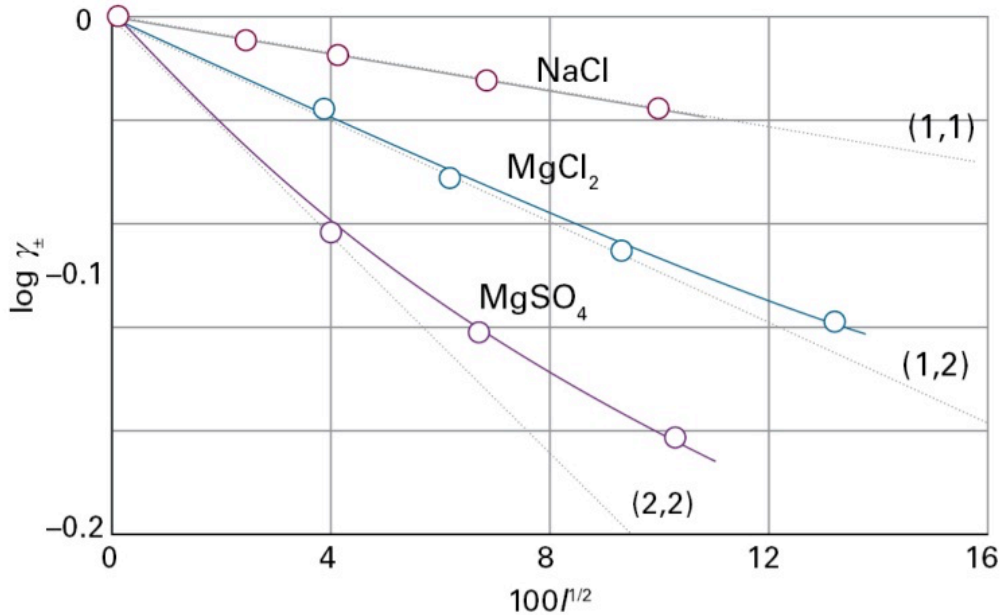
2. **There will be a new WebAssign homework set (Homework #7) available on Saturday night (November 11). This will be due on November 18. This will probably be the last homework assignment before the second midterm.**

3. **Second Midterm exam: Wednesday, November 22 second midterm will cover Chapters 1—6, 19**

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



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

$$\log_{10} \gamma_{\pm} = -0.509 \left| z_+ z_- \right| I^{1/2}$$

Shown by light gray straight lines

Phase Rule

One component system:

F = 3 – P

if P = 1, then F = 2

if P = 2, then F = 1 (phase boundary line)

if P = 3, then F = 0 (triple point)

In General:

