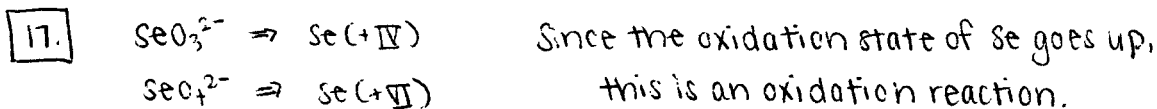


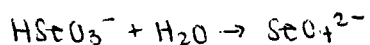
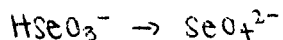
1.725 Problem Set #5 Solutions

Ch. 2 - 17, 35

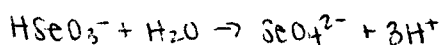
(including a couple of problems that weren't assigned this year... mostly because I'm lazy. But you might find them useful, too.)



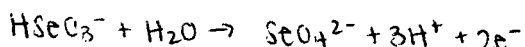
Writing a balanced half-reaction:



balance O by adding H_2O

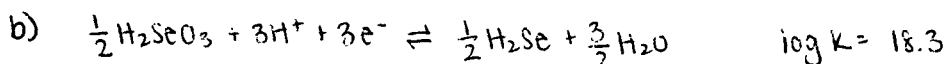
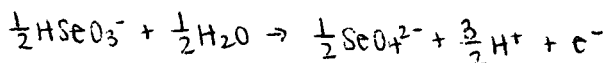


balance H by adding H^+



balance charge by adding e^-

these are often written per electron:



$$\frac{[\text{H}_2\text{Se}]^{1/2}}{[\text{H}_2\text{SeO}_3]^{1/2} [\text{H}^+]^3 \{\text{e}^-\}^3} = 10^{18.3}$$

assuming pH 7, $[\text{H}_2\text{SeO}_3] = [\text{H}_2\text{Se}]$, find pE

$$\{\text{e}^-\}^3 = \frac{[\text{H}_2\text{Se}]^{1/2}}{[\text{H}_2\text{SeO}_3]^{1/2} (10^{-7})^3 (10^{18.3})} = 10^{2.7}$$

$$\{\text{e}^-\} = 10^{0.9}$$

$$\text{pE} = -\log \{\text{e}^-\} = \boxed{-0.9}$$

if $E_h = -0.1\text{V}$, find $[\text{H}_2\text{SeO}_3] / [\text{H}_2\text{Se}]$

$$\text{pE} = \frac{E_h}{0.059} = -1.69 \Rightarrow \{\text{e}^-\} = 10^{1.69}$$

$$\frac{[\text{H}_2\text{SeO}_3]^{1/2}}{[\text{H}_2\text{Se}]^{1/2}} = \frac{1}{(10^{-7})^3 (10^{1.69})^3 (10^{18.3})} = 10^{-2.37}$$

$$\frac{[\text{H}_2\text{SeO}_3]}{[\text{H}_2\text{Se}]} = 10^{-4.74} = \boxed{1.8 \times 10^{-5}}$$

35.

$$\text{Alk} = 0.2 \text{ meq/L} = 2 \times 10^{-4} \text{ eq/L}$$

$$\text{pH} = 7$$

a) using Deffeyes diagram, $C_T = 2.4 \times 10^{-4} \text{ mol/L}$

b) pH is affected by C_T and Alkalinity; how do these change?

C_T : 0.5 mM organic carbon \rightarrow all mineralized (converted to inorganic carbon)

$$C_T = 2.4 \times 10^{-4} \text{ mol/L} + 5 \times 10^{-4} \text{ mol/L} = 7.4 \times 10^{-4} \text{ mol/L}$$

Alk: organic N \rightarrow NH_4^+ , which counts as a strong base

* strange and confusing * explanation...

NH_4^+ is not itself a strong base (it's not a base at all!). But if you derive $\text{Alk} = C_B - C_A$ from electroneutrality, as Harry did in class, it turns out to come from the counterions:

$$\text{Alk} = [\text{Na}^+] + [\text{K}^+] + 2[\text{Mg}^{2+}] - [\text{Cl}^-] - [\text{NO}_3^-] \quad (\text{for class example})$$

\uparrow from NaOH \uparrow from HCl

So, since NH_4OH is a strong base (i.e. it fully dissociates), it contributes to the C_B term of the Alk expression.

