

## Class CEE 543 Homework 3 Solution

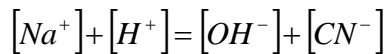
1. **(2.0 points)** Using LogC approach, find the system points and determine the pH of following solutions. Provide all necessary equations and graphs.

- a) 0.005M NaCN and 0.005 HCN. pK of this acid (HCN) is 9.24.
- b) 0.005 M NaHCO<sub>3</sub> and 0.0025 M Na<sub>2</sub>CO<sub>3</sub>. pK<sub>1</sub> and pK<sub>2</sub> of carbonic acid are 6.3 and 10.3, respectively.
- c) 0.0001 M NH<sub>4</sub>Cl. pK of NH<sub>4</sub><sup>+</sup> is 9.25.
- d) 0.001 M of sodium acetate NaCH<sub>3</sub>COO (pK of acetic acid CH<sub>3</sub>COOH is 4.76) and 0.001 M NH<sub>4</sub>Cl.

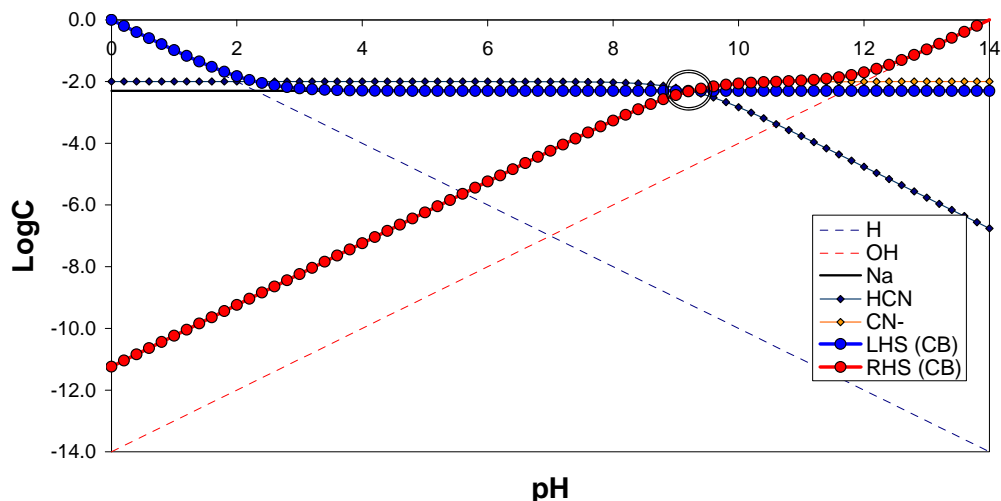
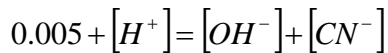
### Problem 1a (pH of solution containing 0.005M NaCN and 0.005 HCN)

#### **Charge balance approach**

Charge balance equation



Total sodium in this system is known (it is 0.005 M), while the total cyanide concentration is 0.01 M. Therefore we can operate using the charge balance equations rewritten as show below. Its LHS and RHS are shown in Figure HW3.1.



**Figure HW3.1 LogC plot and system point for problem HW1.a (charge balance condition)**

**Proton condition approach #1 (CN<sup>-</sup> as the reference species)**

The table of proton-excess and proton-deficient species is shown below. This table assumes that for the HCN system, CN<sup>-</sup> is the reference species.

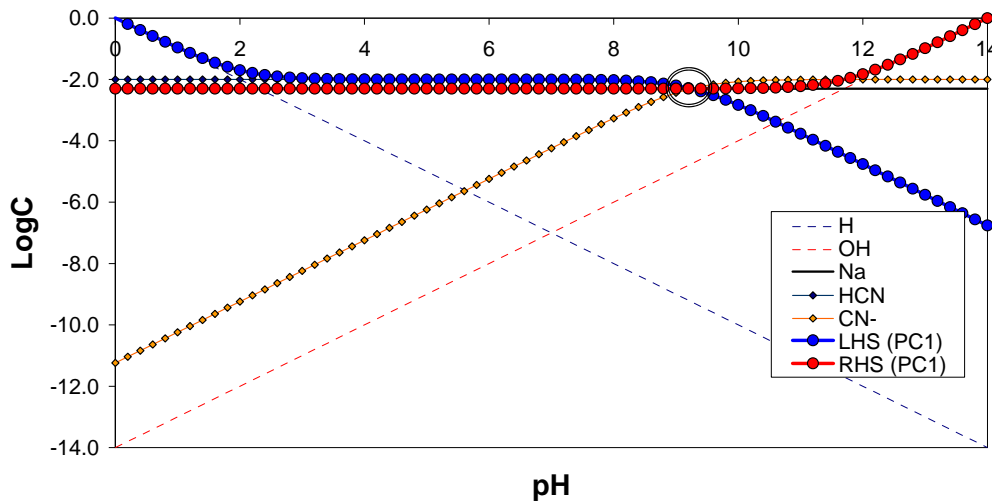
-1	0	+1		Concentration
OH <sup>-</sup>	H <sub>2</sub> O	H <sup>+</sup>		
	CN <sup>-</sup>	HCN		
	Na <sup>+</sup>			
Initial concentrations				
	CN <sup>-</sup>			0.005 M
		HCN		0.005 N

The proton condition defined in agreement with this table is therefore

$$\sum_i c_{initial} n_i = 0.005 = \sum_i c_{equilibrium} = [H^+] + [HCN] - [OH^-]$$

$$[H^+] + [HCN] = 0.005 + [OH^-]$$

The LHS and RHS for this equation are shown in Figure HW3.2.



