ANSWER KEY

Ocean 421
Chemical Oceanography
Spring 2000

Your Name__________________

155
+135
290 TOTAL POINTS

Final Exam

(Use the back of the pages if necessary)(More than one answer may be correct.)

1. Due to the water molecule's (H_2O) great abundance in seawater: (10 pts)
   a) Seawater has a high heat capacity
   b) The activity of H_2O is 1 in all equilibrium calculations
   c) Salts dissolve easily in seawater
   d) The activity coefficients of all dissolved constituents are equal
   e) The activity of Ca^{2+} is greater than its concentration.

2. Due to the great abundance of dissolved salts in seawater: (10 pts)
   a) sea water has a higher density than freshwater
   b) sea water has a higher molar volume than freshwater
   c) sea water has a higher boiling point than freshwater
   d) sea water has a high ionic strength
   e) sea water has a higher sound absorption than freshwater

3. Some elements in seawater are considered to be conservative.

   a) What is the definition of a conservative element? (5 pts)

   a non reactive element whose ratio to salinity (S) is constant in the ocean.

   b) There are statements in the literature that uranium (U) is a conservative element in seawater. How would you design a study to show this is true or not true? (5 pts)

   measure uranium together with a conservative element or property – such as salinity (S), potential temperature (θ) or Cl^-, Ca^+ etc.

   If U is conservative it will make a linear plot versus another conservative property

30

4. Both equilibrium and kinetic (dynamic) models have been proposed for the composition of seawater. What arguments can be given favoring the kinetic model relative to the equilibrium approach? (10 pts)

1. CLAYS COME FROM DETRITAL SOURCES RATHER THAN REVERSE WEATHERING
2. LACK OF EVIDENCE FOR SUFFICIENT MINERALS OF REVERSE WEATHERING ORIGIN
3. SW. COMPOSITION HAS CHANGED WITH TIME WHICH IS ALLOWED BY THE KINETIC MODEL BUT NOT THE EQUILIBRIUM MODEL.

5. As deep water flows from the North Atlantic to the North Pacific the carbonate alkalinity increases from 2350 µEq to 2475 µEq while total CO_2 (e.g., DIC) increases from 2200 µM to 2375 µM. Estimate the average contributions of $CaCO_3$ dissolution and organic carbon respiration that create this increase in DIC. (15 pts)

Δ ALK = 2475 - 2350 = 125 µEq / 2 = 62.25

Δ DIC = 2375 - 2200 = 175 µM - 62.25 = 112.75

ASSUME:

$CaCO_3 = Ca^{2+} + CO_3^{2-}$ $\quad$ ΔDIC = 1 $\quad$ ΔALK = 2

$org C + O_2 = CO_2 + H_2O$ $\quad$ ΔDIC = 1 $\quad$ ΔALK = 0

$$\frac{\Delta DIC_{org C}}{\Delta DIC_{CaCO_3}} = \frac{112.75}{62.25} = 1.8$$

6. $CaCO_3$ is added to water and it dissolves. How will the following parameters vary? (10 pts)

pH ~~↓~~ ↑
alkalinity ↑
total CO_2 ↑
Ca^{2+} ↑
P_{CO2} ↓

35

7. ^{238}U ($t_{1/2} = 4.5 \times 10^9$ yr) decays to ^{234}Th ($t_{1/2} = 24.1$ d)

a) Define, and give the conditions for, secular equilibrium (5 pts)

DECAY ONLY

$t_{1/2P} >> t_{1/2D}$

b) Assuming the activity of $^{238}U = 2.3$ dpm kg^{-1} what is the molar concentration of ^{234}Th? (10pts)

$$A_{238U} = A_{234Th} = 2.3 \frac{dpm}{kg} = \lambda_{Th} N_{Th}$$

$t_{1/2} = \frac{\ln 2}{\lambda}$

$\lambda = \frac{0.693}{24.1 d} = 0.028 d^{-1}$

$$N_{Th} = \frac{2.3 \text{ dpm kg}^{-1}}{0.028 d^{-1}}$$

c) Assume there has been an extreme bloom period with intensive scavenging that removes most of the ^{234}Th from the water column in the euphotic zone. Suddenly the bloom stops. How long will it take for ^{234}Th to reach secular equilibrium with ^{238}U? (5 pts)

