KEY

1. Carbonate/CO_2 equilibria, and ramifications.
   a) Calculate the solubility of $CaCO_3$ (s) in H_2O. Assuming no reaction between CO_3^{-2} and H_2O takes place ($K_{sp}=4.9 \times 10^{-9}$).

   b) Now, consider the reaction between CO_3^{-2} and H_2O, add this to the reaction in "a". Calculate the equilibrium constant for the net reaction, and use it to (re)calculate the solubility of $CaCO_3$. $K_b = 2.1 \times 10^{-4}$

   c) Explain the increase in solubility (between a & b) in terms of *LeChatlier's principle*.

   d) Calculate the pH of a saturated solution of $CaCO_3$ (using results from b).

   e) Suppose the water reservoir in question was such that $CaSO_4$ minerals were present in the sediments, rather than $CaCO_3$. What would the pH be is this "solution" if it were saturated w/ $CaSO_4$ (s)?
   $K_{sp}(CaSO_4) = 2.4 \times 10^{-5}$ and $K_b(SO_4^{-2}) = 8.3 \times 10^{-13}$.

   f) How, ultimately does the predominance of SO_4^{-2} over CO_3^{-2} rather affect the system's ability to buffer acid input.

2. In class, we discussed how dissolved CO_2 enhanced the solubility of $CaCO_3$ – and vice versa. Explain both of these effects in terms of *LeChatlier's Principle*, and identify a couple of *positive feedback* loops in this process.

3. Oxidation numbers:

a) Calculate oxidation numbers for both elements in the following: CO_2, CO_3^{-2}, CH_4, H_2S, SO_4^{-2}, NH_4^+, NO_3^-
b) Which would be referred to as "oxidized" C, S, or N species, and which would be "reduced" C, S, N?

4. a) What is the main oxidant in the *hydrosphere* (the Earth's water reserves)?
   b) What are its two main sources?
   c) What is the main sink for this oxidant (the primary reducing species)?
   d) Why is the concentration of this oxidant such a key parameter in overall water quality assessment?

5. a) The Henry's Law constant (K_H) of water at 25°C is 1.3×10^{-3} M/atm. Use this to calculate the solubility of O_2 in water (units of M and ppm).

b) The solubilities of O_2 at 15°C and 35 °C 10.13 and 7.07 ppm, respectively, use these data to calculate the Henry's Law constants at these temperatures.

Bonus question: Based on the results of "b", is the process of dissolving O_2 in water *endothermic* or *exothermic*?

c) *Thermal pollution* refers to the (potentially unwelcome) addition of heat to some ecosystem – such as pumping warm water from a power plant into a cold lake. What negative effect would such an activity have?

6. a) Define the quantity pE.

b) Does a high pE value mean the water is oxidizing or reducing? What about a low pE value?

c) In class we noted the pE value for an anaerobic water reservoir, based on the equilibrium between "oxidized carbon" (i.e. CO_2) and "reduced carbon" (CH_4), and found it to be negative. Based on this, what negative effect might result from a large injection of reduced carbon into a stream or river? (This is the case with a manure spill, or even when manure is spread over frozen ground such that is runs off before it sinks into the soil. The additional nutrient load due to the nitrogen would only amplify the problem.)

7. Describing the chemistry of a thermally stratified lake. Consider the sources and sinks of dissolved oxygen, the pE scale, and answer the questions below.