**Figure HW3.2 LogC plot and system point for problem HW1.a (proton condition #1)**

**Proton condition #2 (HCN as the reference species)**

-1	0	+1		Concentration
OH <sup>-</sup>	H <sub>2</sub> O	H <sup>+</sup>		
CN <sup>-</sup>	HCN			
	Na <sup>+</sup>			

Initial concentrations				
CN-				0.005 M
	HCN			0.005 N

$$\sum_i c_{initial} n_i = -0.005 = \sum_i c_{equilibrium} = [H^+] - [OH^-] - [CN^-]$$

$$0.005 + [H^+] = [OH^-] + [CN^-]$$

This is the same condition as that defined by the charge balance for this system. In all cases the system point is located at pH 9.2.

### **Problem 1b (pH of solution containing 0.005 M NaHCO<sub>3</sub> and 0.0025 M Na<sub>2</sub>CO<sub>3</sub>)**

#### **Charge balance condition**

$$[Na^+] + [H^+] = [OH^-] + [HCO_3^-] + 2[CO_3^{2-}]$$

Total concentration of sodium 0.01 M (0.005+2x0.0025)

Total concentration of carbonate 0.0075 M

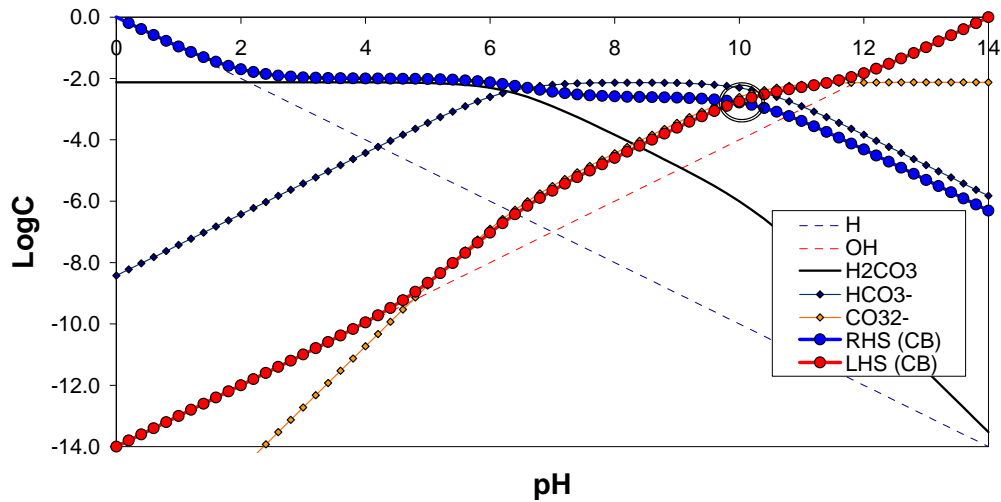
The molar ratio of total sodium to total carbonate concentrations is 0.01/0.0075=1.33. Therefore, based on the stoichiometry of dissolution, we can write that

$$1.33[H_2CO_3] + 1.33[HCO_3^-] + 1.33[CO_3^{2-}] + [H^+] = [OH^-] + [HCO_3^-] + 2[CO_3^{2-}]$$

Or

$$1.33[H_2CO_3] + 0.33[HCO_3^-] + [H^+] = [OH^-] + 0.67[CO_3^{2-}]$$

The RHS and LHS for this system are shown in Figure HW3.3. They indicate that the system point is at pH 10.0.



**Figure HW3.3 LogC plot and system point for problem HW1.b (charge balance condition)**

***Proton condition approach #1 (HCO<sub>3</sub><sup>-</sup> as the reference species)***

The table of proton-excess and proton-deficient species is shown below. This table assumes that for the H<sub>2</sub>CO<sub>3</sub> system, HCO<sub>3</sub><sup>-</sup> is the reference species

