CEE 680 12 December 2012

FINAL EXAM

Closed book, three pages of notes allowed.
Answer all Three Questions. 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).

Miscellaneous Information:
R = 1.987 cal/mole°K = 8.314 J/mole°K
Absolute zero = -273.15°C
1 joule = 0.239 calories

1. Buffers (25%)

You have prepared a 10 mM phosphate buffer designed to hold pH at 8.1 (25°C, assume I~0). The two chemicals at your disposal are Na_2HPO_4 and KH_2PO_4.

A. How much of each compound (in mM concentration) would you add to create your buffer?
B. If you were to elevate the solution pH to 12.0, how much NaOH would you need to add (again in mM)?

A. This is a good use for the empiricial Henderson Hasselbach Equation

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

Where C_A is the Na_2HPO_4 and C_{HA} is the KH_2PO_4

$$\frac{C_A}{C_{HA}} = 10^{pH-pK_a} = 10^{8.1-7.2} = 7.943$$

And since $C_A + C_{HA} = 10$ mM,

$$\frac{C_A}{0.010 - C_A} = 7.943$$
$$C_A = 0.07943 - 7.943C_A$$
$$8.943C_A = 0.07943$$
$$C_A = 0.00888M = Na_2HPO_4$$
$$C_{HA} = 0.00112M = KH_2PO_4$$

B. Now determine the new mixture at pH 12 and determine amount of protons that need to be neutralized, but this time we're closer to the third K_a, so C_A is PO_4^{-3} and C_{HA} is HPO_4^{-2}

$$\frac{C_A}{C_{HA}} = 10^{pH-pK_a} = 10^{12.0-12.3} = 0.501$$

$$\frac{C_A}{0.010 - C_A} = 0.501$$

$$C_A = 0.00501 - 0.501 C_A$$

$$1.501 C_A = 0.00501$$

$$C_A = 0.00334M = PO_4^{-3}$$

$$C_{HA} = 0.00666M = HPO_4^{-2}$$

So the change in protons is:

ΔH^+ in Phosphates = 2*0.00122+0.00888-0.00666 = **0.00466M or 4.66mM**

But you also have significant hydroxide in the amount of 10^{-2}M or 10 mM. Therefore the overall hydroxide addition must be equal to the sum or:

NaOH dose = 0.010+0.00466 = **0.01466M or 14.66mM**

2. Redox (25%)

Sulfide and sulfate are two forms of sulfur that commonly exist in the aquatic environment. They often are found in groundwaters with both reduced and oxidized iron.

A. Write a balanced equation for the oxidation of hydrogen sulfide (HS^-) to sulfate by reaction with amorphous ferric hydroxide, liberating free ferrous iron.
B. Determine the net cell potential (E^o_{net}) and the equilibrium constant for this reaction and comment on what thermodynamics tells you about whether this is a favorable reaction in a typical groundwater and surface water systems.
C. At what pH does the eqilibrium rest half-way between the two sulfur species? Assume a free ferrous iron concentration of 0.56 mg/L. Which species (sulfate or bisulfide) will predominate at lower pHs?

So we use redox #1 and #14, but we need to reverse #14 and cut its stiochiometry by a factor of 2 so that the electrons balance.

14	$Fe(OH)_{3(am)} + 3H^+ + e^- = Fe^{+2} + 3H_2O$	+0.95
15	$SO_4^{-2} + 9H^+ + 8e^- = HS^- + 4H_2O$	+0.25

This requires that we reverse the sign on the ΔE^o, but since the potentals are expressed on a per-electron basis, the change in stoichiometric factors doesn't result in any additional change in ΔE^o.

Red	$8Fe(OH)_{3(am)} + 24H^+ + 8e^- = 8Fe^{+2} + 24H_2O$	+0.95
Ox	$HS^- + 4H_2O = SO_4^{-2} + 9H^+ + 8e^-$	-0.25
Net	$\mathbf{8Fe(OH)_{3(am)} + 15H^+ + HS^- = 8Fe^{+2} + SO_4^{-2} + 20H_2O}$	**+0.70**

$$
\begin{aligned}
\log K &= \frac{n}{0.059} E^{o}_{net} \\
&= \frac{8}{0.059}(0.70) \\
&= 94.9
\end{aligned}
$$

$$10^{+94.9} = \frac{[Fe^{+2}]^{8}[SO_4^{-2}]}{[H^{+}]^{15}[HS^{-}]}$$

Now substituing in for 10^{-5}M Fe^{+2} (0.56 mg/L) we get:

$$10^{+94.9} = \frac{[10^{-5}]^{8}[SO_4^{-2}]}{[H^{+}]^{15}[HS^{-}]}$$

$$\frac{[SO_4^{-2}]}{[HS^{-}]} = 10^{+134.9}[H^{+}]^{15}$$

So when the quotient on the left is unity, the pH must be 134.9/15 or **9.0**. Below this pH sulfate will predominate and above it will be bisulfide.

3. *Solubility (50%)*

Ferrous Sulfide (Troilite, a form of Pyrrhotite) is a rather insoluble mineral with a K_{so} of about $10^{-18.1}$. One would expect this to form in reduced groundwaters and sediments where ferrous iron and sulfide are major forms of Fe and S. $Fe(OH)_{2(s)}$ would, of course form under the right conditions as well.

#	Reaction	pK
1[1]	$FeS_{(s)} = Fe^{+2} + S^{-2}$	18.1
2	$Fe(OH)_{2(s)} + 2H^{+} = Fe^{+2} + 2H_2O$	-12.9
3	$FeOH^{+} + H^{+} = Fe^{+2} + H_2O$	-9.5
4	$Fe(OH)_2^{o} + 2H^{+} = Fe^{+2} + 2H_2O$	-20.6
5	$Fe(OH)_3^{-} + 3H^{+} = Fe^{+2} + 3H_2O$	-31.0

A. Prepare a combined Ferrous Hydroxide and Ferrous Sulfide solubility diagram assumng you have a total sulfide concentration of 10^{-6}M. The x-axis should be pH and the y-axixs should be log concentration. Show lines for the four soluble iron species based on each precipitate. Identify the key precipitation zones with Fe_T lines.
B. At what pH can both precipitates co-exist?
C. If the sulfide concentration was to increase, would the pH where the precipitates co-exist increase or decrease?
D. Describe in qualitative terms how the presence of 10^{-3}M total carbonate would affect the hydroxide and sulfide precipitation zones.
E. Describe in qualitative terms how the presence of 10^{-6}M mercury would affect the hydroxide and sulfide precipitation zones

Development of hydroxide solubility diagram

a. Using the equilibria for ferric hydroxide from above:

$$K = \frac{[Fe^{+2}]}{[H^{+}]^2} = 10^{+12.9}$$

we get the following for the free aquo ion:

$$\log[Fe^{+2}] = +12.9 - 2pH$$

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

---

[1] Because of uncertainty over K_2 for the sulfide system, this equilibrium are often expressed in terms of HS^{-} rather than S^{-2}. However, to be consistant, I have converted it to the more conventional Kso form in a way that is internally consistent with our value of $10^{-13.9}$ for the sulfide K_2. These pK values were taken from Morel & Hering, 1993.

$$K = \frac{[Fe^{+2}]}{[FeOH^{+}][H^{+}]} = 10^{+9.5}$$

$$\log[FeOH^{+}] = -9.5 + \log[Fe^{+2}] - \log[H^{+}]$$

$$\log[FeOH^{+}] = -9.5 + \log[Fe^{+2}] + pH$$

$$\log[FeOH^{+}] = -9.5 + (12.9 - 2pH) + pH$$

$$\log[FeOH^{+}] = +3.4 - pH$$

now for the dihydroxide:

$$K = \frac{[Fe^{+2}]}{[Fe(OH)_2^{o}][H^{+}]^2} = 10^{+20.6}$$

$$\log[Fe(OH)_2^{o}] = -20.6 + \log[Fe^{+2}] - 2\log[H^{+}]$$

$$\log[Fe(OH)_2^{o}] = -20.6 + (12.9 - 2pH) + 2pH$$

$$\log[Fe(OH)_2^{o}] = -7.7$$

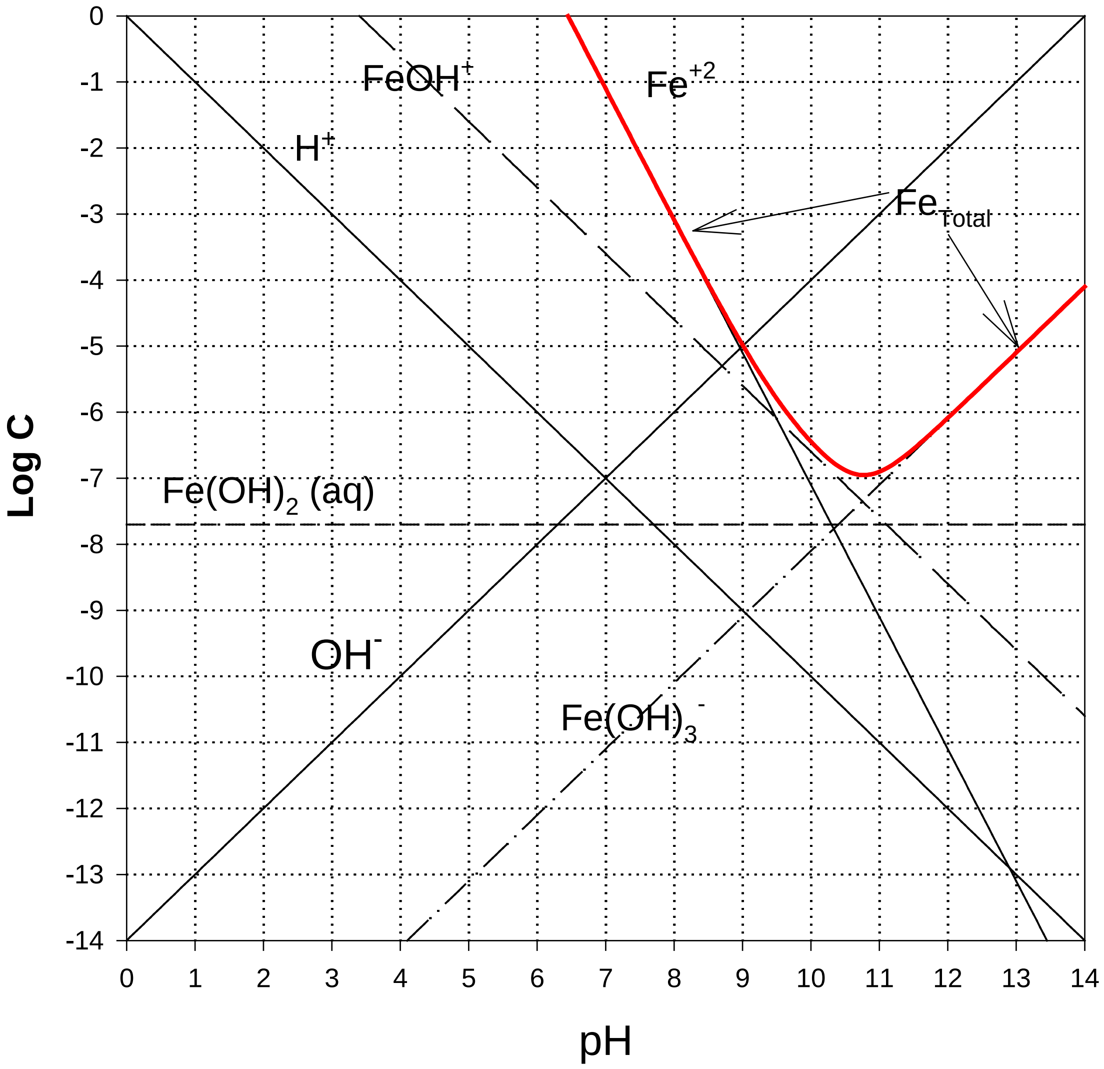
now for the trihydroxide:

