

## PRACTICE PROBLEMS IN CARBONATE/ACID-BASE CHEMISTRY

1. What is Alk  $\left( \text{Alk} = -[\text{H}^+] + [\text{OH}^-] + [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] \right)$

a)  $[\text{NaOH}]_T = 10^{-3} \text{ M} = [\text{OH}^-]_{\text{Tot}}$

$[\text{NaHCO}_3]_T = 10^{-2} \text{ M} = [\text{HCO}_3^-]_{\text{Tot}}$

$P_{\text{CO}_2} = 10^{-2.5}$  ← "Red herring" here:  
CO<sub>2</sub> does not alter Alk

$\text{Alk} = [\text{OH}^-]_T + [\text{HCO}_3^-]_T = \boxed{1.1 \times 10^{-2} \text{ eq/L}} \text{ (a)}$

b)  $[\text{Na}_2\text{CO}_3]_T = 10^{-4} \text{ M}$

$\text{Alk} = 2[\text{CO}_3^{2-}] = \boxed{2 \times 10^{-4} \text{ eq/L}} \text{ (b)}$

(Again,  $P_{\text{CO}_2}$  means nothing)

c) Now HERE  $P_{\text{CO}_2}$  is important because that's our only info about carbonate-species concs.

$[\text{H}_2\text{CO}_3^*] = K_H P_{\text{CO}_2} = 10^{-1.5} \cdot 10^{-3.5} = 10^{-5.0} \text{ M}$

$\frac{[\text{HCO}_3^-][\text{H}^+]}{[\text{H}_2\text{CO}_3^*]} = K_{a1} \Rightarrow [\text{HCO}_3^-] = \frac{10^{-6.3} \cdot 10^{-5.0}}{10^{-7.3}} = 10^{-4.0}$

at pH 7.3

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

$\swarrow$   
 $\sim 10^{-7} \text{ M}$        $\swarrow$   
 $10^{-4} \text{ M}$        $\swarrow$   
 $\sim 1000$  times less than  $[\text{HCO}_3^-]$

$\boxed{\text{Alk} = [\text{HCO}_3^-] = 10^{-4.0} \text{ eq/L}}$

(Cont'd) d)  $[H_2SO_4]_T = 10^{-3} M \Rightarrow [H^+] = 2 \times 10^{-3} \text{ eq/L}$

$[NaHCO_3]_T = 10^{-3} = [HCO_3^-]$

$Alk = -[H^+] + [HCO_3^-] = -(2 \times 10^{-3} \text{ eq/L}) + (1 \times 10^{-3} \text{ eq/L})$

$Alk = -1 \times 10^{-3} \text{ eq/L}$  NEGATIVE Alk  $\equiv$  "Mineral Acidity"

CALCULATE pH

a)  $Alk = 10^{-3} M = -[H^+] + [OH^-] + [HCO_3^-] + 2[CO_3^{2-}]$

$C_T = 10^{-3} M = [H_2CO_3^*] + [HCO_3^-] + [CO_3^{2-}]$

To find pH, need a ratio of any TWO carbonate species.  
We also know that  $[H^+] + [OH^-]$  usually negligible

So:  $[HCO_3^-] + 2[CO_3^{2-}] \approx [H_2CO_3^*] + [HCO_3^-] + [CO_3^{2-}]$

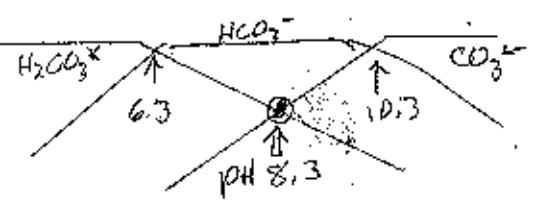
$2[CO_3^{2-}] \approx [H_2CO_3^*] + [CO_3^{2-}]$

$[CO_3^{2-}] \approx [H_2CO_3^*] \Leftrightarrow$  OK AT WHAT pH DOES THIS OCCUR?

TWO SOLUTION APPROACHES

MORE INTUITIVE

Notice on predominance diagram that  $[H_2CO_3^*] + [CO_3^{2-}]$  are equal at midpoint between  $pH = pK_{a1} = 6.3$  and  $pH = pK_{a2} = 10.3$   
OR AT  $pH \ 8.3$



MORE RIGOROUS

$\frac{[CO_3^{2-}][H^+]^2}{[H_2CO_3^*]} = 10^{-6.3} \cdot 10^{-10.3} = 10^{-16.6}$

$\frac{[CO_3^{2-}]}{[H_2CO_3^*]} = \frac{1}{1}$  (i.e., they're equal) so...