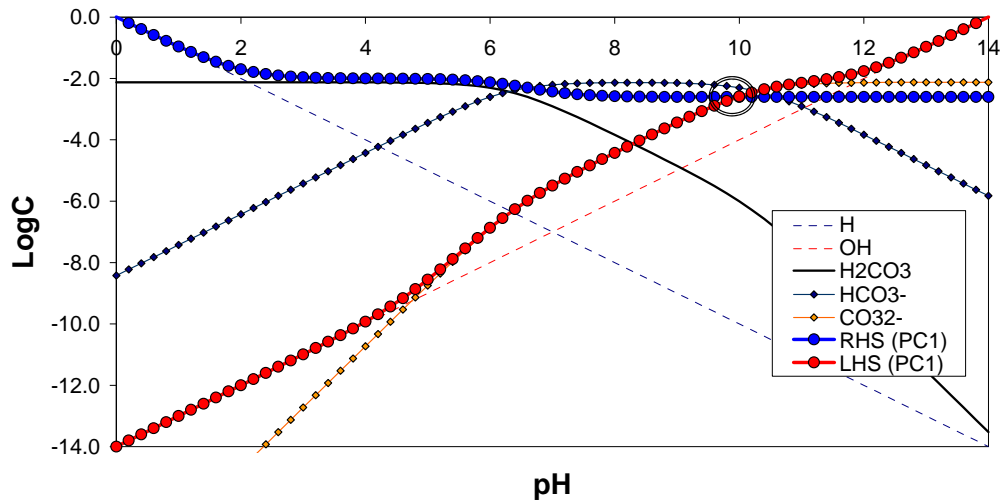
-1	0	+1		Concentration
OH <sup>-</sup>	H <sub>2</sub> O	H <sup>+</sup>		
CO <sub>3</sub> <sup>2-</sup>	HCO <sub>3</sub> <sup>-</sup>	H <sub>2</sub> CO <sub>3</sub>		
	Na <sup>+</sup>			
Initial concentrations				
	HCO <sub>3</sub> <sup>-</sup>			0.0050 M
CO <sub>3</sub> <sup>2-</sup>				0.0025 M

The proton condition defined in agreement with this table is therefore

$$\sum_i c_{initial} n_i = -0.0025 = \sum_i c_{equilibrium} = [H^+] + [H_2CO_3] - [OH^-] - [CO_3^{2-}]$$

$$[H^+] + [H_2CO_3] + 0.0025 = [OH^-] + [CO_3^{2-}]$$

The LHS and RHS for this equation are shown in Figure HW3.4.



**Figure HW3.4 LogC plot and system point for problem HW1.b (proton condition #1)**

***Proton condition approach #2 ( $\text{CO}_3^{2-}$  as the reference species)***

The table of proton-excess and proton-deficient species is shown below. This table assumes that for the  $\text{H}_2\text{CO}_3$  system,  $\text{CO}_3^{2-}$  is the reference species

-1	0	+1	+2	Concentration
$\text{OH}^-$	$\text{H}_2\text{O}$	$\text{H}^+$		
	$\text{CO}_3^{2-}$	$\text{HCO}_3^-$	$\text{H}_2\text{CO}_3$	
	$\text{Na}^+$			
Initial concentrations				
		$\text{HCO}_3^-$		0.0050 M
	$\text{CO}_3^{2-}$			0.0025 M

The proton condition defined in agreement with this table is therefore

$$\sum_i c_{\text{initial}} n_i = 0.005 = \sum_i c_{\text{equilibrium}} = [\text{H}^+] + [\text{HCO}_3^-] + 2[\text{H}_2\text{CO}_3] - [\text{OH}^-]$$

$$[\text{H}^+] + [\text{HCO}_3^-] + 2[\text{H}_2\text{CO}_3] = [\text{OH}^-] + 0.005$$

The LHS and RHS for this equation are shown in Figure HW3.5.

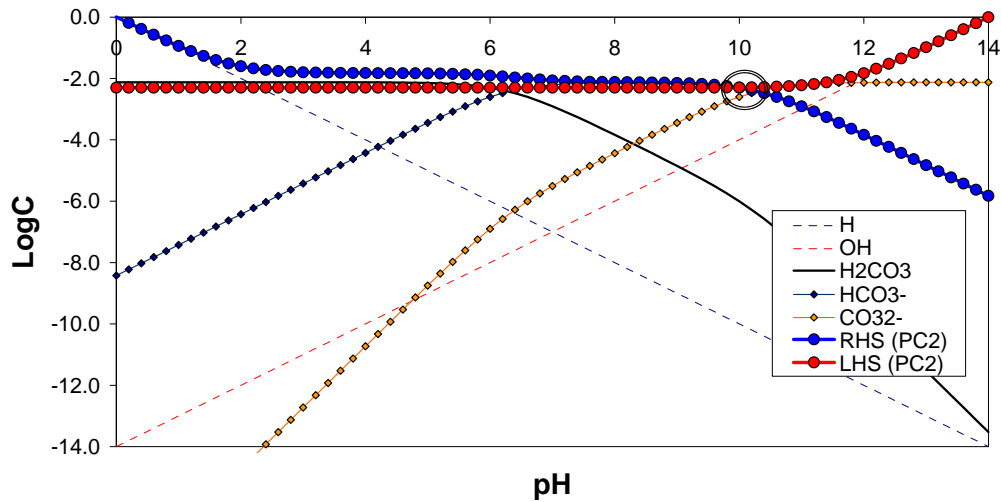


Figure HW3.5 LogC plot and system point for problem HW1.b (proton condition #2)