F = C – P + 2

For a 2 component system: C = 2

F = 4 – P

New Topic: Chapter 6

Chemical Equilibrium and Equilibrium Constants

Chemical Equilibrium and Spontaneous Reactions

A simple reaction: A $\rightleftharpoons$ B

$$dn_A = -d\xi$$

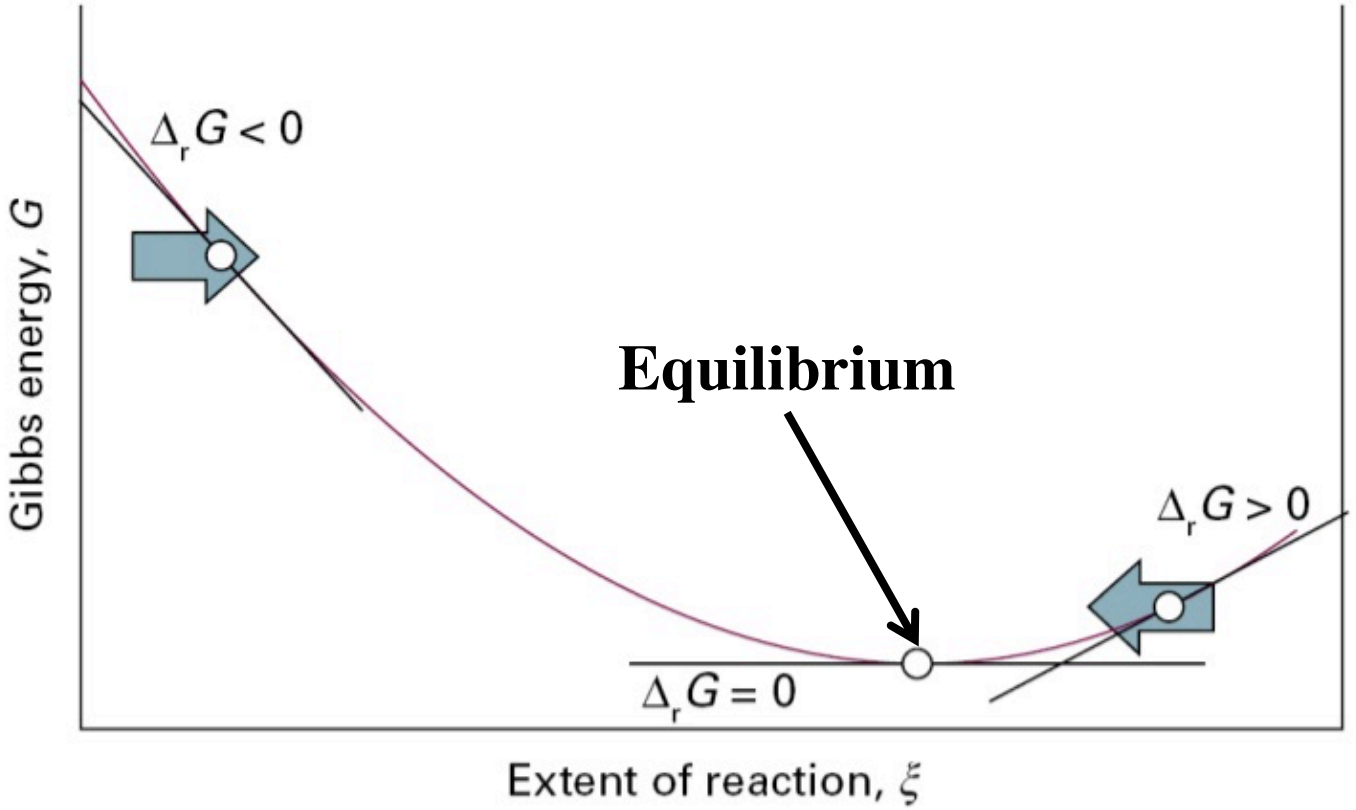
$$dn_B = +d\xi$$

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

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

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

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

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

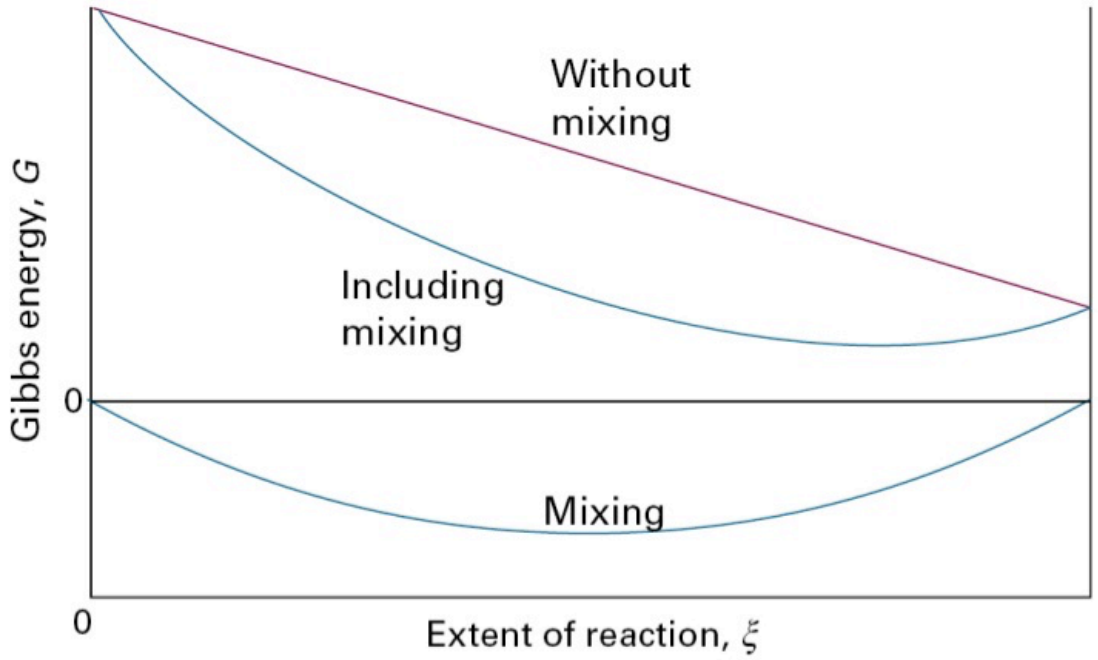
At equilibrium: $\Delta G_r = 0$

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



Non-ideal case ΔH can contribute

Anything Different from Introductory Chemistry?

A + B ⟷ C + D

$$K = \frac{a_C a_D}{a_A a_B}$$

K should be written in terms of activities

$$K = \frac{a_C a_D}{a_A a_B} = \frac{\gamma_C b_C \gamma_D b_D}{\gamma_A b_A \gamma_B b_b} = \frac{\gamma_C \gamma_D}{\gamma_A \gamma_B} \frac{b_C b_D}{b_A b_B}$$

$$K = K_\gamma K_b$$

Temperature Dependence of K

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

$$\ln K = -\frac{\Delta_r G^0}{RT}$$

$$\frac{d \ln K}{dT} = -\frac{1}{R} \frac{d\left(\frac{\Delta_r G^0}{T}\right)}{dT}$$

$$= -\frac{1}{R} \frac{d\left(\frac{\Delta_r H^0 - T\Delta S^0}{T}\right)}{dT} = -\frac{1}{R} \frac{d\left(\frac{\Delta_r H^0}{T} - \Delta S^0\right)}{dT}$$

$$\frac{d \ln K}{dT} = -\frac{1}{R} \frac{d\left(\frac{\Delta_r H^0}{T}\right)}{dT} = -\frac{1}{R} \frac{d\left(\Delta_r H^0 * T^{-1}\right)}{dT} = \frac{\Delta_r H^0}{RT^2}$$

$$\frac{d(1/T)}{dT} = -\frac{1}{T^2}$$

$$dT = -T^2 d(1/T)$$

$$\frac{d \ln K}{d(1/T)} = -\frac{\Delta_r H^0}{R}$$

$$\ln K_2 - \ln K_1 = -\frac{\Delta_r H^0}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Le Chatelier's Principle

Equilibrium shifts to offset any perturbation

e.g. effect of pressure:

$N_2 + 3H_2 = 2NH_3$
increased pressure causes shift toward NH_3

Effect of temperature (heat)
- **Endothermic**
- **Exothermic**

Electrochemical Cells and Cell Potentials

Chapter 6C and 6D

You should know this material from Introductory Chemistry

Read and review 6C and 6D

- **Balancing half-reactions and overall Redox reactions**
- **Standard potentials**
- **Nernst Equation**

THE END

SEE YOU Wednesday