Homework #3

1. *Acid/Base Equilibria II: graphical method (4 POINTS)*

Solve the following problems (A. and B.) graphically. Later in HW #4, I will ask you to solve them exactly using MINEQL. Show the graphs and circle your solution point. Then present the approximate concentrations in a table.

A). Construct a log C vs pH diagram for a 0.10 F phosphate (H3PO4, H2PO4-, HPO4-2, PO4-3) system. Using it, calculate the pH and the concentration of all species in the following solutions:

i) 0.10 F NaH2PO4

ii) 0.10 F Na2HPO4

iii) 0.10 F Na3PO4

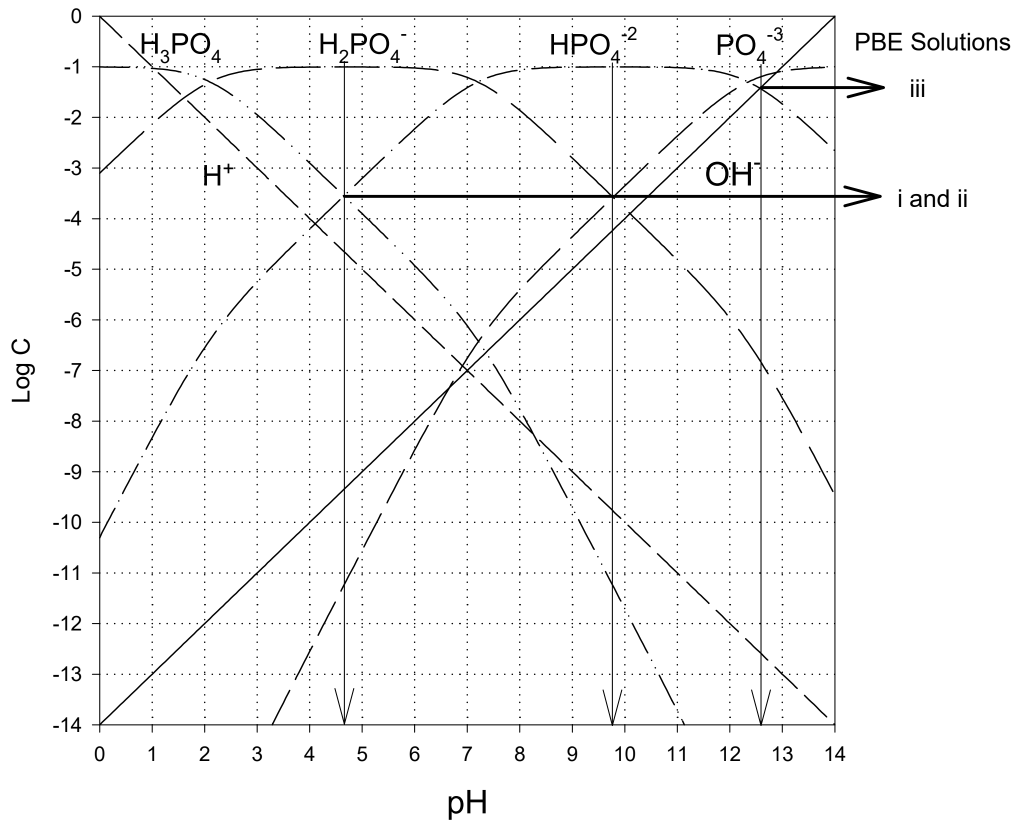
Approach

* prepare Log C vs pH diagram
* write PBE for each solution
* locate pHs for each solution
* read off concentrations for each species

Log C vs pH Diagram

* pKs are 2.1, 7.2, and 12.35
* Log C_T is -1

Log C vs pH Diagram



i) 0.10 F NaH2PO4

PBE

$$[HPO_4^{-2}] + 2[PO_4^{-3}] + [OH^-] = [H^+] + [H_3PO_4]$$

which reduces to:

$$[HPO_4^{-2}] = [H_3PO_4]$$

Solution Composition

Species	Graph	
	C	pC
H^+	2.2e-5	4.65
OH^-	4.5e-10	9.35
H_3PO_4	2.8e-4	3.55
$H_2PO_4^-$	1e-1	1.0
HPO_4^{-2}	2.8e-4	3.55
PO_4^{-3}	8e-12	11.1
Na^+	1e-1	1