**Problem 1c (pH of solution containing 0.0001 M NH<sub>4</sub>Cl)**

Charge balance condition

$$[NH_4^+] + [H^+] = [OH^-] + [Cl^-]$$

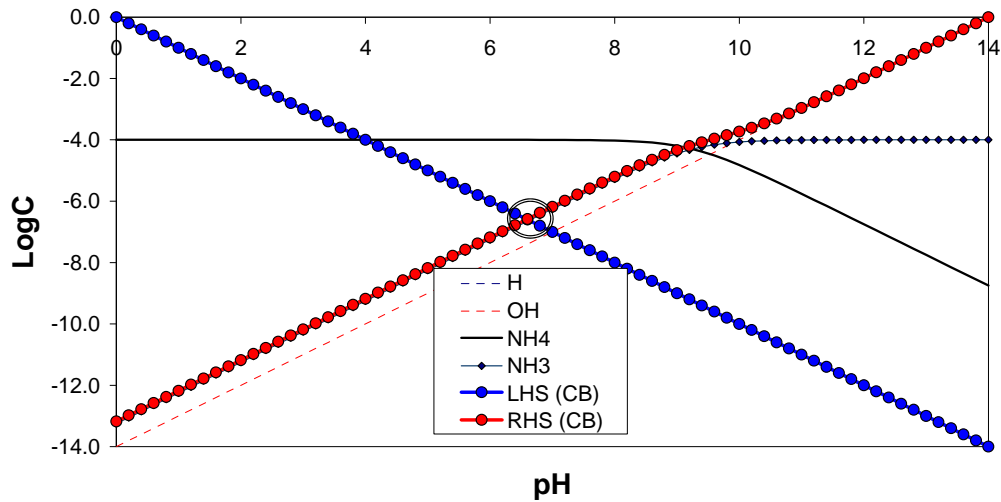
The stoichiometry condition

$$[NH_4^+] + [NH_3] = [Cl^-]$$

Modified charge balance condition

$$[H^+] = [OH^-] + [NH_3]$$

The RHS and LHS for this system are shown in Figure HW3.6. They indicate that the system point is at pH 6.6.



**Figure HW3.6 LogC plot and system point for problem HW1.c (charge balance condition)**

***Proton condition approach #1 (NH<sub>3</sub> as the reference species)***

The table of proton-excess and proton-deficient species is shown below. This table assumes that for the ammonium system, NH<sub>3</sub> is the reference species.

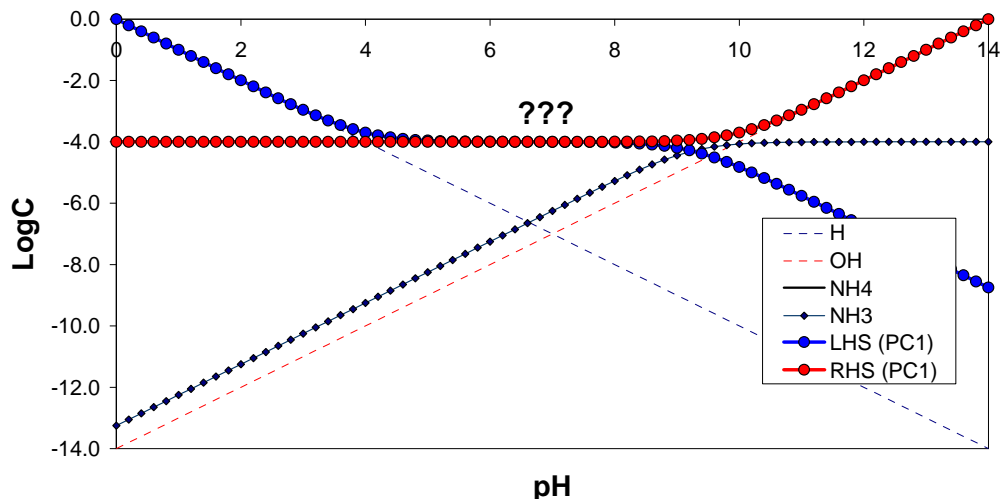
-1	0	+1		Concentration
OH <sup>-</sup>	H <sub>2</sub> O	H <sup>+</sup>		
	NH <sub>3</sub>			
		NH <sub>4</sub> <sup>+</sup>		
	Cl <sup>-</sup>			
Initial concentrations				
		NH <sub>4</sub> <sup>+</sup>		0.0001 M

The proton condition defined in agreement with this table is therefore

$$\sum_i c_{initial} n_i = 0.0001 = \sum_i c_{equilibrium} = [H^+] + [NH_4^+] - [OH^-]$$

$$[H^+] + [NH_4^+] = [OH^-] + 0.0001$$

The LHS and RHS for this equation are shown in Figure HW3.7. This figure shows that choosing NH<sub>3</sub> as the reference species in the system is not very helpful in finding the system point.