$$K = \frac{[Fe^{+2}]}{[Fe(OH)_3^{-1}][H^{+}]^3} = 10^{+31.0}$$

$$\log[Fe(OH)_3^{-1}] = -31.0 + \log[Fe^{+2}] - 3\log[H^{+}]$$

$$\log[Fe(OH)_3^{-1}] = -31.0 + (12.9 - 2pH) + 3pH$$

$$\log[Fe(OH)_3^{-1}] = -18.1 + pH$$



Development of Sulfide-based lines

b. Using the solubility product constant for ferrous sulfide from above:

$$K = [Fe^{+2}][S^{-2}] = 10^{-18.1}$$

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

$$\log[Fe^{+2}] = -18.1 - \log[S^{-2}]$$

$$\log[Fe^{+2}] = -18.1 - \log[S_T] - \log \alpha_2$$

And for 10^{-6} M total sulfides:

$$\log[Fe^{+2}] = -18.1 - \log[10^{-6}] - \log \alpha_2$$

$$\log[Fe^{+2}] = -12.1 - \log \alpha_2$$

For Sulfide Calculations:

$$\alpha_2 = \frac{1}{\frac{[H^+]^2}{K_1K_2} + \frac{[H^+]}{K_2} + 1}$$

For pH<7.02, $\alpha_2 \approx \frac{K_1K_2}{[H^+]^2}$, or $\log\alpha_2 \approx -20.92 + 2pH$

For pH=7.02-13.9, $\alpha_2 \approx \frac{K_2}{[H^+]}$, or $\log\alpha_2 \approx -13.9 + pH$

For pH>13.9, $\alpha_2 \approx 1$, or $\log\alpha_2 \approx 0$

So for pH<7.02, we have:

$$\log[Fe^{+2}] = -12.1 - (-20.92 + 2pH)$$

$$\log[Fe^{+2}] = 8.82 - 2pH$$, @pH<7.02

And for pH=7.02-13.9, we have:

$$\log[Fe^{+2}] = -12.1 - (-13.9 + pH)$$

$$\log[Fe^{+2}] = +1.8 - pH$$, @pH=7.02-13.9

And for pH>13.9, we have:

$$\log[Fe^{+2}] = -12.1 - (0)$$

$$\log[Fe^{+2}] = -12.1$$, @pH>13.9

b2. and for the monohydroxide:

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

$$\log[FeOH^+] = -9.5 + \log[Fe^{+2}] + pH$$

And now substituting in the $FeS_{(s)}$-based free iron equation for pH<7.02, we have:

$$\log[FeOH^+] = -9.5 + (8.82 - 2pH) + pH$$

$$\log[FeOH^+] = -0.68 - pH$$, @pH<7.02

And for pH=7.02-13.9, we have:

$$\log[FeOH^+] = -9.5 + (1.8 - pH) + pH$$

$$\log[FeOH^+] = -7.7$$, @pH=7.02-13.9

And for pH>13.9, we have:

$$\log[FeOH^+] = -9.5 + (-12.1) + pH$$

$$\log[FeOH^+] = -21.6 + pH$$, @pH>13.9

b3. now for the dihydroxide:

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

$$\log[Fe(OH)_2^o] = -20.6 + \log[Fe^{+2}] - 2\log[H^+]$$

And now substituting in the $FeS_{(s)}$-based FeOH equation for pH<7.02, we have:

$$\log[Fe(OH)_2^o] = -20.6 + (8.82 - 2pH) + 2pH$$

$$\log[Fe(OH)_2^o] = -11.78$$, @pH<7.02

And for pH=7.02-13.9, we have:

$$\log[Fe(OH)_2^o] = -20.6 + (1.8 - pH) + 2pH$$

$$\log[Fe(OH)_2^o] = -18.8 + pH$$, @pH=7.02-13.9

And for pH>13.9, we have:

$$\log[Fe(OH)_2^o] = -20.6 + (-12.1) + 2pH$$

$$\log[Fe(OH)_2^o] = -32.7 + 2pH$$, @pH>13.9

B4. now for the trihydroxide:

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

$$\log[Fe(OH)_3^{-1}] = -31.0 + \log[Fe^{+2}] - 3\log[H^+]$$

$$\log[Fe(OH)_3^{-1}] = -31.0 + \log[Fe^{+2}] + 3pH$$

And now substituting in the $FeS_{(s)}$ based $Fe(OH)_2$ equation for pH<7.02, we have:

$$\log[Fe(OH)_3^{-1}] = -31.0 + (8.82 - 2pH) + 3pH$$

$$\log[Fe(OH)_3^{-1}] = -22.18 + pH$$, @pH<7.02

And for pH=7.02-13.9, we have:

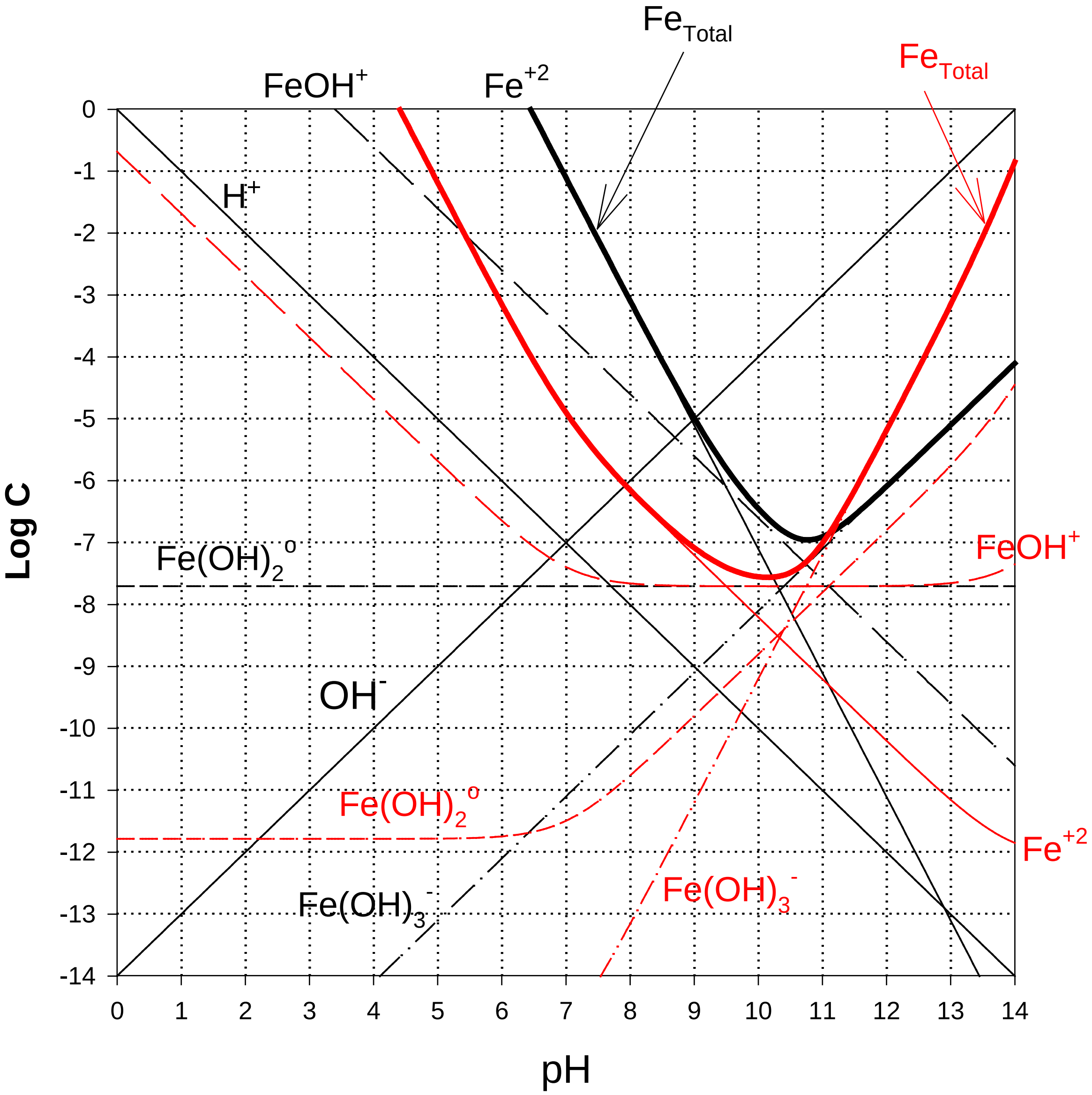
$$\log[Fe(OH)_3^{-1}] = -31.0 + (1.8 - pH) + 3pH$$

