Answers - Chemistry 301 - MIDTERM #1 2007

1) *(8 points) True or false? And* <u>*briefly explain why*</u> *(for both T and F). If the statement is false, correct it. No credit is given for T or F alone! (2 points each)*

(a) *At a given pH, Fe(III) is more likely than Fe(II) to exist as a hydroxo complex rather than an aquo complex.*

True – Metal with **higher charge** (formal oxidation state, or "z") increases chances of hydroxo vs. aquo. Metal **pulls on electrons** from oxygen in water, weakening the O-H bond and making it easier for the H to leave.

(b) *Al (III), being an A-type metal, will typically be found bound to F^- in aqueous environments.*

False – Although **Al (III) is an A-type** metal and **prefers F^-**, F^- is typically much less abundant in the environment than oxygen, so **Al usually ends up with its second choice, "O", due to availability.**

(c) *Humic substances are divided into three groups based on what functional groups they contain.*

False – Humic substances are divided into three groups based on their behaviour in laboratory tests (treatment with strong acid and with strong base) – this is an **operationally defined separation**, **not based on functional groups** or any other specific chemical structure.

(d) *The climate in British Columbia is milder than the rest of Canada due to its location near the Pacific Ocean.*

True – Water has a **high heat capacity** which means it has smaller changes in temperature for the same amount of heat transfer. In British Columbia we get our **dominant weather from the ocean** (prevailing winds from west), rather than from the continent, so we have mild climate (eastern Canada is also on an Ocean, but gets its weather from the continent).

2) *(4 points) Explain why basic waters are typically high in alkalinity. Make sure to define the terms "basic" and "alkalinity" in your answer.*

Definitions: **"Basic" means water with a high pH** (low $[H^+]$, high $[OH^-]$), while **"alkalinity" is a measure of the ability of water to absorb protons** (its buffering capacity) and is due to the **sum of all conjugate bases of weak acids** that are in water – not just OH^-. The main species that contribute to alkalinity are bicarbonate (HCO_3^-) and carbonate (CO_3^{-2}).

Why the link?: Basic water is typically produced by (the water becomes basic due to) the **dissolution of carbonate minerals**, which add CO_3^{-2} to the water. This is mosty converted to HCO_3^- at natural pH (pH < 10) thus removing protons from the water.

2) *(cont)*

Removing protons raises the pH (increasing basicity), and **adding bicarbonate and carbonate to the water raises the alkalinity** (increasing alkalinity).

An alternate way to explain this: Basic water can absorb more CO_2, due to the reactions:

$$CO_2 + H_2O \rightleftharpoons HCO_3^- + H^+$$

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

Which show that at high pH (low H^+) you can have more bicarbonate and carbonate in the water, and this leads to more dissolution of carbonate from solids, via the reaction:

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

This provides additional carbonate to the system (without adding H^+), thus raising both the pH (basicity) and the alkalinity.

3) *(3 points) According to Wikipedia: "A limnic eruption, also referred to as a lake overturn or exploding lake, is a rare type of natural disaster in which CO_2 suddenly erupts from deep lake water, posing the threat of suffocating wildlife, livestock and humans". Describe the effect of pressure on gas solubility, and how this contributes to these "limnic eruptions". Why is this phenomenon is rare?*

Solubility increases with increasing pressure, and **pressure increases with depth under water**. Thus, more gas is soluble at the bottom of a lake than at the top. If there is a source of gas at depth (which is rare), then the bottom can become saturated. At this point, any addition of gas or any disturbance that causes **deep waters to mix upwards, will lead to supersaturation and degassing**. As the gas bubbles rise, they pull up more deep waters, which leads to more extreme supersaturation and more degassing. Hence, the exploding lake (a violent overturn). This is **rare because there is not typically a source of gas to the bottom of a lake** (the exceptions are the lakes in Africa where volcanic gases, such as carbon dioxide, are supplied to the bottom of the lake).

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

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

Since **input = output**,

$(1 \times 10^{-3}$ M$)(1$ $m^3/hr) = (x$ M$)(1 \times 10^3$ $m^3/hr)$

where x = conc. of Pb in outflow

= conc. of Pb in lake (in Molar Units)

$$x = \frac{(1 \times 10^{-3}\ M)(1\ m^3/hr)}{(1 \times 10^3\ m^3/hr)} = \mathbf{10^{-6}\ M\ Pb}$$

(b) (2 points) Calculate the residence time of Pb^{+2} in the lake, and explain what residence time means.

$$\textbf{Residence time} = \frac{\textbf{inventory}}{\textbf{input (or output)}} = \frac{(10^{-6}\text{ M Pb})(5 \times 10^{7}\text{ m}^3)}{(10^{-6}\text{ M Pb})(1 \times 10^{3}\text{ m}^3\text{/hr})}$$

$$= \frac{(5 \times 10^{7})}{(1 \times 10^{3})}\text{ hr} = \mathbf{5 \times 10^{4}\ hours}$$

The residence time is the **average time** a given atom or molecule (Pb+2 in this case) **spends in the lake** (or other defined "reservoir") – time between input and output.