$\frac{C}{N} = 5$ so we have 0.1 mM of NH_4^+ after mineralization

$$\frac{1 \times 10^{-4} \text{ mol}}{\text{L}} \times \frac{1 \text{ equiv}}{\text{mol}} = 1 \times 10^{-4} \text{ eq/L}$$

$$\text{Alk} = 2 \times 10^{-4} \text{ eq/L} + 1 \times 10^{-4} \text{ eq/L} = 3 \times 10^{-4} \text{ eq/L}$$

Summarize: $C_T(\text{new}) = 7.4 \times 10^{-4} \text{ mol/L}$
 $\text{Alk}(\text{new}) = 3 \times 10^{-4} \text{ eq/L}$

$$\Rightarrow \boxed{\text{pH} \approx 6.2}$$

40. a) The methanogenesis reaction is at the bottom of the ecological redox sequence. Since the other reactions are more favorable (ΔG is more negative), methanogenesis will not occur if any other oxidant is present in significant quantities. The concentrations of NO_3^- , $\text{Fe}(\text{OH})_3$, MnO_2 , and SO_4^{2-} must be small enough that methanogenesis is the most favorable reaction.

b) assumptions:

- bioreactor is not pressurized, so $P_{\text{tot}} = 1 \text{ atm}$
- water still contains dissolved N_2 in equil. so $P_{\text{N}_2} = 0.8 \text{ atm}$
- \Rightarrow remaining 0.2 atm from methane

$$H = \frac{C_{\text{air}}}{C_{\text{water}}} = 27RT = 27(0.082 \frac{\text{L atm}}{\text{mol K}})(303\text{K}) = 671 \frac{\text{atm}}{\text{mol/L}}$$

$$C_{\text{water}} = \frac{C_{\text{air}}}{H} = \frac{0.2 \text{ atm}}{671 \text{ atm/M}} = \boxed{3.0 \times 10^{-4} \text{ M}}$$

c) initial: $\text{Alk} = 8 \times 10^{-4} \text{ eq/L}$, $\text{pH} = 7$

$$\Rightarrow C_T = 9.7 \times 10^{-4} \text{ M from diagram}$$

methanogenesis reaction: $\text{CH}_2\text{O} \rightarrow \frac{1}{2}\text{CH}_4 + \frac{1}{2}\text{CO}_2$

(1:1 ratio) so $3.0 \times 10^{-4} \text{ M CO}_2$ has been produced

$$\text{final: } C_T = 9.7 \times 10^{-4} \text{ M} + 3.0 \times 10^{-4} \text{ M} = 1.3 \times 10^{-3} \text{ M}$$

$\text{Alk} = 8 \times 10^{-4} \text{ eq/L}$ (unchanged, no hard acid/base)

$$\Rightarrow \boxed{\text{pH} = 6.5}$$

If you wanted to do the calculations instead of using the diagram:

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

at neutral pH, $\text{Alk} \approx [\text{HCO}_3^-] = 8 \times 10^{-4} \text{ M}$

$$\frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3^*]} = 10^{-6.3} \quad [\text{H}_2\text{CO}_3^*] = \frac{10^{-7}(8 \times 10^{-4})}{10^{-6.3}} = 1.6 \times 10^{-4}$$

$$C_T \approx [\text{H}_2\text{CO}_3^*] + [\text{HCO}_3^-] = 9.6 \times 10^{-4} \text{ M}$$

pH calculation:

$$[\text{HCO}_3^-] \approx 8 \times 10^{-4} \text{ M}$$

$$[\text{H}_2\text{CO}_3^*] = C_T - [\text{HCO}_3^-] = 4.6 \times 10^{-4} \text{ M}$$

$$[\text{H}^+] = \frac{10^{-6.3} [\text{H}_2\text{CO}_3^*]}{[\text{HCO}_3^-]} = \frac{10^{-6.3} (4.6 \times 10^{-4})}{8 \times 10^{-4}} = 2.9 \times 10^{-7} \Rightarrow \text{pH} = 6.5$$

$$46. \quad \text{BCF} = \frac{C_{\text{fish}}}{C_{\text{water}}} = \frac{\text{mg chemical / kg fish}}{\text{mg chemical / L H}_2\text{O}}$$

