

FINAL EXAM

Closed book, three pages of notes allowed.

Answer both Question A and Question B. Please state any additional assumptions you made, and **show all work.** If you don't have time to complete a section, please describe how you would solve the problem (without using a computer program such as MINEQL).

Part I: Answer Question A

A. Solubility & Predominance. (70%)

Zinc carbonate ($\text{ZnCO}_3(\text{s})$) and Zinc Hydroxide ($\text{Zn}(\text{OH})_2(\text{s})$) are two important solid phases that may control zinc solubility in water¹. In the attached pages is a detailed solution leading to a zinc hydroxide solubility diagram². Please use this to help solve the following problems.

1. Prepare a solubility diagram ($\log C$ vs pH) for a water that is potentially in equilibrium with zinc hydroxide and zinc carbonate. Assume the water has 10^{-2} M total carbonates (i.e., 10 mM C_T). Show all soluble species along with the Zn_T line and indicate where precipitation will occur and the type of precipitate. Please feel free to use any of the hydroxide calculations in developing the answer to part 1 or part 2. It could save you some time. **(35%)**
2. Prepare a predominance diagram, showing the precipitates and major soluble species (in areas where there are no precipitates). As would be typical for a problem of this type, make pH the x-axis, and \log total carbonate (CO_{3T}), the y-axis. Assume a total soluble zinc concentration of 10^{-4} M (i.e., 0.1 mM Zn_T). Again you may find that using the solubility diagram provided or the one you did for part 1 can help in directing your work for part 2. **(35%)**

<u>Equilibrium</u> ³	<u>Log K</u>
$\text{ZnOH}^+ = \text{Zn}^{+2} + \text{OH}^-$	-5.04
$\text{Zn}(\text{OH})_2^0 = \text{ZnOH}^+ + \text{OH}^-$	-6.06
$\text{Zn}(\text{OH})_3^{-1} = \text{Zn}(\text{OH})_2^0 + \text{OH}^-$	-2.50
$\text{Zn}(\text{OH})_4^{-2} = \text{Zn}(\text{OH})_3^{-1} + \text{OH}^-$	-1.20
$\text{Zn}(\text{OH})_2(\text{s}) = \text{Zn}^{+2} + 2\text{OH}^-$	-15.55
$\text{ZnCO}_3(\text{s}) = \text{Zn}^{+2} + \text{CO}_3^{-2}$	-10.26

Development of hydroxide solubility diagram (already provided).

¹ Hydrozincite is also an important solid, but it will not be considered here for the purpose of simplicity.

² Note that this considers only mononuclear species, as the known polynuclear species are never dominant

³ For the purposes of this problem, we are ignoring all soluble zinc carbonate species.

a. Using the equilibria for zinc hydroxide from above:

$$K = [Zn^{+2}][OH^-]^2 = 10^{-15.55}$$

we get the following for the free aquo ion:

$$\log[Zn^{+2}] = -15.55 - 2\log[OH^-]$$

$$\log[Zn^{+2}] = -15.55 - 2\log\frac{K_w}{[H^+]}$$

$$\log[Zn^{+2}] = 12.45 - 2pH$$

From this we use the hydroxide equilibria to get hydroxide species concentrations:

and for the monohydroxide:

$$K = \frac{[Zn^{+2}][OH^-]}{[ZnOH^+]} = 10^{-5.04}$$

$$\log[ZnOH^+] = +5.04 + \log[Zn^{+2}] + \log[OH^-]$$

$$\log[ZnOH^+] = +5.04 + \log[Zn^{+2}] - 14 - \log[H^+]$$

$$\log[ZnOH^+] = -8.96 + \log[Zn^{+2}] + pH$$

$$\log[ZnOH^+] = -8.96 + (12.45 - 2pH) + pH$$

$$\log[ZnOH^+] = +3.49 - pH$$

now for the dihydroxide:

$$K = \frac{[ZnOH^+][OH^-]}{[Zn(OH)_2^0]} = 10^{-6.06}$$

$$\log[Zn(OH)_2^0] = +6.06 + \log[ZnOH^+] + \log[OH^-]$$

$$\log[Zn(OH)_2^0] = +6.06 + \log[ZnOH^+] - 14 - \log[H^+]$$

$$\log[Zn(OH)_2^0] = -7.94 + \log[ZnOH^+] + pH$$

$$\log[Zn(OH)_2^0] = -7.94 + (3.49 - pH) + pH$$

$$\log[Zn(OH)_2^0] = -4.45$$

now for the trihydroxide:

$$K = \frac{[Zn(OH)_2^0][OH^-]}{[Zn(OH)_3^{-1}]} = 10^{-2.50}$$

$$\log[Zn(OH)_3^{-1}] = +2.50 + \log[Zn(OH)_2^0] + \log[OH^-]$$

$$\log[Zn(OH)_3^{-1}] = +2.50 + \log[Zn(OH)_2^0] - 14 - \log[H^+]$$

$$\log[Zn(OH)_3^{-1}] = -11.50 + \log[Zn(OH)_2^0] + pH$$

$$\log[\text{Zn}(\text{OH})_3^{-1}] = -11.50 + (-4.45) + \text{pH}$$

$$\log[\text{Zn}(\text{OH})_3^{-1}] = -15.95 + \text{pH}$$

now for the tetrahydroxide:

$$K = \frac{[\text{Zn}(\text{OH})_3^{-1}][\text{OH}^{-}]}{[\text{Zn}(\text{OH})_4^{-2}]} = 10^{-1.20}$$

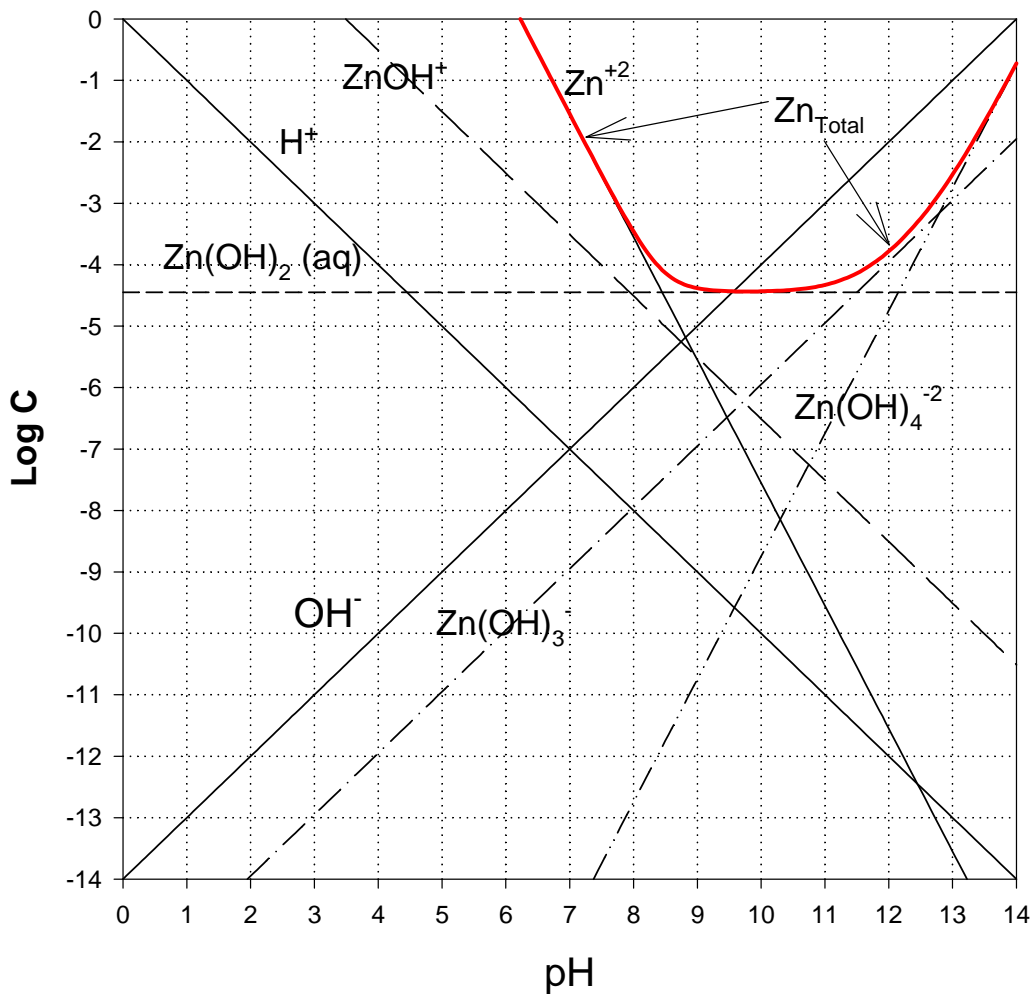
$$\log[\text{Zn}(\text{OH})_4^{-2}] = +1.20 + \log[\text{Zn}(\text{OH})_3^{-1}] + \log[\text{OH}^{-}]$$

