Chemistry 301 - Midterm Exam #1 - Answers

1. Considering the equilibrium between Fe^{2+} and $Fe(OH)_2$, Fe is more likely to precipitate:
   a) when the total amount of Fe is high, regardless of the pH
   b) when the total amount of Fe is high and pH is low
   c) when the total amount of Fe is high and pH is high
   d) when the total amount of Fe is low, regardless of the pH
   e) when the total amount of Fe is low and pH is low
   f) when the total amount of Fe is low and pH is high

2. Given the hypothetical information in Table A below, if total M is 10^{-5} M which solid forms do you expect to find at equilibrium?
   a) only $MX_{(s)}$
   b) only $MY_{(s)}$
   c) only $MZ_{(s)}$
   d) $MX_{(s)}$ and $MY_{(s)}$
   e) $MX_{(s)}$ and $MZ_{(s)}$
   f) $MY_{(s)}$ and $MZ_{(s)}$
   g) all three ($MX_{(s)}$, $MY_{(s)}$ and $MZ_{(s)}$)
   h) no solid forms are expected

Table A

Reaction	**Ksp**	**Calculated [M^{n+}] at equil.**
$MX_{(s)} \rightleftharpoons M^{n+} + X^{n-}$	1×10^{-12}	10^{-8} M
$MY_{(s)} \rightleftharpoons M^{n+} + Y^{n-}$	1×10^{-8}	10^{-6} M
$MZ_{(s)} \rightleftharpoons M^{n+} + Z^{n-}$	1×10^{-10}	10^{-4} M

3. Given the information in Table A above:
   a) $[X^{n-}] < [Y^{n-}] < [Z^{n-}]$
   b) $[X^{n-}] < [Z^{n-}] < [Y^{n-}]$
   c) $[Y^{n-}] < [Z^{n-}] < [X^{n-}]$
   d) $[Y^{n-}] < [X^{n-}] < [Z^{n-}]$
   e) $[Z^{n-}] < [Y^{n-}] < [X^{n-}]$
   f) $[Z^{n-}] < [X^{n-}] < [Y^{n-}]$

4. Supersaturated oxygen levels are likely to be found in surface waters when there has been recent:
   a) Phytoplankton growth and cooling
   b) Phytoplankton growth and windy weather
   c) Phytoplankton growth and rain
   d) Phytoplankton decay and cooling
   e) Phytoplankton decay and windy weather
   f) Phytoplankton decay and rain

5. Gases are most soluble in:
   a) cold freshwater
   b) warm freshwater
   c) cold seawater
   d) warm seawater
   e) a warm 50:50 mixture of seawater and freshwater
   f) cold 50:50 mixture of seawater and freshwater

6. The climate in Vancouver is moderate relative to the rest of Canada because:
    a) sea breezes develop in the late afternoon in Vancouver
    b) the Pacific Ocean is warmer than the Atlantic Ocean
    c) oceans are warmer than land
    d) water has a higher specific heat capacity than land
    e) Vancouver is at a lower latitude than any other part of Canada
    f) Vancouver is close to granitic mountains

7. Which of the following statements about soap scum is true:
    a) Scum forms when hard water is heated
    b) Scum is more likely to form in Vancouver than in Calgary or Toronto
    c) Scum forms when Fe is oxidized
    d) Scum forms when CO_2 is added to water
    e) Scum makes soap less effective

8. On a sketch of the hydrological cycle, which arrows would be bigger (represent a larger flux)?
    a) Evaporation from land > precipitation to land, evaporation from ocean > precipitation to ocean
    b) Evaporation from land > precipitation to land, evaporation from ocean < precipitation to ocean
    c) Evaporation from land < precipitation to land, evaporation from ocean > precipitation to ocean
    d) Evaporation from land < precipitation to land, evaporation from ocean < precipitation to ocean
    e) Evaporation from land = precipitation to land, evaporation from ocean = precipitation to ocean

9. For a Cr^{6+} ion, what transformation would you expect if you changed the pH from acidic to basic conditions?
    a) aqua to hydroxo
    b) aqua to oxo
    c) hydroxo to aqua
    d) hydroxo to oxo
    e) oxo to hydroxo
    f) oxo to aqua

10. Water is a good solvent because:
    a) It is polar
    b) It forms hydrogen bonds
    c) It has a high heat capacity
    d) It forms small clusters
    e) Ice is less dense than water
    f) It has a temperature of maximum density above the freezing point