ii) 0.10 F Na2HPO4

PBE

$$[PO_4^{-3}] + [OH^-] = [H^+] + 2[H_3PO_4] + [H_2PO_4^-]$$

which reduces to:

$$[PO_4^{-3}] = [H_2PO_4^-]$$

Solution Composition

Species	Graph	
	C	pC
H^+	1.7e-10	9.75
OH^-	5.6e-5	4.25
H_3PO_4	8e-12	11.1
$H_2PO_4^-$	2.8e-4	3.55
HPO_4^{-2}	1e-1	1
PO_4^{-3}	2.8e-4	3.55
Na^+	2e-1	0.7

iii) 0.10 F Na3PO4

PBE

$$[OH^-] = [H^+] + 3[H_3PO_4] + 2[H_2PO_4^-] + [HPO_4^{-2}]$$

which reduces to:

$$[OH^-] = [HPO_4^{-2}]$$

Solution Composition

Species	**Graph**	
	C	pC
H^+	2.5e-13	12.6
OH^-	4e-2	1.4
H_3PO_4	1e-17	17
$H_2PO_4^-$	2e-7	6.7
HPO_4^{-2}	4e-2	1.4
PO_4^{-3}	6.3e-2	1.2
Na^+	3e-1	0.5

B) Construct similar log C vs pH diagrams for 0.10 F carbonate system (H2CO3, HCO3-, CO3-2) and 0.20 F ammonia system (NH4+, NH3), and use this to calculate pH and composition of the following systems:

i) 0.10 F $NaHCO_3$

ii) 0.10 F $NaHCO_3$ + 0.20 F NH_4Cl

iii) 0.10 F $(NH_4)_2CO_3$

iv) 0.10 F Na_2CO_3

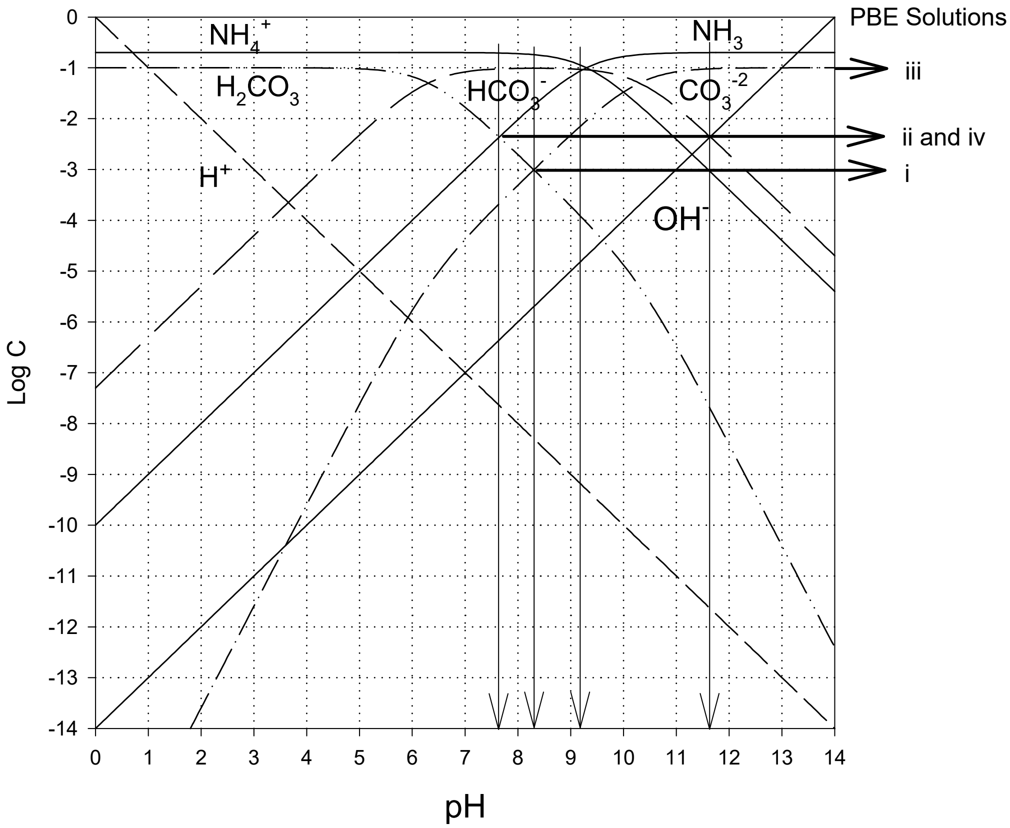
Approach

- prepare Log C vs pH diagram
- write PBE for each solution
- locate pHs for each solution
- read off concentrations for each species

