CEE 543 Aut 2011 Final Exam

Solubility product values at 25°C: $\log {}^{*}K_{s0} = 13.49$ for $Fe(OH)_2(s)$; $\log K_{s0} = -10.59$ for $FeCO_3(s)$; $\log K_{s0} = -8.48$ for $CaCO_3(s)$;

Acidity constants at 25°C: $pK_{a1} = 9.40$ for Fe^{2+}; ignore pK_{a2} and pK_{a3}; $pK_{a1} = 6.35$ and $pK_{a2} = 10.33$ for H_2CO_3.

Henry's constant at 25°C: 29.4 atm/(mol/L) for $CO_2(g)$

$pe^{o} = 21.50$ for the reaction: $O_2(aq) + 4H^{+} + 4e^{-} \rightarrow 2 H_2O$

$pe^{o} = 18.154$ for the reaction: $SeO_4^{2-} + 3H^{+} + 2e^{-} \rightarrow HSeO_3^{-} + H_2O$

1. (30) A solution that is well-buffered at pH 8.4 contains $2 \times 10^{-4} M$ TOTFe(II) and $10^{-4} M$ TOTCO$_3$.

   (a) (15) Do you expect either $FeCO_3(s)$ or $Fe(OH)_2(s)$, or both, to begin precipitating, based on the initial solution composition?
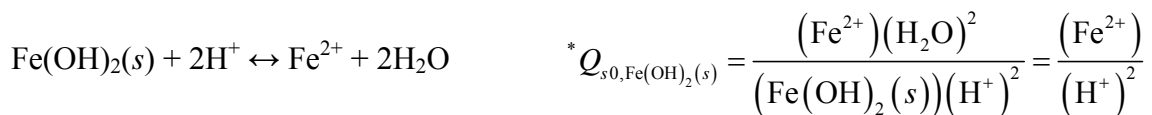
   (b) (15) For this part of the problem, consider the possible precipitation of $FeCO_3(s)$, but assume that $Fe(OH)_2(s)$ does not precipitate, even if it is supersaturated. If you determined in part *a* that $FeCO_3(s)$ is likely to precipitate, write out the equations and describe the steps that would need to be taken to determine the equilibrium composition of the solution. If you determined that $FeCO_3(s)$ does not precipitate from the initial solution, write out the equations and describe the steps that would need to be taken to determine how much $FeCl_2$ must be added to cause the solid to form. Assume ideal solute behavior.
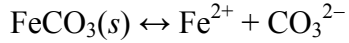
Answer. (a) The pH of the solution is one unit below pK_{a1} for Fe^{2+}, so the concentration of Fe^{2+} is 10 times that of $FeOH^{+}$ and is 10/11 of TOTFe(II). The pH is in a range where almost all the TOTCO$_3$ is present as HCO_3^{-}, so the CO_3^{2-} concentration can be approximated based on the K_{a2} expression for H_2CO_3. Thus,

$$\left(Fe^{2+}\right) = \frac{10}{11} TOTFe = 1.82 \times 10^{-4}$$

$$\left(CO_3^{2-}\right) = \frac{\left(HCO_3^{-}\right) K_{a2}}{\left(H^{+}\right)} \approx \frac{\left(10^{-4}\right)\left(10^{-10.33}\right)}{10^{-8.4}} = 10^{-5.93} = 1.17 \times 10^{-6}$$

The reactions and activity quotient expressions for the dissolution of the two solids are:

$$Fe(OH)_2(s) + 2H^{+} \leftrightarrow Fe^{2+} + 2H_2O \qquad {}^{*}Q_{s0,Fe(OH)_2(s)} = \frac{\left(Fe^{2+}\right)\left(H_2O\right)^2}{\left(Fe(OH)_2(s)\right)\left(H^{+}\right)^2} = \frac{\left(Fe^{2+}\right)}{\left(H^{+}\right)^2}$$

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$$FeCO_3(s) \leftrightarrow Fe^{2+} + CO_3^{2-} \qquad\qquad Q_{s0,FeCO_3(s)} = \left(Fe^{2+}\right)\left(CO_3^{2-}\right)$$

Inserting appropriate values into the activity quotient expressions, we find:

$$^*Q_{s0,Fe(OH)_2(s)} = \frac{\left(Fe^{2+}\right)}{\left(H^+\right)^2} = \frac{1.82x10^{-4}}{\left(10^{-8.5}\right)^2} = 1.82x10^{13} = 10^{13.26} < {}^*K_{s0,Fe(OH)_2(s)}$$

$$Q_{s0,FeCO_3(s)} = \left(Fe^{2+}\right)\left(CO_3^{2-}\right) = \left(1.82x10^{-4}\right)\left(1.17x10^{-6}\right) = 2.14x10^{-10} = 10^{-9.57} > K_{s0,FeCO_3(s)}$$

Thus, Fe(OH)$_2$(s) is undersaturated and will not precipitate, whereas FeCO$_3$(s) is supersaturated and will precipitate.