a) Above the *thermocline* (the top layer of the lake):
      i) Would the conditions be described as *aerobic* or *anaerobic*?
      ii) In terms of sources and/or sinks of dissolved O_2 – why?
      iii) Would the pE value be high or low (perhaps relative to that below the thermocline)?
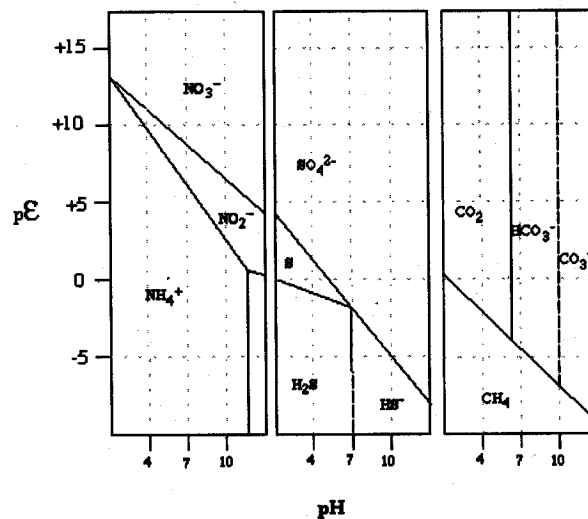
b) Below the *thermocline* (the bottom layer of the lake):
      i) Would the conditions be described as *aerobic* or *anaerobic*?
      ii) In terms of sources and/or sinks – why?
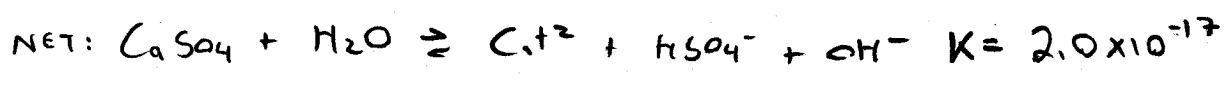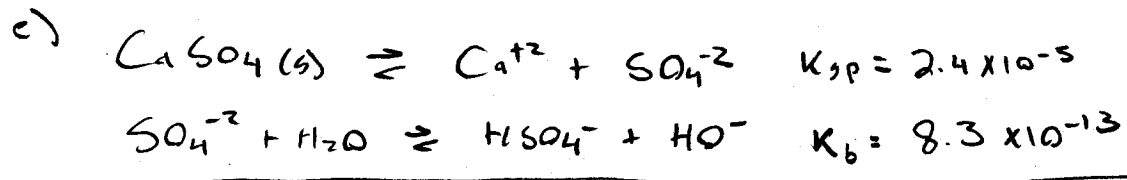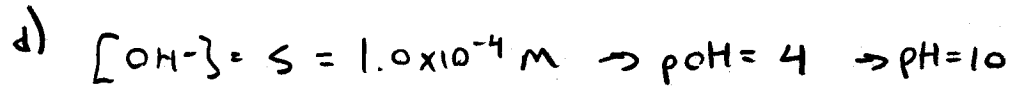   iii) Would the pE value be high or low (perhaps relative to that above the thermocline)?
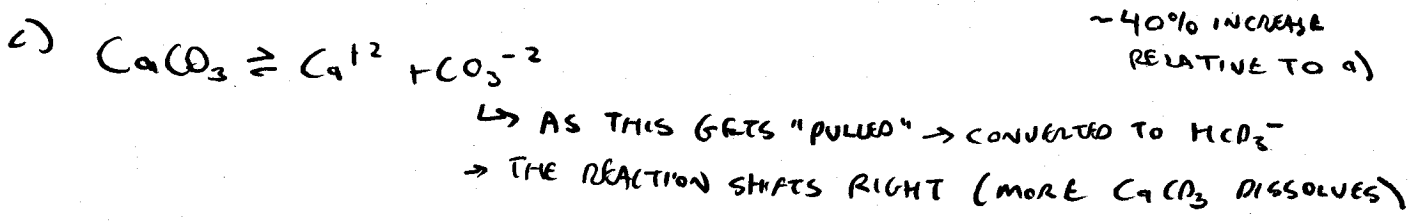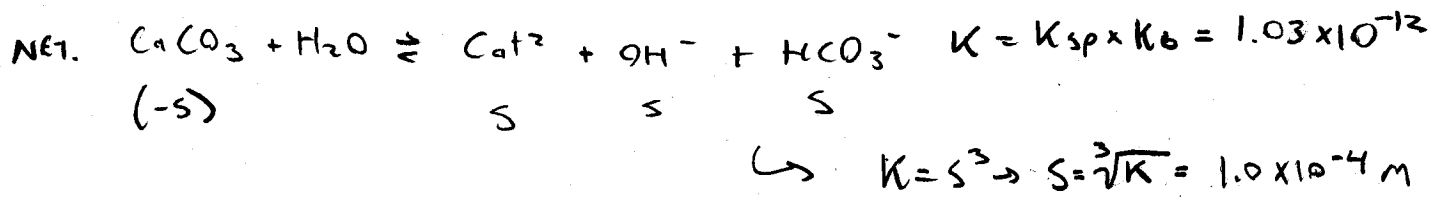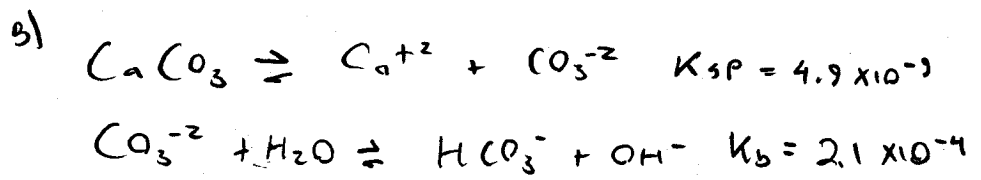
8. Explain how H+ input from acid rain can lead to significant concentrations of aqueous Al^{+3} ions ($Al(OH)_3$ is quite insoluble), and how this leads to fish mortality in acidified waters.