Log C vs pH Diagram

- pKs are 6.3 and 10.3 for carbonate system; 9.3 for ammonia
- Log C_T is -1 for carbonate system; -0.7 for ammonia

Log C vs pH Diagram



i) 0.10 F $NaHCO_3$

PBE

$$[CO_3^{-2}] + [OH^-] = [H^+] + [H_2CO_3]$$

which reduces to:

$$[CO_3^{-2}] = [H_2CO_3]$$

Solution Composition

Species	Graph	
	C	pC
H^+	5e-9	8.3
OH^-	2e-6	5.7
H_2CO_3	1e-3	3
HCO_3^-	1e-1	1
CO_3^{-2}	1e-3	3
Na^+	1e-1	1

** this is the sum of $[CO_3^{-2}]$ (5.69e-4) and $[NaCO_3^-]$ (9.93e-4).

ii) 0.10 F $NaHCO_3$ + 0.20 F NH_4Cl

PBE

$$[CO_3^{-2}] + [NH_3] + [OH^-] = [H^+] + [H_2CO_3]$$

which reduces to:

$$[NH_3] = [H_2CO_3]$$

Solution Composition

Species	Graph	
	C	pC
H^+	2.5e-8	7.6
OH^-	4e-7	6.4
H_2CO_3	5e-3	2.3
HCO_3^-	1e-1	1
CO_3^{-2}	1.8e-4	3.75
NH_4^+	2e-1	0.7
NH_3	5e-3	2.3
Cl^-	2e-1	0.7
Na^+	1e-1	1

iii) 0.10 F $(NH_4)_2CO_3$

PBE

$$[NH_3] + [OH^-] = [H^+] + 2[H_2CO_3] + [HCO_3^-]$$

which reduces to:

$$[NH_3] = [HCO_3^-]$$

Solution Composition

Species	Graph	
	C	pC
H^+	5.6e-10	9.25
OH^-	1.8e-5	4.75
H_2CO_3	7e-5	4.2
HCO_3^-	1e-1	1
CO_3^{-2}	8e-3	2.1
NH_4^+	1e-1	1.0
NH_3	1e-1	1.0

iv) 0.10 F Na_2CO_3

PBE

$$[OH^-] = [H^+] + 2[H_2CO_3] + [HCO_3^-]$$

which reduces to:

$$[OH^-] = [HCO_3^-]$$

Solution Composition

Species	Graph	
	C	pC
H^+	2.2e-12	11.65
OH^-	4.5e-3	2.35
H_2CO_3	2e-8	7.7
HCO_3^-	4.5e-3	2.35
CO_3^{-2}	1e-1	1
Na^+	2e-1	0.7

** this is the sum of $[CO_3^{-2}]$ (2.8e-2) and $[NaCO_3^-]$ (6.9e-2).

2. Acid/Base Equilibria III: Acids & Conjugate Bases (2 POINTs)

A. Calculate the composition and pH of the following solutions:

i) 0.10 F NaCOOH + 0.40 F HCOOH

ii) 0.20 F NH_3 + 0.50 F NH_4Cl

General Approach

* these are solutions of acids and conjugate bases
* use the buffer equation, and its simplifying assumptions:

$$pH = pK_a + \log\{C_A/C_{HA}\}$$

* pK_a's are 3.75 for formic acid and 9.3 for ammonia

i) 0.10 F NaCOOH + 0.40 F HCOOH

$$pH = pK_a + \log\{C_A/C_{HA}\}$$
$$pH = 3.75 + \log\{0.1/0.4\}$$
$$pH = 3.15$$

Species	Equation	C	pC
H^+	buffer eq.	7.1e-4	3.15
OH^-	K_w	1.4e-11	10.85
HCOOH	$=C_{HA}$	0.4	0.40
$COOH^-$	$=C_A$	0.1	1
Na^+	$=C_A$	0.1	1