5 half lives of daughter

or

$5 \times 24.1 d = 120 d$

8. Which of the following is a first order process? (10 pts)

a) River input
b) Downwelling
c) Biological Production, with respect to DIC
d) Biological Production, with respect to N,P, Fe or another biolimiting element
e) Radioactive decay

9. The Redfield (or RKR) ratio represents (10 pts)

a) C:N:P content of organic matter formed during photosynthesis
b) C:N:P content of nutrients released during respiration
c) C:N:P of preformed nutrients in the surface ocean
d) C:N:P of nutrient uptake during photosynthesis
e) C:N:P of organic matter found in sediments

40

10. Relative to the Atlantic, Pacific deepwater (10 pts)

a) pH is higher
b) P_{CO2} is higher
c) Alkalinity is higher due to a larger organic C respiration: $CaCO_3$ dissolution rate ratio
d) Alkalinity is higher due to a smaller organic C respiration: $CaCO_3$ dissolution rate ratio
e) Total CO_2 is higher than alkalinity

11. In which situations is it advantageous to use K', the apparent equilibrium constant (10 pts)

a) Ion activites (but not concentrations) can be measured and free energies are known
b) Trace metal speciation calculations
c) At ionic strength, I=0
d) Carbonate system equilibria in seawater
e) When Q > K.

12. Due to the input of radionuclides during bomb testing in the 1960s, which information has been gained? (10 pts)

a) Water mass ventilation using chlorofluorocarbon (CFC) tracers
b) N-S mixing across the equator using ^3H as a tracer
c) Export production using $C/^{234}Th$ ratios
d) Stagnant boundary layer thickness using a ^{14}C steady state box model
e) The rate of turbulent mixing in the bottom boundary layer.

13. The oxidation of organic matter (10 pts)

a) produces dissolved organic carbon
b) produces dissolved inorganic carbon
c) consumes energy
d) provides bacteria with energy for growth and function
e) is not possible in the absence of oxygen

14. Trace elements with nutrient-like distributions, such as barium and copper (10 pts)

a) show a linear relationship with salinity and $[Cl^-]$
b) are depleted at the surface
c) are enriched at the surface
d) are regenerated (i.e. increase) with depth
e) have fixed stoichiometric ratios to P

50

15. CO_2 and climate. There is evidence that the ocean's circulation varied in a regular way during the past glacial periods. This has to do with the different sources and strengths of bottom water formation.

a) Broecker (1997) used a conservative geochemical tracer called PO_4^* to determine the intensity of the northern and southern sources, where waters of southern origin are described by:

$$PO_4^* = PO_4 + O_2 / 175 - 1.95 \text{ mmol kg}^{-1}$$

$O_2 \downarrow$
$PO_4 \uparrow$

and waters of northern origin by:

$$PO_4^* = PO_4 + O_2 / 175 - 0.73 \text{ mmol kg}^{-1}$$

Explain the origin of these equation and how it can be used for this purpose and why they are different for the norther and southern sources.(5 pts)

THE SUM OF $PO_4 + \frac{O_2}{175}$ SHOULD REMAIN CONSTANT BECAUSE AS $PO_4 \uparrow$ $O_2 \downarrow$ DUE TO RESPIRATION

THE LAST NUMBER IS THE PREFORMED PO_4 WITH IS DIFFERENT IN THE NORTHERN AND SOUTHERN SOURCES

WHY? PERHAPS BECAUSE THE SOUTHERN SOURCE IS UNDER THE ICE AND PO_4 IS HIGHER BECAUSE THERE IS LESS BIOLOGICAL REMOVAL

b) What were the reorganizations in ocean circulation that occurred in the past and what was their origin?(5 pts)

NADW WAS SHUT DOWN AT SEMI-REGULAR INTERVALS DUE TO FRESHENING OF THE N. ATLANTIC SURFACE WATER

c) If there are ocean reorganizations in the future, will they be caused by the same mechanism? If not what will be the cause? (5 pts)

AS $CO_2 \uparrow$ SST $\uparrow$ SO NADW MAY BE SHUT OF BUT BECAUSE OF WARMING RATHER THAN FRESHENING.