$[H^+]^2 = 10^{-16.6}$

$[H^+] = \sqrt{10^{-16.6}} = 10^{-8.3}$

$pH \ 8.3$

2 (cont'd)

$$b) P_{CO_2} = 10^{-3.5} \text{ atm}$$

$$[H_2CO_3^*] = 10^{-5.0} \text{ M}$$

Alk =  $10^{-3} \text{ M}$   $\Leftarrow$  Can try assuming  $\text{Alk} \approx [HCO_3^-]$   
as before (OK for pH 6~8).

$$[H^+] = \frac{K_{a1} [H_2CO_3^*]}{[HCO_3^-]} = \frac{10^{-6.3} 10^{-5.0}}{10^{-3.0}} = \frac{10^{-11.3}}{10^{-3.0}} = 10^{-8.3}$$

$$\boxed{\text{pH} = 8.3}$$

THINK LOGS!

$$c) \text{Alk} = -10^{-2} \text{ M}$$

Only term that makes Alk negative is  $[H^+]$ .

$$\text{So, try } [H^+] = 10^{-2} \text{ M}$$

$$\boxed{\text{pH} = 2.0}$$

At this pH  $[OH^-]$ ,  $[HCO_3^-]$ , &  $2[CO_3^{2-}]$  all negligible

So the assumption that  $\text{Alk} = -[H^+]$  is good,  
(only)

# SOLUTIONS

3)  $\text{pH} = 7.0$      $\text{Alk} \cong 10^{-3} \text{ eq/L}$

APPROACH: Need to get carbonate species from these data. If we can get the concentration of at least ONE species, we can calculate all the rest by knowing the pH, plus  $\text{pK}_{a1} = 6.3$ ,  $\text{pK}_{a2} = 10.3$ .

$$\text{Alk} = \underbrace{-[\text{H}^+]}_{10^{-7}} + \underbrace{[\text{OH}^-]}_{\ll 10^{-3}} + [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] = 10^{-3} \text{ eq/L}$$

At pH 7 we are far away from  $\text{pK}_{a2} = 10.3$

so  $[\text{CO}_3^{2-}] \ll [\text{HCO}_3^-]$

$$\text{Alk} \cong [\text{HCO}_3^-] = 10^{-3} \text{ eq/L}$$

$$[\text{H}_2\text{CO}_3^*] = \frac{[\text{HCO}_3^-][\text{H}^+]}{10^{6.3}} = \frac{10^{-3} \cdot 10^{-7}}{10^{6.3}} = \frac{10^{-10}}{10^{6.3}} = 10^{-3.7}$$

$$[\text{CO}_3^{2-}] = \frac{10^{-10.3} [\text{HCO}_3^-]}{[\text{H}^+]} = \frac{10^{-10.3} 10^{-3}}{10^{-7}} = \frac{10^{-13.3}}{10^{-6}} = 10^{-7.3}$$

$$[\text{H}_2\text{CO}_3^*] = 10^{-3.7} > 10^{-5.0}$$

EQUIL. w/  
ATMOS.

was OK to ignore in Alk eqn.

Has  $10^{-3.7+5} = 10^{1.3} \times = 20\times$  as much  $\text{H}_2\text{CO}_3^*$  as would in equilibrium

Probably a lot of respiration by those pesky goldfish in the pond ☹️

Keep  $\Delta pH \leq 0.2$  units

How much strong acid (HCl) could you add?

Really saying, "How much Alk can we remove?"

APPROACH: Lower Alk will lower pH.

- Lowering Alk in this range means lowering  $[HCO_3^-]$
- Recall that ratio of  $[HCO_3^-]$  to other species (e.g.,  $[H_2CO_3^*]$ ) is function of pH.
- So, set up that ratio and see how much you can change  $[HCO_3^-]$  to get a 0.2 unit  $\Delta pH$ .

$$\frac{[HCO_3^-]}{[H_2CO_3^*]} = \frac{Alk}{10^{-3.7}} = \frac{10^{-6.3}}{[H^+]}$$

↑  
Assume  $H_2CO_3^*$  remains steady at the original  $10^{-3.7} M$ .

