Name Answer Key **Student #** ____________

Chemistry 301 - MIDTERM EXAM #2

Wednesday, November 9, 2011, 9:00 am

Only the standard UBC Science calculator (Sharp 510B) is permitted.
Worth ~~27~~ 28 points (20% of course)

PART I (multiple choice – 11 points)

One point for each correct answer. No penalty for wrong answers - if you don't know, then guess. There is only one best answer for each question.

1. In a low nutrient, anoxic oceanic region, what do you expect to be the primary oxidant used in the breakdown of organic matter?
   - a) MnO_2
   - [✓ b) SO_4^{2-}]
   - c) NO_3^-
   - d) CO_2
   - e) FeOOH

2. During nitrate assimilation, ____ is converted into ____.
   - [✓ a) NO_3^-, organic N]
   - b) Organic N, NO_3^-
   - c) NO_3^-, NO_2^-
   - d) NH_4^+, NO_3-
   - e) NO_3^-, NH_4^+

3. Colloids aggregate at ____ ionic strength due to _____.
   - a) higher, increased attractive forces
   - [✓ b) higher, decreased repulsive forces]
   - c) higher, both increased attractive and decreased repulsive forces
   - d) lower, increased attractive forces
   - e) lower, decreased repulsive forces
   - f) lower, both increased attractive and decreased repulsive forces

4. What is the most likely reason for methanogenesis to occur?
   - a) it is more energetically favorable than the reaction with oxygen
   - b) it is more efficient because it uses CO_2, which is always present
   - [✓ c) organic matter is still present, when all other oxidants are used up]
   - d) the bacteria present in this environment prefer this process
   - e) it produces products needed for organic matter formation

Using this reaction, answer the following two questions:

$1/8\ CO_2 + H^+ + e^- \rightarrow 1/8CH_4 + 1/4H_2O \quad (p\varepsilon^o = 2.86)$

5. What species is being reduced in this reaction?
   - [✓ a) C]
   - b) O
   - c) H (attached to C)
   - d) H (attached to O)

6. If $pCO_2 = 100[pCH_4]$ and pH = 7.86, what is the pε of an environment controlled by this redox pair?
   - a) -3.0
   - [✓ b) -4.75]
   - c) -5.0
   - d) -5.25
   - e) -7.0

7. Why are clay minerals often slightly negatively charged in the aqueous environment?
   - a) van der Waals forces
   - b) electric double layer formation
   - [✓ c) charge generation from ion substitution]
   - d) polarity of surrounding water molecules
   - e) oxidation/reduction reactions of surface atoms

8. Acid mine drainage has large environmental impact due to:
   - a) The oxidation of S releasing excess sulfur species such as yellowboy
   - b) The release of high concentrations of metals
   - c) The formation of H_2SO_4
   - [✓ d) b and c]
   - e) All of the above

9. On a pε-pH diagram, which of the following transitions will change based on the total concentration set for the diagram?
   - a) HSO_4^- to $SO4^{2-}$
   - b) SO_4^{2-} to HS^-
   - c) $H_2S(aq)$ to $SO4^{2-}$
   - [✓ d) $H_2S(aq)$ to $S(s)$]
   - e) H_2S to HS^-

10. Why is treating acid mine drainage with $CaCO_3$ not as helpful as it could be?
    - a) the carbonate dissolves too quickly to be effective
    - b) the pH in the environment is too low for CO_3^{2-} to be a prevalent species
    - [✓ c) $Fe(OH)_3$ forms on its surface, lowering its effectiveness]
    - d) SO_4^{2-} is produced in the reaction, which is a harmful byproduct
    - e) Limestone is not readily available to use for treatment

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11. The process of denitrification can be represented on a pε/pH diagram by an arrow pointing:

a) from the bottom to the top
b) from the top to the bottom
c) from the bottom to the middle
[✓ d)] from the top to the middle
e) from the left to the right
f) from the right to the left
g) from the left to the middle
h) from the right to the middle

PART II (short answer – 16 pts)

12. A 50g sediment sample was equilibrated with NH_4^+ ions, which were later displaced by Na^+ for analysis. A total of 24×10^{-3} moles of NH_4^+ was measured after the addition of Na^+.

a) (1pt) Explain CEC in words.

Cation exchange capacity
The total amount of cation charges that can stick to clay surfaces and be removed (exchanged).

b) (1pt) What is the CEC of the above sample in meq/100g?

24×10^{-3} moles in 50g $\xrightarrow{\times 2}$ $\underline{\underline{48}}$ meq/100g

c) ~~(1pt)~~ 2pt The sediment sample above was found to contain the following cations (in mmoles)

Ca^{2+}: 3.5 Mg^{2+}: 2.7
Na^+: 5.2 K^+: 0.8

H^+ concentration was not directly measured. Calculate the H^+ ECS in meq/100g.

$$\left.\begin{array}{lll} Ca^{2+} & 3.5 \times \underline{2} & 7 \\ Mg^{2+} & 2.7 \times \underline{2} & 5.4 \\ Na^+ & 5.2 & \multirow{2}{*}{\}\ 6} \\ K^+ & 0.8 & \end{array}\right\} 18.4 \text{ in } 50g \overset{\times 2}{=} \underline{36.8} \text{ in } 100g$$

meq

CEC = Σ ECS

$$\boxed{ECS_{(H^+)} = CEC - \Sigma ECS_{others}}$$

= 48 − 36.8

$\underline{ECS_{H^+} = 11.2 \text{ meq}/100g}$

13. (2 pts) Given the data in the table below, over what time period is the bacterial growth in log phase? What is the generation time for this population of bacteria during log phase growth?