**Figure HW3.7 LogC plot and system point for problem HW1.c (proton condition #1)**

**Proton condition approach #2 ( $\text{NH}_4^+$  as the reference species)**

The table of proton-excess and proton-deficient species is shown below. This table assumes that for the ammonium system,  $\text{NH}_4^+$  is the reference species.

-1	0	+1		Concentration
$\text{OH}^-$	$\text{H}_2\text{O}$	$\text{H}^+$		
$\text{NH}_3$				
	$\text{NH}_4^+$			
	$\text{Cl}^-$			
Initial concentrations				
	$\text{NH}_4^+$			0.0001 M

The proton condition defined in agreement with this table is therefore

$$\sum_i c_{\text{initial}} n_i = 0 = \sum_i c_{\text{equilibrium}} = [\text{H}^+] - [\text{NH}_3] - [\text{OH}^-]$$

$$[\text{H}^+] = [\text{OH}^-] + [\text{NH}_3]$$

This is exactly the same condition as that defined by the charge balance equation indicating that the system point is at pH 6.6.

**Problem 1d (pH of solution containing 0.001 M of sodium acetate  $\text{NaCH}_3\text{COO}$  and 0.001 M  $\text{NH}_4\text{Cl}$ )**



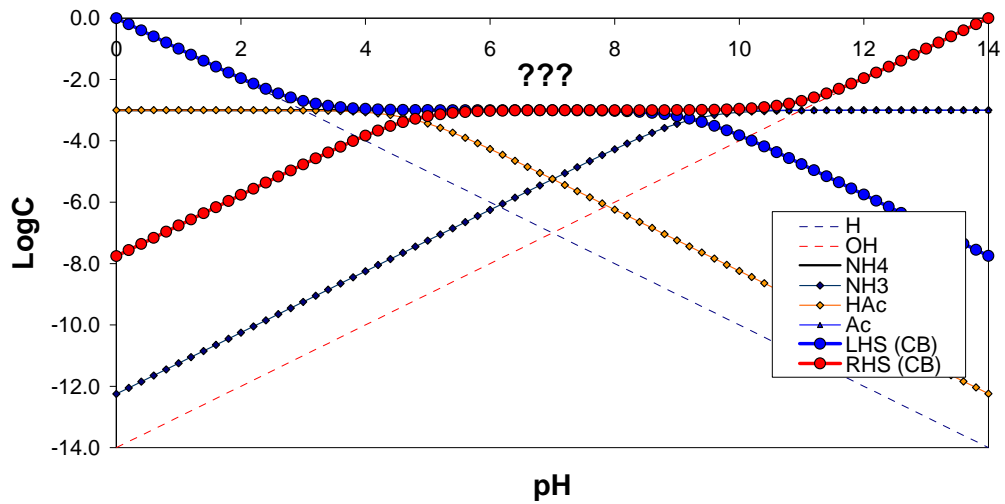
**Charge balance condition**

$$[NH_4^+] + [H^+] + [Na^+] = [OH^-] + [Cl^-] + [Ac^-]$$

Because the molar concentrations of chloride and sodium are equal in this case, the above equation can be rewritten

$$[NH_4^+] + [H^+] = [OH^-] + [Ac^-]$$

The RHS and LHS for this system are shown in Figure HW3.8. It indicates that the charge balance approach is not useful here.



**Figure HW3.8 LogC plot and system point for problem HW1.d (charge balance condition)**

**Proton condition approach #1 ( $NH_4^+$  and  $Ac^-$  as the reference species)**

The table of proton-excess and proton-deficient species is shown below. This table assumes that for the ammonium and acetate systems,  $NH_4^+$  and  $Ac^-$  are the reference species, respectively.

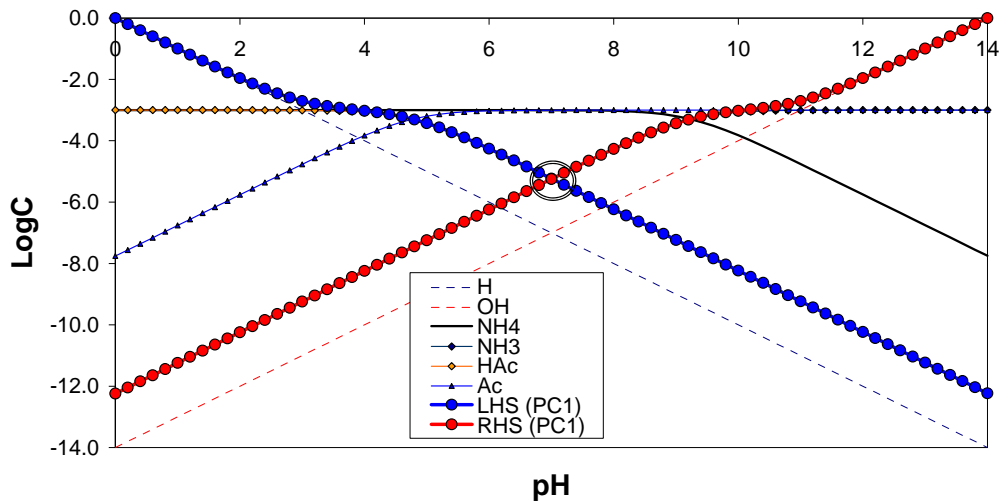
-1	0	+1		Concentration
$OH^-$	$H_2O$	$H^+$		
$NH_3$	$NH_4^+$			
	$Ac^-$	HAc		
	$Na^+$			
	$Cl^-$			
Initial concentrations				
	$NH_4^+$			0.001 M
	$Ac^-$			0.001 M