(b) The expressions required to determine the solution composition comprise a combination of mass balances and equilibrium expressions. The problem statement indicates that the solution is well-buffered at pH 8.4, so the α values for Fe^{2+} and CO$_3^{2-}$ in the equilibrated solution will be the same as those computed in part a; i.e., (Fe^{2+})/TOTFe(II) will be 10/11, or 0.91, and

(CO$_3^{2-}$)/TOTCO$_3$ will be approximately $\dfrac{10^{-10.33}}{10^{-8.4}} = 10^{-1.93}$. Combining this information with mass

balances that indicate that the total dissolved concentrations of Fe(II) and CO$_3$ after precipitation of the solid will equal the corresponding initial total dissolved concentrations minus the concentration of FeCO$_3$(s) that forms, we can write:

$$\left(Fe^{2+}\right) = \frac{10}{11} TOTFe_{diss} = \frac{10}{11}\left\{2x10^{-4} - \left[FeCO_3\left(s\right)\right]\right\}$$

$$\left(CO_3^{2-}\right) \approx 10^{-1.93} TOTCO_{3,diss} = 10^{-1.93}\left\{10^{-4} - \left[FeCO_3\left(s\right)\right]\right\}$$

$$\left(Fe^{2+}\right)\left(CO_3^{2-}\right) = K_{s0} = 10^{-10.59}$$

$$\left[\frac{10}{11}\left\{2x10^{-4} - \left[FeCO_3\left(s\right)\right]\right\}\right]\left[10^{-1.93}\left\{10^{-4} - \left[FeCO_3\left(s\right)\right]\right\}\right] = 10^{-10.59}$$

The final equation has the concentration of FeCO$_3$(s) as the only unknown, so it can be solved to determine that value. The mass balances noted above can then be solved to determine TOTFe(II) and TOTCO$_3$, and those values can be used in conjunction with the α values to determine the concentrations of the individual species.

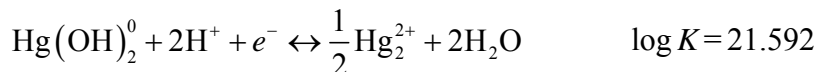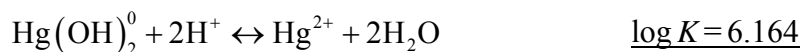2. (25) Dissolved mercury in the +I oxidation state is unusual in that it is present primarily as a dimer, Hg$_2^{2+}$.

(a) (10) Write out the 'pe° half-reaction' for forming this species by reduction of Hg^{2+}. The value of pe° for this half-reaction is 15.428.

(b) (15) As you might recall, the default species for Hg(II) in Visual Minteq is $Hg(OH)_2^0$. A portion of the tableau for a system containing Hg in the +1 and +2 oxidation states is shown below, using H_2O, H^+, e^-, and $Hg(OH)_2^0$ as components. Fill in all the values on the Hg_2^{2+} row. (Note that this tableau has been prepared without considering the dummy species $\overline{Hg_2^{2+}/Hg^{2+}}$, so it is not the tableau that would be generated in Visual Minteq.)

