Mid-Term Exam

October 28, 2010

Closed Book, one sheet of notes allowed
Please answer any 4 of the following 9 questions on separate sheets of paper (except for the T/F questions that may be answered directly on this paper. Each is worth 25 points.

Show all work. Be neat, and box-in your answer. Hand in your answer pages and the exam handout together.

1. A tanker of hydrochloric acid overturns on Rte 128. A Hazmat team springs into action ready to neutralize the spill with a tanker of 50% (by weight) NaOH solution. If the overturned tanker spills 400 gallons of 12 M hydrochloric acid, how many gallons of the 50% NaOH is needed to exactly neutralize it?

Note that a 50% NaOH solution has a specific gravity of 1.53, meaning that 1 liter of this solution weights 1.53 kg.

i. First calculate the number of moles of HCl that were spilled
\[ \text{HCl spill} = 400 \text{gal} \left(\frac{3.7854 \text{L}}{\text{gal}}\right)12 \frac{\text{moles}}{L} = 18,170 \text{ moles} - \text{HCl} \]

ii. Determine Stoichiometry
\[ \text{NaOH} + \text{HCl} = \text{NaCl} + \text{H}_2\text{O} \]

iii. Determine GFW of NaOH
\[ \text{GFW} = 23 + 16 + 1 = 40 \text{ g-NaOH/mole-NaOH} \]

iv. Determine mass of NaOH needed
\[ \text{NaOH needed} = 18,170 \text{ moles} - \text{HCl} \left(\frac{1 \text{mole-NaOH}}{\text{mole-HCl}}\right)40 \frac{\text{g-NaOH}}{\text{mole-NaOH}} \]
\[ = 726,800 \text{ g-NaOH} = 726.8 \text{ Kg} = \text{NaOH} \]

v. Calculate mass concentration of NaOH solution
\[ \text{conc} = 0.50 \times 1.53 \text{ kg/L} = 0.765 \text{ kg/L} \]

vi. Calculate volume of NaOH solution
\[ \text{Volume} = \frac{726.8 \text{ Kg}}{0.765 \frac{\text{Kg}}{L}} = 950 \text{L} = 251 \text{ gallons} \]
2. **Calculate the ThOD of the following solutions and indicate which family of organic compounds each comes from:**

a. \(10^{-3}\) moles/L of hexane, \(C_6H_8\)

b. \(3 \times 10^{-3}\) moles/L of oxalic acid, \(C_2H_2O_4\)

c. 30 mg/L of ethanol, \(CH_3CH_2OH\)

**Solution to a.**
The balanced stoichiometric equation is:
\[
C_6H_8 + 8O_2 \rightarrow 6CO_2 + 4H_2O
\]
The ThOD is then:
\[
ThOD = 8 \frac{\text{moles oxygen}}{\text{mole hexane}} \times 10^{-3} \frac{\text{moles hexane}}{L} \times \frac{32,000\text{mg O}_2}{\text{mole O}_2}
\]
\[
ThOD = \frac{256\text{mg O}_2}{L}
\]
Hexane is a member of the **Alkane** family

**Solution to b.**
The balanced stoichiometric equation is:
\[
C_2H_2O_4 + \frac{1}{2}O_2 \rightarrow 2CO_2 + H_2O
\]
The ThOD is then:
\[
ThOD = 0.5 \frac{\text{moles oxygen}}{\text{mole oxalic acid}} \times 3 \times 10^{-3} \frac{\text{moles oxalic acid}}{L} \times \frac{32,000\text{mg O}_2}{\text{mole O}_2}
\]
\[
ThOD = \frac{48\text{mg O}_2}{L}
\]
Oxalic Acid is a member of the **Carboxylic Acid** family

**Solution to c.**
The balanced stoichiometric equation is:
\[
\frac{46}{3}CH_3CH_2OH + 3O_2 \rightarrow 2CO_2 + 3H_2O
\]
The ThOD is then:
\[
ThOD = 30 \frac{\text{mg CH}_3\text{CH}_2\text{OH}}{L} \times \left(\frac{96\text{mg O}_2}{46\text{mg CH}_3\text{CH}_2\text{OH}}\right)
\]
Ethanol is a member of the **Alcohol** family

### 3. You’re checking on the suitability of an urban groundwater as a drinking water source. You request a complete analysis of major inorganic ions from a commercial laboratory and the results are shown below.