$$\log[\text{Zn}(\text{OH})_4^{-2}] = +1.20 + \log[\text{Zn}(\text{OH})_3^{-1}] - 14 - \log[\text{H}^{+}]$$

$$\log[\text{Zn}(\text{OH})_4^{-2}] = -12.80 + \log[\text{Zn}(\text{OH})_3^{-1}] + \text{pH}$$

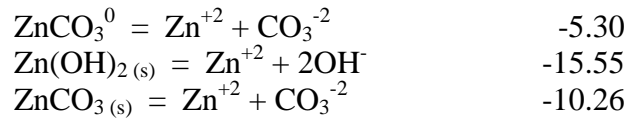
$$\log[\text{Zn}(\text{OH})_4^{-2}] = -12.80 + (-15.95 + \text{pH}) + \text{pH}$$

$$\log[\text{Zn}(\text{OH})_4^{-2}] = -28.75 + 2\text{pH}$$



Answer to A.1.

And for the carbonate, we must consider:



b. Using the equilibria for zinc carbonate from above:

$$K = [\text{Zn}^{+2}][\text{CO}_3^{-2}] = 10^{-10.26}$$

b1. we get the following for the free aquo ion:

$$\log[\text{Zn}^{+2}] = -10.26 - \log[\text{CO}_3^{-2}]$$

$$\log[\text{Zn}^{+2}] = -10.26 - \log[C_T] - \log \alpha_2$$

And for 10 mM total carbonates:

$$\log[\text{Zn}^{+2}] = -10.26 - \log[10^{-2}] - \log \alpha_2$$

$$\log[\text{Zn}^{+2}] = -8.26 - \log \alpha_2$$

For Carbonate Calculations:

$$\alpha_2 = \frac{1}{\frac{[\text{H}^+]^2}{K_1 K_2} + \frac{[\text{H}^+]}{K_2} + 1}$$

For pH < 6.3, $\alpha_2 \approx \frac{K_1 K_2}{[\text{H}^+]^2}$, or $\log \alpha_2 \approx -16.6 + 2pH$

For pH = 6.3-10.3, $\alpha_2 \approx \frac{K_2}{[\text{H}^+]}$, or $\log \alpha_2 \approx -10.3 + pH$

For pH > 10.3, $\alpha_2 \approx 1$, or $\log \alpha_2 \approx 0$

So for pH < 6.3, we have:

$$\log[\text{Zn}^{+2}] = -10.26 - \log[C_T] - (-16.6 + 2pH)$$

$$\log[\text{Zn}^{+2}] = -8.26 - (-16.6 + 2pH)$$

$$\log[\text{Zn}^{+2}] = 8.34 - 2pH, \text{ @pH} < 6.3$$

And for pH = 6.3-10.3, we have:

$$\log[\text{Zn}^{+2}] = -10.26 - \log[C_T] - (-10.3 + pH)$$

$$\log[\text{Zn}^{+2}] = -8.26 - (-10.3 + pH)$$

$$\log[\text{Zn}^{+2}] = 2.04 - pH, \text{ @pH} = 6.3-10.3$$

And for $\text{pH} > 10.3$, we have:

$$\log[\text{Zn}^{+2}] = -10.26 - \log[C_T] - (0)$$

$$\log[\text{Zn}^{+2}] = -8.26 - (0)$$

$$\log[\text{Zn}^{+2}] = -8.26, \text{ @pH} > 10.3$$

b2. and for the monohydroxide:

from the $\text{Zn}(\text{OH})_{2(s)}$ based calculations, we know that:

$$\log[\text{ZnOH}^+] = -8.96 + \log[\text{Zn}^{+2}] + \text{pH}$$

And now substituting in the $\text{ZnCO}_{3(s)}$ -based free zinc equation for $\text{pH} < 6.3$, we have:

$$\log[\text{ZnOH}^+] = -8.96 + (8.34 - 2\text{pH}) + \text{pH}$$

$$\log[\text{ZnOH}^+] = -0.62 - \text{pH}, \text{ @pH} < 6.3$$

And for $\text{pH} = 6.3-10.3$, we have:

$$\log[\text{ZnOH}^+] = -8.96 + (2.04 - \text{pH}) + \text{pH}$$

$$\log[\text{ZnOH}^+] = -6.92, \text{ @pH} = 6.3-10.3$$

And for $\text{pH} > 10.3$, we have:

$$\log[\text{ZnOH}^+] = -8.96 + (-8.26) + \text{pH}$$

$$\log[\text{ZnOH}^+] = -17.22 + \text{pH}, \text{ @pH} > 10.3$$

b3. now for the dihydroxide:

from the $\text{Zn}(\text{OH})_{2(s)}$ -based calculations, we know that:

$$\log[\text{Zn}(\text{OH})_2^0] = -7.94 + \log[\text{ZnOH}^+] + \text{pH}$$

And now substituting in the $\text{ZnCO}_{3(s)}$ -based ZnOH equation for $\text{pH} < 6.3$, we have:

$$\log[\text{Zn}(\text{OH})_2^0] = -7.94 + (-0.62 - \text{pH}) + \text{pH}$$

$$\log[\text{Zn}(\text{OH})_2^0] = -8.56, \text{ @pH} < 6.3$$

And for $\text{pH} = 6.3-10.3$, we have:

$$\log[\text{Zn}(\text{OH})_2^0] = -7.94 + (-6.92) + \text{pH}$$

$$\log[\text{Zn}(\text{OH})_2^0] = -14.86 + \text{pH}, \text{ @pH} = 6.3-10.3$$

And for $\text{pH} > 10.3$, we have:

$$\log[\text{Zn}(\text{OH})_2^0] = -7.94 + (-17.22 + \text{pH}) + \text{pH}$$

$$\log[\text{Zn}(\text{OH})_2^0] = -25.16 + 2\text{pH}, \text{ @pH} > 10.3$$

B4. now for the trihydroxide:

from the $\text{Zn}(\text{OH})_{2(s)}$ -based calculations, we know that:

$$\log[\text{Zn}(\text{OH})_3^{-1}] = -11.50 + \log[\text{Zn}(\text{OH})_2^0] + pH$$