$$\log[Fe(OH)_3^{-1}] = -29.2 + 2pH$$, @pH=7.02-13.9

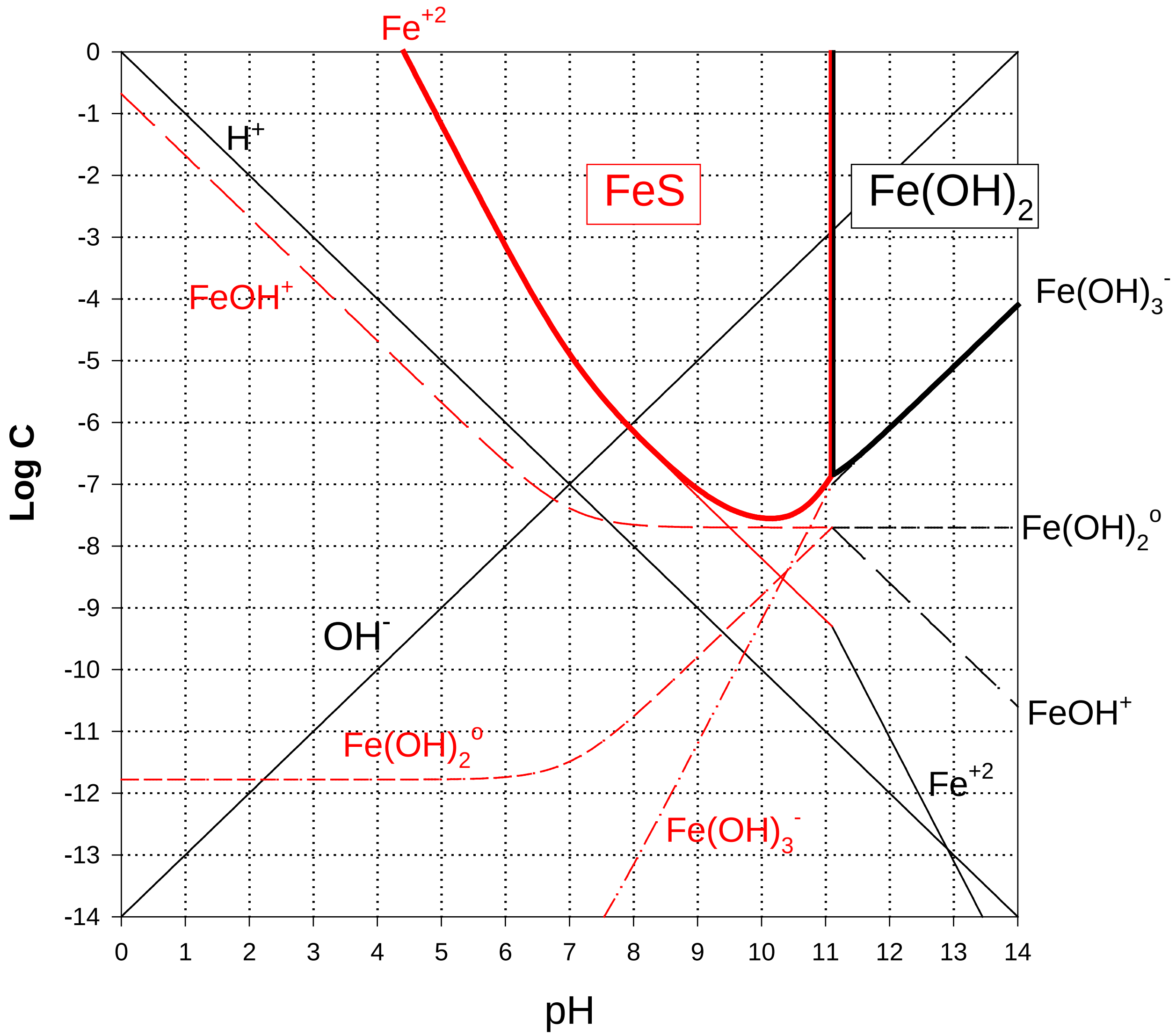
And for pH>13.9, we have:

$$\log[Fe(OH)_3^{-1}] = -31.0 + (-12.1) + 3pH$$

$$\log[Fe(OH)_3^{-1}] = -43.1 + 3pH$$, @pH>13.9



Red lines are based on sulfide solubility and black are based on hydroxide



Now combining, we find that the hydroxide controls at pHs of 11.15 and above. Below this level, the carbonate is less soluble.

A. (30 points) see above

B. (5 points) The co-exist at a pH of about **11.1**

C. (5 points) pH **increases**; it forms over a wider pH range

D. (5 points) it forms a 3rd solid phase ($FeCO_3$) which would infringe on the $FeS_{(s)}$ zone mostly

E. (5 points) it would precipitate HgS quite extensively, depressing the sulfide concentrations and thereby diminish the $FeS_{(s)}$ zone, allowing $Fe(OH)_{2(s)}$ to expand into lower pHs.

4. Predominance (50%) Answer this or #3, your choice

Lead carbonate ($PbCO_{3(s)}$) and red Lead Oxide ($PbO_{(s)}$) are two important solid phases that may control lead solubility in water[2]. In the attached pages is a detailed solution leading to a zinc hydroxide solubility diagram. Please use this to help solve the following problems.

A. Prepare a solubility diagram (log C vs pH) for a water that is potentially in equilibrium with lead hydroxide and lead carbonate. Assume the water has $\underline{10^{-3}\text{ M}}$ total carbonates (i.e., 1 mM C_T). Show all soluble species along with the Pb_T line and indicate where precipitation will occur and the type of precipitate. To help you, there is a full solubility diagram for lead hydroxide only below. Feel free to work from this to prepare the combined carbonate-hydroxide diagram

B. Below is a partially completed predominance diagram for the lead oxide – lead carbonate system. This was prepared for a total soluble lead concentration of $\underline{10^{-4}\text{ M}}$ (i.e., 0.1 mM Pb_T). Please complete this diagram showing the line(s) separating the two precipitates (C lines) and also determine and show the last remaining B line that separates the PbCO3 precipitation zone from the $Pb(OH)_3^-$ zone (no precipitate). Show your work.

Stumm & Morgan Present the following data in Table A6.1

	OH^-		CO_3^{-2}	
Pb^{2+}	PbL	6.3		
	PbL_2	10.9	PbL • s	13.1
	PbL_3	13.9		
	PbL_2 • s	15.3		

They note that the numerical values are Log formation contstants.

Using these data you can rearrange the equilibrium quotients to get the following

In equilibrium with PbO(s):

$\text{Log}[Pb^{+2}] = +12.7 - 2pH$

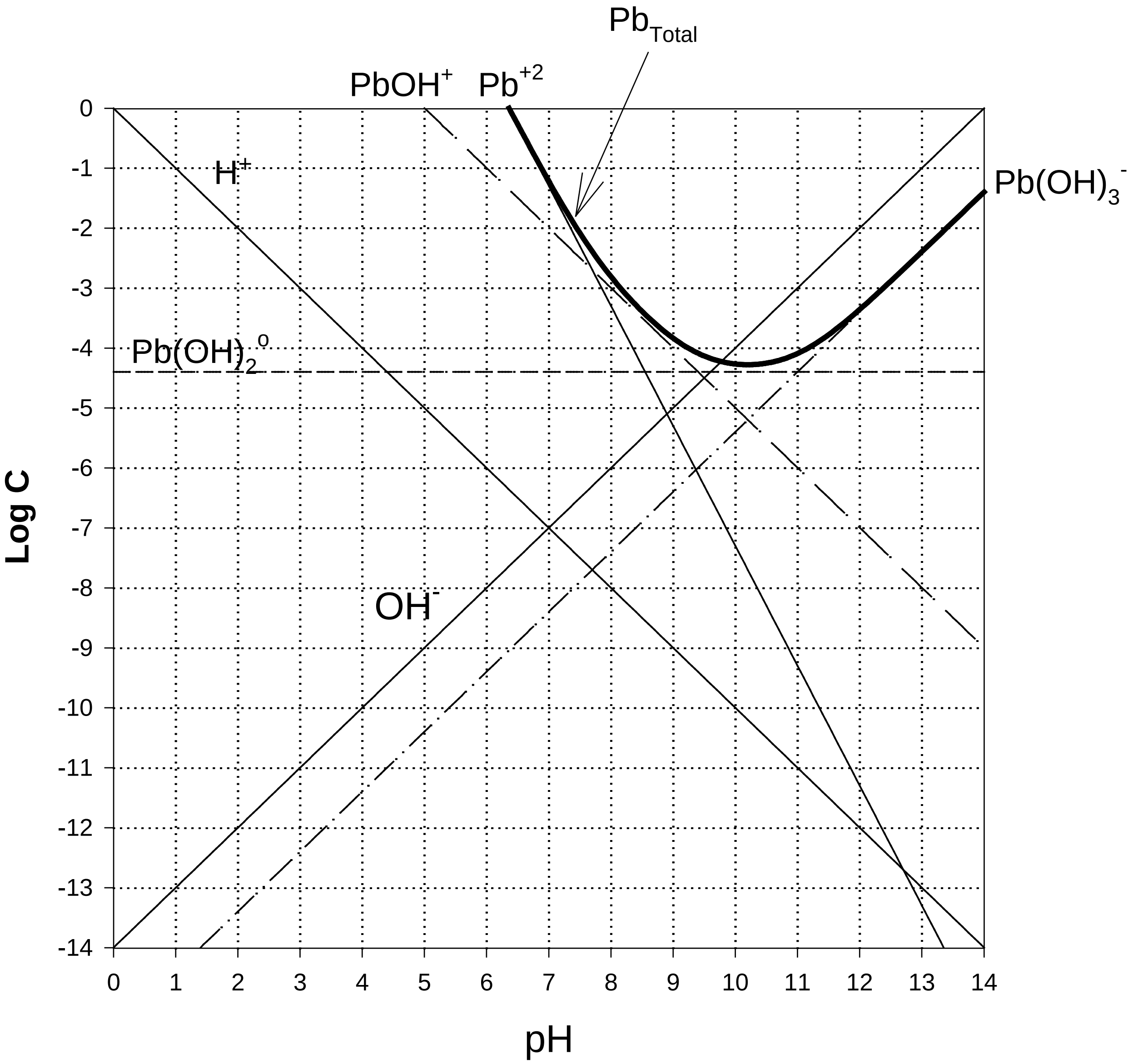
$\text{Log}[PbOH^{+}] = +5.0 - pH$

$\text{Log}[Pb(OH)_2] = -4.4$

$\text{Log}\ [Pb(OH)_3] = -15.4 + pH$

---

[2] Some mixed carbonate-hydroxide species may, in fact, be the most important, but they will not be considered here for the purpose of simplicity.