<table>
<thead>
<tr>
<th>Chemical Substance</th>
<th>Conc. (mg/L)</th>
<th>GFW</th>
<th>Conc. (mM)</th>
<th>Conc. (meq/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na⁺</td>
<td>31.1</td>
<td>22.9898</td>
<td>1.3528</td>
<td>1.3528</td>
</tr>
<tr>
<td>K⁺</td>
<td>7.7</td>
<td>39.0983</td>
<td>0.1969</td>
<td>0.1969</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>21.2</td>
<td>40.0800</td>
<td>0.5289</td>
<td>1.0579</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>3.5</td>
<td>24.3050</td>
<td>0.1440</td>
<td>0.2880</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>2.1</td>
<td>62.0049</td>
<td>0.0339</td>
<td>0.0339</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>5.6</td>
<td>96.0576</td>
<td>0.0583</td>
<td>0.1166</td>
</tr>
<tr>
<td>Br⁻</td>
<td>0.5</td>
<td>35.4530</td>
<td>0.0141</td>
<td>0.0141</td>
</tr>
<tr>
<td>HCO₃⁻</td>
<td>87.9</td>
<td>61.0171</td>
<td>1.4406</td>
<td>1.4406</td>
</tr>
<tr>
<td><strong>Sum</strong></td>
<td><strong>159.6</strong></td>
<td></td>
<td><strong>71.2</strong></td>
<td></td>
</tr>
</tbody>
</table>

\[ \text{Sum} = 159.6 \text{ mg/L} \]
\[ \text{Sum} = 71.2 \text{ mg/L} \]

with loss of CO₂

cations = 2.896 meq/L
anions = 1.605 meq/L

% diff. = 44.57%

**A. Check the results by performing a charge balance. What is the percent difference between the anions and cations?**

There appears to be a large deficit in anions (45% difference). This is too large for normal laboratory error. It suggests a gross error or some major omission.

**B. The lab also measured 117 mg/L total dissolved solids. What value would you expect based on the data in the table above?**

Direct assessment results in an estimate of 71.2 mg/L TDS presuming that the bicarbonate is lost to CO₂ upon drying. This is much lower than the measured value of 117 mg/L

**C. Do these results seem to be complete and accurate based on your answers in A and B? Explain.**
The results seem to have substantial error. Either there was a large error of measurement, or an error of omission. The lab shows data for bromide but not chloride. Since chloride is a very common anion in natural waters and it is often associated with sodium, we would have expected to see some chloride. Perhaps it was omitted by accident and the missing chloride would account for the apparent anion deficit and the low calculated TDS.

4. You’re examining a 1st order batch reaction that occurs with a half-life of 90 minutes.

A. What is the value of the reaction rate constant in units of min⁻¹?

\[ t_{1/2} = \frac{0.693}{k} \]

\[ k = \frac{0.693}{t_{1/2}} = \frac{0.693}{90 \text{min}} = 0.0077 \text{min}^{-1} = 7.7 \times 10^{-3} \text{min}^{-1} \]

B. How long will it take to reach 99% removal?

\[ C = C_0 e^{-kt} \]

\[ \frac{C}{C_0} = e^{-kt} \]

\[ 0.01 = e^{-0.0077\text{min}(t)} \]

\[ \ln(0.01) = -0.0077\text{min}(t) \]

\[ t = -\frac{1}{0.0077\text{min}} \ln(0.01) = 598 \text{ min} = 9.97 \text{ hrs} \]

C. What would the fraction remaining be if you were doing this in a CMFR with a retention time of 5 hours

\[ \frac{C}{C_0} = \frac{1}{1 + \theta k} = \frac{1}{1 + 5\text{hr}(0.0077\text{min}^{-1})60\text{min/hr}} = 0.302 \]

5. Intercontinental Paper and the Mill River

The Intercontinental Paper Co. is discharging its wastewater directly into the Mill River. The discharge flow is 3.8 ft³/s (cfs). They obtain half of this water from an intake 0.5 miles upstream of the wastewater outfall, and half from groundwater via a nearby well field. On average, the Mill River water upstream of IPC has a total suspended solids concentration (TSS) of 2.5 mg/L. If the Mill River has a flow of 12 cfs upstream of the IPC intake, and if the state permits a maximum TSS concentration of 15 mg/L in the Mill...
River, what will the allowable effluent concentration of suspended solids be for IPC? Assume that TSS is conservative in this stretch of the Mill River.