And now substituting in the $\text{ZnCO}_3(\text{s})$ based $\text{Zn}(\text{OH})_2$ equation for $\text{pH} < 6.3$, we have:

$$\log[\text{Zn}(\text{OH})_3^{-1}] = -11.50 + (-8.56) + pH$$

$$\log[\text{Zn}(\text{OH})_3^{-1}] = -20.06 + pH, \text{ @pH} < 6.3$$

And for $\text{pH} = 6.3 - 10.3$, we have:

$$\log[\text{Zn}(\text{OH})_3^{-1}] = -11.50 + (-14.86 + pH) + pH$$

$$\log[\text{Zn}(\text{OH})_3^{-1}] = -26.36 + 2pH, \text{ @pH} = 6.3 - 10.3$$

And for $\text{pH} > 10.3$, we have:

$$\log[\text{Zn}(\text{OH})_3^{-1}] = -11.50 + (-25.16 + 2pH) + pH$$

$$\log[\text{Zn}(\text{OH})_3^{-1}] = -36.66 + 3pH, \text{ @pH} > 10.3$$

b5. now for the tetrahydroxide:

from the $\text{Zn}(\text{OH})_2(\text{s})$ -based calculations, we know that:

$$\log[\text{Zn}(\text{OH})_4^{-2}] = -12.80 + \log[\text{Zn}(\text{OH})_3^{-1}] + pH$$

And now substituting in the $\text{ZnCO}_3(\text{s})$ based $\text{Zn}(\text{OH})_3$ equation for $\text{pH} < 6.3$, we have:

$$\log[\text{Zn}(\text{OH})_4^{-2}] = -12.80 + (-20.06 + pH) + pH$$

$$\log[\text{Zn}(\text{OH})_4^{-2}] = -32.86 + 2pH, \text{ @pH} < 6.3$$

And for $\text{pH} = 6.3 - 10.3$, we have:

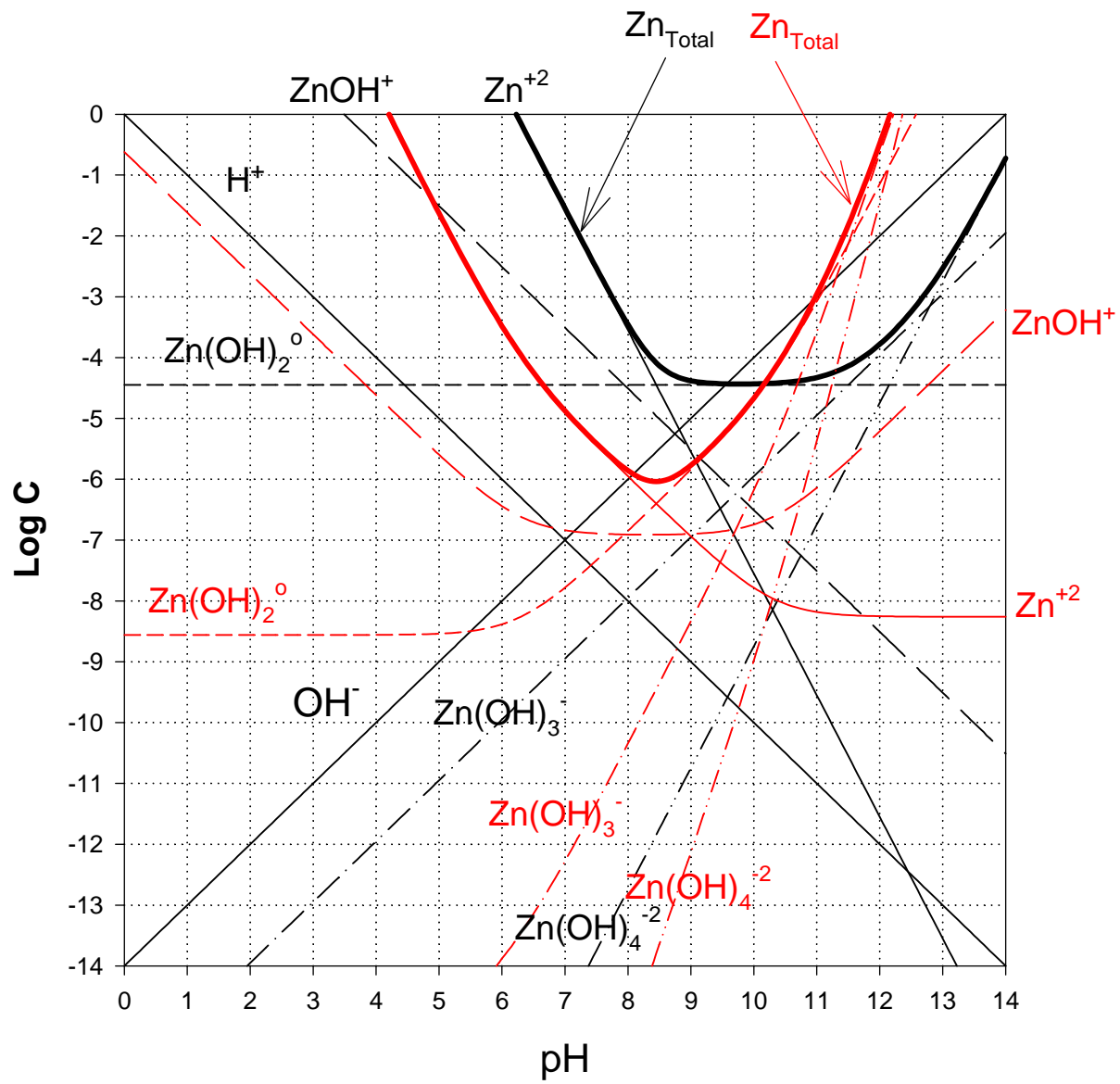
$$\log[\text{Zn}(\text{OH})_4^{-2}] = -12.80 + (-26.36 + 2pH) + pH$$

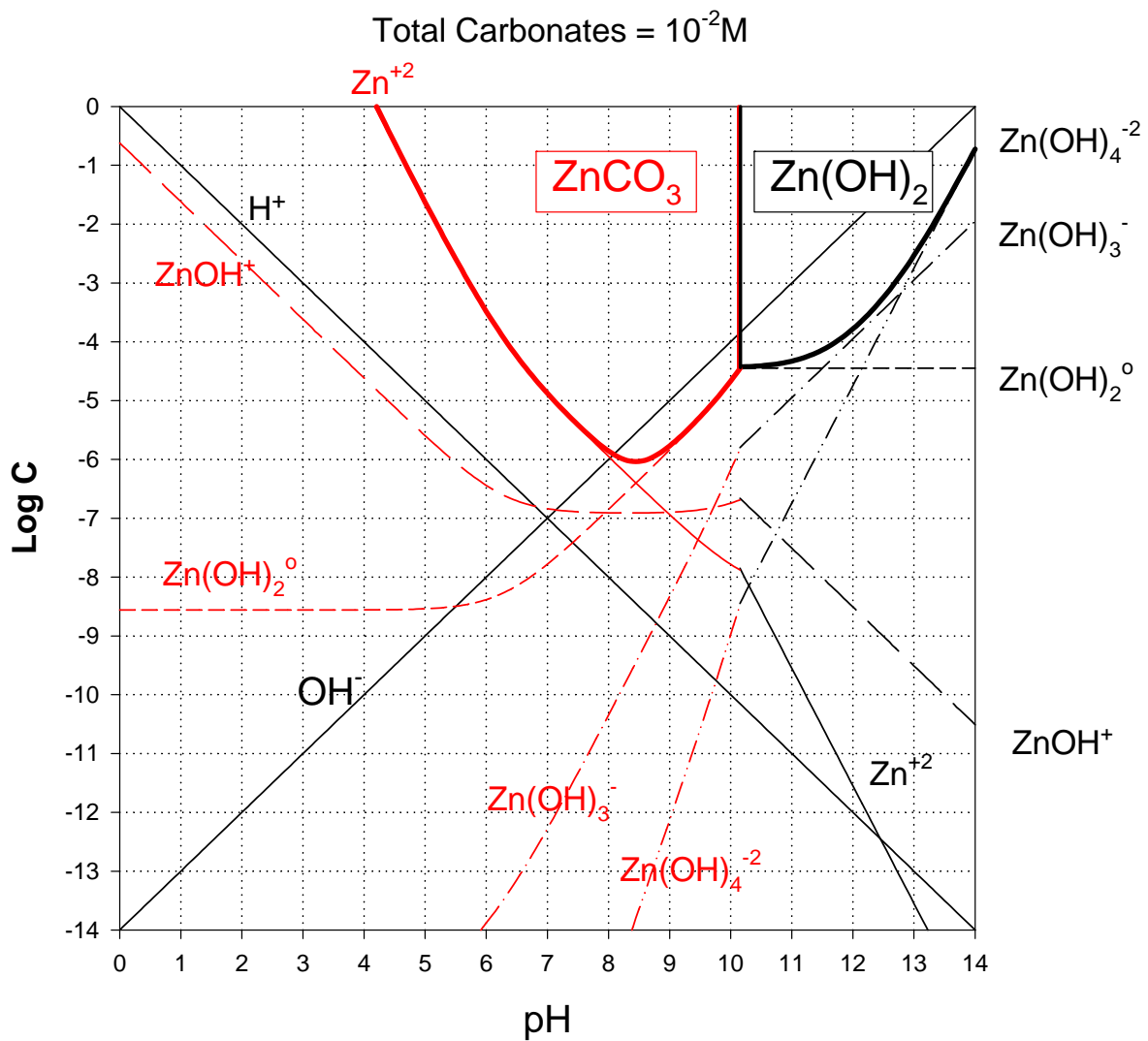
$$\log[\text{Zn}(\text{OH})_4^{-2}] = -39.16 + 3pH, \text{ @pH} = 6.3 - 10.3$$