The proton condition defined in agreement with this table is therefore

$$\sum_i c_{initial} n_i = 0 = \sum_i c_{equilibrium} = [H^+] + [HAc] - [OH^-] - [NH_3]$$

$$[H^+] + [HAc] = [OH^-] + [NH_3]$$

The corresponding graph is shown in Figure HW3.9. It indicates that the system point is at pH 7.0.



**Figure HW3.9 LogC plot and system point for problem HW1.d (proton condition #1)**

2. **(2.0 points)** Using MINEQL+, determine the following:

- Determine the pH of solution containing 0.001 M  $CH_3COOH$ , 0.0005 M  $KCH_3COO$  and 0.0005 M  $NaCH_3COO$  at ionic strength of the solution 0.01 M.
- Determine the pH of solution containing 0.015 M  $Na_2SO_4$ , 0.027 M  $NaHCO_3$ , 0.009 M  $NH_4Cl$  at the following concentrations of  $Na_2CO_3$ : 0, 0.005 M, 0.01 M, 0.015 M, 0.02 M and 0.025 M. The ionic strength of the solution is defined by the actual concentrations of all salts present in it.
- Generate linear and logC plots of the speciation of 0.0001 M citric acid in the range of pH 0 to 14 at ionic strength of 0.001 M. Provide all necessary graphs.
- Carry out same calculations for 0.0001 M EDTA (ethylenediaminetetraacetic acid) at 0.001 M ionic strength and

temperatures 5, 25 and 45°C. Compare changes of EDTA speciation caused by changes of the temperature. Provide all necessary graphs.

### Problem 2a

The pH of this system is 4.73, largely coinciding with the pK of acetic acid (4.76). This is to be expected, given the equal concentrations of the protonated and deprotonated forms of acetic acid defined in this problem.

### Problem 2b

pH values calculated for the system at varying concentrations of  $\text{Na}_2\text{CO}_3$  are shown below

$\text{Na}_2\text{CO}_3$ concentration 0 M	pH 7.90
$\text{Na}_2\text{CO}_3$ concentration 0.005 M	pH 8.87
$\text{Na}_2\text{CO}_3$ concentration 0.010 M	pH 9.17
$\text{Na}_2\text{CO}_3$ concentration 0.015 M	pH 9.35
$\text{Na}_2\text{CO}_3$ concentration 0.020 M	pH 9.47
$\text{Na}_2\text{CO}_3$ concentration 0.025 M	pH 9.56

### Problem 2c

Results of required calculations are shown in two figures below (Figure HW3.10 and Figure HW3.11).

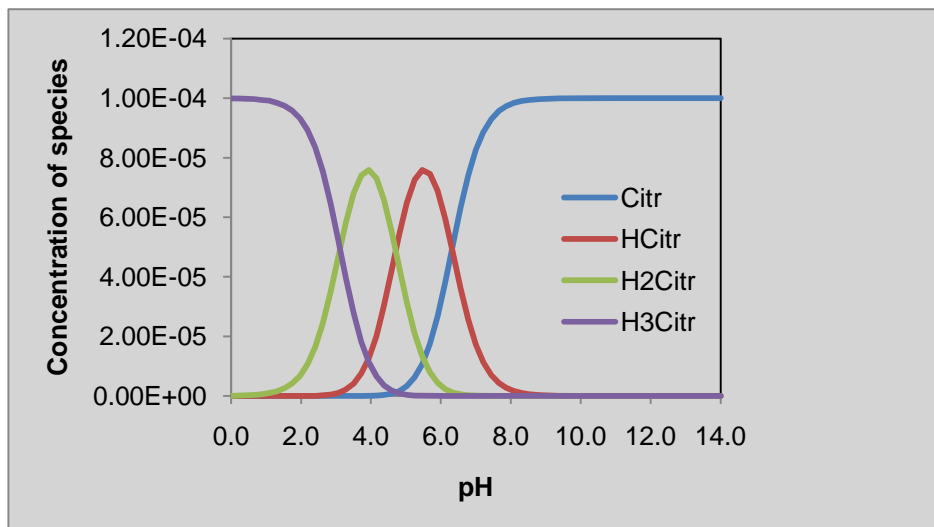


Figure HW3.10 Effects of pH on the speciation of citric acid (linear representation)