Time (hrs)	# cells
0	20
1	25
2	50
3	100
4	200
5	400
6	800
10	1600
15	3200
20	4000

same time interval

doubling

log phase 1 – 6 hrs

generation time = 1 hr

(time interval for doubling)

14. (2 pts) Discuss the properties and structure revealed by the following clay mineral formula: $(Na^{+}.nH_2O)(Mg_{3-x}K_x)Si_2(OH)_4O_5$

a) Is this [✓ a 1:1] or a 2:1 clay?

b) What generates charge in this mineral?

Substitution of K for Mg

c) Does the charge generation occur in the tetrahedral layer or [✓ the octahedral] layer ?

d) What is the counter ion?

Na

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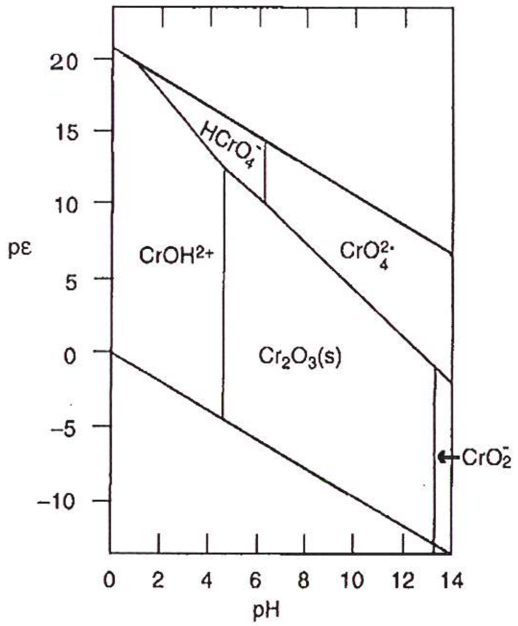
15. Using the pε/pH diagram for Cr shown here, answer the questions that follow:



pε vs. pH diagram for Cr. Total dissolved Cr = 10^{-6} M 25°C.

a) (1 pt) When converting between Cr_2O_3 and $CrO_2^{\cancel{2}-}$ CrO_2^-, do you expect an electron transfer? Why?

No. Dominant species only changes when pH changes, not when pε changes. Vertical line

b) (1 pt) What is the oxidation state of Cr in $Cr_2O_7^{2-}$ (not shown in figure)?

$O = -2$ $7x - 2 = -14$, $Cr_2 = +12$ (overall charge = −2)

$\boxed{Cr = +6}$

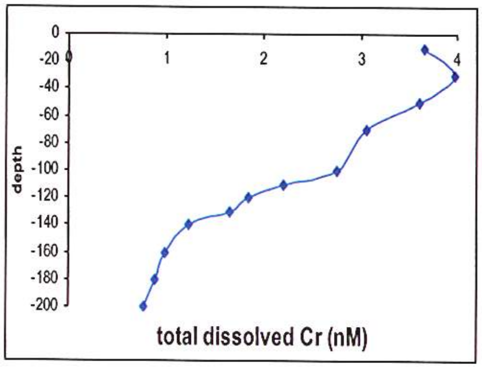
c) (1 pt) If you add some $Cr_2O_7^{2-}$ to a swamp, do you expect a change in the Cr oxidation state? Why? If yes, what will the oxidation state change to?

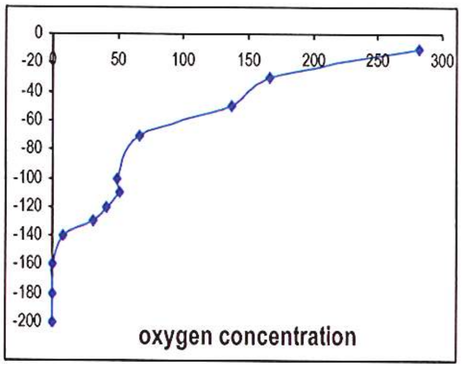
Yes in swamp, pε low (anoxic) ∴ expect Cr^{III} (either $CrOH^{2+}$ or $Cr_2O_3(s)$, depending on pH). Cr will be reduced from Cr^{VI} to Cr^{III}

d) (1 pt) If you add some $Cr_2O_7^{2-}$ to oxygenated surface water do you expect a change in the Cr oxidation state? Why? If yes, what will the oxidation state change to?

No in oxygenated surface water pε high (oxic) ∴ expect Cr^{VI} (CrO_4^{2-} or $HCrO_4^-$ depending on pH). Cr will stay as Cr^{VI}

16. Using both the pε/pH diagram on the previous page and the data below from Saanich Inlet, a seasonally anoxic fjord on Vancouver Island, answer the questions that follow:





a) (2 pts) Propose an explanation as to why the total dissolved Cr concentration is lower in the deeper waters than in the surface waters.

Cr is lower when O_2 is lower because low O_2 means low pε, and at low pε Cr is reduced to Cr^{III}, which exists primarily as a solid ($Cr_2O_3(s)$) at most of natural pH range

b) (1pt) What limits can you set for the pH of the deep waters in Saanich Inlet, based on the Cr data above?

pH range where Cr^{III} exists as a solid is ~4.5 – ~13.5, so pH must be within this range.

17. (2 pts) From the measured concentration of Al in a river, after accounting for dilution, you come up with a prediction of the levels of Al you expect to find in seawater off the coast where this river enters the ocean. If the observed concentration of Al in the seawater is much lower than you predicted, what explanation can you provide for this observation? What process do you think is occurring? Why?

1) Al in river could be mostly colloidal. When river water mixes with seawater ionic strength increases and colloids aggregate. Colloidal Al would therefore be removed.

2) Seawater pH is higher than river water, so Al could be precipitating as $Al(OH)_3(s)$ (favoured at higher pH)

(Either explanation OK, don't need both)