

# Chem132A Discussion 5 Solutions

Moises Romero, Shane Flynn

November 2017

## 1 Ionic Solutions; Answer Key

In this problem we are given various equations to analyze and apply. DO NOT worry about knowing any of these equations other than the Debye-Huckel Limiting Law!

### 1.1 Units

$$\ln \gamma_{\pm} = \frac{-|z_+ z_-| \kappa}{8\pi\epsilon_0\epsilon_r k_B T} \quad (1)$$

We can re-write this equation in terms of the dimensionality of each constant.

The unit of charge is the Coulomb (C). The Boltzmann constant is in terms of J/K. The vacuum permittivity is given by  $C^2/Nm^2$ .

$$\ln \gamma_{\pm} = \frac{C^2 - K - N - m^2}{m - C^2 - J - K} \quad (2)$$

Note that a Joule is equal to a N-m and we do see that all the dimensions cancel.

### 1.2 Water

If we do some fancy math and massage Equation 1 we can show that it can be re-written as

$$\log \gamma_{\pm} = \frac{1.8248 \times 10^6 \sqrt{\rho_s}}{(D_s T)^{3/2}} |z_+ z_-| \sqrt{I} \quad (3)$$

Show that this equation evaluates to the Debye-Huckel Limiting Law presented in class for water at 25°C.

For water at room temperature the density  $\rho_s$  is 1 kg/L and the dielectric constant for water at 25 °C is 78.42.

$$\log \gamma_{\pm} = \frac{-1.8248 \times 10^6 \sqrt{1}}{(78.42 * 298)^{3/2}} |z_+ z_-| \sqrt{I} = -0.51 |z_+ z_-| \sqrt{I} \quad (4)$$

### 1.3 Mean Activity

Compute the mean activity coefficient ( $\gamma_{\pm}$ ) for a 0.005 (molal) aqueous solution of  $AlCl_3$  (assume complete dissociation) at  $T = 96.85^\circ C$ .

Let's first compute the ionic strength of the solution. We know each chlorine will contribute a negative 1 charge and each aluminum will contribute a positive 3 charge. If we take our reference state to be 1 molal, we find

$$\begin{aligned} I &\equiv \frac{1}{2} \sum_i z_i^2 \left( \frac{b_i}{b^0} \right) = \frac{b}{2} (1 \times 3^2 + 3 \times 1^2) \\ &= \frac{0.005}{2} (12) = 0.03 \frac{\text{mol}}{\text{kg}} \end{aligned} \quad (5)$$

Next we need to compute our A coefficient. Note the solvent is water, but we are at a different temperature, therefore we must look up the density of water at 370k ( $\rho_s = 0.96 \text{ kg/L}$ ) and the dielectric constant of water at this temperature ( $D_s = 30.04$ ).

$$A = \frac{-1.8248 \times 10^6 \sqrt{0.96}}{(30.04 * 370)^{3/2}} = -1.526 \quad (6)$$

Finally we can use the Debye-Huckel Limiting Equation to determine the average activity for our system.

$$\log \gamma_{\pm} = -1.526 | -1 \times 3 | \sqrt{0.03} = -0.793 \quad (7)$$

## 2 Chemical Equilibrium

Chemical Equilibrium for a non-ideal gas.

### 2.1 Real Gases

Develop an expression for  $K_\gamma$  and evaluate it using data from :

Total Pressure(Bar)	$K_p(10^{-3})$	$K_f(10^{-3})$
10	6.59	6.55
30	6.76	6.59
50	6.90	6.50
100	7.25	6.36
300	8.84	6.08
600	12.94	6.42

### Solution

We can write the fugacity coefficient as :

$$f_i = \gamma_i P_i \quad (8)$$

We can then substitute this in to our express of  $K_f$  to describe the relationship between the three K expressions :

$$K_f = \frac{f_C^{(V_C)} f_D^{(V_D)}}{f_A^{(V_A)} f_B^{(V_B)}} = \frac{\gamma_P^{(V_C)} P_C^{(V_C)} \gamma_D^{(V_D)} P_D^{(V_D)}}{\gamma_A^{(V_A)} P_A^{(V_A)} \gamma_B^{(V_B)} P_B^{(V_B)}} = \left( \frac{\gamma_C^{(V_C)} \gamma_D^{(V_D)}}{\gamma_A^{(V_A)} \gamma_B^{(V_B)}} \right) \left( \frac{P_C^{(V_C)} P_D^{(V_D)}}{P_A^{(V_A)} P_B^{(V_B)}} \right) = K_\gamma \dot{K}_P \quad (9)$$