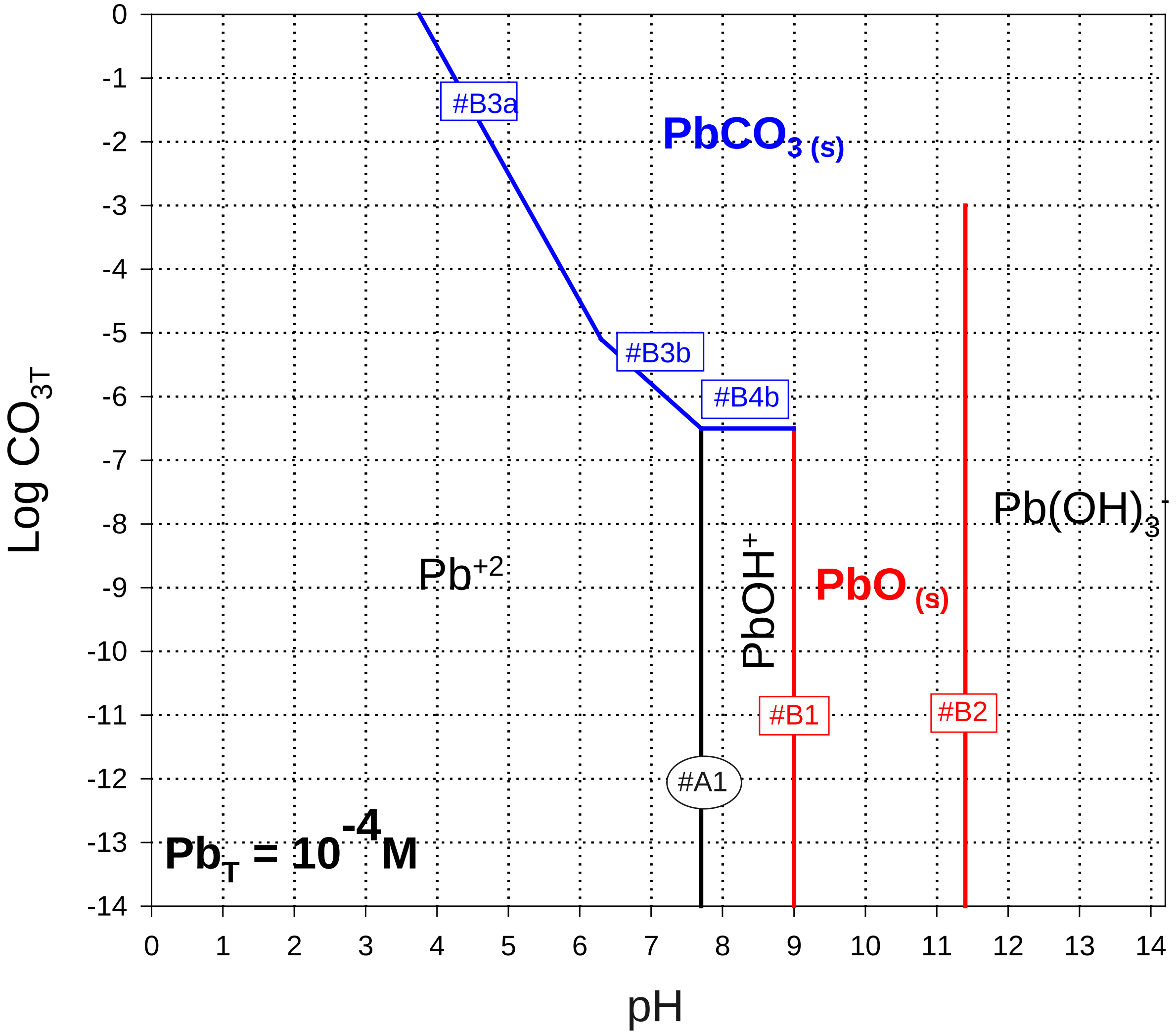
In equilibrium with $PbCO_3(s)$:

$Log[Pb^{+2}] = -13.1 - log[CO_3^{-2}]$

$Log[PbOH^{+}] = -20.8 + pH - log[CO_3^{-2}]$

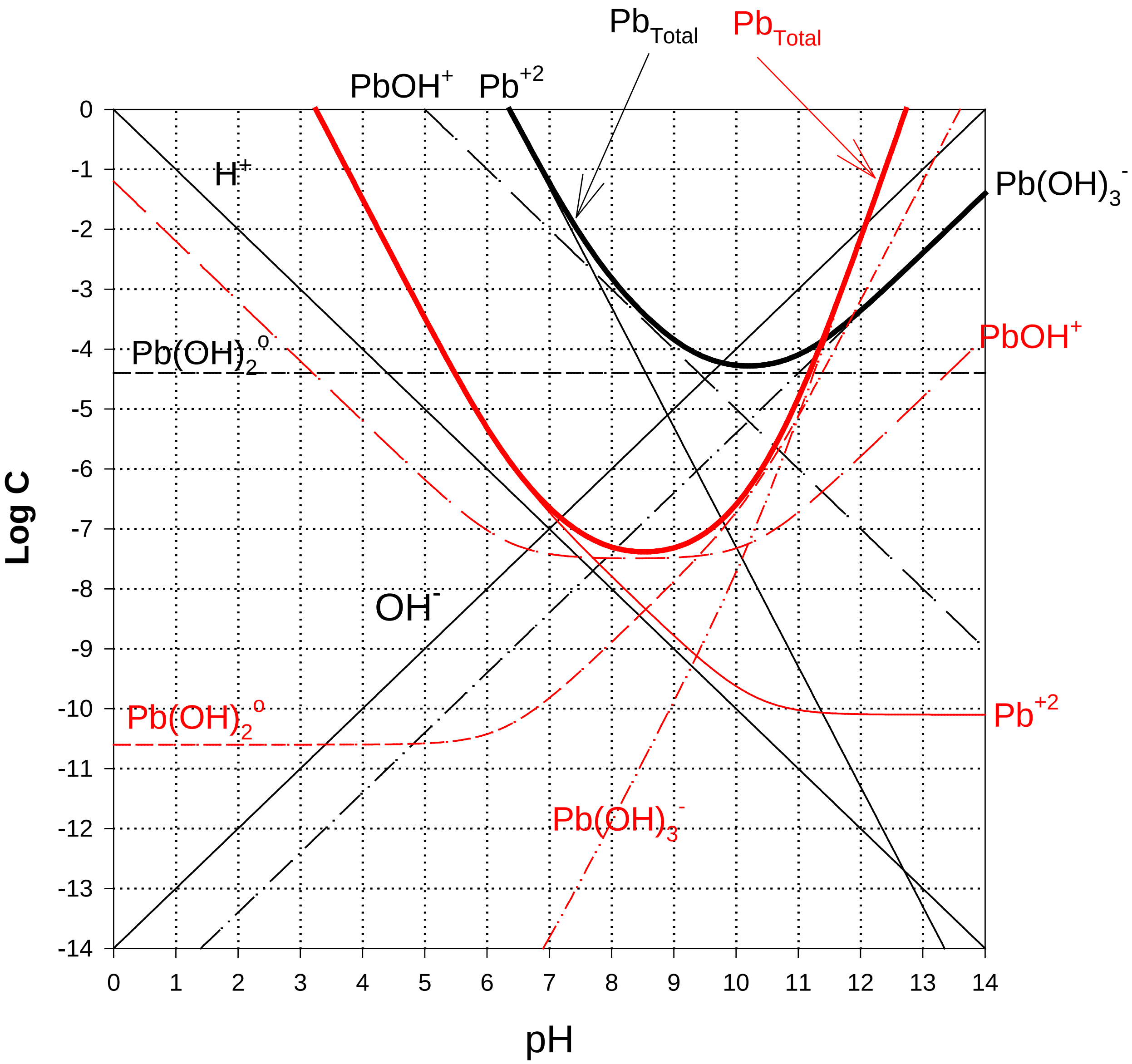
$Log[Pb(OH)_2] = -30.2 + 2pH - log[CO_3^{-2}]$