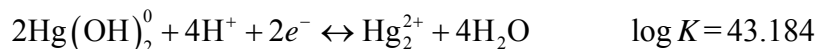|	H_2O	H^+	e^-	$Hg(OH)_2^0$	$\log K$
Hg^{2+}	−2	2	0	1	6.164
Hg_2^{2+}					

Answer. (a) The 'pe° half-reaction' is the reduction half-reaction written for a stoichiometry such that one electron is consumed. That reaction and corresponding equilibrium constant (given in the problem statement) is:

$$Hg^{2+} + e^- \leftrightarrow \frac{1}{2} Hg_2^{2+} \qquad \log K = pe° = 15.428$$
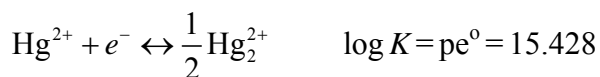
(b) In the tableau, the reaction forming Hg_2^{2+} must be written using the component $Hg(OH)_2^0$ as a reactant, but the reaction in part a shows formation of Hg_2^{2+} using Hg^{2+} as the reactant. To derive the desired reaction and corresponding equilibrium constant, we need to add the reaction in part a to the reaction represented the first row of the tableau. The summation can be represented as follows:

$$Hg^{2+} + e^- \leftrightarrow \frac{1}{2} Hg_2^{2+} \qquad\qquad \log K = 15.428$$

$$\underline{Hg(OH)_2^0 + 2H^+ \leftrightarrow Hg^{2+} + 2H_2O} \qquad\qquad \underline{\log K = 6.164}$$

$$Hg(OH)_2^0 + 2H^+ + e^- \leftrightarrow \frac{1}{2} Hg_2^{2+} + 2H_2O \qquad \log K = 21.592$$

Finally, we note that the reaction in the tableau must be written for formation of one molecule or mole of the species of interest, in this case Hg_2^{2+}. We can write that reaction by doubling the one derived above, i.e.:

$$2Hg(OH)_2^0 + 4H^+ + 2e^- \leftrightarrow Hg_2^{2+} + 4H_2O \qquad \log K = 43.184$$

This result is incorporated into the tableau as follows:

	H_2O	H^+	e^-	$Hg(OH)_2^0$	$\log K$
Hg^{2+}	-2	2	0	1	6.164
Hg_2^{2+}	-4	4	2	2	43.184

3. (45) Selenium (Se) is a trace element present in natural systems that is a required nutrient for plants but can be toxic at high concentrations. The chemistry of selenium is similar to that of sulfur, and it can be present in the $-II$, $+IV$, and $+VI$ oxidation states. A $\log c - pe$ diagram is shown below for a solution at pH 8.4 containing $10^{-4}\,M\ TOT$Se. The selenium is initially split evenly between the $+IV$ and $+VI$ oxidation states (i.e., as selenite and selenate species, respectively). pK_{a2} for H_2SeO_3 is 8.4, so that the curves for $HSeO_3^-$ and SeO_3^{2-} overlap. pK_{a1} for H_2SeO_4 is <0. The initial solution contains 6 mg/L $O_2(aq)$.

(a) (30) Assuming the pH remains constant, estimate the pe and the concentrations of SeO_3^{2-} and $HSeO_3^-$ at equilibrium.

(b) (15) If the redox reaction reaches equilibrium, how much will the alkalinity increase or decrease, and how large will the change be, expressed in mg/L as $CaCO_3$? (Note: If you don't have an answer for part a, make a reasonable guess for pe and answer this question based on that guess.)