Solution

First the downstream flow is:

\[ Q_d = Q_u + Q_e = [12 - (0.5)3.8] + 3.8 = 13.9 \text{ cfs} \]

The solve for the effluent concentration using a mass balance:

\[ C_e = \frac{Q_d C_d - Q_u C_u}{Q_e} = \frac{13.9 \text{ cfs}(15 \text{ mg/L}) - 10.1(2.5 \text{ mg/L})}{3.8 \text{ cfs}} \]

\[ = \frac{48.2 \text{ mg}}{L} \approx 48 \frac{\text{mg}}{L} \]

6. True/False. Indicate whether the following statements are true (T) or false (F).
1. **F** Procaryotic organisms include all higher plants and animals

2. **F** A triprotic acid has three times the strength as a monoprotic acid

3. **T** A conjugate base is what forms when an acid loses a proton

4. **F** When an organic compound name ends in “al”, it usually means the compound is an alcohol

5. **T** Proteins are composed mostly of amino acids

6. **F** When Gibbs Free Energy increases, the reaction will tend to go forward

7. **F** Ethers have carbon-nitrogen bonds

8. **T** Henry’s law describes the relationship between partial pressure and dissolved concentration

9. **T** Autotrophs can use inorganic carbon for cell synthesis

10. **T** Changes in ionic strength can cause shifts in chemical equilibria

11. **F** An element of high electronegativity will share its bonding electrons equally with an element of low electronegativity

12. **F** Cryptosporidium is a type of prion

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7. **The equilibrium constant for the following reaction is $10^{-6.3}$. What percent of the total carbonate is in the form of bicarbonate at pH 5.5?**

\[ \text{H}_2\text{CO}_3 = \text{HCO}_3^- + \text{H}^+ \]

First you need to recognize that bicarbonate is: \( \text{HCO}_3^- \)

The equilibrium expression for this reaction is:

\[ K_{eq} = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = 10^{-6.3} \]

So:

\[ \frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = 10^{-6.3} \]

And therefore:

\[ \frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = \frac{10^{-6.3}}{10^{-5.5}} = 10^{-0.8} \]

Thus:

\[ \frac{[\text{H}_2\text{CO}_3] + [\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = 1 + 10^{-0.8} \]
And recognizing that at such a low pH, virtually all of the carbonates are in the form of bicarbonate and carbonic acid (i.e., there is essentially no carbonate):

\[
\frac{[H_2CO_3]}{C_T} = \frac{1}{1 + 10^{-0.8}}
\]

= 0.863

And what’s left is bicarbonate:

\[
\frac{HCO_3^-}{\text{total carbonate}} \approx 1 - 0.863 = 0.137 = 13.7\%
\]

8. A rapidly growing suburb has a population of 11,500 in 2000 and 16,300 in 2010.

A. Predict the 2030 population assuming an exponential growth model.

B. Make a second prediction for 2030, but this time presume that the housing availability will limit the maximum population to 30,000. Assume the population approaches this limit at a rate of 0.1 yr\(^{-1}\).

A. this is a simple exponential model

\[N = N_o e^{rt}\]

Which first requires that the exponential growth rate be calculated

\[r = \frac{1}{t} \ln\left(\frac{N}{N_o}\right) = \frac{1}{10\text{yr}} \ln\left(\frac{16,300}{11,500}\right) = 0.03488 \text{yr}^{-1}\]

\[N = N_o e^{rt} = 16,300 e^{0.03488 \text{yr}^{-1}(20\text{yr})} = 32,747\]

B. This is a logistics model with a carrying capacity (K) of 30,000 and an r of 0.1 yr\(^{-1}\).

You could use either year (2000 or 2010) as the baseline, but 2010 would be a better choice as there’s no guarantee that the period between 2000 and 2010 actually conformed to a logistics model. All you really know is that you’re assuming the model fits in the future.

\[N_t = \frac{KN_o}{N_o + (K - N_o)e^{-rt}} = \frac{30,000(16,300)}{16,300 + (30,000 - 16,300)e^{-0.1\text{yr}^{-1}(20\text{yr})}} = 26,936\]

9. An urban area receives 48 inches of rain per year. Using the rational formula, calculate the average runoff for this area in cubic feet per second (cfs).