$Log\ [Pb(OH)_3] = -41.2 + 3pH - log[CO_3^{-2}]$

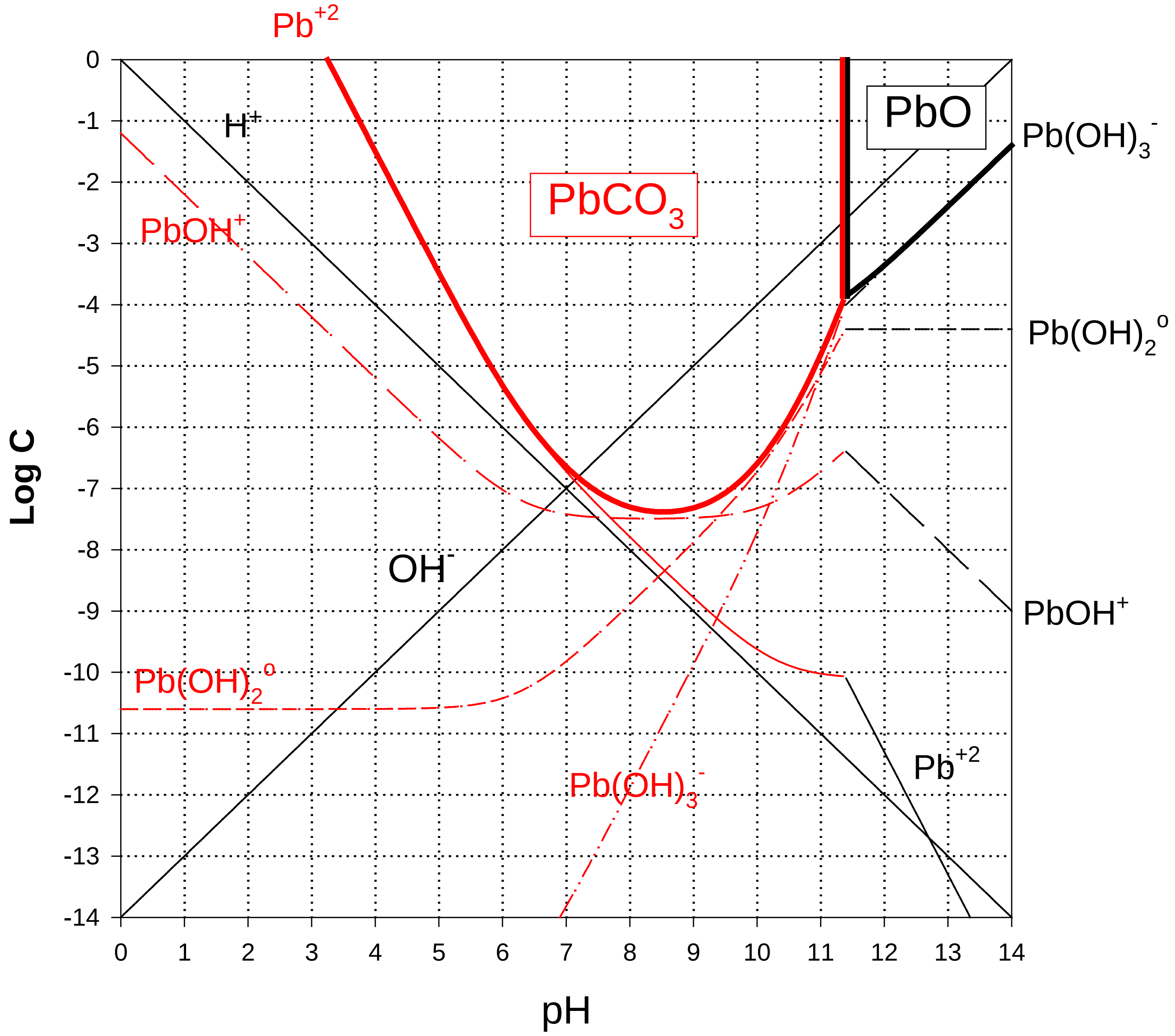


0
-1
-2
-3
-4
-5
-6
-7
-8
-9
-10
-11
-12
-13
-14
Log CO_{3T}
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
pH
#B3a
$PbCO_{3\ (s)}$
#B3b
#B4b
$Pb(OH)_3^-$
Pb^{+2}
$PbOH^+$
$PbO_{\ (s)}$
#B1
#B2
#A1
$Pb_T = 10^{-4}$ M

Answer to A.1.



PbTotal
PbTotal
PbOH+
Pb+2
H+
Pb(OH)3-
Pb(OH)2o
PbOH+
OH-
Pb(OH)2o
Pb+2
Pb(OH)3-
Log C
pH
0
-1
-2
-3
-4
-5
-6
-7
-8
-9
-10
-11
-12
-13
-14
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14



Answer to A.2.

Type A lines

First, lets consider the boundary between the aquo ion and the monohydroxide (**line A1**)

At this point the two are equal, so we can take both equations and set them equal:

$$\mathrm{Log}[Pb^{+2}] = \mathrm{Log}[PbOH^{+}]$$

$$+12.7 - 2pH = +5.0 - pH$$

$$pH = 12.7 - 5.0$$

$$pH = 7.7$$

following the same approach, we get the remaining A lines

A2:

$$\mathrm{Log}[PbOH^{+}] = \mathrm{Log}[Pb(OH)_2]$$

$$+5.0 - pH = -4.4$$

$$pH = 5.0 + 4.4$$

$$pH = 9.4$$

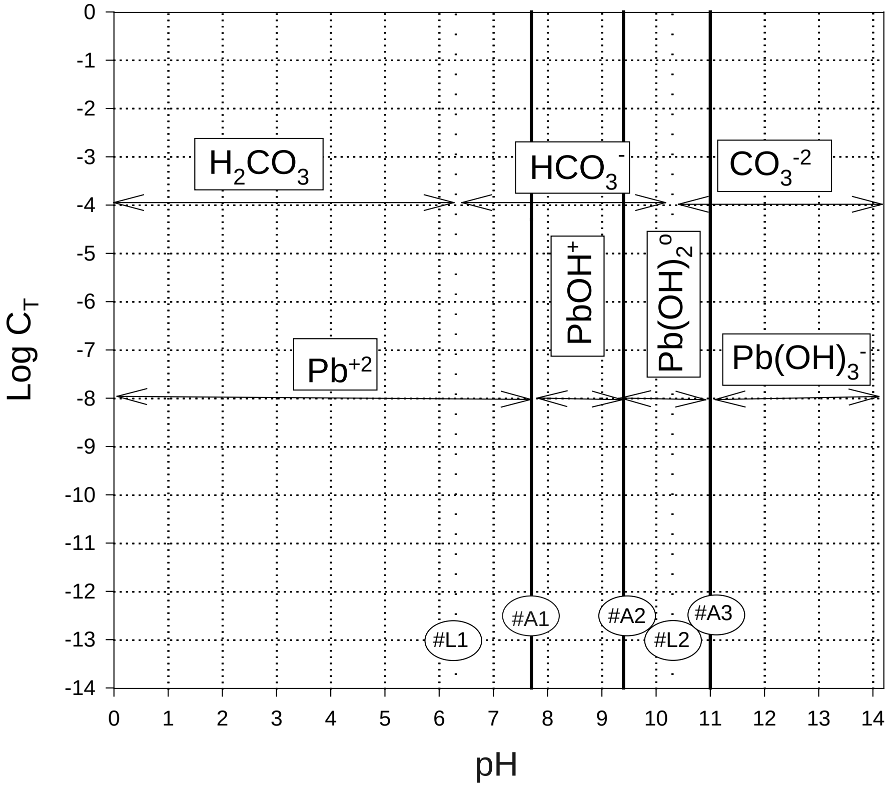
A3:

$$\mathrm{Log}[Pb(OH)_2] = \mathrm{Log}\ [Pb(OH)_3]$$

$$-4.4 = -15.4 + pH$$

$$pH = -4.4 + 15.4$$

$$pH = 11.0$$



Type B lines

First let's examine the hydroxide equilibria. By looking at the PbO solubility graph, its appears that only free lead (Pb^{+2}) and the trihydroxide ($Pb(OH)_3^-$) are the dominant soluble species in equilibrium with the hydroxide precipitate at a total soluble lead concentration of 10^{-4} M.

B1:

So, first let's look at the $Pb^{+2}/PbOH^{+}$ precipitate boundary. From the solubility product equation:

$$\text{Log}[PbOH^{+}] = +5.0 - pH$$

And presuming that this soluble species is the dominant one at the onset of precipitation, we set the concentration equal to the $Me_T = 10^{-4}M$:

$$-4 = +5.0 - pH$$

$$pH = 9$$

this is in the range where the monohydroxide predominates, so our assumption is correct.

B2:

Now let's look at the $Pb(OH)_3^{-}/PbO$ precipitate boundary. From the given solubility calculations, we have:

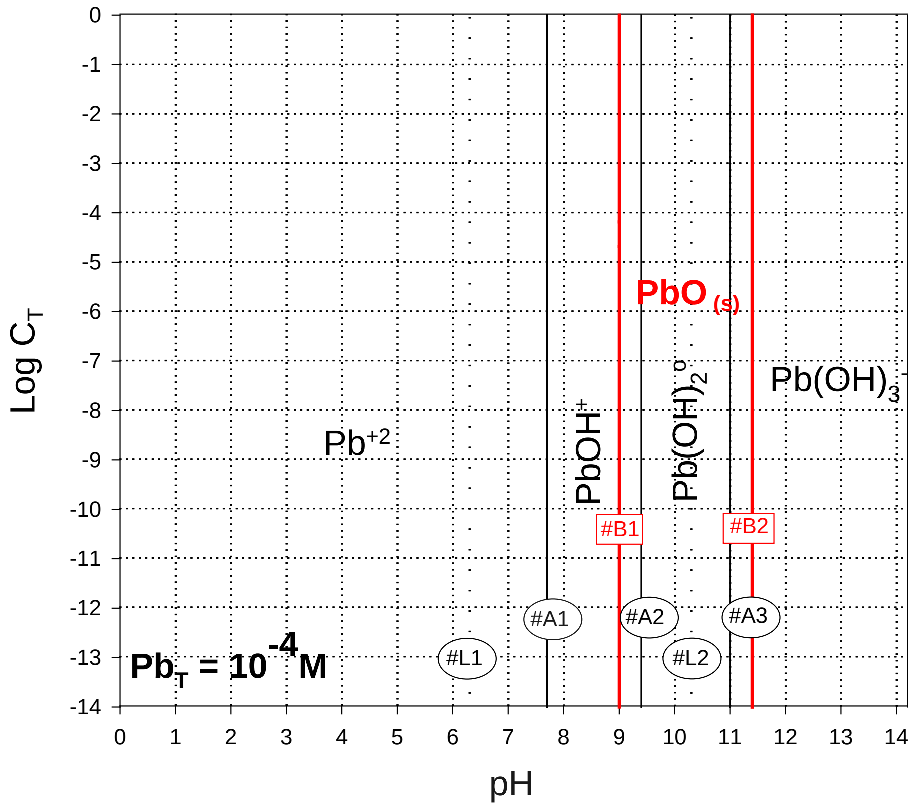
$$\text{Log}\ [Pb(OH)_3] = -15.4 + pH$$

And presuming that this soluble species is the dominant one at the onset of precipitation, we set the concentration equal to the $Me_T = 10^{-4}M$:

$$-4 = -15.4 + pH$$

$$pH = 11.4$$

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



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

B3

So, lets look at the $Pb^{+2}/PbCO_3$ boundary: We may need to develop as many as three line segments due to carbonate's pH dependence.:

For Carbonate Calculations:

$$\alpha_2 = \frac{1}{\frac{[H^+]^2}{K_1K_2} + \frac{[H^+]}{K_2} + 1}$$

For pH<6.3, $\alpha_2 \approx \frac{K_1K_2}{[H^+]^2}$, or $\log\alpha_2 \approx -16.6 + 2pH$

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

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

Now looking at the given equilibrium expression:

$$\text{Log}[Pb^{+2}] = -13.1 - \log[CO_3^{-2}]$$

And presuming that this soluble species is the dominant one at the onset of precipitation, we set the concentration equal to the $Me_T = 10^{-4}$M:

$$-4 = -13.1 - \log[CO_3^{-2}]$$

$$-4 = -13.1 - \log[C_T] - \log\alpha$$

$$\text{Log}[C_T] = -9.1 - \log\alpha$$

B3a:

Substituting in for the simplified logα at pH < 6.3

$$\text{Log}[C_T] = -9.1 - (-16.6 + 2pH)$$

$$\log[C_T] = +7.5 - 2pH, \quad @pH<6.3$$

B3b:

And for pH=6.3-10.3, we have:

$$\log[C_T] = -9.1 - (-10.3 + pH)$$

$$\log[C_T] = +1.2 - pH, \quad @pH<6.3\text{-}7.7$$

Note that this is only valid up to pH 7.7, the limit of free lead's predominance (A1 line)

Now we need to look at the $PbOH^+/PbCO_3$ 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:

B4

Now looking at the next given equilibrium expression:

$$\log[PbOH^+] = -20.8 + pH - \log[CO_3^{-2}]$$

And presuming that this soluble species is the dominant one at the onset of precipitation, we set the concentration equal to the $Me_T = 10^{-4}M$:

$$-4 = -20.8 + pH - \log[CO_3^{-2}]$$

$$-4 = -20.8 + pH - \log[C_T] - \log\alpha$$

$$\log[C_T] = -16.8 + pH - \log\alpha$$

B4b:

And for pH=6.3-10.3, we have:

$$\log[C_T] = -16.8 + pH - (-10.3 + pH)$$

$$\log[C_T] = -6.5, \quad @pH = 7.7\text{-}9.4$$

Note that this is only valid up to pH 9.4, the limit of lead monohydroxide's predominance (A2 line)

At this point, we're well into the PbO precipation zone, so let's look at the other side where lead carbonate may re-emerge at high pHs. This is beyond the A3 line, so we must consider the trihydroxide.

B5

Now looking at the final given equilibrium expression:

$$\text{Log}\ [Pb(OH)_3] = -41.2 + 3pH - \log[CO_3^{-2}]$$

And presuming that this soluble species is the dominant one at the onset of precipitation, we set the concentration equal to the $Me_T = 10^{-4}M$:

$$-4 = -41.2 + 3pH - \log[CO_3^{-2}]$$

$$-4 = -41.2 + 3pH - \log[C_T] - \log\alpha$$

$$\text{Log}[C_T] = -37.2 + 3pH - \log\alpha$$

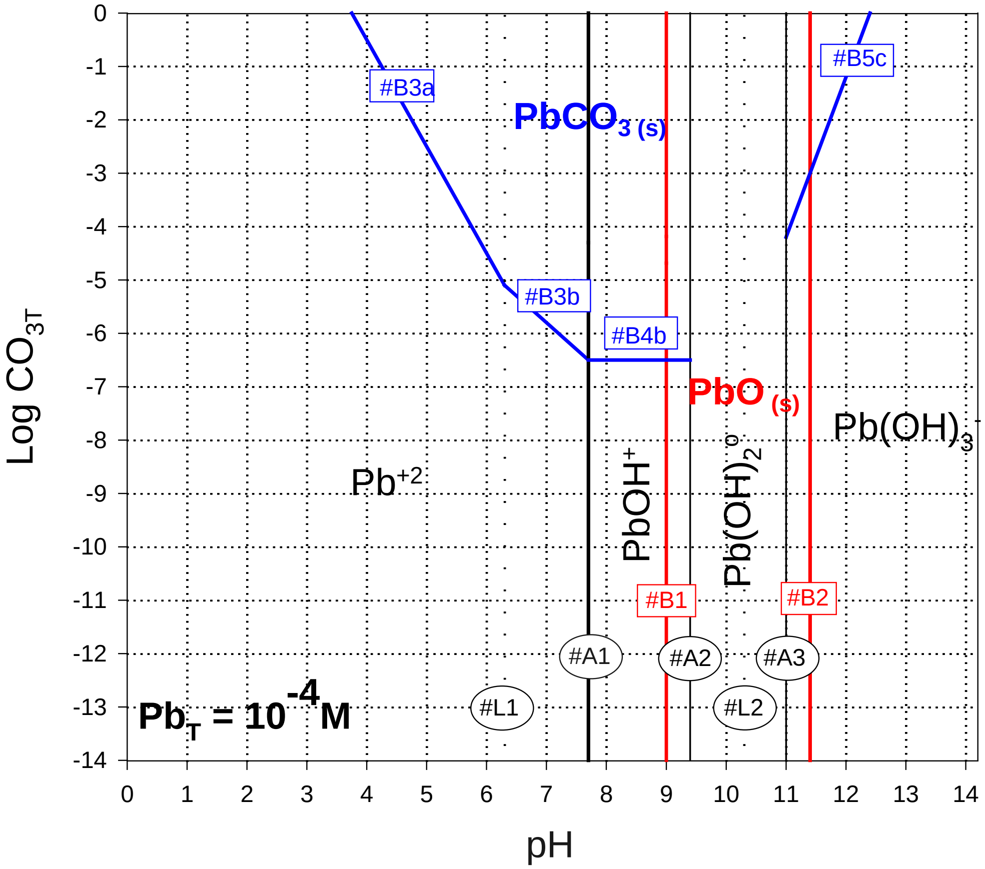
B5c:

And for pH> 10.3, we have:

$$\text{Log}[C_T] = -37.2 + 3pH - (0)$$

$$\log[C_T] = -37.2 + 3pH, \quad @pH > 11.0$$

Note that this is only valid beyond pH 11, the lower limit of lead trihydroxide's predominance (A3 line)



Type C lines

Finally, lets consider the boundary between the two solid phases. This line will start on the low pH side, were the B lines intersect (pH=9). This is well within the zone where bicarbonate is the dominant carbonate species.

To determine this, we can pick from any one of the matched equations. Each will give us the same answer, so let's just arbitrarily pick free lead. Now we set them equal to each other:

$$\mathrm{Log}[Pb^{+2}] = +12.7 - 2pH = \mathrm{Log}[Pb^{+2}] = -13.1 - \log[CO_3^{-2}]$$

$$+12.7 - 2pH = -13.1 - \log[CO_3^{-2}]$$

$$\log[CO_3^{-2}] = -25.8 + 2pH$$

or:

$$\log[C_T] = -25.8 + 2pH - \log\alpha$$

C1b:

And for pH=6.3-10.3, we have:

$$\mathrm{Log}[C_T] = -25.8 + 2pH - (-10.3 + pH)$$

$$\log[C_T] = -15.5 + pH, \quad @pH = 9.0\text{-}10.3$$

C1c:

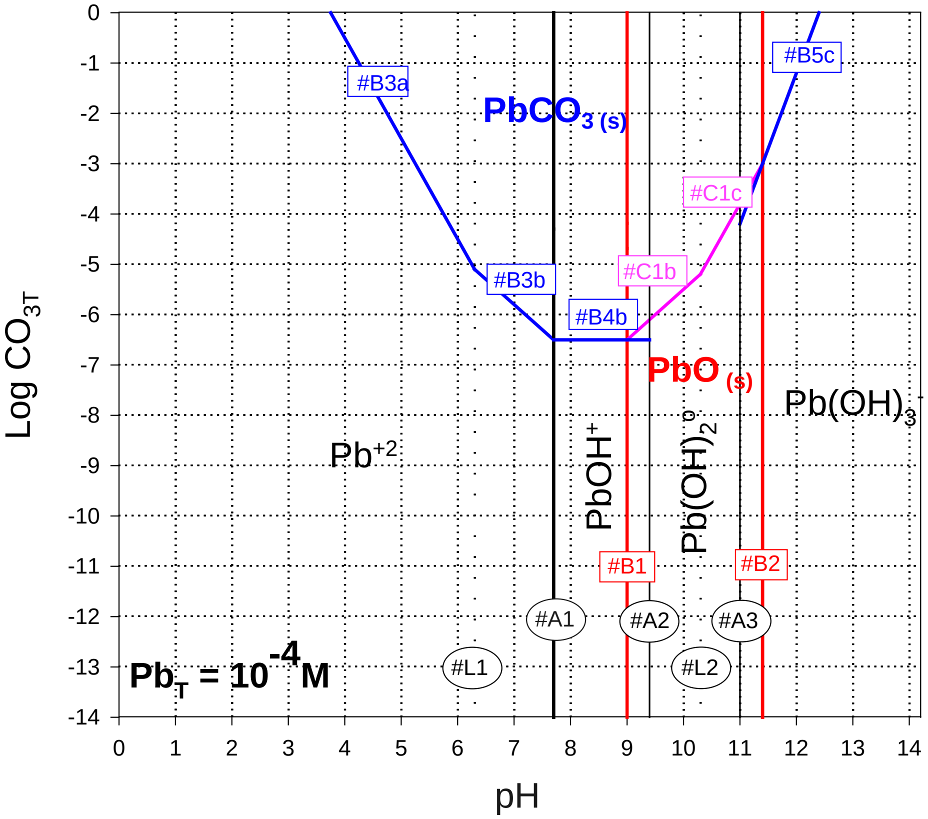
And for the carbonate zone; pH>10.3, we determined:

$$\mathrm{Log}[C_T] = -25.8 + 2pH - (0)$$

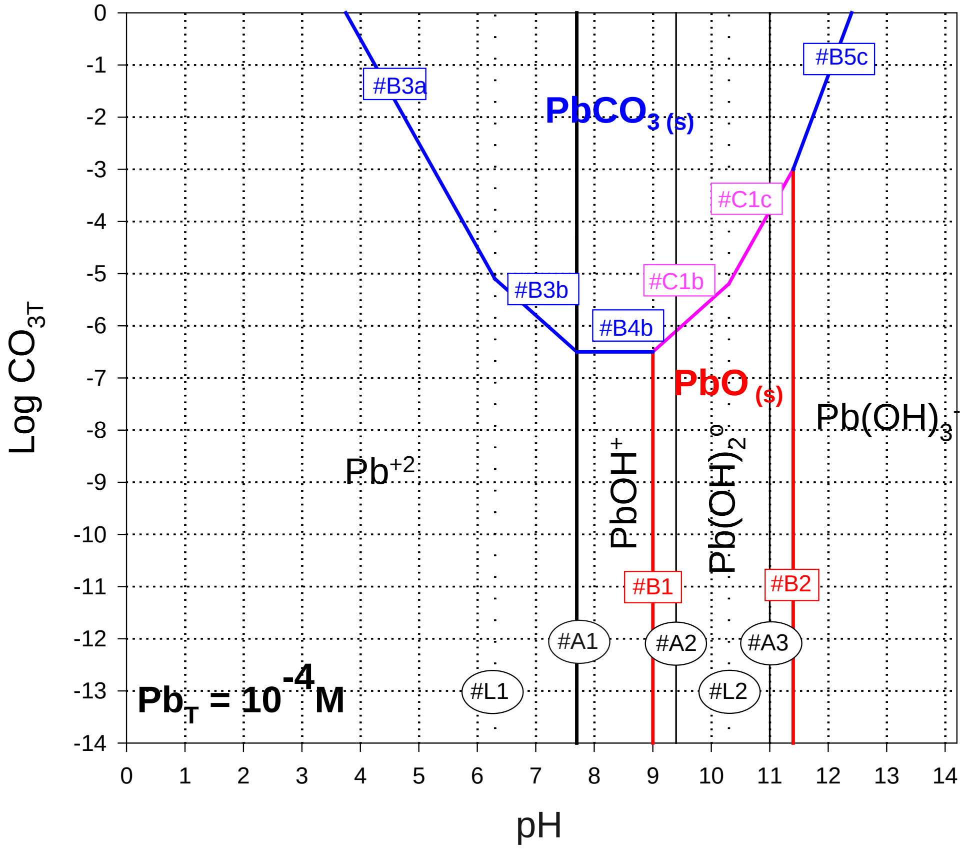
$$\mathrm{Log}[C_T] = -25.8 + 2pH, \quad @pH>10.3\text{-}11.4$$

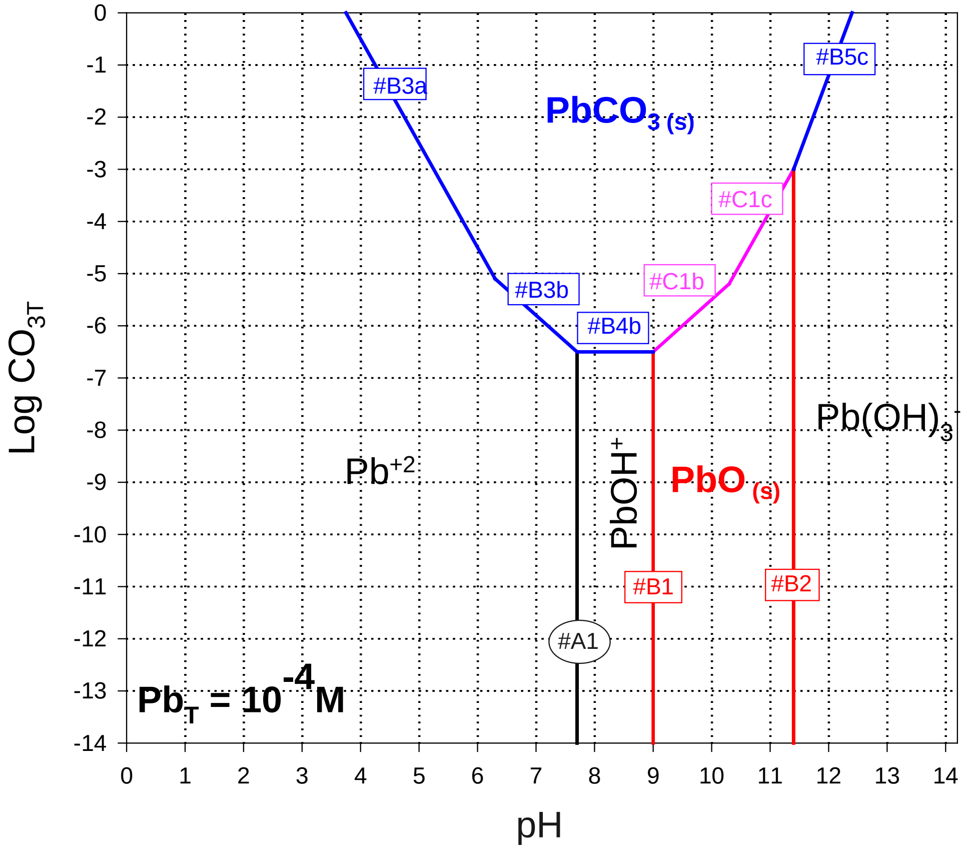
Note that this is only valid beyond pH 11.4, the upper limit of lead oxide's insolubility (B2 line)

The complete lines are as follows:

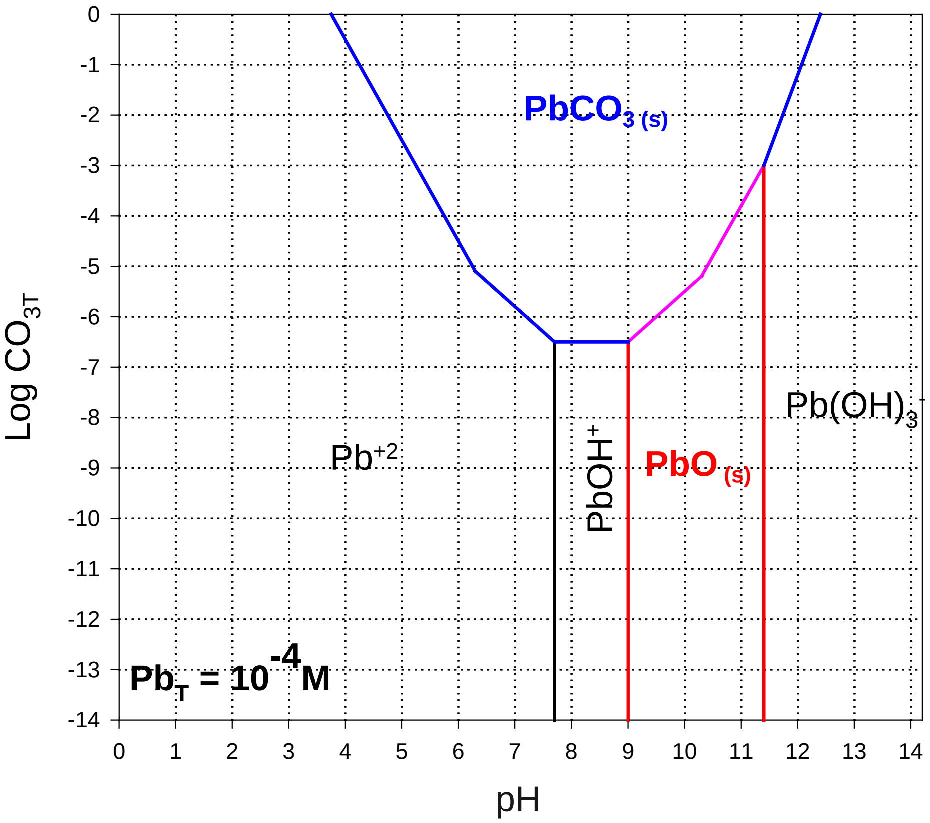


And removing extra line segments and lead species that do not exist at 0.1 mM concentration (e.g., those "under" the precipitates, we get the final diagram:


PbCO$_{3\,(s)}$
PbO $_{(s)}$
Pb^{+2}
PbOH$^+$
Pb(OH)$_2^o$
Pb(OH)$_3^-$
Pb$_T$ = 10^{-4}M
#B3a
#B3b
#B4b
#B5c
#C1b
#C1c
#B1
#B2
#A1
#A2
#A3
#L1
#L2
Log CO$_{3T}$
0
-1
-2
-3
-4
-5
-6
-7
-8
-9
-10
-11
-12
-13
-14
pH
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14



PbCO$_{3\,(s)}$
#B3a
#B3b
#B4b
#B5c
#C1b
#C1c
Pb^{+2}
PbOH^{+}
PbO$_{(s)}$
Pb(OH)$_3^-$
#A1
#B1
#B2
Pb$_T$ = 10^{-4}M
Log CO$_{3T}$
pH
0
-1
-2
-3
-4
-5
-6
-7
-8
-9
-10
-11
-12
-13
-14
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14



0
-1
-2
-3
-4
-5
-6
-7
-8
-9
-10
-11
-12
-13
-14
Log CO_{3T}
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
pH
$PbCO_{3\,(s)}$
Pb^{+2}
$PbOH^{+}$
$PbO_{(s)}$
$Pb(OH)_3^-$
$Pb_T = 10^{-4}M$

Some important equilibrium constants:

Equilibria	Log K
$Mg(OH)_{2\,(s)} = Mg^{+2} + 2OH^-$	-11.6
$Mg^{+2} + H_2O = MgOH^+ + H^+$	-11.44
$MgCO_{3\,(s)} = Mg^{+2} + CO_3^{-2}$	-7.5
$CaCO_{3(s)} = Ca^{+2} + CO_3^{-2}$	-8.34
$Ca(OH_2)_{(s)} = Ca^{+2} + 2OH^-$	-5.19
$CaSO_4 \cdot 2H_2O_{(s)} = Ca^{+2} + SO_4^{-2} + 2H_2O$	-4.62
$CaOH^+ = Ca^{+2} + OH^-$	-1.15
$FeCO_{3(s)} = Fe^{+2} + CO_3^{-2}$	-10.7
$AlOH^{+2} = Al^{+3} + OH^-$	-9.01
$CdOH^+ = Cd^{+2} + OH^-$	-3.92
$CoOH^+ = Co^{+2} + OH^-$	-4.80
$CuOH^+ = Cu^{+2} + OH^-$	-6.00
$HgOH^+ = Hg^{+2} + OH^-$	-10.60
$NiOH^+ = Ni^{+2} + OH^-$	-4.14
$PbOH^+ = Pb^{+2} + OH^-$	-6.29
$ZnOH^+ = Zn^{+2} + OH^-$	-5.04
$HgS_{(s)} = Hg^{+2} + S^{-2}$	-42.7