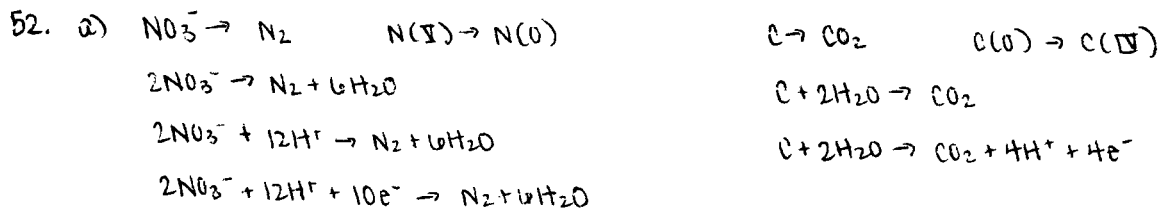
$$\text{BCF} = 10^4 \text{ L/kg}$$

$$V_{\text{water}} = 10^4 \text{ m}^3 = 10^9 \text{ L}$$

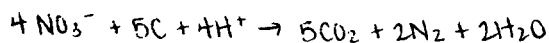
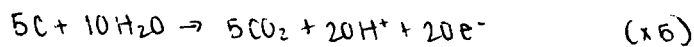
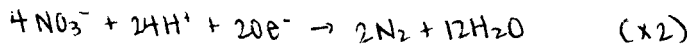
$$M_{\text{fish}} = 1000 \text{ kg}$$

$$\text{fraction in fish} = \frac{C_{\text{F}} M_{\text{F}}}{C_{\text{F}} M_{\text{F}} + C_{\text{W}} V_{\text{W}}} = \frac{\text{BCF}(C_{\text{W}} M_{\text{F}})}{\text{BCF}(C_{\text{W}} M_{\text{F}}) + C_{\text{W}} V_{\text{W}}}$$

$$\text{cancel } C_{\text{W}}: \text{ fraction} = \frac{10^4 \text{ L/kg} (1000 \text{ kg})}{10^4 \text{ L/kg} (1000 \text{ kg}) + 10^9 \text{ L}} = \frac{10^9 \text{ L}}{2 \times 10^9 \text{ L}} = \boxed{0.5}$$



Multiply reactions so that electrons cancel out:



$$\Rightarrow \boxed{\frac{4}{5} \text{ mol NO}_3^-}$$

$$\text{b)} \quad 12 \text{ oz. C} \times \frac{28.3 \text{ g}}{\text{oz}} \times \frac{\text{mol C}}{12 \text{ g C}} \times \frac{4/5 \text{ mol NO}_3^-}{\text{mol C}} = 22.7 \text{ mol NO}_3^-$$

$$\text{KNO}_3 \cdot 101 \text{ g/mol} \quad 22.7 \text{ mol} \times \frac{101 \text{ g}}{\text{mol}} = \boxed{2.3 \text{ kg or 81 oz}}$$

Ex. pH = 8, $C_T = 1.5 \times 10^{-3} \text{ M}$

a) compare actual $[\text{H}_2\text{CO}_3^*]$ to $[\text{H}_2\text{CO}_3^*]$ in equilibrium w/ atmosphere

at pH 8, $C_T \approx [\text{HCO}_3^-]$

$$\frac{[\text{HCO}_3^-][\text{H}^+]}{[\text{H}_2\text{CO}_3^*]} = 10^{-6.3} \quad [\text{H}_2\text{CO}_3^*] = \frac{(1.5 \times 10^{-3})(10^{-8})}{10^{-6.3}} = 3.0 \times 10^{-5} \text{ M}$$

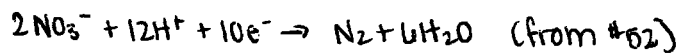
$[\text{H}_2\text{CO}_3^*] < [\text{HCO}_3^-]$ by about 2 orders of magnitude \Rightarrow assumption is reasonable if in equil. w/ atmosphere:

$$\frac{[\text{H}_2\text{CO}_3^*]}{p\text{CO}_2} = 10^{-1.5} \text{ mol/atm}\cdot\text{L} \quad [\text{H}_2\text{CO}_3^*] = 10^{-1.5} \frac{\text{mol}}{\text{atm}\cdot\text{L}} (10^{-3.5} \text{ atm}) = 10^{-5} \text{ M}$$

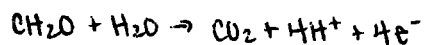
Since the actual $[\text{H}_2\text{CO}_3^*]$ is higher than the equilibrium value, the water will lose CO_2 when brought into contact with the atmosphere.

b) The result is consistent. Since the DO is zero, we know that respiration reactions (with O_2 and other electron acceptors) have been happening, and this produces CO_2 . The lake is stratified, so CO_2 accumulates in the hypolimnion.