ii) 0.20 F NH_3 + 0.50 F NH_4Cl

$$pH = pK_a + \log\{C_A/C_{HA}\}$$
$$pH = 9.3 + \log\{0.2/0.5\}$$
$$pH = 8.90$$

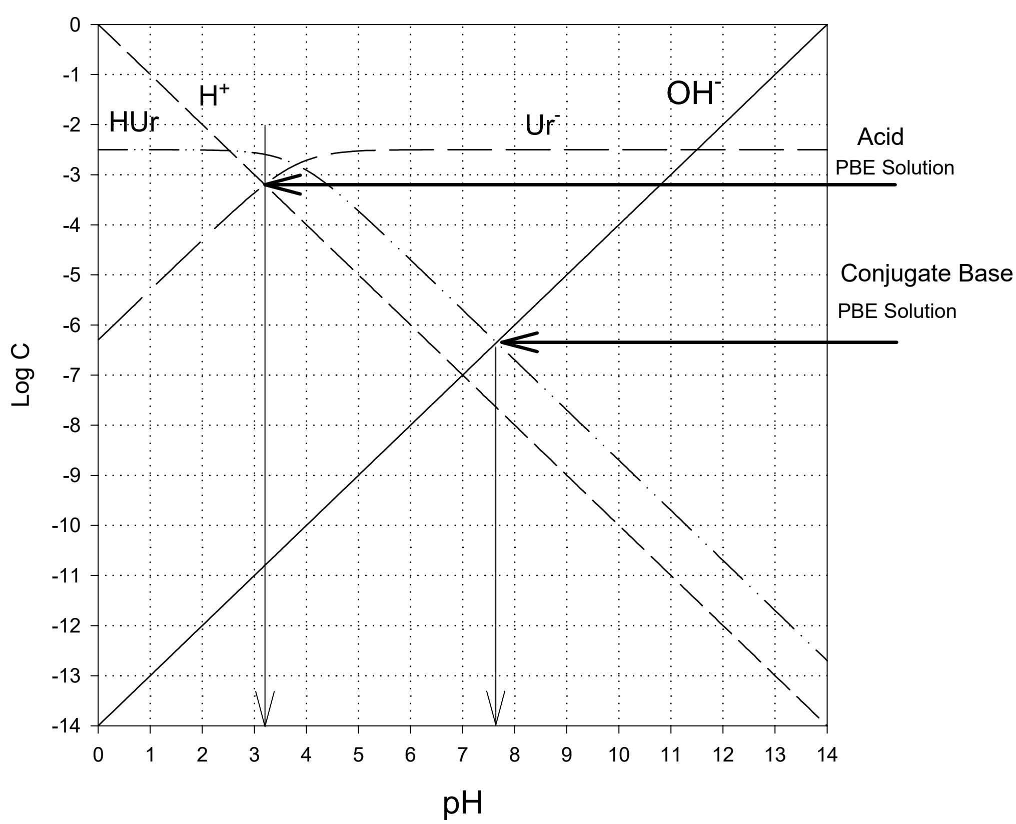
Species	Equation	C	pC
H^+	buffer eq.	1.2e-9	8.90
OH^-	K_w	8.0e-5	5.10
NH_4^+	$=C_{HA}$	0.5	0.3
NH_3	$=C_A$	0.2	0.7
Cl^-	$=C_{HA}$	0.5	0.3

B. A 3.16x10-3 F solution of uric acid has a pH of 3.2. What is the pH of an equimolar solution (i.e., 3.16x10-3 F) of the Na+ salt of its conjugate base (Na-urate)?

Approach

* prepare a Log C vs pH diagram, but working backwards
* known C_T, and known pH, find pK_a
* PBE suggests that pH lies at intersection of urate (Ur^-) line and the H^+ line
* draw line with +1 slope passing through H^+ line at pH=3.2
* where it intersects C_T is the pK_a (about 3.8)
* then write PBE for base addition (i.e., NaUr) and solve

Log C vs pH Diagram



PBE for Base Addition (NaUr)

$$[HUr] + [H^+] = [OH^-]$$

which reduces to:

$$[HUr] = [OH^-]$$

Read pH from Graph

$$pH = 7.65$$