Some important half-cell reactions

Equ#	Half Cell Reaction	ΔE^o (Volts)
1	$O_2(aq) + 4H^+ + 4e^- = 2H_2O$	+1.23
2	$Mn^{+3} + e^- = Mn^{+2}$	+1.51
3	$Mn^{+4} + e^- = Mn^{+3}$	+1.65
4	$MnO_4^- + 8H^+ + 5e^- = Mn^{+2} + 4H_2O$	+1.49
5	$Fe^{+3} + e^- = Fe^{+2}$	+0.77
6	$Cu^{+2} + e^- = Cu^+$	+0.16
7	$\frac{1}{2}HOBr + \frac{1}{2}H^+ + e^- = \frac{1}{2}Br^- + \frac{1}{2}H_2O$	+1.33
8	$O_{3\,(g)} + 2H^+ + 2e^- = O_{2\,(g)} + H_2O$	+2.07
9	$Al^{+3} + 3e^- = Al_{(s)}$	-1.68
10	$\frac{1}{2}HOCl + \frac{1}{2}H^+ + e^- = \frac{1}{2}Cl^- + \frac{1}{2}H_2O$	+1.48
11	$\frac{1}{2}OCl^- + H^+ + e^- = \frac{1}{2}Cl^- + \frac{1}{2}H_2O$	+1.64
12	$BrO_3^- + 5H^+ + 4e^- = HOBr + 2H_2O$	+1.45
13	$\frac{1}{2}NH_2Cl + H^+ + e^- = \frac{1}{2}Cl^- + \frac{1}{2}NH_4^+$	+1.40
14	$Fe(OH)_{3(am)} + 3H^+ + e^- = Fe^{+2} + 3H_2O$	+0.95
15	$SO_4^{-2} + 9H^+ + 8e^- = HS^- + 4H_2O$	+0.25
16	$S_{(s)} + 2H^+ + 2e^- = H_2S_{(g)}$	+0.17
17	$Zn^{+2} + 2e^- = Zn(s)$	-0.76
18	$Ni^{+2} + 2e^- = Ni(s)$	-0.24
19	$Pb^{+2} + 2e^- = Pb(s)$	-0.126
20	$ClO_2 + e- = ClO_2-$	+0.95
21	$PbO_2(s) + 4H^+ + 2e^- = Pb^{+2} + 2H_2O$	+1.451

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
Iron	Fe	26	55.845	0,2,3	1.83
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
Lead	Pb	82	207.19	2,4	

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

NAME	FORMULA	pK_a
Perchloric acid	$HClO_4 = H^+ + ClO_4^-$	-7
Hydrochloric acid	$HCl = H^+ + Cl^-$	-3
Sulfuric acid	$H_2SO_4 = H^+ + HSO_4^-$	-3
Nitric acid	$HNO_3 = H^+ + NO_3^-$	0
Bisulfate ion	$HSO_4^- = H^+ + SO_4^{-2}$	2
Phosphoric acid	$H_3PO_4 = H^+ + H_2PO_4^-$	2.15
o-Phthalic acid	$C_6H_4(COOH)_2 = H^+ + C_6H_4(COOH)COO^-$	2.89
p-Hydroxybenzoic acid	$C_6H_4(OH)COOH = H^+ + C_6H_4(OH)COO^-$	4.48
Nitrous acid	$HNO_2 = H^+ + NO_2^-$	4.5
Acetic acid	$CH_3COOH = H^+ + CH_3COO^-$	4.75
Aluminum ion	$Al(H_2O)_6^{+3} = H^+ + Al(OH)(H_2O)_5^{+2}$	4.8
Carbonic acid	$H_2CO_3 = H^+ + HCO_3^-$	6.35
Hydrogen sulfide	$H_2S = H^+ + HS^-$	7.02
Dihydrogen phosphate	$H_2PO_4^- = H^+ + HPO_4^{-2}$	7.2

Hypochlorous acid	$HOCl = H^+ + OCl^-$	7.5
Hypobromous acid	$HOBr = H^+ + OBr^-$	8.71
Ammonium ion	$NH_4^+ = H^+ + NH_3$	9.24
Bicarbonate ion	$HCO_3^- = H^+ + CO_3^{-2}$	10.33
Monohydrogen phosphate	$HPO_4^{-2} = H^+ + PO_4^{-3}$	12.3
Sulfide	$HS^- = H^+ + S^{-2}$	13.9

Atmospheric Gases

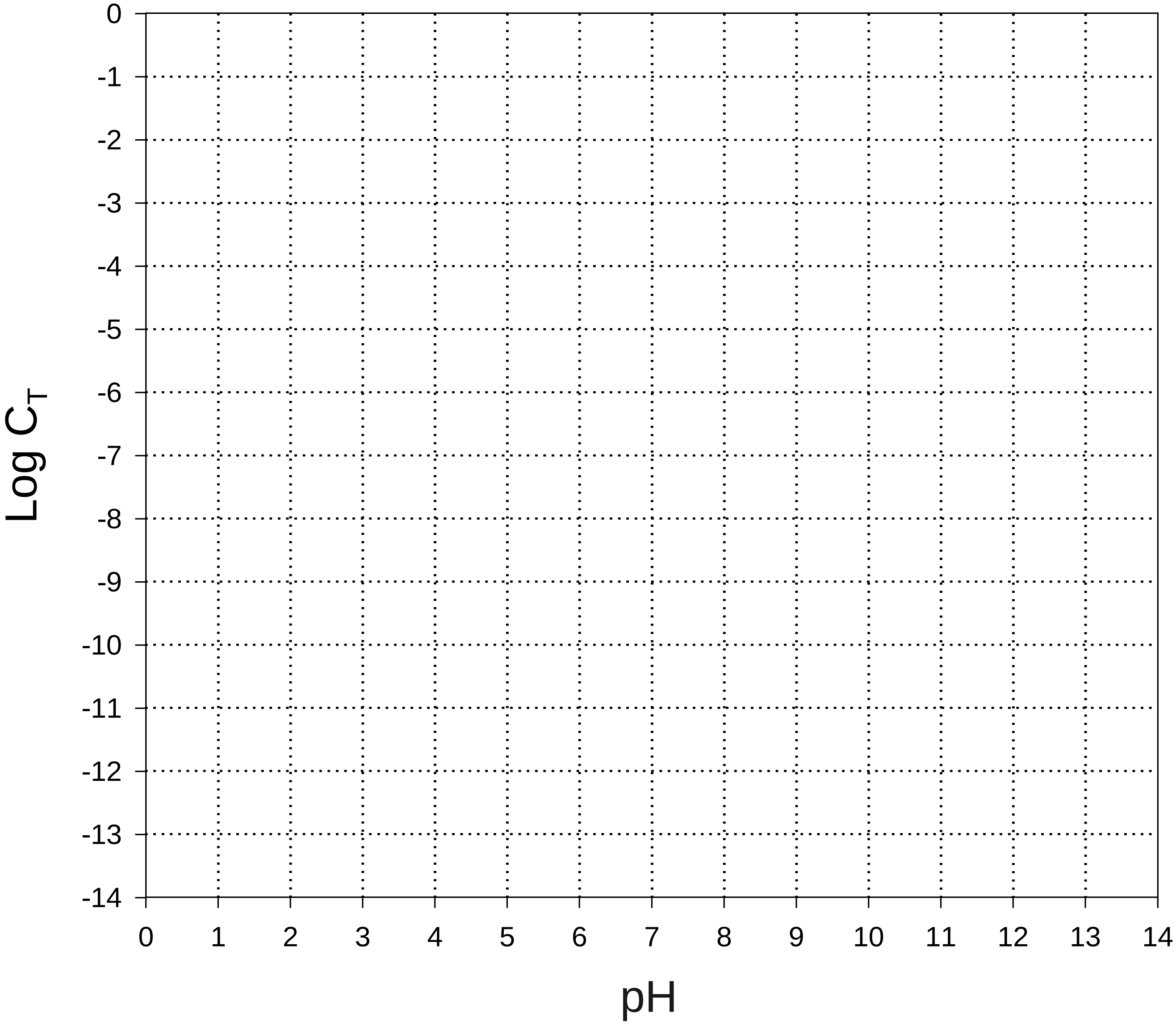
Gas	Atmospheric Abundance	Henry's Law Const[3]
Nitrogen (N_2)	780,840 ppmv (78.084%)	6.1×10^{-4}
Oxygen (O_2)	209,460 ppmv (20.946%)	1.3×10^{-3}
Argon (Ar)	9,340 ppmv (0.9340%)	1.4×10^{-3}
Carbon dioxide (CO_2)	387 ppmv (0.0387%)	3.4×10^{-2}
Neon (Ne)	18.18 ppmv (0.001818%)	4.5×10^{-4}
Helium (He)	5.24 ppmv (0.000524%)	3.7×10^{-4}
Methane (CH_4)	1.79 ppmv (0.000179%)	
Krypton (Kr)	1.14 ppmv (0.000114%)	
Hydrogen (H_2)	0.55 ppmv (0.000055%)	7.8×10^{-4}
Nitrous oxide (N_2O)	0.3 ppmv (0.00003%)	
Xenon (Xe)	0.09 ppmv (9×10^{-6}%)	

α_2 for a diprotic acid:

$$\alpha_2 = \frac{1}{\frac{[H^+]^2}{K_1K_2} + \frac{[H^+]}{K_2} + 1}$$

---

[3] In: moles/L/atm


0
-1
-2
-3
-4
-5
-6
-7
-8
-9
-10
-11
-12
-13
-14
Log C_T
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
pH