And for $\text{pH} > 10.3$, we have:

$$\log[\text{Zn}(\text{OH})_4^{-2}] = -12.80 + (-36.66 + 3pH) + pH$$

$$\log[\text{Zn}(\text{OH})_4^{-2}] = -49.46 + 4pH, \text{ @pH} > 10.3$$





Now combining, we find that the hydroxide controls at pHs of 10.15 and above. Below this level, the carbonate is less soluble.

Answer to A.2.

Type A lines

First, let's consider the boundary between the aquo ion and the monohydroxide

$$K_1 = \frac{[Zn^{+2}][OH^-]}{[ZnOH^+]} = 10^{-5.04}$$

When they're present at equal concentrations:

$$K_1 = \frac{x[OH^-]}{x} = 10^{-5.04}$$

or:

$$[OH^-] = 10^{-5.045}$$

And this gives us A1:

$$pH = 8.96$$

following the same approach, we get the remaining A lines

$$K_2 = \frac{[ZnOH^+][OH^-]}{[Zn(OH)_2^0]} = 10^{-6.06}$$

Gives us A2:

$$pH = 7.94$$

but since this is less than A1, it tells us that the monohydroxide never predominates, so we need to look at the boundary between the free zinc and the dihydroxide

$$K_1 K_2 = \frac{[Zn^{+2}][OH^-][ZnOH^+][OH^-]}{[ZnOH^+][Zn(OH)_2^0]} = 10^{-5.04} 10^{-6.06}$$

$$K_1 K_2 = \frac{[Zn^{+2}][OH^-]^2}{[Zn(OH)_2^0]} = 10^{-5.04} 10^{-6.06}$$

$$\text{At the boundary, } K_1 K_2 = [OH^-]^2 = 10^{-11.10}$$

$$[OH^-] = 10^{-5.55}$$

Gives us the revised A1:

$$pH = 8.45$$

$$K = \frac{[Zn(OH)_2^0][OH^-]}{[Zn(OH)_3^{-1}]} = 10^{-2.50}$$

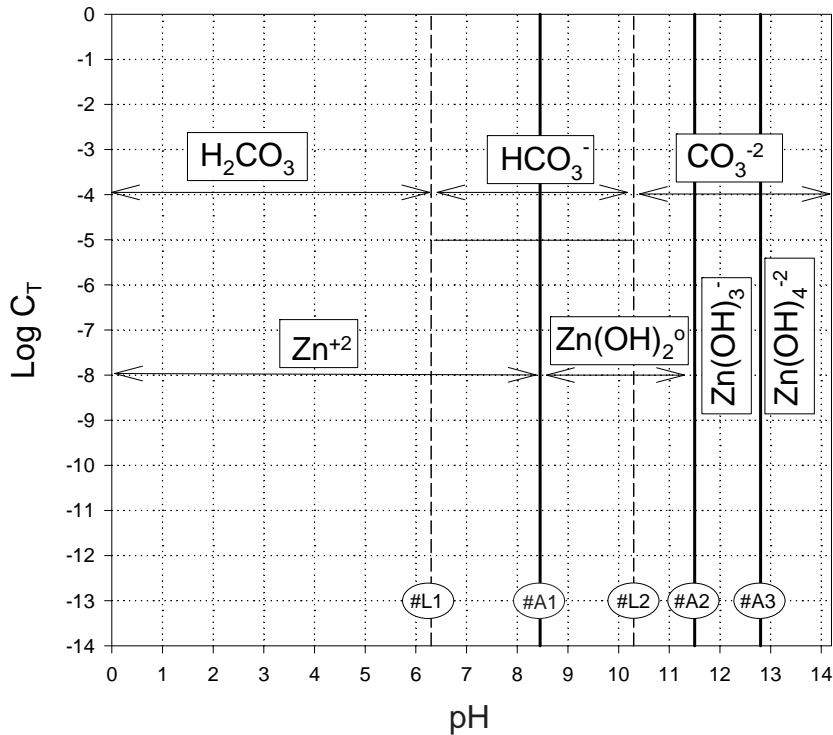
Gives us the revised A2:

$$pH = 11.50$$

$$K = \frac{[Zn(OH)_3^{-1}][OH^-]}{[Zn(OH)_4^{-2}]} = 10^{-1.20}$$

Gives us A3:

$$pH = 12.80$$



Type B lines

First let's examine the hydroxide equilibria. By looking at the $Zn(OH)_2$ solubility graph, it appears that only free zinc (Zn^{+2}) and the tetrahydroxide ($Zn(OH)_4^{-2}$) are the dominant soluble species in equilibrium with the hydroxide precipitate at a total soluble zinc concentration of 10^{-4} M.

B1:

So, first let's look at the $Zn^{+2}/Zn(OH)_2$ precipitate boundary. From the solubility product equation:

$$\begin{aligned}
 K_{so} &= [Zn^{+2}][OH^-]^2 = 10^{-15.55} \\
 \log[Zn^{+2}] &= -15.55 - 2\log[OH^-] \\
 &= -15.55 - 2\log\left(\frac{K_w}{[H^+]}\right) \\
 &= -15.55 + 28 + 2\log[H^+] \\
 &= 12.45 - 2pH
 \end{aligned}$$

Of course, this is just a re-derivation of the equation that was already provided as part of the hydroxide solubility calculations:

$$\log[Zn^{+2}] = 12.45 - 2pH$$

now adopting a total Zn of 0.1 mM, we get:

$$-4 = 12.45 - 2pH$$

or:

$$pH = 8.225$$

this line is valid as the A lines show Zn^{+2} to be dominant at this pH, albeit just barely

B2:

Now let's look at the $Zn(OH)_4^{-2}/Zn(OH)_2$ precipitate boundary. From the given solubility calculations, we have:

$$\log[Zn(OH)_4^{-2}] = -28.75 + 2pH$$

Once again, adopting a total Zn of 0.1 mM, we get:

$$-4 = -28.75 + 2pH$$

or:

$$pH = 12.375$$

This falls below the A3 line, and well into the $Zn(OH)_3^{-1}$ zone, so it's not valid

