HW #11 Solutions

(1) Show that f, for the titration of a monobasic acid with a strong base (NaOH) can be expressed as:

$$f = \alpha_1 + \left(\frac{K_w}{[H^+]} - [H^+]\right)\left(\frac{V_o + V}{C_o V_o}\right)$$

C_o = conc of acid
V_o = total vol of acid soln
C = conc of base titrant
V = vol of base titrant added

Solution:

by definition

$$f = \frac{\text{eqv of NaOH added}}{\text{moles of } (HA + A^-)} = \frac{CV}{C_o V_o}$$

$$HA \rightleftharpoons H^+ + A^-$$

Equilibrium $\quad K_A = \dfrac{[H^+][A^-]}{[HA]}$

mass balance:

$$C_{T,A} = [HA] + [A^-]$$

$$C_{T,A} = \frac{\text{moles of acid present}}{\text{total vol of soln}} = \frac{C_o V_o}{V_o + V}$$

Charge Balance

$$[Na^+] + [H^+] = [A^-] + [OH^-]$$

$$[Na^+] = \frac{\text{moles of base added}}{\text{tot vol of soln}} = \frac{CV}{V_o + V}$$

Using knowledge of ionization fractions $\alpha_1 = \dfrac{[A^-]}{C_{T,A}}$

Substitute into charge balance

$$\frac{CV}{V_o + V} + [H^+] = [OH^-] + \alpha_1 \frac{C_o V_o}{V_o + V}$$

USE algebra skills to simplify

$$\frac{CV}{C_0 V_0} + \frac{[H^+](V_0+V)}{C_0 V_0} = \frac{(V_0+V)[OH^-]}{C_0 V_0} + \alpha_1 \frac{(V_0+V)}{(V_0+V)}$$

$$f = \left([OH^-] - [H^+]\right)\frac{(V_0+V)}{C_0 V_0} + \alpha_1$$

$$\boxed{f = \alpha_1 + \left(\frac{K_w}{[H^+]} - [H^+]\right)\left(\frac{V_0+V}{C_0 V_0}\right)}$$

(2) FIND pH SEE DIAGRAM ON NEXT PAGE

10^{-1} M HAc + 2×10^{-1} M $NaHCO_3$

10^{-1} M HAc $\Rightarrow$ $pC_{1,HAc} = 1$ $\quad pK_A = 4.7$

2×10^{-1} M $NaHCO_3$ $\Rightarrow$ $pC_{T,CO_3^{2-}} = 0.7$ $\quad pK_{a_1} = 6.3$