16. Acantharian protozoa use strontium to form celestite, $SrSO_4(s)$ skeletons. Is the formation of celestite thermodynamically favorable in seawater? The solubility of celestite is written as:

$$SrSO_4(s) = Sr^{2+} + SO_4^{2-}$$

a) Calculate the equilibrium constant for this reaction at 25°C given the following free energies of formation (ΔG_f^o) and using (ΔG_r^o)=-2.3RT log K=-5.708 log K at 25°C. (10 pts)

Species	ΔG_f^o (kJ mol^{-1})
$SrSO_4(s)$	-1340.9
$Sr^{2+}(aq)$	-563.83
$SO_4^{2-}(aq)$	-744.53

$$\Delta G_r^o = -563.83 + -744.53 - -1340.9$$
$$= -1308.36 + 1340.9$$
$$= +32.54 \text{ kJ mol}^{-1}$$
$$\log K = \frac{\Delta G_r^o}{-5.708} = \frac{32.54}{-5.708} = -5.70$$
$$K = 10^{-5.70}$$

b) What is the equilibrium expression? (5 pts)

$$K = \frac{(Sr^{2+})(SO_4^{2-})}{\cancel{(SrSO_4(s))}} \quad 1$$

c) If seawater has $[Sr^{2+}]_T$=0.0928 mmol/L and $[SO_4^{2-}]$= 28.93 mmol/L and the total activity coefficients are γ_{Sr}=0.25 and γ_{SO4}=0.065, what is ΔG_r? Is the formation of celestite thermodynamically favorable in seawater? (10 pts)

$$Q = (Sr^{2+})(SO_4^{2-})$$
$$= [Sr^{2+}]\gamma_{Sr,T}[SO_4]\gamma_{SO_4,T}$$
$$= (9.28\times10^{-5}\text{ M})(0.25)(28.93\times10^{-3})(0.065)$$
$$= 4.36\times10^{-8}$$
$$= 10^{-7.36}$$

$$\Delta G_r = \Delta G_r^o + 2.3RT\log Q$$
$$= +32.54 + (5.708)(-7.36)$$
$$= 32.54 - 42.01$$
$$= -9.47 \text{ kJ mol}^{-1}$$

RXN TO RIGHT

17. A recent paper reported data for the gas nitrous oxide (N_2O) in the surface waters of the Arabian Sea (Lal and Patra, 1998, Global Biogeochemical Cycles, 12, 321-327).

The average partial presure of N_2O in the atmosphere over the Arabian Sea was 313 ppbv or $10^{-6.50}$ atm. The Henry's Law constant for N_2O solubility at 25°C is $K_H = 10^{-1.59}$ mol l^{-1} atm^{-1}.

313×10^{-9}
3.13×10^{-7}

a. What was the mean saturated concentration of N_2O in surface water in mol l^{-1}. (5 points)

$$
\begin{aligned}
[N_2O] &= K_H P_{N_2O} = 10^{-1.59} \; 10^{-6.50} \\
&= 10^{-8.09} \\
&= 10^{0.91} \times 10^{-9} \\
&= 8.12 \times 10^{-9} \text{ M}
\end{aligned}
$$

b. The average degree of supersaturation was 130% and the average piston velocity for the average wind speed was 22.7 cm hr^{-1} . Calculate the average gas exchange flux in mol cm^{-2} d^{-1} using the stagnant boundary layer model. (10 points)

$$
\begin{aligned}
\text{Flux} &= \frac{D}{Z_{FILM}} (C - C_{SAT}) \\
&= \frac{D}{Z_{FILM}} \left(1.30 \times 10^{-8.09} - 10^{-8.09}\right) \\
&= 22.7 \frac{cm}{hr} \left(10.57 \times 10^{-9} - 8.12 \times 10^{-9}\right) \\
&= 22.7 \frac{cm}{hr} \left(2.37 \times 10^{-9} \frac{mol}{l}\right) \frac{l}{10^3 cm^3} \\
&= \left(22.7 \frac{cm}{hr}\right)\left(2.37 \times 10^{-12} \frac{mol}{cm^3}\right) \\
&= 53.7 \times 10^{-12} \frac{mol}{cm^2\, hr} \times 24 \frac{hr}{d} \\
&= 1289 \times 10^{-12} \frac{mol}{cm^2\, d} \\
&= 1.289 \times 10^{-9} \frac{mol}{cm^2\, d}
\end{aligned}
$$

18. Sometimes different oxidation states of the same element can be both oxidants and reductants. In one case the oxidized form of sulfur (SO_4^{2-}) can react with the reduced form (H_2S) to form solid elemental sulfur (S°). Such as reaction may occur at the oxic-anoxic interface in the Black Sea.