11. Water in Vancouver is soft because:
    a) Temperatures in Vancouver rarely get below 4°C
    b) Vancouver is close to the Pacific Ocean
    c) Vancouver is close to steep mountains
    d) Vancouver is close to granitic mountains
    e) Vancouver is close to sedimentary mountains

12. Which of the following could cause a body of water become anoxic?
    a) A low amount of photosynthesis
    b) A deep thermocline
    c) High B.O.D.
    d) Oligotrophic conditions
    e) A recent change in temperature

13. How is humin different than humic acic?
    a) Solubility in strong acid
    b) Solubility in strong base
    c) Functional groups attached
    d) molecular weight
    e) electronegativity

14. Adding CO_2 to water:
    a) increases total CO_2 and increases pH
    b) decreases total CO_2 and increases pH
    c) increases total CO_2 and decreases pH
    d) decreases total CO_2 and decreases pH
    e) increases total CO_2 with no change to pH

15. Give the following pKa's for phosphoric acid:
    $pKa_1 = 2.17$
    $pKa_2 = 7.13$
    $pKa_3 = 12.36$

    What form(s) of phosphate do you expect to be significant at pH = 12?
    a) PO_4^{3-} only
    b) PO_4^{3-} and HPO_4^{2-}
    c) HPO_4^{2-} only
    d) HPO_4^{2-} and $H_2PO_4^-$
    e) $H_2PO_4^-$ only
    f) $H_2PO_4^-$ and H_3PO_4
    g) H_3PO_4 only

16. You take a sample of water with a "total CO_2" of 1.00 x 10^{-4} mol/litre and a pH of 9.33.

a) (1 pt) What is the ratio of $[HCO_3^-]$ to $[CO_3^{-2}]$?

$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$

$K_a = [H^+][CO_3^{2-}]/[HCO_3^-] = 10^{-10.33;}$ $[H^+] = 10^{-9.33}$

$10^{-10.33}/10^{9.33} = [CO_3^{2-}]/[HCO_3^-]$

$10^{-1} = [CO_3^{2-}]/[HCO_3^-]$; $10 = [HCO_3^-]/[CO_3^{2-}]$

b) (1 pt) What is $[HCO_3^-]$?

"total CO_2" = 1.00 X 10^{-4} M = ~~$[CO_2]$~~ + $[HCO_3^-]$ + $[CO_3^{2-}]$

At pH = 9.33, you can assume the CO_2 concentration is insignificant compared to the other two.

From previous question: $10[CO_3^{2-}] = [HCO_3^-]$ OR $0.1[HCO_3^-] = [CO_3^{2-}]$

$1.00 \times 10^{-4} = 0.1[HCO_3^-] + [HCO_3^-]$

$1.00 \times 10^{-4}/1.1 = 9.09 \times 10^{-5} \approx 0.9 \times 10^{-4}$(without calculator)

c) (2pt) If 1 millimole of acid is added to 1000 litres of this water, what do you expect the pH to be, assuming the reaction goes to completion? (Explain using words and/or calculations.)

Because this system is a buffer system with a high alkalinity, adding a small amount of acid will not significantly change the pH.

$[H^+]$ = 1mmol · 1 mol/1000 mmol = 0.001 mol / 1000 L = $1x10^{-6}$ M

The protons will be absorbed by the base $[CO_3^{2-}]$.

Amount of $[HCO_3^-]$ = $9.09x10^{-5}$ + $1X10^{-6}$ = $9.19x10^{-5}$
Amount of $[CO_3^{2-}]$= $9.01X10^{-6}$ – $1X10^{-6}$ = $8.01x10^{-6}$

solve for H^+ / pH (can use Ka expression or the Henderson-Hasselbalch equation)

pH = 10.33 + $\log([CO_3^{2-}]/[HCO_3^-])$

pH = 10.33 + $\log(8.01X10^{-6}/9.19X10^{-5})$

pH = 10.33 – 1.05 = 9.28

pH changed by only 0.05 units

d) (1 pt) If the alkalinity were essentially zero, what would the pH be after the addition of the same amount of acid?