9. Ocean pH has decreased by about 0.1 pH units from a (variable) average of 8.2. How would this change affect CO_3^{-2} concentrations, and what are the ecological ramifications.

10. pH/pE Digrams: e.g below...

a) What is the primary sulfur species present at pH = 8 and pE=0.

b) What is the primary carbon species present at pE=0 and pH=7.

c) What is the primary nitrogen species present at pH=7 and pE=0.

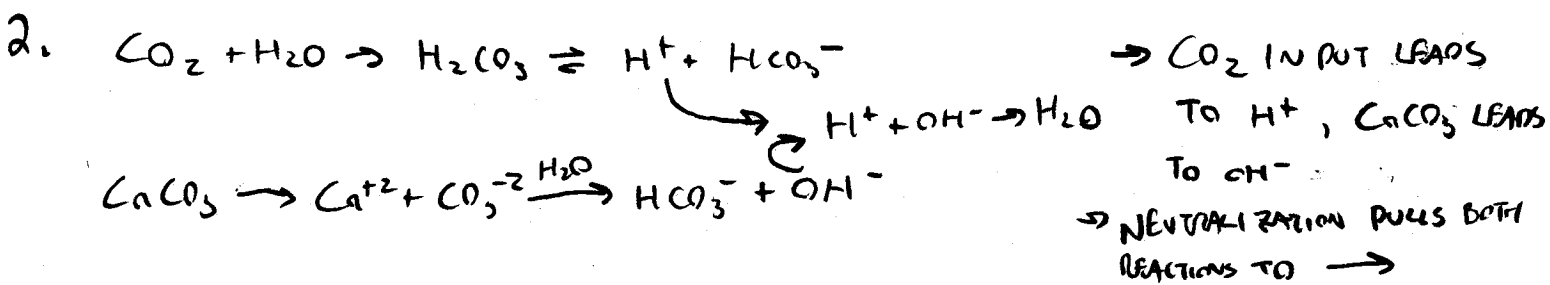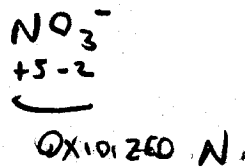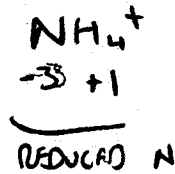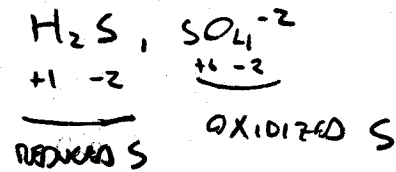1. A) $CaCO_3 \rightleftharpoons Ca^{+2} + CO_3^{-2}$ $K_{sp} = 4.9 \times 10^{-9}$