c)



organic matter is CH_2O



\Rightarrow 4 mol NO_3^- oxidizes 5 mol CH_2O (producing 5 mol CO_2)

$$1 \text{ mmol } \text{NO}_3^- \times \frac{5 \text{ mol } \text{CH}_2\text{O}}{4 \text{ mol } \text{NO}_3^-} = 1.25 \text{ mmol } \text{CH}_2\text{O}$$

$C_T = 2.75 \text{ mM}$ $\Delta C_T = 1.25 \text{ mM}$

57. a) $[\text{CO}_2]_{\text{air}}: \frac{n}{V} = \frac{P}{RT} = \frac{10^{-3.5} \text{ atm}}{0.082 \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}} (298\text{K})} = 1.29 \times 10^{-5} \text{ mol/L}$

amount in air: $[\text{CO}_2]_{\text{air}} V_{\text{air}} = 1.29 \times 10^{-5} \frac{\text{mol}}{\text{L}} \times 400 \text{ m}^3 \times \frac{1000 \text{ L}}{\text{m}^3} = 5.2 \text{ mol}$

$[\text{H}_2\text{CO}_3^*]_{\text{water}}: \frac{[\text{H}_2\text{CO}_3^*]}{p\text{CO}_2} = 10^{-1.5} \text{ mol/L}\cdot\text{atm}$

$$[\text{H}_2\text{CO}_3^*] = 10^{-1.5} \frac{\text{mol}}{\text{L}\cdot\text{atm}} (10^{-3.5} \text{ atm}) = 10^{-5} \text{ M}$$

amount in water: $[H_2CO_3^*] v_w = 10^{-5} \frac{\text{mol}}{\text{L}} \times 4 \text{ m}^3 \times \frac{1000 \text{ L}}{\text{m}^3} = 0.04 \text{ mol}$

ratio = $\frac{5.2 \text{ mol}}{0.04 \text{ mol}} = \boxed{130}$

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

at pH 7.3, $\frac{[H_2CO_3^*]}{[HCO_3^-]} = \frac{[H^+]}{10^{-6.3}} = \frac{10^{-7.3}}{10^{-6.3}} = \boxed{0.1}$

0.04 mol $H_2CO_3^*$, so 0.4 mol HCO_3^-

since $[CO_3^{2-}]$ is negligible at pH 7.3:

$C_T = H_2CO_3^* + HCO_3^- + CO_2(\text{air})$

$= 0.04 \text{ mol} + 0.4 \text{ mol} + 5.2 \text{ mol} = \boxed{5.6 \text{ mol}}$

c) pH = 7.3

$C_T = 10^{-5} \text{ M} + 10(10^{-5} \text{ M}) = 1.1 \times 10^{-4} \text{ M} \quad \left. \vphantom{C_T} \right\} \text{Alk} = 10^{-4} \text{ eq/L}$

d) assume 6 kg is all CH_2O

$1\% = 60 \text{ g } CH_2O \times \frac{\text{mol}}{30 \text{ g}} \times \frac{1 \text{ mol } CO_2}{1 \text{ mol } CH_2O} = 2 \text{ mol } CO_2$

after mineralization, $C_T = 1.1 \times 10^{-4} \text{ M} + \frac{2 \text{ mol}}{4000 \text{ L}} = 6.1 \times 10^{-4} \text{ M}$

$\text{Alk} = 10^{-4} \text{ eq/L} \Rightarrow \boxed{\text{pH} \approx 5.7}$

e) Adding NaOH will increase alkalinity, thereby increasing pH.

$C_T = 6.1 \times 10^{-4} \text{ M} \quad \left. \vphantom{C_T} \right\} \text{Alk} = 5.4 \times 10^{-4} \text{ eq/L}$
 pH = 7.3

$\Delta \text{Alk} = 5.4 \times 10^{-4} \text{ eq/L} - 10^{-4} \text{ eq/L} = 4.4 \times 10^{-4} \text{ eq/L}$

$4.4 \times 10^{-4} \frac{\text{eq}}{\text{L}} \times \frac{1 \text{ mol NaOH}}{1 \text{ eq}} = \boxed{4.4 \times 10^{-4} \text{ M}}$

f) The carbonate system is a buffer, so it tends to resist changes in pH. However, in this system, there is not enough inorganic carbon to deal with possible perturbations (even 1% of Brutus was more than C_T). This allows for significant changes in pH, so the plants will die and then the people will be in trouble...