In this system, the pH will change significantly because there is no buffer system to stabilize the pH.

pH = $-\log[H^+]$ = $-\log(1.0x10^{-6})$ = 6

17. A lead recycling plant begins operation on the shores of a formerly clean lake of capacity 1 x 10^7 m^3. It discharges into the lake 1 m^3 per hour of waste containing 1 x 10^{-5} M Pb^{+2}. The other inflow to the lake is a river with a flow rate of 1 x 10^3 m^3 per hr. Once the lake is allowed to reach a new steady state:

(a) (2 pts) Calculate the residence time of Pb^{+2} in the lake and explain what the term residence time means.

Residence time is the amount of time the average particle spends in a system.

τ = inventory / input

$1x10^7$ m^3/ $1x10^3$ m^3/hr = $1x10^4$ hr

Note: Lead will leave the system at the same rate as the water does.

(b) (2 pts) Calculate the concentration of Pb^{+2} in the lake, which is well mixed, and has no other sources or sinks for $Pb^{+2.}$

There are two ways to calculate this:

#1: rate of input = rate of output

$1x10^3\ m^3/hr \cdot [Pb^{2+}]_{eq} = 1x10^{-5}\ mol/L \cdot 1\ m^3/hr$

$[Pb^{2+}]_{eq} = 10^{-8}\ mol/L$

#2 Inventory = $[Pb]_{eq}$·lake volume = input ·τ

$[Pb]_{eq} = input_{Pb} \cdot \tau/\text{lake volume} = 1x10^4\ hr \cdot 1x10^{-5}\ mol/L \cdot 1m^3/hr\ /\ 1x10^7\ hr$

$[Pb^{2+}]_{eq} = 10^{-8}\ mol/L$

(c) (3 pts) If the pH of this lake is 9, do you expect the added lead to form an insoluble hydroxide precipitate? What if the pH is 5? Taking each case separately, what is the concentration of Pb^{+2} in the lake (after considering precipitation)?

$Pb(OH)_2 \rightleftharpoons Pb^{2+} + 2OH^-$

$Ksp = [Pb^{2+}][OH^-]^2 \approx 10^{-20}$

When pH = 9:

$[OH-] = 10^{-5}\ M;\ 10^{-20} = [Pb^{2+}][10^{-5}]^2 = 10^{-20}/10^{-10} = 10^{-10}\ M$

10^{-10} M < 10^{-8} M from the previous question; precipitate will form and the new steady state concentration will be 10^{-10} M.

When pH = 5:

$[OH-] = 10^{-9}\ M;\ 10^{-20} = [Pb^{2+}][10^{-9}]^2 = 10^{-20}/10^{-18} = 10^{-2}\ M$

10^{-2} M > 10^{-8} M from the previous question; precipitate will NOT form and the steady state concentration will stay at 10^{-8} M.

(d) **(3 pts) If the lake also has a steady state concentration of NTA at $1x10^{-4}$ M along with the Pb^{+2}, how will this affect the amount of soluble Pb in the lake? If you predicted precipitation at any pH in part (c), will this prediction change with the added NTA? To make any calculations easier, feel free to round off pK's as needed.**

NTA addition makes lead more soluble and thus less likely to precipitate out.

$HNTA^{2-} \rightleftharpoons H^+ + NTA^{3-}$ $pK_a = 10.28$, k_a $10^{-10.28}$
$Pb^{2+} + NTA^{3-} \rightleftharpoons PbNTA^-$ $pK_f = -11.4$, $k_f = 10^{11.4}$
$Kt \approx 10^1 = 10$

$10 = ([PbNTA^-][H^+]) / ([Pb^{2+}][HNTA^{2-}])$

At pH 9, $HNTA^{2-}$ is the dominant form of NTA because the pK_a is significantly higher than the pH, favoring the acidic form.

$[HNTA^{2-}]= 10^{-4}$ M

We then calculate a ratio between $PbNTA^-$ and Pb^{2+}. Because of the formation constant, we expect this ratio to be very high.

$10^1 \cdot 10^{-4} / 10^{-9} = 10^6 = [PbNTA^-] / [Pb^{2+}]$

This tells us that the dominant form of Pb is now $PbNTA^-$. This will be the same concentration as our original lake water, which is 10^{-8} M.

$10^6 = 10^{-8} / [Pb^{2+}]$
$[Pb^{2+}]= 10^{-8} / 10^6 = 10^{-14}$ M

The precipitate at pH 9 will no longer form because Pb has been chelated to NTA.

Since pH 5 conditions did not precipitate anyway, it would not change the prediction.