So, now we need to consider the $Zn(OH)_3^{-1}/Zn(OH)_2$ precipitate boundary. From the given solubility calculations, we have:

$$\log[Zn(OH)_3^{-1}] = -15.95 + pH$$

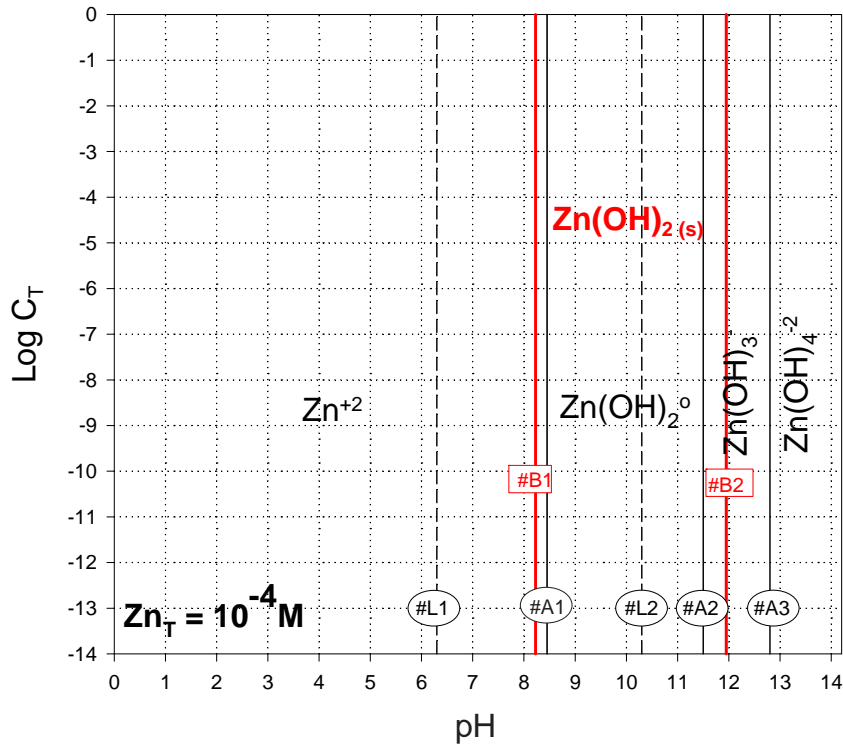
Once again, adopting a total Zn of 0.1 mM, we get:

$$-4 = -15.95 + pH$$

or:

$$pH = 11.95$$

This falls between the A2 and A3 lines, so we're in the $Zn(OH)_3^{-1}$ zone, and the line is valid



Inspection of the carbonate/hydroxide solubility diagram leads one to conclude that free zinc is the only soluble species that needs to be considered for the B lines defining carbonate solubility.

So, let's look at the $Zn^{+2}/ZnCO_3$ boundary: From the solubility calculations we had developed three line segments. We can conveniently take the equation for each, retaining the total carbonate term in its general form:

B3a:

For $pH < 6.3$, we had:

$$\log[Zn^{+2}] = -10.26 - \log[C_T] - (-16.6 + 2pH)$$

And setting the free zinc equation to 0.1 mM, we get

$$-4 = -10.26 - \log[C_T] - (-16.6 + 2pH)$$

$$\log[C_T] = 10.34 - 2pH, \text{ @ } pH < 6.3$$

B3b:

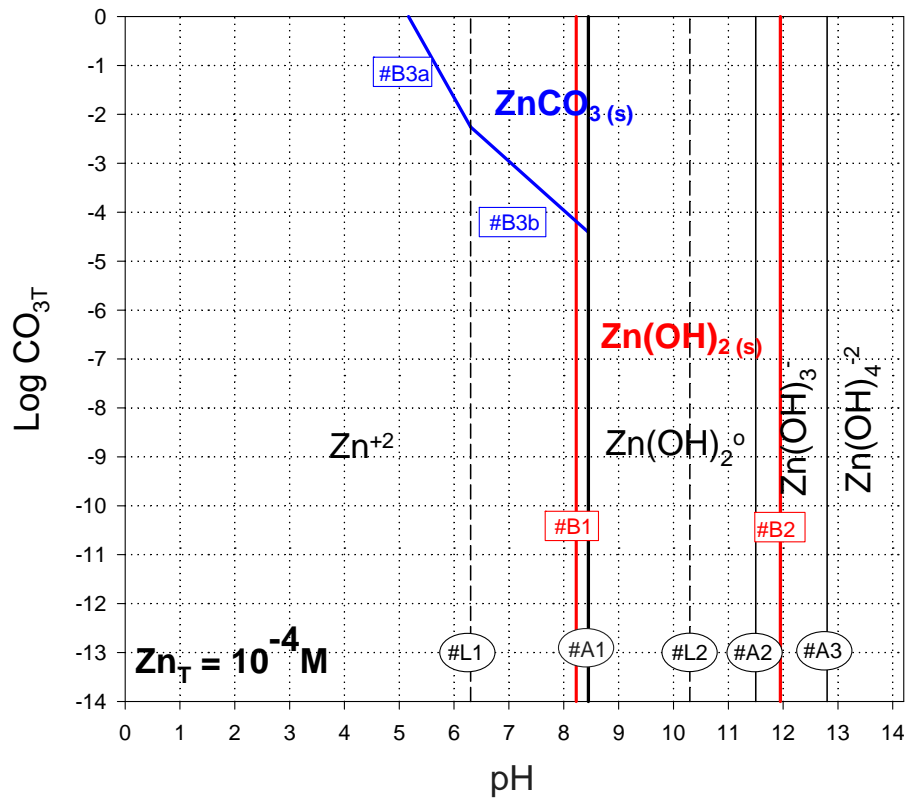
And for $pH = 6.3 - 10.3$, we have:

$$\log[Zn^{+2}] = -10.26 - \log[C_T] - (-10.3 + pH)$$

$$-4 = -10.26 - \log[C_T] - (-10.3 + pH)$$

$$\log[C_T] = 4.04 - pH, \text{ @ } pH = 6.3 - 8.45$$

However, this is only valid up to pH 8.45, the limit of free zinc's predominance (A1 line)



We could go on and graph the lines defining the border between the various zinc hydroxides, but it's clear that they won't be necessary. This was determined from inspection of the carbonate/hydroxide solubility graph. It's also clear from the emerging predominance diagram (above). The zinc carbonate lines already extend into the zinc hydroxide precipitate zone. This border is defined by type C lines.

Type C lines

Finally, let's consider the boundary between the two solid phases. This line will start on the low pH side, where the B lines intersect (pH=8.225). This is well within the zone where bicarbonate is the dominant carbonate species.