Here are two relevant half reactions:

$1/6\ SO_4^{2-} + 8/6\ H^+ + e- = 1/6\ S° + 4/6\ H_2O$ log K = 6.03
$1/8\ SO_4^{2-} + 10/8\ H^+ + e- = 1/8\ H_2S + 4/8\ H_2O$ log K = 5.12

a) write the balanced oxidation-reduction reaction (10 pts)

log K

$1/6\ SO_4 + 8/6\ H + e^- = 1/6\ S° + 4/6\ H_2O$ 6.03
$1/8\ H_2S + 4/8\ H_2O = e^- + 1/8\ SO_4 + 10/8\ H$ - 5.12
$1/6\ SO_4 + 1/8\ H_2S + 8/6\ H + 4/8\ H_2O = 1/6\ S° + 1/8\ SO_4 + 4/6\ H_2O + 10/8\ H$ 0.91
×48
$8\ SO_4 + 6\ H_2S + 64\ H^+ + 24\ H_2O = 8\ S^0 + 6\ SO_4 + 32\ H_2O + 60\ H^+$ 43.68
or
$SO_4 + 3\ H_2S + 2H^+ = 4\ S° + 4\ H_2O$ $\frac{43.68}{2} = 21.84$

b) which compounds are oxidants in this reaction (note that there are two oxidants) (5 pts) SO_4 AND H_2O

c) what is the equilibrium constant for this reaction (5pts)

$$K = \frac{(S^0)^8 (H_2O)^8}{(SO_4)^2 (H_2S)^6 (H)^4}$$ but $(S^0) = 1$, $(H_2O) = 1$

$$K = \frac{1}{(SO_4)^2 (H_2S)^6 (H^+)^4} = 10^{43.68}$$ $$\frac{1}{(SO_4)(H_2S)^3(H)^2} = 10^{21.84}$$

d) Is S° stable with regard to this reaction at the point of reaction in the Black Sea where pH = 7.5, SO_4^{2-} = 17 mM, H_2S = 1 µM. Assume for this calculation that concentrations and activities are equal. (10 pts)

$$Q = \frac{1}{(17\times10^{-3})^2 (1\times10^{-6})^6 (10^{-7.5})^4}$$
$$= \frac{1}{(289\times10^{-6})(10^{-36})(10^{-30})}$$
$$= \frac{1}{(10^{-3.53})(10^{-36})(10^{-30})}$$
$$= \frac{1}{10^{-69.5}}$$

so $Q = 10^{69.5}$
$K = 10^{43.7}$
$Q/K = 10^{25.8} > 1$

$$Q = \frac{1}{(17\times10^{-3})(1\times10^{-6})^3(10^{-7.5})^2}$$
$$Q = \frac{1}{10^{-24.7}}$$

$Q = 10^{24.7}$
$K = 10^{21.8}$
$Q/K > 1$

SO REACTION TO LEFT, S° NOT STABLE!

19. Fossil fuel CO_2 is on its way up from the pre-industrial value of about P_{CO2} = 300 µatm to about 600 µatm. By one scenario we can assume that alkalinity will stay constant at 2100 µEq.

Remember that the equilibrium constants for CO_2 and carbonic acid are:

$K_H' = [H_2CO_3^*] / P_{CO2} = 10^{-1.5}$
$K_1' = [HCO_3^-][H^+] / [H_2CO_3] = 10^{-6.0}$
$K_2' = [CO_3^{2-}][H^+] / [HCO_3^-] = 10^{-9.0}$

300×10^{-6}
3×10^{-4}
$10^{-3.52}$

a) Calculate the $[H_2CO_3^*]$ in equilibrium with an atmospheric P_{CO2} = 300 µatm. (10 pts)

$[H_2CO_3^*] = K_H P_{CO_2} = 10^{-1.5}\, 10^{-3.52} = 10^{-5.02}$

600×10^{-6}
6×10^{-4}
$10^{-3.22}$

b) Calculate pH for this open carbonate system when P_{CO2} has doubled to 600 µatm. (10 pts)