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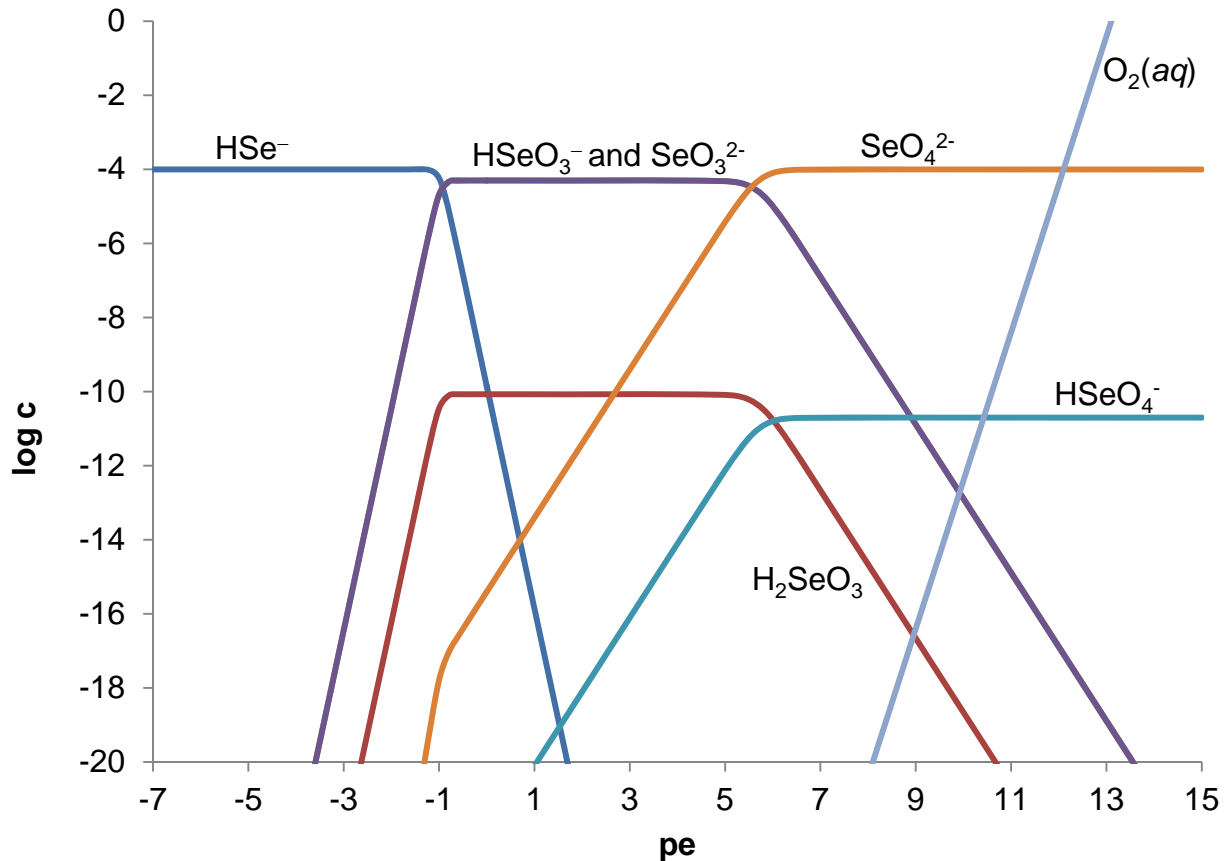
Answer. (a) The oxidation state of Se in the selenite species (H_2SeO_3, $HSeO_3^-$, and SeO_3^{2-}) is +IV, and that of Se in the selenate species species (H_2SeO_4, $HSeO_4^-$, and SeO_4^{2-}) is +VI. Because the pH remains constant, the $\log c - pe$ diagram will apply to the equilibrated solution as well as the initial solution. The problem statement indicates that the initial solution contains $2.5 \times 10^{-5}\,M$ each of $HSeO_4^-$ and SeO_3^{2-} and $5.0 \times 10^{-5}\,M$ SeO_4^{-5}, along with the dissolved oxygen, which has a molar concentration of

$$\left(O_2\left(aq\right)\right) = \frac{6\text{ mg/L}}{32{,}000\text{ mg/mol}} = 1.875 \times 10^{-4}\,M$$

There are at least two, equivalent approaches for determining the equilibrium pe, both of which will be presented. The first approach involves preparing the system tableau and solving the *TOTe* equation in conjunction with the $\log c - pe$ diagram. To prepare the tableau, we need to choose a component set. The choice of which selenium species to use as a component is arbitrary, although it makes sense to choose a species that is dominant over at least some range of pe values; for oxygen, the only reasonable choice is H_2O, because it is the dominant oxygen-containing species in the system under all conditions. The tableau using SeO_4^{2-}, H_2O, H^+, and e^- as components is shown below. Because we only need to solve the *TOTe* equation, only the data in the e^- column is needed. We can therefore combine all the Se(IV) species in a single row, and do the same for the Se(VI) species.

| | Stoichiometric Coefficient | | | | |
	H_2O	SeO_4^{2-}	H^+	e^-	Conc'n
Species					
H^+	0	1	1	0	
$H_mSeO_4{}^{m-2}$	0	1	m	0	
OH^-	1	0	−1	0	
$H_nSeO_3{}^{n-2}$	−1	1	n	2	
$O_2(aq)$	2	0	-4	-4	
Inputs					
$H_mSeO_4{}^{m-2}$	0	1	m	0	$5.0x10^{-5}$
$H_nSeO_3{}^{n-2}$	−1	1	n	2	$5.0x10^{-5}$
$O_2(aq)$	2	0	-4	-4	$1.875x10^{-4}$