   $(-s) \rightarrow \quad S \qquad S \qquad K_{sp} = S^2 \rightarrow S = \sqrt{K_{sp}} = 7.0 \times 10^{-5} M$

   B) $CaCO_3 \rightleftharpoons Ca^{+2} + CO_3^{-2}$ $K_{sp} = 4.9 \times 10^{-9}$

   $CO_3^{-2} + H_2O \rightleftharpoons HCO_3^- + OH^-$ $K_b = 2.1 \times 10^{-4}$

   ───

   NET. $CaCO_3 + H_2O \rightleftharpoons Ca^{+2} + OH^- + HCO_3^-$ $K = K_{sp} \times K_b = 1.03 \times 10^{-12}$

   $(-s) \qquad\qquad\quad S \quad S \quad S$

   $\rightsquigarrow K = S^3 \rightarrow S = \sqrt[3]{K} = 1.0 \times 10^{-4} M$

   ~40% INCREASE RELATIVE TO a)

   c) $CaCO_3 \rightleftharpoons Ca^{+2} + CO_3^{-2}$

   $\rightsquigarrow$ AS THIS GETS "PULLED" $\rightarrow$ CONVERTED TO HCO_3^-
   $\rightarrow$ THE REACTION SHIFTS RIGHT (MORE $CaCO_3$ DISSOLVES)

   d) $[OH^-] = S = 1.0 \times 10^{-4} M \rightarrow pOH = 4 \rightarrow pH = 10$

   e) $CaSO_4 (s) \rightleftharpoons Ca^{+2} + SO_4^{-2}$ $K_{sp} = 2.4 \times 10^{-5}$

   $SO_4^{-2} + H_2O \rightleftharpoons HSO_4^- + HO^-$ $K_b = 8.3 \times 10^{-13}$

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   NET: $CaSO_4 + H_2O \rightleftharpoons Ca^{+2} + HSO_4^- + OH^-$ $K = 2.0 \times 10^{-17}$
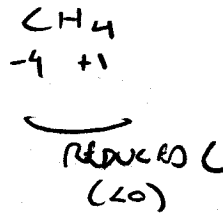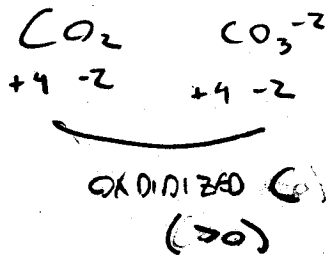
   AS ABOVE $S = \sqrt[3]{K} = 2.7 \times 10^{-6} = [OH^-]$

   $\rightarrow pOH = -\log[OH^-] = 5.6 \rightarrow pH = 8.4$ (MUCH LESS BASIC!)

   f) MORE SO_4^{-2} DISSOLVES - BUT CO_3^{-2} IS A MUCH STRONGER BASE. SO_4^{-2} IS NOT AN EFFECTIVE BUFFER AGAINST ACID INPUT B/C OF ITS VERY SLIGHT BASICITY.

2. $CO_2 + H_2O \rightarrow H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$

   $\rightarrow H^+ + OH^- \rightarrow H_2O$

   $CaCO_3 \rightarrow Ca^{+2} + CO_3^{-2} \xrightarrow{H_2O} HCO_3^- + OH^-$

   $\rightarrow CO_2$ INPUT LEADS TO H^+, $CaCO_3$ LEADS TO OH^-

   $\rightarrow$ NEUTRALIZATION PULLS BOTH REACTIONS TO $\rightarrow$

3. A/B

CO_2 CO_3^{-2} CH_4 H_2S, SO_4^{-2}
+4 -2   +4 -2   -4 +1   +1 -2   +6 -2

OXIDIZED C (>0)   REDUCED C (<0)   REDUCED S   OXIDIZED S

NH_4^+ NO_3^-
-3 +1   +5 -2

REDUCED N   OXIDIZED N.

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4. A) DISSOLVED O_2 B) PLANTS, DIRECT CONTACT W/ ATM   C) DISSOLVED ORGANIC MATTER $(CH_2O)_n$

d) ORGANISMS (ANIMAL KINGDOM ANYWAYS) DEPEND ON IT!