$pK_{a_2} = 10.3$

Charge balance

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

solution of charge balance is long line

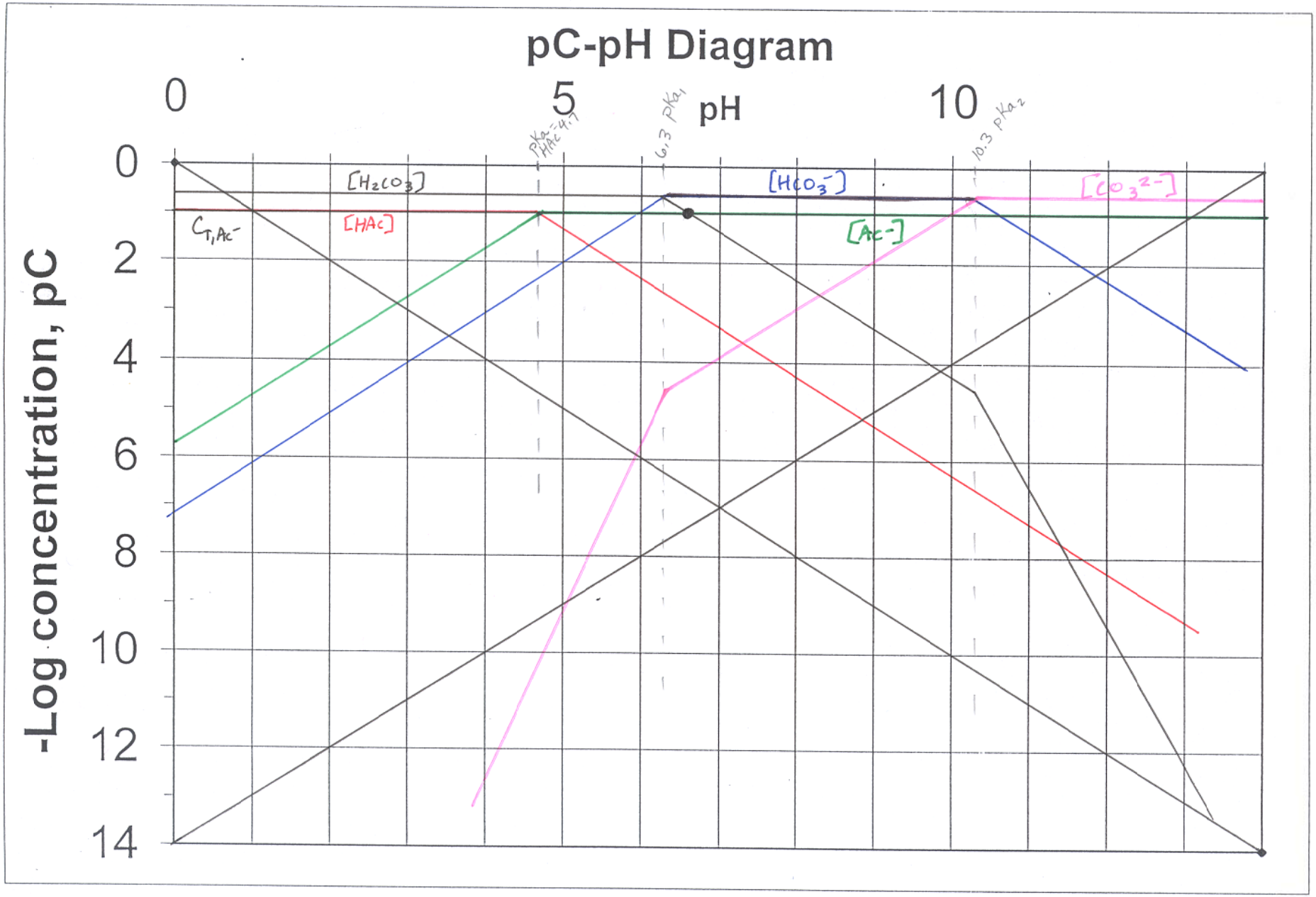
$$[Na^+] = [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}]$$

$$[H_2CO_3] + [HCO_3^-] + [CO_3^{2-}] + [H^+] = [OH^-] + [Ac^-] + [HCO_3^-] + \tfrac{1}{2}[CO_3^{2-}]$$

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

ONLY POINT WHERE THIS IS SATISFIED $\rightarrow$ $\boxed{pH \approx 6.5}$

#2


pC-pH Diagram
0
5
10
pH
pKa HAc 4.7
6.3 pKa1
10.3 pKa2
0
2
4
6
8
10
12
14
-Log concentration, pC
[H2CO3]
[HCO3-]
[CO3 2-]
CT,Ac-
[HAc]
[Ac-]

(3) Calculate pH

10^{-2} M propionic acid $\quad HPr \rightleftharpoons H^+ + Pr^- \quad pC_{T,Pr} = 2$

$pK_a = 4.9$

10^{-2} M HAc $\quad pK_a = 4.7 \quad pC_{T,Ac^-} = 2$

10^{-1} M $NaHCO_3 \quad pK_{a_1} = 6.3 \quad pC_{T,CO_3^{2-}} = 1$

$pK_{a_2} = 10.3$

Charge balance

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

$$[Na^+] = 10^{-1}\,M = [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}]$$