So we can calculate  $K_\gamma$  at each given pressure to get :

Total Pressure(Bar)	$K_\gamma$
10	.994
30	.975
50	.942
100	.877
300	.688
600	.4996

As expected, the higher the pressure, the less ideal the system becomes.

### 2.2 Equilibrium expressed in terms of activity

The change in standard molar Gibbs Free Energy for the conversion of graphite to diamond is  $2.9 \text{ kJ}\cdot\text{mol}^{-1}$  at 298K. The density for graphite and diamond are  $2.27 \text{ g}\cdot\text{cm}^{-3}$  and  $3.52 \text{ g}\cdot\text{cm}^{-3}$ . At What pressure will these two compounds be at equilibrium?

### Solution

First we will start by finding an expression for the activity in terms of pressure. Then we will solve for the pressure.

To prove the relationship we will start with the fundamental equation for Gibbs Free Energy. At constant temperature the fundamental equation can be expressed as follows :

$$dG = VdP - SdT \rightarrow dG = d\mu = VdP \quad (10)$$

Combining this result with:

$$d\mu = RTd\ln(a) \quad (11)$$

We see that

$$\bar{V}dP = RTd\ln(a) \quad (12)$$

We then need to simply integrate both sides to find our relationship.

$$d \ln(a) = \frac{\bar{V}}{RT} dP \Rightarrow \int_{a=1}^a d \ln(a) = \frac{1}{RT} \int_1^P \bar{V} P \quad (13)$$

We integrate from an assigned standard state (a=1 and P=1 bar) , once we integrate we are left with :

$$\ln(a) = \frac{\bar{V}}{RT} (P - 1) \quad (14)$$

We can now use this relationship to determine our pressure at equilibrium.

$$\Delta_r G^o = -RT \ln(K_a) = -RT \ln \left( \frac{a_{diamond}}{a_{graphite}} \right) = -RT \left[ \frac{\Delta \bar{V}}{RT} (P - 1) \right] \quad (15)$$

We can rearrange this equation :

$$\frac{2900 J mol^{-1}}{(8.3145 J mol^{-1} K^{-1})(298 K)} = - \frac{(3.41 cm^3 mol^{-1} - 5.29 cm^3 mol^{-1} (\frac{1 dm^3}{1000 cm^3})(P - 1) bar)}{(.083145 dm^3 bar mol^{-1} K^{-1})(298 K)} \quad (16)$$

Which can then be simplified :

$$1.17 = -(-7.59 \times 10^{-5})(P - 1) \quad (17)$$

$$P \approx 15,000 \text{ Bar} \quad (18)$$

### 3 Enthalpy and Equilibrium

Consider the chemical reaction



The equilibrium constant as a function of temperature has been measured as

T(Kelvin)	K
900	1.32
1000	0.47
1100	0.21
1200	0.10

From this data estimate the standard Enthalpy of Reaction.

#### Solution

We can derive the Van't Hoff equation by starting with the Gibbs-Helmholtz equation.

$$\left( \frac{\partial(\Delta_r G^o/T)}{\partial T} \right) = \frac{-\Delta_r H^o}{T^2} \quad (20)$$

At equilibrium we know that

$$\Delta_r G^o = -RT \ln K \quad (21)$$

Equating these expressions we find

$$\left( \frac{\partial \ln K}{\partial T} \right) = \frac{\Delta_r H^o}{T^2 R} \quad (22)$$

Let's now integrate the expression

$$\int_{\ln K_1}^{\ln K_2} \left( \frac{\partial \ln K}{\partial T} \right) = \int_{T_1}^{T_2} \frac{\Delta_r H^o}{RT^2} \quad (23)$$

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

This equation means we can plot  $\ln K$  versus  $1/T$ , the slope will be  $\frac{\Delta_r H^o}{R}$