First, from the hydroxide solid solubility as given, we have:

$$\log[Zn^{+2}] = 12.45 - 2pH$$

And from the carbonate solubility we had calculated:

C1b:

For the bicarbonate zone; pH=6.3-10.3:

$$\log[\text{Zn}^{+2}] = -10.26 - \log[C_T] - (-10.3 + pH)$$

$$\log[\text{Zn}^{+2}] = +0.04 - \log[C_T] - pH$$

Substituting in the hydroxide-based equation, we get:

$$12.45 - 2pH = +0.04 - \log[C_T] - pH$$

$$\log[C_T] = -12.41 + pH, \text{ @pH=6.3-10.3}$$

C1c:

And for the carbonate zone; $pH > 10.3$, we determined:

$$\log[\text{Zn}^{+2}] = -10.26 - \log[C_T]$$

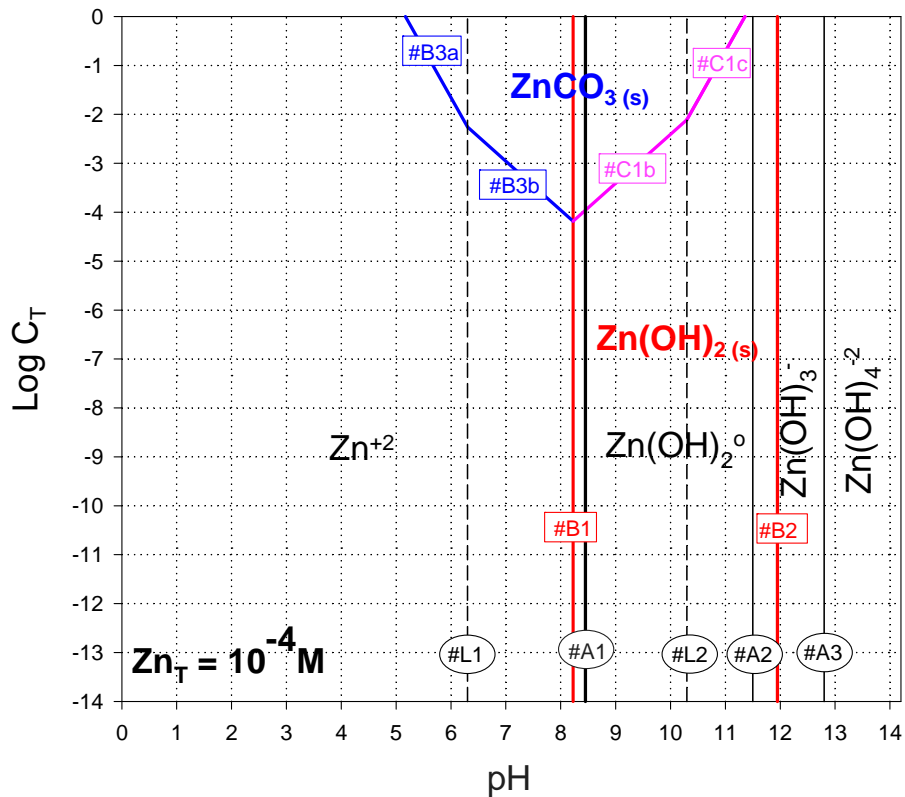
Substituting in the hydroxide-based equation, we get:

$$12.45 - 2pH = -10.26 - \log[C_T]$$

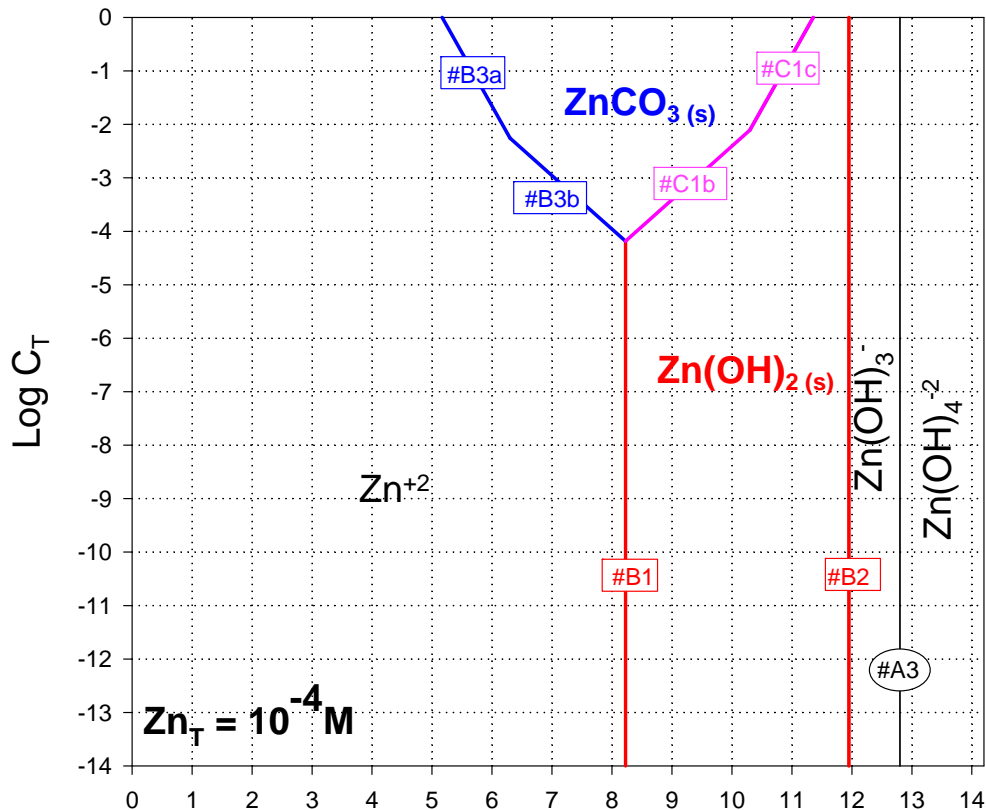
$$\log[C_T] = -22.71 + 2pH$$

$$\log[C_T] = -22.71 + 2pH, \text{ @pH} > 10.3$$

The complete lines are as follows:



And removing extra line segments and zinc species that do not exist at 0.1 mM concentration (e.g., those “under” the precipitates), we get the final diagram:



Part II:. Answer either B or C

B. Redox (30%)

It has long been known that ozonation of a drinking water or wastewater containing bromide will lead to the formation of bromate. Because of its status as a suspected human carcinogen, bromate concentrations in finished drinking water have been regulated by the US EPA at 0.010 mg/L (10 $\mu\text{g/L}$). For this reason, the bromate regulation has inadvertently resulted in diminished use of ozone with waters naturally high in bromide.

With more frequent use of marginal drinking water supplies, the treatment of waters with high chloride and bromide levels is becoming more common. Given the concern over bromate formation from ozonation, these more saline sources are treated almost exclusively with chlorine. Only systems with ozonation processes are required to monitor for bromate. However, recently the possibility that chlorine can oxidize bromide to bromate has been raised.

1. Write a balanced equation for the oxidation of bromide to bromate by reaction with aqueous chlorine (use dominant species at pH 7) (10%)
2. Determine the stoichiometry of this reaction (e.g., $\text{mg-BrO}_3^-/\text{mg-chlorine as Cl}_2$). (5%)

- Determine the equilibrium constant (K) for this reaction and comment on what thermodynamics tells you about whether this is a favorable reaction in pure sea water (assume 0.5 M chloride, 1 mM bromide, and pH 8) when the chlorine residual is 0.7 mg/L. In the interest of simplifying this problem, assume that all active chlorine is in the form of HOCl. (10%)
- Now estimate the residual equilibrium HOBr concentration under these conditions. Assume the same conditions as in #3. Assume that all of the bromine atoms are either in bromate or bromide. Consider that there is a very large molar excess of bromide as compared to the added HOCl. (5%)

Answer to B.1.

Use the following redox constants:

Equ#	Half Cell Reaction	ΔE^0 (Volts)
7	$\frac{1}{2}\text{HOBr} + \frac{1}{2}\text{H}^+ + \text{e}^- = \frac{1}{2}\text{Br}^- + \frac{1}{2}\text{H}_2\text{O}$	+1.33
10	$\frac{1}{2}\text{HOCl} + \frac{1}{2}\text{H}^+ + \text{e}^- = \frac{1}{2}\text{Cl}^- + \frac{1}{2}\text{H}_2\text{O}$	+1.48
12	$\text{BrO}_3^- + 5\text{H}^+ + 4\text{e}^- = \text{HOBr} + 2\text{H}_2\text{O}$	+1.45

Now there is one reduction reaction and two oxidation reactions. The two oxidation reactions must be combined so that the intermediate (HOBr) cancels out. This also requires that we determine the average potential per electron for the two oxidation steps.