(c) (4 points) If the pH of this lake is 8, do you expect the added lead to form an insoluble hydroxide precipitate? What if the pH is 6? In each case, what is the concentration of Pb^{+2} in the lake (after considering precipitation)?

$$Pb(OH)_2(s) \rightleftharpoons Pb^{+2} + 2OH^- \qquad pK_{sp} = 19.79$$

$$[Pb^{+2}] = \frac{K_{sp}}{[OH^-]^2} = \frac{10^{-pK_{sp}}}{[OH^-]^2}$$

at **pH = 8**; $[OH^-] = 10^{-6}$ $(K_W = [H^+][OH^-] = 10^{-14})$

$$\mathbf{[Pb^{+2}]} = \frac{10^{-19.79}}{(10^{-6})^2} = \frac{10^{-19.79}}{(10^{-12})} = \mathbf{10^{-7.79}\ M}$$

Saturation concentration of dissolved Pb^{+2} with respect to (w.r.t.) lead hydroxide ($10^{-7.79}$ M) is lower than the concentration expected from the pollution source (part a: 10^{-6} M Pb), so there **will be precipitation of the lead**, and **the concentration will be $10^{-7.79}$ M Pb**.

at **pH = 6**; $[OH^-] = 10^{-8}$ $(K_W = [H^+][OH^-] = 10^{-14})$

$$\mathbf{[Pb^{+2}]} = \frac{10^{-19.79}}{(10^{-8})^2} = \frac{10^{-19.79}}{(10^{-16})} = \mathbf{10^{-3.79}\ M}$$

Saturation concentration of dissolved Pb^{+2} with respect to (w.r.t.) lead hydroxide ($10^{-3.79}$ M) is higher than the concentration expected from the pollution source (part a: 10^{-6} M Pb), so there **will NOT be precipitation of the lead**, and **the concentration will be 10^{-6} M Pb**.

(d) *(3 points) If the lead recycling plant waste also contains 1 x 10^{-1} M NTA, along with the Pb^{+2}, how will this effect 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.*

Total NTA >> Total Pb, therefore $Pb(NTA)^-$ is insignificant compared to total NTA
Dominant form of NTA at pH 6 or 8 is $HNTA^{-2}$
Total NTA in lake = (10^{-3}) x (NTA in waste) *(as for Pb – see part a)*
= 10^{-4} M

Under these conditions, the relevant equations for calculating the speciation are:

$$Pb^{+2} + (NTA)^{-3} \rightleftharpoons Pb(NTA)^- \qquad pK_f = -11.4$$

$$\underline{H(NTA)^{-2} \rightleftharpoons (NTA)^{-3} + H^+} \qquad pK_{a3} = 10.28$$

$$\mathbf{Pb^{+2} + H(NTA)^{-2} \rightleftharpoons Pb(NTA)^- + H^+}$$

$$K_T = \frac{[Pb(NTA)^-]\,[H^+]}{[H(NTA)^{-2}][Pb^{+2}]}$$

$$= K_f K_{a3} = (10^{+11.4})(10^{-10.28}) = (10^{+1.12}) \cong 10^1$$

therefore, at pH=8 (where ppt was predicted in part c):

$$\frac{[Pb(NTA)^-]}{[Pb^{+2}]} = \frac{K_T\,[H(NTA)^{-2}]}{[H^+]} = \frac{(10^1)(10^{-4})}{(10^{-8})} = 10^5$$

therefore **all Pb is as $Pb(NTA)^-$**

$$\text{and } [Pb^{+2}] = \frac{[Pb(NTA)^-]}{10^5} = \frac{\text{total Pb}}{10^5} = \frac{(10^{-6})}{10^5} = 10^{-11}\text{ M}$$

which is well below saturation, so **all Pb will remain in solution as $Pb(NTA)^-$ therefore no precipitation in this case**. (At pH = 6, never predicted precipitation, and calculation for this pH also shows all Pb will remain in solution as $Pb(NTA)^-$).

Note: Could also get credit for a logical explanation, rather than a calculation, as long as you noted that:

- Total NTA >> Total Pb, therefore you expect NTA complexation to be significant
- NTA complexation solubilizes Pb from hydroxides by lowering free $[Pb^{+2}]$
- At pH 6 to 8, even though NTA is mostly protonated (in the form of $HNTA^{-2}$), there is still a tendency for the overall reaction (above) to go toward products.