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5. A)

$$O_{2(l)} \rightleftharpoons O_{2(g)} \quad K_H = \frac{[O_2]}{P_{O_2}} \rightarrow [O_2] = K_H \cdot P_{O_2} = 1.3 \times 10^{-3} \cdot .21$$
$$= 2.2 \times 10^{-4} M$$

$$2.7 \times 10^{-4} \frac{mol}{L} \times \frac{1000 \, mg}{g} \times \frac{32 \, g}{mol} = 8.64 \frac{mg}{L} \cong 8.64 \, ppm$$

B)

$$10.13 \, ppm \left(\frac{mg}{L}\right) \times \frac{1 \, mol}{32 \, g} \times \frac{1 \, g}{1000 \, mg} = 3.17 \times 10^{-4} M \cdot [O_2]$$

$$K_H = \frac{[O_2]}{P_{O_2}} = \frac{3.17 \times 10^{-4}}{.21} = 1.5 \times 10^{-3} \frac{M}{atm} \, (LARGER \, THAN \, 25°C)$$

FOR 7.07 ppm $\rightarrow [O_2] = 2.2 \times 10^{-4} \rightarrow K_H = 1.05 \times 10^{-3} \frac{M}{atm}$

BONUS: IF $O_{2(l)} \rightleftharpoons O_{2(g)}$ GOES $\rightarrow$ W/ LOWER TEMP, HEAT IS A PRODUCT $\rightarrow$ PROCESS IS <u>EXO</u> THERMIC.

C) WARMER WATER HAS LESS DISSOLVED O_2 (AT SATURATION).
(AT THE SAME TIME METABOLISM IS GOING ↑ $\rightarrow$ THIS LEADS TO STRESS!)

6. A) pE IS EFFECTIVE e⁻ CONCENTRATION — THE QUANTITY
   CONVEYES OXIDIZING/REDUCING CHARACTER OF H_2O.

   B) HI pE → OXIDIZING , LO pE → REDUCING

   C) $$pE = pE^° - \log \left(\frac{P_{CH_4}^{1/8}}{P_{CO_2}^{1/4} [H^+]} \right)$$
   → INCREASING THIS "OXIDIZABLE" CARBON LOAD WILL LOWER pE!
   (ORGANICS WILL CONSUME DISSOLVED O_2 ...)

7. A) TOP LAYER   i) AEROBIC ii) DIRECT CONTACT w/ ATM + PLANTS
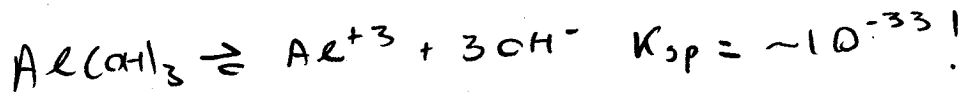   iii) HI pE (OXIDIZED SPECIES)

   B) BOTTOM LAYER i) ANAEROBIC ii) NO PLANTS OR DIRECT CONTACT w/ ATM
   iii) LO pE (REDUCED SPECIES)

8. MUCH Al^{+3} IS TIED UP IN HYDROXIDES (VRY INSOLUBLE AT pH=7)

   $$Al(OH)_3 \rightleftharpoons Al^{+3} + 3OH^- \quad K_{sp} = \sim 10^{-33} !$$

   BUT H^+ INPUT : $H^+ + OH^- \rightarrow H_2O$ "PULLS" RXN TO PRODUCTS
   → MORE Al^{+3} IN SOLUTION!

   WHEN THIS HITS FISH GILLS (pH~7) IT RE-PRECIPITATES
   + SUFFOCATES FISH ($Al(OH)_3$ IS GELATINOUS + STICKY).

9. MORE H^+ WILL CONVERT $CO_3^{-2} \xrightarrow{H^+} HCO_3^-$ THUS MOLLUSKS + CORALS
   CAN'T USE !

10. a) SO_4^{-2} b) HCO_3^- c) NH_4