Based on this tableau, the *TOTe* equation is

$$2\left[TOT\text{Se}(IV)\right]-4\left[O_2(aq)\right]=2\left(5.0x10^{-5}\right)-4\left(1.875x10^{-4}\right)$$

$$2\left[TOT\text{Se}(IV)\right]+7.4x10^{-4}=4\left[O_2(aq)\right]$$

$$2\left[TOT\text{Se}(IV)\right]+10^{-3.13}=4\left[O_2(aq)\right]$$

Scanning the $\log c - $pe diagram, we see that this equation is solved at a relatively high pe where *TOT*Se(IV) is much less than $10^{-3.13}$. As a result, the equilibrium pe is approximately at the point where $[O_2(aq)]$ equals, $10^{-3.13}/4$, or $10^{-3.73}$. If we had the spreadsheet that was used to prepare the diagram, it would be easy to identify this pe accurately. Alternatively, we could insert the known value of $[O_2(aq)]$ into the Nernst equation to solve for the pe. However, for the exam, it is satisfactory to note that the equilibrium pe will be slightly higher than that at the intersection of the lines representing $[O_2(aq)]$ and SeO_4^{2-} (because, at that intersection point, $[O_2(aq)]$ is 10^{-4}). The remaining parts of this question are answered after the alternative approach for determining the equilibrium pe is presented.

The alternative approach for finding the equilibrium pe involves representing the inputs as an equivalent mixture of oxidized species and electrons. The equilibration process can then be represented as though the available electrons combine with the oxidized species sequentially, from the strongest to weakest oxidant, until all the available electrons have been consumed. Thus, considering for now only the total concentrations in each oxidation state, we can think of the inputs as

$$1.00 \times 10^{-4} M \text{ Se}(\text{VI}) \qquad + 1.0 \times 10^{-4} M \ e^{-}$$

$$3.75 \times 10^{-4} M \text{ O}(0)$$
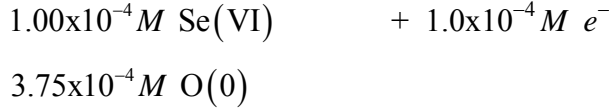
The $\log c - \text{pe}$ diagram shows that the initial $O_2(aq)$ concentration would be the equilibrium concentration at a pe near 12, and that under those conditions, essentially all the Se is in the +VI state (primarily as SeO_4^{2-}, with a negligible concentration of $HSeO_4^{-}$). If the pe declines even one or two units below 12, essentially all of the $O_2(aq)$ disappears, due to the reduction of O(0) to O(−II) in the form of H_2O and OH^{-}, while the overwhelming majority of the Se remains as Se(+VI). Thus, $O_2(aq)$ is a stronger oxidant than Se(VI) species, and it will be reduced first.

Because two moles of electrons are required to reduce each mole of O(0), complete reduction of the O(0) in the initial solution would consume $7.5 \times 10^{-4} M \ e^{-}$. However, only $1.0 \times 10^{-4} M \ e^{-}$ are available, so only $0.5 \times 10^{-4} M \text{ O}(0)$, corresponding to $0.25 \times 10^{-4} M \text{ O}_2(aq)$, is actually reduced, leaving $1.625 \times 10^{-4} M \text{ O}_2(aq)$ in solution. The pe in the equilibrated solution can be computed by applying the Nernst equation in conjunction with this value:

$$\text{pe} = \text{pe}^{o} - \frac{1}{4}\log\frac{(H_2O)}{\left(O_{2(aq)}\right)} - \frac{4}{4}\text{pH} = 21.50 - \frac{4}{4}\log\frac{1.0}{1.625 \times 10^{-4}} - 8.5 = 12.053$$

As noted above and as is clear from the diagram, essentially all of the Se is in the +VI oxidation state at this pe and is present as SeO_4^{2-}. The reaction for the reduction of SeO_4^{2-} to $HSeO_3^{-}$ is given in the problem statement, and pe^{o} for this reaction is given as 18.154. We can apply the Nernst equation to that reaction, now with the known pe computed based on the $O_2(aq)/H_2O$ couple, to find:

$$12.053 = 18.154 - \frac{1}{2}\log\frac{\left(HSeO_3^{-}\right)}{\left(SeO_4^{2-}\right)} - \frac{3}{2}\text{pH}$$