By inspecting this ratio, you see that to lower  $[H^+]$  by  $10^{0.2}$  (0.2 pH units) you'd lower Alk by  $10^{0.2}$  also. (I.e., change exponent by -0.2 units)

So:

Original Alk	=	$10^{-3.0}$	=	$1 \times 10^{-3}$ eq/L
New Alk	=	$10^{-3.2}$	=	$6.3 \times 10^{-4}$ eq/L

$\Delta Alk = HCl \text{ Added}$	=	$3.7 \times 10^{-4}$ eq/L	ANS
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c) Reduce  $[SO_4] = 3 \times 10^{-4} M$

We know from P. set #6 that this is same as ADDING  $3 \times 10^{-4}$  eq/L of Alk.

$$Alk_{hyp} = 1 \times 10^{-3} \text{ eq/L} + 2 \times 10^{-3} \text{ eq/L} = 3 \times 10^{-3} \text{ eq/L} = \boxed{10^{-2.5} \text{ eq/L}} \approx [HCO_3^-]$$

$$[H_2CO_3^*] = 10^{-3.7} \text{ (as in epilimnion; given in problem)}$$

$$[H^+] = \frac{10^{-6.3} [H_2CO_3^*]}{[HCO_3^*]} = \frac{10^{-6.3} 10^{-3.7}}{10^{-2.5}} = 10^{-7.5}$$

**pH 7.5**

$$[CO_3^{2-}] = \frac{10^{-10.3} 10^{-2.5}}{10^{-7.5}} = 10^{-5.3} M = \boxed{5 \times 10^{-6} M} \text{ (still negligible in Alk)}$$

d) Mix two layers, w/ mass & volumes proportional to depth (1 m epilimnion, 2 m hypolimnion)

$$Alk_{mix} = \frac{[1L \times (1 \times 10^{-3} \text{ eq/L})] + [2L \times (3 \times 10^{-3} \text{ eq/L})]}{(1+2)L} = \frac{7 \times 10^{-3} \text{ eq}}{3L}$$

ALK

$$= \boxed{2.3 \times 10^{-3} \text{ eq/L}} = 10^{-2.63} M \approx [HCO_3^-]$$

$$C_T^{Epi} = [H_2CO_3] + [HCO_3^-] + \underset{\substack{\downarrow \\ \text{Negligible}}}{[CO_3^{2-}]} = 10^{-3.7} + 10^{-3.0} = 1.2 \times 10^{-3} M$$

C<sub>T</sub>

$$C_T^{Hyp} = 10^{-3.7} + 10^{-2.5} = 3.2 \times 10^{-3} M$$

$$C_T^{MIX} = \frac{1L(1.2 \times 10^{-3} M) + 2L(3.2 \times 10^{-3} M)}{(1+2)L} = \boxed{2.5 \times 10^{-3} M}$$

$$[H_2CO_3^*] \approx (C_T - Alk) \text{ [if we neglect } [CO_3^{2-}]] = \boxed{2 \times 10^{-4} M = 10^{-3.70}}$$

cont'd →

So now we have

$$[\text{HCO}_3^-]_{\text{MIX}} = \text{Alk} = 10^{-2.63} \text{ M}$$

$$[\text{H}_2\text{CO}_3^*]_{\text{MIX}} = (C_T - \text{Alk}) = 10^{-3.7}$$

We're all set to calculate pH:

$$[\text{H}^+] = \frac{10^{6.3} [\text{H}_2\text{CO}_3^*]}{[\text{HCO}_3^-]} = \frac{10^{6.3} \cdot 10^{-3.70}}{10^{-2.63}} = 10^{-7.37}$$

$$\text{pH} \approx 7.4$$

Notice this is NOT the average pH of epilimnion (7.0) and hypolimnion (7.5), even if we do the "correct" averaging of  $\{\text{H}^+\}$ 's.

$$\frac{1 \times \{\text{H}^+\}_{\text{Epi}} + 2 \times \{\text{H}^+\}_{\text{Hypo}}}{1+2} = \frac{(1 \times 10^{-7}) + (2 \times 3 \times 10^{-8})}{3}$$
$$= 5.4 \times 10^{-8} = 10^{-7.26}$$

pH is an intensity of acid content, NOT a

direct QUANTITY, so it is not additive or "averageable"

WRONG

Alk is the "QUANTITY" you must average,

⇒ REMEMBER THIS IF YOU ARE EVER DEALING WITH TWO WATERS THAT MIX WITH DIFFERENT INITIAL pH.

- EX'S:
- Turnover of a stratified lake
  - Mixing of river and seawater
  - Mixing of acid mine drainage into a river.