Assume it encompasses 20,000 acres, including 3000 acres of urban business land, 6000 acres of urban single family housing land, 6000 acres of multi-family housing, 3000 acres of land occupied by apartments and 2000 acres of parks and cemeteries.
<table>
<thead>
<tr>
<th>Area Description</th>
<th>average runoff coefficient</th>
<th>acres</th>
<th>C<em>I</em>A (acre-ft/yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Urban Business</td>
<td>0.8</td>
<td>3000</td>
<td>9600</td>
</tr>
<tr>
<td>Urban single family</td>
<td>0.4</td>
<td>6000</td>
<td>9600</td>
</tr>
<tr>
<td>multifamily homes</td>
<td>0.5</td>
<td>6000</td>
<td>12000</td>
</tr>
<tr>
<td>Apartments</td>
<td>0.6</td>
<td>3000</td>
<td>7200</td>
</tr>
<tr>
<td>Parks &amp; Cemeteries</td>
<td>0.15</td>
<td>2000</td>
<td>1200</td>
</tr>
</tbody>
</table>

|               | total                     | 20000 | 39600             |

\[ Q = \sum CIA = 39,600 \frac{acre-ft}{yr} \left( \frac{43560 ft^2}{acre} \right) \left( \frac{yr}{365.25 d} \right) \left( \frac{d}{24 hr} \right) \left( \frac{hr}{60 min} \right) \left( \frac{min}{60 s} \right) \]

\[ = 54.7 \text{ cfs} \]
### Appendix

#### Selected Chemical Constants

<table>
<thead>
<tr>
<th>Element</th>
<th>Symbol</th>
<th>Atomic #</th>
<th>Atomic Wt.</th>
<th>Valence</th>
<th>Electronegativity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum</td>
<td>Al</td>
<td>13</td>
<td>26.98</td>
<td>3</td>
<td>1.47</td>
</tr>
<tr>
<td>Boron</td>
<td>B</td>
<td>5</td>
<td>10.81</td>
<td>3</td>
<td>2.01</td>
</tr>
<tr>
<td>Bromine</td>
<td>Br</td>
<td>35</td>
<td>79.9</td>
<td>1,2,5,7</td>
<td>large</td>
</tr>
<tr>
<td>Calcium</td>
<td>Ca</td>
<td>20</td>
<td>40.08</td>
<td>2</td>
<td>1.04</td>
</tr>
<tr>
<td>Carbon</td>
<td>C</td>
<td>6</td>
<td>12.01</td>
<td>2,4</td>
<td>2.50</td>
</tr>
<tr>
<td>Chlorine</td>
<td>Cl</td>
<td>17</td>
<td>35.453</td>
<td>1,3,5,7</td>
<td>2.83</td>
</tr>
<tr>
<td>Chromium</td>
<td>Cr</td>
<td>24</td>
<td>52.00</td>
<td>many</td>
<td>1.56</td>
</tr>
<tr>
<td>Helium</td>
<td>He</td>
<td>2</td>
<td>4.00</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Holmiuum</td>
<td>Ho</td>
<td>67</td>
<td>164.93</td>
<td>3</td>
<td>1.10</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>H</td>
<td>1</td>
<td>1.01</td>
<td>1</td>
<td>2.20</td>
</tr>
<tr>
<td>Magnesium</td>
<td>Mg</td>
<td>12</td>
<td>24.31</td>
<td>2</td>
<td>1.23</td>
</tr>
<tr>
<td>Manganese</td>
<td>Mn</td>
<td>25</td>
<td>54.94</td>
<td>2,3,4,6,7</td>
<td>1.60</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>N</td>
<td>7</td>
<td>14.01</td>
<td>many</td>
<td>3.07</td>
</tr>
<tr>
<td>Oxygen</td>
<td>O</td>
<td>8</td>
<td>16.00</td>
<td>2</td>
<td>3.50</td>
</tr>
<tr>
<td>Potassium</td>
<td>K</td>
<td>19</td>
<td>39.10</td>
<td>1</td>
<td>0.91</td>
</tr>
<tr>
<td>Sodium</td>
<td>Na</td>
<td>11</td>
<td>22.99</td>
<td>1</td>
<td>1.01</td>
</tr>
<tr>
<td>Sulfur</td>
<td>S</td>
<td>16</td>
<td>32.06</td>
<td>2,4,6</td>
<td>2.44</td>
</tr>
</tbody>
</table>