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

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

Follow LHS and RHS to find solution

Notice from graph that solution is where $[H_2CO_3] = [Ac^-] + [Pr^-]$

$$[Ac^-] + [Pr^-] = 2 \times 10^{-2}$$

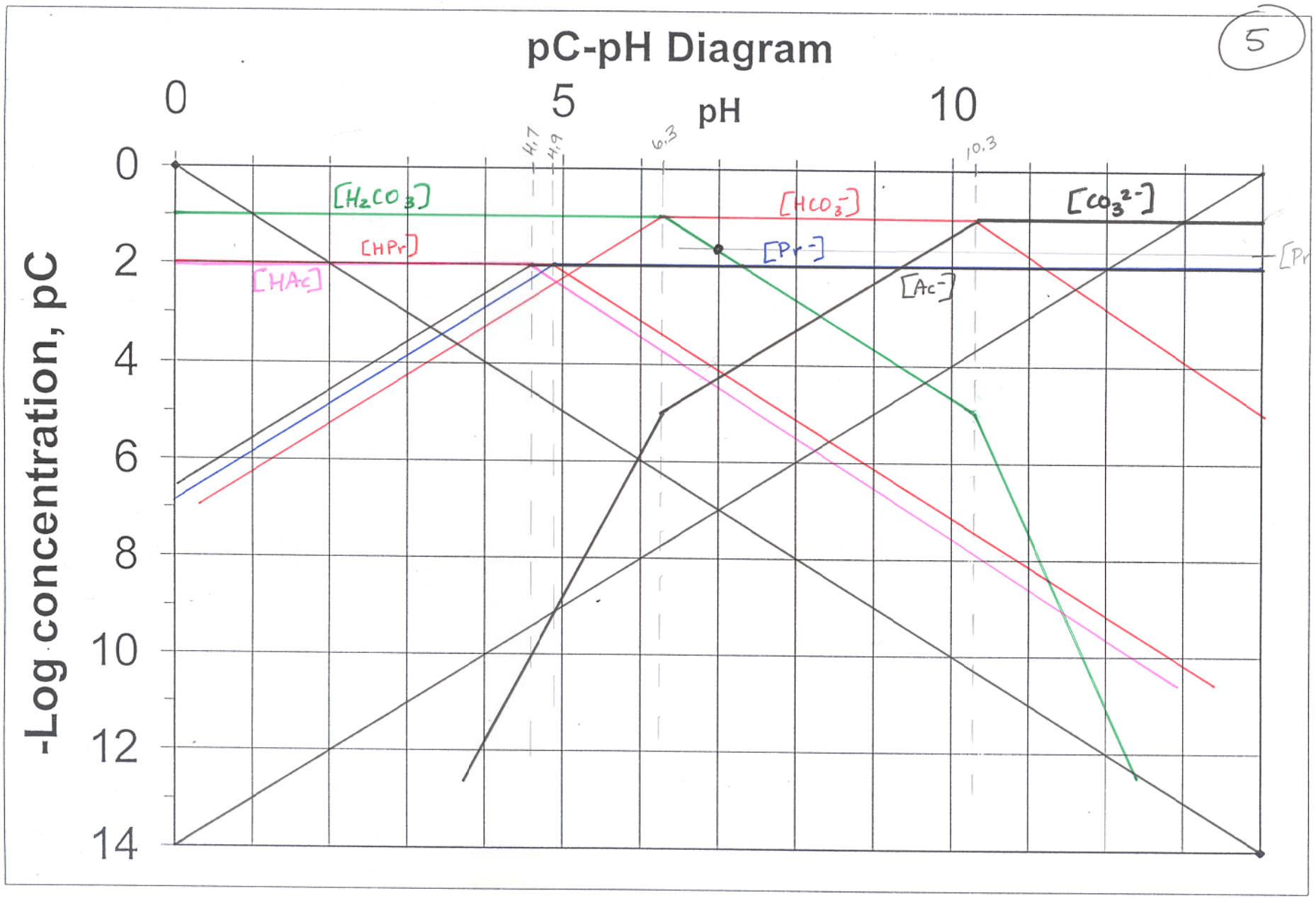
$$C_T\ [Ac^-] + [Pr^-] = -\log(2 \times 10^{-2})$$

$$= 1.7$$

Solution

$$[H_2CO_3] = 1.7$$

$$pH \cong 7.0$$


pC-pH Diagram
pH
-Log concentration, pC
0
5
10
0
2
4
6
8
10
12
14
4.7
4.9
6.3
10.3
[H2CO3]
[HCO3-]
[CO3 2-]
[HPr]
[Pr-]
[HAc]
[Ac-]
[Pr-] + [Ac-]