$$ALK \cong HCO_3 + 2CO_3$$
$$= C_T(\alpha_1 + 2\alpha_2)$$
$$= \frac{K_H P_{CO_2}}{\alpha_0}(\alpha_1 + 2\alpha_2)$$
$$ALK = K_H P_{CO_2}\left(\frac{HK_1 + 2K_1K_2}{H^2}\right)$$
$$2100 \times 10^{-6} = 10^{-1.5}\, 10^{-3.22}\left(\frac{H\, 10^{-6} + 2\, 10^{-6}\, 10^{-9}}{H^2}\right)$$
$$2.1 \times 10^{-3} = 10^{-4.72}\left(\frac{H\, 10^{-6} + 2 \times 10^{-15}}{H^2}\right)$$
$$10^{-2.67} H^2 = 10^{-10.72} H - 10^{-19.42}$$
$$10^{-2.67} H^2 - 10^{-10.72} H + 10^{-19.42} = 0$$
$$H^+ \cong 10^{-7.97}$$
$$pH \cong 7.97$$

20. Nitrogen fixation has become the latest "hot topic". Lets assess its importance. A Construct a two-box ocean model for fixed nitrogen as nitrate. Include river inflow, atmospheric input to the surface box, nitrification input to the surface box at the air-sea surface, upwelling, downwelling, denitrification in the deep box and a biological flux of organic N (B). The removal rate to the sediments (S) is expressed as S = f x B.

From the literature we find so information that we may (or may not) need:

$Q_{DENITRIF}$ Global denitrification = 175 TgN y^{-1} — f = 0.01

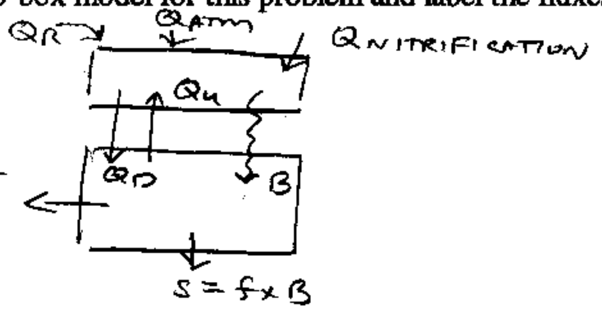
Q_R River Input = 76 TgN y^{-1} — Area = 3.61×10^8 km^2 $\frac{10^6 \, m^2}{km^2}$ $\frac{10^4 \, cm^2}{m^2}$

Q_{ATM} Atmospheric Deposition = 30 TgN y^{-1} — $= 3.61 \times 10^{18}$ cm^2

S Sediment Burial = 25 TgN y^{-1}.

Q_u Q_D Upwelling rate V = 300 cm y^{-1}

a) Draw the two-box model for this problem and label the fluxes.(5 pts)



b) Write the mass balance equations for the surface and deep boxes. (10 pts)

ASSUME Steady STate

SURFACE $\quad 0 = Q_R + Q_{NITRIF} + V_m C_D - V_m C_s - B$

DEEP $\quad 0 = V_m C_s - Q_{DENITRIF} + B - fB - V_m C_D$

c) If the average concentration of nitrate in the deep box is C_D = 30 µM, and the surface box is C_S = 0 µM, what is the rate of nitrogen fixation required for a steady state balance? (10 pts)

SURF $\quad 0 = Q_R + Q_{NITRIF} + V_m C_D - B \quad \therefore \quad B = Q_R + Q_{NITRIF} + V_m C_D$