### Selected Acidity Constants (Aqueous Solution, 25°C, I = 0)

<table>
<thead>
<tr>
<th>NAME</th>
<th>FORMULA</th>
<th>pKₐ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrochloric acid</td>
<td>HCl = H⁺ + Cl⁻</td>
<td>-3</td>
</tr>
<tr>
<td>Sulfuric acid</td>
<td>H₂SO₄ = H⁺ + HSO₄⁻</td>
<td>-3</td>
</tr>
<tr>
<td>Nitric acid</td>
<td>HNO₃ = H⁺ + NO₃⁻</td>
<td>-0</td>
</tr>
<tr>
<td>Bisulfate ion</td>
<td>HSO₄⁻ = H⁺ + SO₄⁻²</td>
<td>2</td>
</tr>
<tr>
<td>Phosphoric acid</td>
<td>H₃PO₄ = H⁺ + H₂PO₄⁻</td>
<td>2.15</td>
</tr>
<tr>
<td>Hydrofluoric acid</td>
<td>HF = H⁺ + F⁻</td>
<td>3.2</td>
</tr>
<tr>
<td>Nitrous acid</td>
<td>HNO₂ = H⁺ + NO₂⁻</td>
<td>4.5</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>CH₃COOH = H⁺ + CH₃COO⁻</td>
<td>4.75</td>
</tr>
<tr>
<td>Propionic acid</td>
<td>C₂H₅COOH = H⁺ + C₂H₅COO⁻</td>
<td>4.87</td>
</tr>
<tr>
<td>Carbonic acid</td>
<td>H₂CO₃ = H⁺ + HCO₃⁻</td>
<td>6.35</td>
</tr>
<tr>
<td>Hydrogen sulfide</td>
<td>H₂S = H⁺ + HS⁻</td>
<td>7.02</td>
</tr>
<tr>
<td>Dihydrogen phosphate</td>
<td>H₂PO₄⁻ = H⁺ + HPO₄⁻²</td>
<td>7.2</td>
</tr>
<tr>
<td>Hypochlorous acid</td>
<td>HOCl = H⁺ + OCl⁻</td>
<td>7.5</td>
</tr>
<tr>
<td>Ammonium ion</td>
<td>NH₄⁺ = H⁺ + NH₃</td>
<td>9.24</td>
</tr>
<tr>
<td>Hydrocyanic acid</td>
<td>HCN = H⁺ + CN⁻</td>
<td>9.3</td>
</tr>
<tr>
<td>Phenol</td>
<td>C₆H₅OH = H⁺ + C₆H₅O⁻</td>
<td>9.9</td>
</tr>
<tr>
<td>Bicarbonate ion</td>
<td>HCO₃⁻ = H⁺ + CO₃⁻²</td>
<td>10.33</td>
</tr>
<tr>
<td>Monohydrogen phosphate</td>
<td>HPO₄⁻² = H⁺ + PO₄⁻³</td>
<td>12.3</td>
</tr>
<tr>
<td>Bisulfide ion</td>
<td>HS⁻ = H⁺ + S⁻²</td>
<td>13.9</td>
</tr>
</tbody>
</table>
Conversions
7.48 gallon = 1.0 ft³  
1 gal = 3.7854 \times 10^{-3} \text{ m}^3

1 MGD = 694 gal/min = 1.547 \text{ ft}^3/\text{s} = 43.8 \text{ L/s}

1 \text{ ft}^3/\text{s} = 449 \text{ gal/min}

1 acre = 43,560 ft²

g = 32 \text{ ft/s}^2

W=\gamma = 62.4 \text{ lb/ft}^3 = 9.8 \text{ N/L}

1 \text{ hp} = 550 \text{ ft-lbs/s} = 0.75 \text{ kW}

1 mile = 5280 feet  
1 \text{ ft} = 0.3048 \text{ m}

1 \text{ watt} = 1 \text{ N-m/s}

1 psi pressure = 2.3 vertical feet of water (head)

At 60 °F, \nu = 1.217 \times 10^{-5} \text{ ft}^2/\text{s}