Factor	Equ#	Half Cell Reaction	ΔE^0 (Volts)
3	10	$1\frac{1}{2}\text{HOCl} + 1\frac{1}{2}\text{H}^+ + 3\text{e}^- = 1\frac{1}{2}\text{Cl}^- + 1\frac{1}{2}\text{H}_2\text{O}$	+1.48
-1	7	$\frac{1}{2}\text{Br}^- + \frac{1}{2}\text{H}_2\text{O} = \frac{1}{2}\text{HOBr} + \frac{1}{2}\text{H}^+ + \text{e}^-$	1/3 (-1.33)
-1/2	12	$\frac{1}{2}\text{HOBr} + \text{H}_2\text{O} = \frac{1}{2}\text{BrO}_3^- + 2\frac{1}{2}\text{H}^+ + 2\text{e}^-$	2/3 (-1.45)
$1\frac{1}{2}\text{HOCl} + \frac{1}{2}\text{Br}^- = \frac{1}{2}\text{BrO}_3^- + 1\frac{1}{2}\text{Cl}^- + 1\frac{1}{2}\text{H}^+$			+0.07

Or simplifying by making it per bromate ion:



Answer to B.2.

Stoichiometry:

$$\text{stoichiometry} = \frac{3M - \text{HOCl}}{1M - \text{BrO}_3^-}$$

$$\text{stoichiometry} = \frac{3M - \text{HOCl} \left(\frac{52.453 \text{ g-HOCl}}{1M - \text{HOCl}} \right)}{1M - \text{BrO}_3^- \left(\frac{127.904 \text{ g-BrO}_3^-}{1M - \text{BrO}_3^-} \right)}$$

$$\text{stoichiometry} = 1.23 \frac{g - HOCl}{g - BrO_3^-} = 1.23 \frac{mg - HOCl}{mg - BrO_3^-}$$

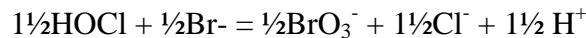
Or:

$$\text{stoichiometry} = 1.66 \frac{g - Cl_2}{g - BrO_3^-} = 1.66 \frac{mg - Cl_2}{mg - BrO_3^-}$$

Answer to B.3.

$$\text{Log}K = \frac{n}{0.059} E_{net}^o$$

If we define the equation as:



This is a 3-electron transfer, so:

$$\log K = \frac{3}{0.059} (0.07)$$

$$\log K = 3.56$$

This means that following is true at equilibrium:

$$K = 10^{3.56} = \frac{[BrO_3^-]^{1.5} [Cl^-]^{1.5} [H^+]^{1.5}}{[HOCl]^{1.5} [Br^-]^{0.5}}$$

Since the concentration of chloride in sea water is about 0.5 M, bromide is about 1 mM, and the typical hydrogen ion concentration is 10^{-8} , the equilibrium bromate concentration would be 47,200 M. In other words, **this is a reaction that essentially goes to completion, from the standpoint of thermodynamics.**

$$K = 10^{3.56} = \frac{[BrO_3^-]^{1.5} [0.5]^{1.5} [10^{-8}]^{1.5}}{[HOCl]^{1.5} [10^{-3}]^{0.5}}$$

$$\frac{[BrO_3^-]^{1.5}}{[HOCl]^{1.5}} = 10^{3.56} \frac{[10^{-3}]^{0.5}}{[0.5]^{1.5} [10^{-8}]^{1.5}}$$

And if the HOCl residual was 0.7 mg/L

$$\frac{[BrO_3^-]^{1.5}}{[10^{-5}]^{1.5}} = 10^{3.56} \frac{[10^{-3}]^{0.5}}{[0.5]^{1.5} [10^{-8}]^{1.5}}$$

$$[BrO_3^-]^{1.5} = 10^{3.56} \frac{[10^{-3}]^{0.5}}{[0.5]^{1.5} [10^{-8}]^{1.5}} [10^{-5}]^{1.5}$$

$$[BrO_3^-]^{1.5} = 10,300$$

$$[BrO_3^-] = 47,200$$

However, if bromide diminishes to low concentrations due to other reactions, the bromate may be quite small.

Answer to B.4.

Returning to the prior equation for bromate formation

$$K = 10^{3.56} = \frac{[BrO_3^-]^{1.5} [Cl^-]^{1.5} [H^+]^{1.5}}{[HOCl]^{1.5} [Br^-]^{0.5}}$$

Now its reasonable to assume that the chlorine will be mostly used up in oxidizing bromide to bromate. Then you can solve for the equilibrium residual chlorine concentration.

$$[HOCl]^{1.5} = 10^{-3.56} \frac{[BrO_3^-]^{1.5} [Cl^-]^{1.5} [H^+]^{1.5}}{[Br^-]^{0.5}}$$

If this is the case, the $[BrO_3^-]$ will be essentially equal to the HOCl dose, and the remaining bromide will still be in the form of bromide.

$$[HOCl]^{1.5} = 10^{-3.56} \frac{[10^{-5}]^{1.5} [0.5]^{1.5} [10^{-8}]^{1.5}}{[10^{-3}]^{0.5}}$$

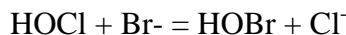
$$[HOCl]^{1.5} = 9.7 \times 10^{-23}$$

$$[HOCl] = 2.12 \times 10^{-15}$$

Now do the calculation for oxidation of bromide to hypobromous acid by hypochlorous acid

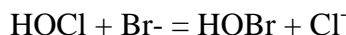
Factor	Equ#	Half Cell Reaction	ΔE° (Volts)
1	10	$\frac{1}{2}HOCl + \frac{1}{2}H^+ + e^- = \frac{1}{2}Cl^- + \frac{1}{2}H_2O$	+1.48
-1	7	$\frac{1}{2}Br^- + \frac{1}{2}H_2O = \frac{1}{2}HOBr + \frac{1}{2}H^+ + e^-$	-1.33
		$\frac{1}{2}HOCl + \frac{1}{2}Br^- = \frac{1}{2}HOBr + \frac{1}{2}Cl^-$	+0.15

Or simplifying by making it per hypobromous acid molecule:



$$\text{Log}K = \frac{n}{0.059} E_{net}^\circ$$

If we define the equation as:



This is a 2-electron transfer, so:

$$\log K = \frac{2}{0.059} (0.15)$$
$$\log K = 5.08$$

This means that following is true at equilibrium:

$$K = 10^{5.08} = \frac{[HOBr][Cl^-]}{[HOCl][Br^-]}$$

Now rearrange, solving for the hypobromous acid concentration

$$[HOBr] = 10^{5.08} \frac{[HOCl][Br^-]}{[Cl^-]}$$

Use the previously calculated equilibrium HOCl value, the raw sea water bromide level, and the chloride level.

$$[HOBr] = 10^{5.08} \frac{[2.12 \times 10^{-15}][10^{-3}]}{[0.5]}$$

$$[HOBr] = 5.1 \times 10^{-13}$$

Some important equilibrium constants:

<u>Equilibria</u>	<u>Log K</u>
$\text{Mg(OH)}_2(s) = \text{Mg}^{+2} + 2\text{OH}^-$	-11.6
$\text{Fe}^{+3} + \text{H}_2\text{O} = \text{FeOH}^{+2} + \text{H}^+$	-2.19
$\text{Mg}^{+2} + \text{H}_2\text{O} = \text{MgOH}^+ + \text{H}^+$	-11.44
$\text{MgCO}_3(s) = \text{Mg}^{+2} + \text{CO}_3^{-2}$	-7.5
$\text{CaCO}_3(s) = \text{Ca}^{+2} + \text{CO}_3^{-2}$	-8.34
$\text{Ca(OH)}_2(s) = \text{Ca}^{+2} + 2\text{OH}^-$	-5.19
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}(s) = \text{Ca}^{+2} + \text{SO}_4^{-2} + 2\text{H}_2\text{O}$	-4.62
$\text{CaOH}^+ = \text{Ca}^{+2} + \text{OH}^-$	-1.15
$\text{AlOH}^{+2} = \text{Al}^{+3} + \text{OH}^-$	-9.01
$\text{CdOH}^+ = \text{Cd}^{+2} + \text{OH}^-$	-3.92
$\text{CoOH}^+ = \text{Co}^{+2} + \text{OH}^-$	-4.80
$\text{CuOH}^+ = \text{Cu}^{+2} + \text{OH}^-$	-6.00
$\text{FeOH}^+ = \text{Fe}^{+2} + \text{OH}^-$	-4.50
$\text{HgOH}^+ = \text{Hg}^{+2} + \text{OH}^-$	-10.60
$\text{NiOH}^+ = \text{Ni}^{+2} + \text{OH}^-$	-4.14
$\text{PbOH}^+ = \text{Pb}^{+2} + \text{OH}^-$	-6.29
$\text{ZnOH}^+ = \text{Zn}^{+2} + \text{OH}^-$	-5.04

Some important half-cell reactions

<u>Equ#</u>	<u>Half Cell Reaction</u>	<u>ΔE° (Volts)</u>
1	$\text{O}_2(\text{g}) + 4\text{H}^+ + 4\text{e}^- = 2\text{H}_2\text{O}$	+1.23
2	$\text{Mn}^{+3} + \text{e}^- = \text{Mn}^{+2}$	+1.51
3	$\text{Mn}^{+4} + \text{e}^- = \text{Mn}^{+3}$	+1.65
4	$\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- = \text{Mn}^{+2} + 4\text{H}_2\text{O}$	+1.49
5	$\text{Fe}^{+3} + \text{e}^- = \text{Fe}^{+2}$	+0.77
6	$\text{Cu}^{+2} + \text{e}^- = \text{Cu}^+$	+0.16
7	$\frac{1}{2}\text{HOBr} + \frac{1}{2}\text{H}^+ + \text{e}^- = \frac{1}{2}\text{Br}^- + \frac{1}{2}\text{H}_2\text{O}$	+1.33
8	$\text{O}_3(\text{g}) + 2\text{H}^+ + 2\text{e}^- = \text{O}_2(\text{g}) + \text{H}_2\text{O}$	+2.07
9	$\text{Al}^{+3} + 3\text{e}^- = \text{Al}(s)$	-1.68
10	$\frac{1}{2}\text{HOCl} + \frac{1}{2}\text{H}^+ + \text{e}^- = \frac{1}{2}\text{Cl}^- + \frac{1}{2}\text{H}_2\text{O}$	+1.48
11	$\frac{1}{2}\text{OCl}^- + \text{H}^+ + \text{e}^- = \frac{1}{2}\text{Cl}^- + \frac{1}{2}\text{H}_2\text{O}$	+1.64
12	$\text{BrO}_3^- + 5\text{H}^+ + 4\text{e}^- = \text{HOBr} + 2\text{H}_2\text{O}$	+1.45
13	$\text{S}(s) + 2\text{H}^+ + 2\text{e}^- = \text{H}_2\text{S}(g)$	+0.17
14	$\frac{1}{2}\text{NH}_2\text{Cl} + \text{H}^+ + \text{e}^- = \frac{1}{2}\text{Cl}^- + \frac{1}{2}\text{NH}_4^+$	+1.40
15	$\text{Zn}^{+2} + 2\text{e}^- = \text{Zn}(s)$	-0.76
16	$\text{Ni}^{+2} + 2\text{e}^- = \text{Ni}(s)$	-0.24
17	$\text{Pb}^{+2} + 2\text{e}^- = \text{Pb}(s)$	-0.13

Properties of Selected Elements

Element	Symbol	Atomic #	Atomic Wt.	Valence	Electronegativity
Aluminum	Al	13	26.98	3	1.47
Bromine	Br	35	79.904	1,3,5,7	2.74
Calcium	Ca	20	40.08	2	1.04
Carbon	C	6	12.01	2,4	2.50
Chlorine	Cl	17	35.453	1,3,5,7	2.83
Copper	Cu	29	63.54	1,2	1.75
Hydrogen	H	1	1.01	1	2.20
Magnesium	Mg	12	24.31	2	1.23
Manganese	Mn	25	54.94	2,3,4,6,7	1.60
Nitrogen	N	7	14.0047	3,5	3.07
Oxygen	O	8	16.00	2	3.50
Potassium	K	19	39.10	1	0.91
Sodium	Na	11	22.99	1	1.01
Strontium	Sr	38	87.62	2	0.99
Sulfur	S	16	32.06	2,4,6	2.44
Zinc	Zn	30	65.39	2	1.65

Selected Acidity Constants
(Aqueous Solution, 25°C, I = 0)

NAME	FORMULA	pK _a
Perchloric acid	$\text{HClO}_4 = \text{H}^+ + \text{ClO}_4^-$	-7
Hydrochloric acid	$\text{HCl} = \text{H}^+ + \text{Cl}^-$	-3
Sulfuric acid	$\text{H}_2\text{SO}_4 = \text{H}^+ + \text{HSO}_4^-$	-3
Nitric acid	$\text{HNO}_3 = \text{H}^+ + \text{NO}_3^-$	0
Bisulfate ion	$\text{HSO}_4^- = \text{H}^+ + \text{SO}_4^{2-}$	2
Phosphoric acid	$\text{H}_3\text{PO}_4 = \text{H}^+ + \text{H}_2\text{PO}_4^-$	2.15
o-Phthalic acid	$\text{C}_6\text{H}_4(\text{COOH})_2 = \text{H}^+ + \text{C}_6\text{H}_4(\text{COOH})\text{COO}^-$	2.89
p-Hydroxybenzoic acid	$\text{C}_6\text{H}_4(\text{OH})\text{COOH} = \text{H}^+ + \text{C}_6\text{H}_4(\text{OH})\text{COO}^-$	4.48
Nitrous acid	$\text{HNO}_2 = \text{H}^+ + \text{NO}_2^-$	4.5
Acetic acid	$\text{CH}_3\text{COOH} = \text{H}^+ + \text{CH}_3\text{COO}^-$	4.75
Aluminum ion	$\text{Al}(\text{H}_2\text{O})_6^{+3} = \text{H}^+ + \text{Al}(\text{OH})(\text{H}_2\text{O})_5^{+2}$	4.8
Carbonic acid	$\text{H}_2\text{CO}_3 = \text{H}^+ + \text{HCO}_3^-$	6.35
Hydrogen sulfide	$\text{H}_2\text{S} = \text{H}^+ + \text{HS}^-$	7.02
Dihydrogen phosphate	$\text{H}_2\text{PO}_4^- = \text{H}^+ + \text{HPO}_4^{2-}$	7.2
Hypochlorous acid	$\text{HOCl} = \text{H}^+ + \text{OCl}^-$	7.5
Hypobromous acid	$\text{HOBr} = \text{H}^+ + \text{OBr}^-$	8.71

Ammonium ion	$\text{NH}_4^+ = \text{H}^+ + \text{NH}_3$	9.24
Bicarbonate ion	$\text{HCO}_3^- = \text{H}^+ + \text{CO}_3^{2-}$	10.33
Monohydrogen phosphate	$\text{HPO}_4^{2-} = \text{H}^+ + \text{PO}_4^{3-}$	12.3