$$\log\left(HSeO_3^{-}\right) = -2\left(12.053 - 18.154 + \frac{3}{2}\text{pH}\right) + \log\left(SeO_4^{2-}\right)$$
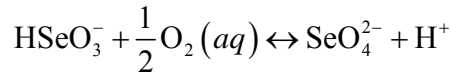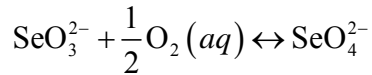
$$= -2\left(12.053 - 18.154 + \frac{3}{2}(8.5)\right) + (-4)$$

$$= -17.298$$

$$\left(HSeO_3^{-}\right) = 5.03 \times 10^{-18} M$$

Because, at the pH of the solution, the SeO_3^{2-} and $HSeO_3^{-}$ concentrations are equal, the concentration of SeO_3^{2-} is also $5.03 \times 10^{-18} M$.

(b) The reactions that take place as equilibrium is approached can be written as

$$SeO_3^{2-} + \frac{1}{2}O_2(aq) \leftrightarrow SeO_4^{2-}$$

$$HSeO_3^- + \frac{1}{2}O_2(aq) \leftrightarrow SeO_4^{2-} + H^+$$

The result in part a indicates that, to a good approximation, the overall reaction destroys $2.5 \times 10^{-5} M$ Se(IV) by each of the above reactions. Correspondingly, based on the stoichiometry, the net effect is that the reactions destroy $2.5 \times 10^{-5} M$ each of $HSeO_3^-$, SeO_3^{2-}, and $O_2(aq)$ and generate $5.0 \times 10^{-5} M$ SeO_4^{2-} and $2.5 \times 10^{-5} M$ H^+.

To assess the effect of these reactions on the alkalinity, we need to know the dominant species in each oxidation state at the endpoint of the alkalinity titration. To identify the species, we need to know K_{a1} for H_2SeO_3 and K_{a2} for H_2SeO_4. Both of these values can be determined from the information in the $\log c - $ pe diagram, along with the known pH of the solution (8.5). For example, at high pe, the concentrations of $HSeO_4^-$ and SeO_4^{2-} are approximately $10^{-11.0}$ and $10^{-4} M$, respectively, so

$$K_{a2,H_2SeO_4} = \frac{\left(10^{-4.0}\right)\left(10^{-8.5}\right)}{10^{-11.0}} = 10^{-1.5}$$

Similarly, at pe near 3, the concentrations of H_2SeO_3 and $HSeO_3^-$ are approximately $10^{-10.3}$ and $5.0 \times 10^{-5} M$, respectively, so

$$K_{a1,H_2SeO_3} = \frac{\left(5.0 \times 10^{-5}\right)\left(10^{-8.5}\right)}{10^{-10.3}} = 10^{-2.50}$$

These K_a values indicate that, at the alkalinity endpoint of pH 4.5, essentially all the Se(IV) is present as $HSeO_3^-$, and all the Se(VI) is present as SeO_4^{2-}. Correspondingly, each mole of SeO_3^{2-} in a solution contributes one equivalent of alkalinity (because it combines with one mole of H^+ during the alkalinity titration), whereas $HSeO_3^-$ and SeO_4^{2-} contribute no alkalinity (because these species do not consume or release H^+ when the solution is titrated to the alkalinity endpoint). Combining this information with the net, overall changes in solution composition identified above, we can write:

Destruction of $5.0 \times 10^{-5} M$ SeO_3^{2-} destroys 5.0×10^{-5} equiv/L alkalinity

Destruction of $5.0 \times 10^{-5} M$ $HSeO_3^-$ has no effect on alkalinity

Destruction of $5.0 \times 10^{-5} M$ $O_2(aq)$ has no effect on alkalinity

Generation of $1.0 \times 10^{-4} M$ SeO_4^{2-} has no effect on alkalinity

Generation of $2.5 \times 10^{-5} M$ H^+ destroys 2.5×10^{-5} equiv/L alkalinity

The sum of these changes indicates that 7.5×10^{-5} equiv/L of alkalinity is destroyed by the reaction. We can express this value in terms of mg/L as $CaCO_3$ as

$$\left(7.5 \times 10^{-5} \frac{\text{equiv}}{\text{L}}\right)\left(\frac{50 \text{ g CaCO}_3}{\text{meq}}\right)\left(1000 \frac{\text{meq}}{\text{equiv}}\right) = 3.75 \frac{\text{mg CaCO}_3}{\text{L}}$$