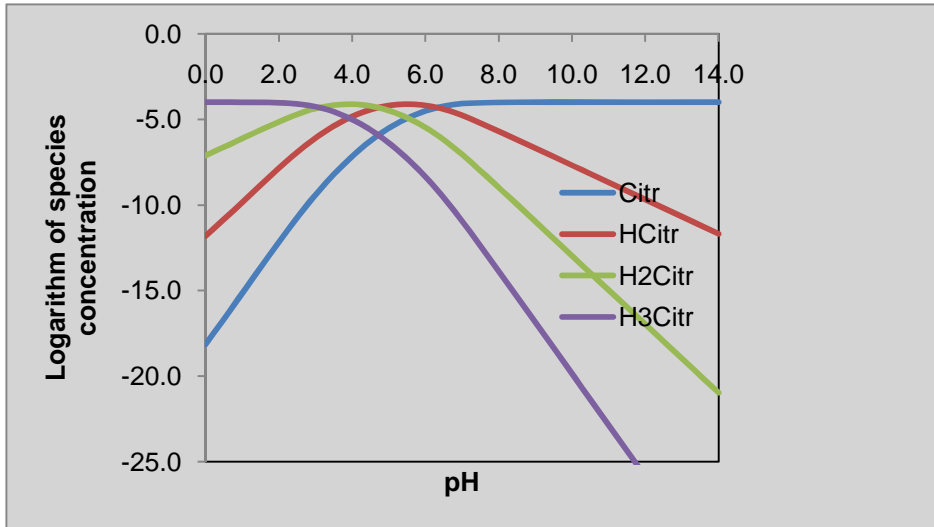


Figure HW3.11 Effects of pH on the speciation of citric acid (logC representation)

### Problem 2d

Results of relevant calculations are shown in Figure HW3.12 to Figure HW3.15. They show that changes of temperature affect relatively little the concentrations of some species of EDTA ( $H_5EDTA^+$ ,  $H_4EDTA$ ,  $H_3EDTA^-$ ). For other species of EDTA ( $H_2EDTA^{2-}$ ,  $HEDTA^{3-}$ ,  $EDTA^{4-}$ ), effects of temperature variations become progressively more prominent.

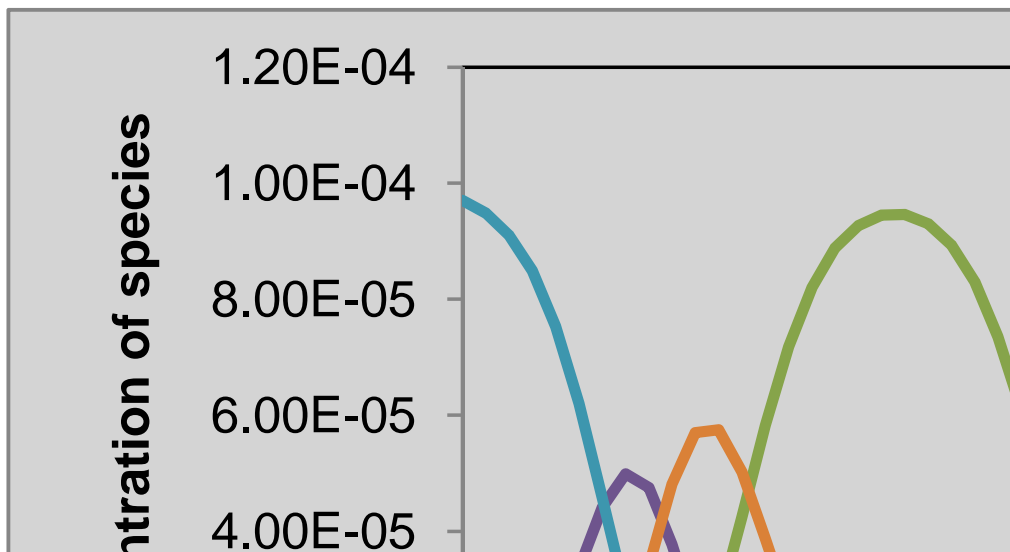
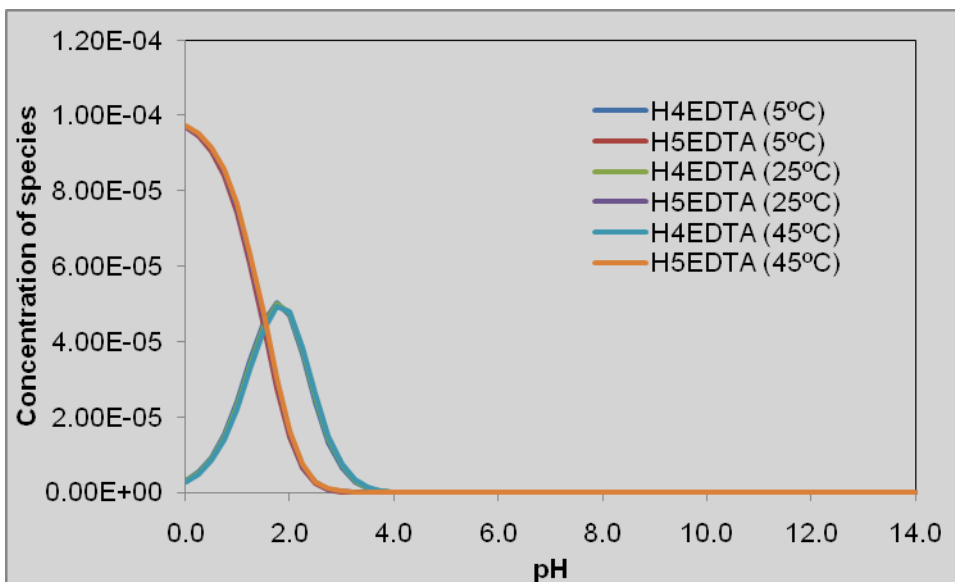
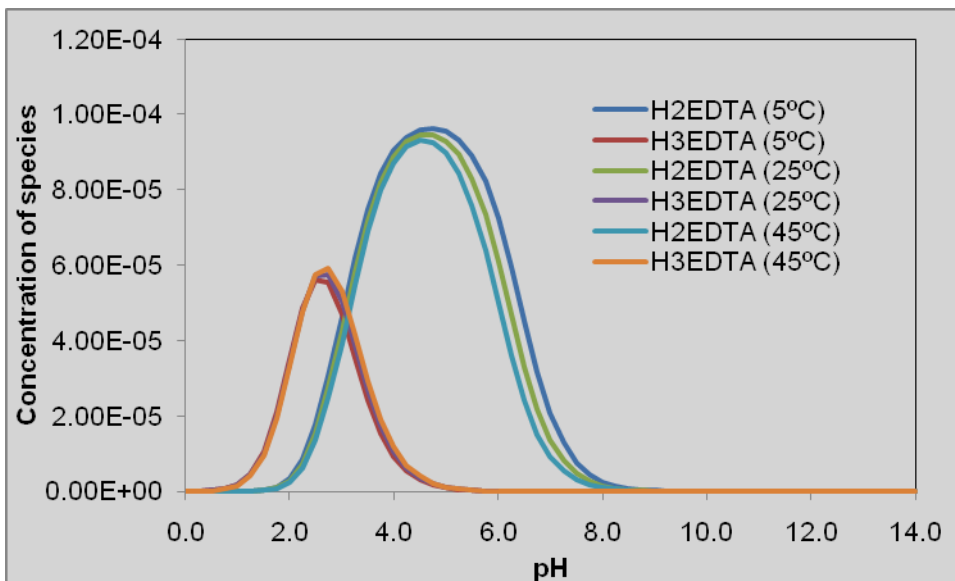