DEEP $\quad 0 = B - Q_{DENITRIF} - f \times B - V_m C_D$

$= (1-f)B - Q_{DENITRIF} - V_m C_D$

$= (1-f)(Q_R + Q_{NITRIF} + V_m C_D) - Q_{DENITRIF} - V_m C_D$

$0 = (1-f)Q_R + (1-f)Q_{NITRIF} + (1-f)V_m C_D - Q_{DENIT} - V_m C_D$

$(1-f)Q_{NITRIF} = Q_{DENITRIF} + V_m C_D - (1-f)V_m C_D - (1-f)Q_R$

$0.99 \, Q_{NITRIF} = Q_{DENITRIF} + 0.01 \, V_m C_D - 0.99 \, Q_R$

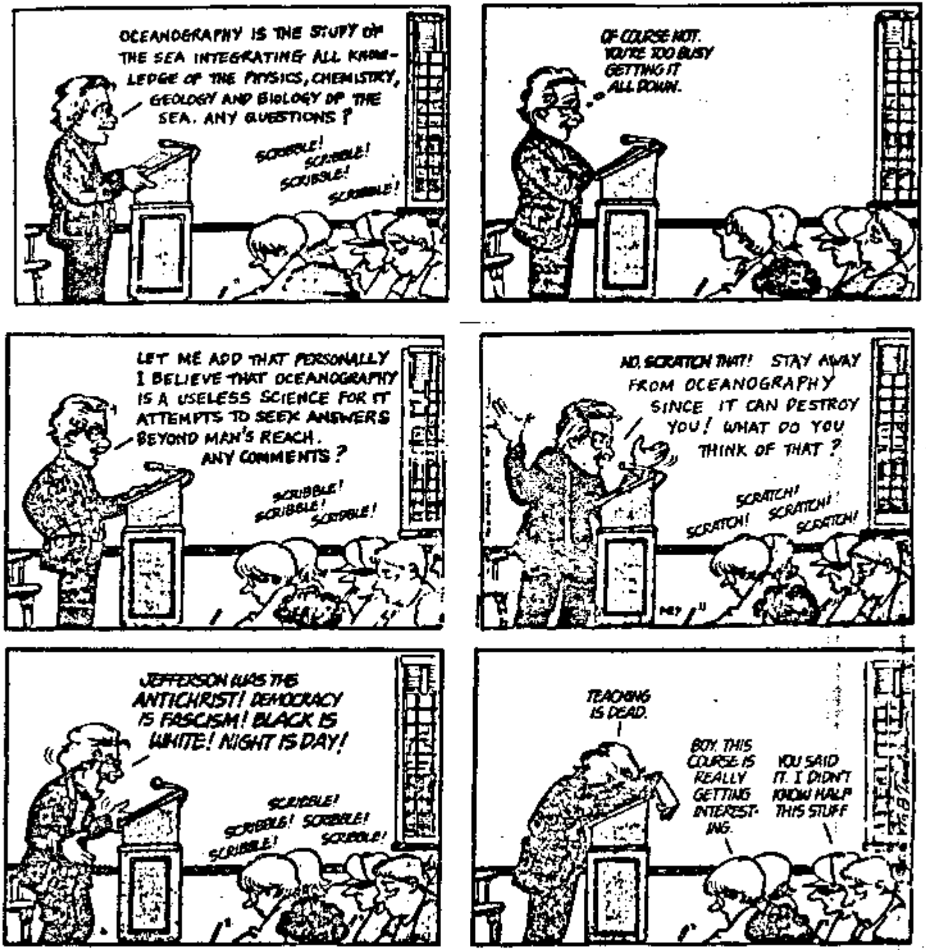
$Q_{NITRIF} = 175 + 0.01(300 \text{ cm/y}) \, 30 \times 10^{-6} \text{ mol}/10^3 \text{ cm}^3 \times A_{OCN} - (0.99)(76)$

d) What is its importance relative to river, atmospheric and upwelling input?(5 pts)

$= 175 + 4.5 - 76$ Tg y^{-1}

$Q_{NITRIF} = 104$ Tg y^{-1}

Q_{NITRIF} larger than river & much larger than upwelling
larger than atmospheric input


OCEANOGRAPHY IS THE STUDY OF THE SEA INTEGRATING ALL KNOWLEDGE OF THE PHYSICS, CHEMISTRY, GEOLOGY AND BIOLOGY OF THE SEA. ANY QUESTIONS?
SCRIBBLE! SCRIBBLE! SCRIBBLE! SCRIBBLE!
OF COURSE NOT. YOU'RE TOO BUSY GETTING IT ALL DOWN.
LET ME ADD THAT PERSONALLY I BELIEVE THAT OCEANOGRAPHY IS A USELESS SCIENCE FOR IT ATTEMPTS TO SEEK ANSWERS BEYOND MAN'S REACH. ANY COMMENTS?
SCRIBBLE! SCRIBBLE! SCRIBBLE!
NO, SCRATCH THAT! STAY AWAY FROM OCEANOGRAPHY SINCE IT CAN DESTROY YOU! WHAT DO YOU THINK OF THAT?
SCRATCH! SCRATCH! SCRATCH! SCRATCH!
JEFFERSON WAS THE ANTICHRIST! DEMOCRACY IS FASCISM! BLACK IS WHITE! NIGHT IS DAY!
SCRIBBLE! SCRIBBLE! SCRIBBLE! SCRIBBLE!
TEACHING IS DEAD.
BOY, THIS COURSE IS REALLY GETTING INTERESTING.
YOU SAID IT. I DIDN'T KNOW HALF THIS STUFF.