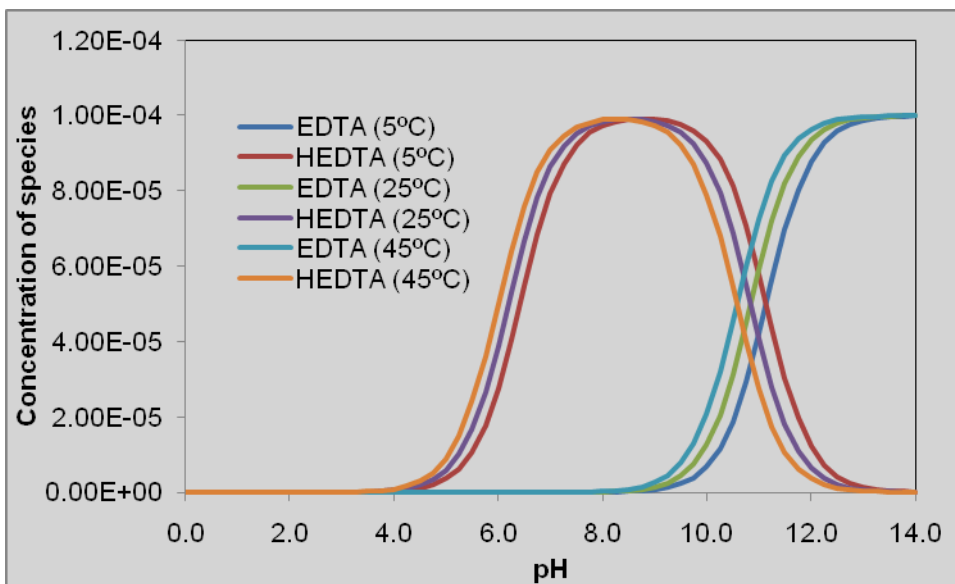
Figure HW3.12 Contributions of different EDTA species at 25°C.



**Figure HW3.13 Effects of temperature of the concentration of  $H_5EDTA^+$  and  $H_4EDTA$  species of EDTA.**



**Figure HW3.14 Effects of temperature of the concentration of  $H_2EDTA^{2-}$  and  $H_3EDTA^-$  species of EDTA.**



**Figure HW3.15 Effects of temperature of the concentration of EDTA<sup>4-</sup> and HEDTA<sup>3-</sup> species of EDTA.**