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

$$HCl\ spill = 400gal\left(\frac{3.7854\text{L}}{gal}\right)12\frac{moles}{L} = 18{,}170\ moles - HCl$$

   ii. Determine Stoichiometry

$$\text{NaOH} + \text{HCl} = \text{NaCl} + \text{H}_2\text{O}$$

   iii. Determine GFW of NaOH

GFW = 23+16+1 = 40 g-NaOH/mole-NaOH

   iv. Determine mass of NaOH needed

$$NaOH\ needed = 18{,}170\ moles - HCl\left(\frac{1mole - NaOH}{mole - HCl}\right)40\frac{g - NaOH}{mole - NaOH}$$

$$= 726{,}800\ g - NaOH\ = 726.8\ Kg = NaOH$$

   v. Calculate mass concentration of NaOH solution

conc = 0.50*1.53 kg/L = 0.765 kg/L

   vi. Calculate volume of NaOH solution

$$Volume = 726.8\ Kg \div 0.765\frac{Kg}{L} = 950L = \mathbf{251\ gallons}$$

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. $3x10^{-3}$ 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:

$$ThOD = 8\frac{moles-oxygen}{mole-hexane}x10^{-3}\frac{moles-hexane}{L}\times\left(\frac{32{,}000mg-O_2}{mole-O_2}\right)$$

$$\boxed{ThOD = 256\frac{mg-O_2}{L}}$$

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:

$$ThOD = 0.5\frac{moles-oxygen}{mole-oxalic\ \text{acid}}x3x10^{-3}\frac{moles-oxalic\ \text{acid}}{L}\times\left(\frac{32{,}000mg-O_2}{mole-O_2}\right)$$

$$\boxed{ThOD = 48\frac{mg-O_2}{L}}$$

Oxalic Acid is a member of the **Carboxylic Acid** family

Solution to c.

The balanced stoichiometric equation is:

$$\underbrace{CH_3CH_2OH}_{46} + \underbrace{3O_2}_{96} \rightarrow 2CO_2 + 3H_2O$$

The ThOD is then:

$$ThOD = 30\frac{mg-CH_3CH_2OH}{L}\times\left(\frac{96mg-O_2}{46mg-CH_3CH_2OH}\right)$$

$$ThOD = 62.6 \frac{mg - O_2}{L}$$

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.

Chemical Substance	Conc. (mg/L)	GFW	Conc. (mM)	Conc. (meq/L)
Na^+	31.1	22.9898	1.3528	1.3528
K^+	7.7	39.0983	0.1969	0.1969
Ca^{+2}	21.2	40.0800	0.5289	1.0579
Mg^{+2}	3.5	24.3050	0.1440	0.2880
NO_3^-	2.1	62.0049	0.0339	0.0339
SO_4^{-2}	5.6	96.0576	0.0583	0.1166
Br^-	0.5	35.4530	0.0141	0.0141
HCO_3^-	87.9	61.0171	1.4406	1.4406
Sum =	159.6	mg/L		

Sum = 159.6 mg/L

Sum = 71.2 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 CO_2 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}?

$$t_{1/2} = \frac{0.693}{k}$$

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{90min} = \mathbf{0.0077 min^{-1} = 7.7x10^{-3} min^{-1}}$$

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

$$C = C_o e^{-kt}$$

$$C/C_o = e^{-kt}$$

$$0.01 = e^{-0.0077min(t)}$$

$$\ln(0.01) = -0.0077min(t)$$

$$t = -\frac{1}{0.0077min} ln(0.01) = \mathbf{598\,min = 9.97\,hrs}$$

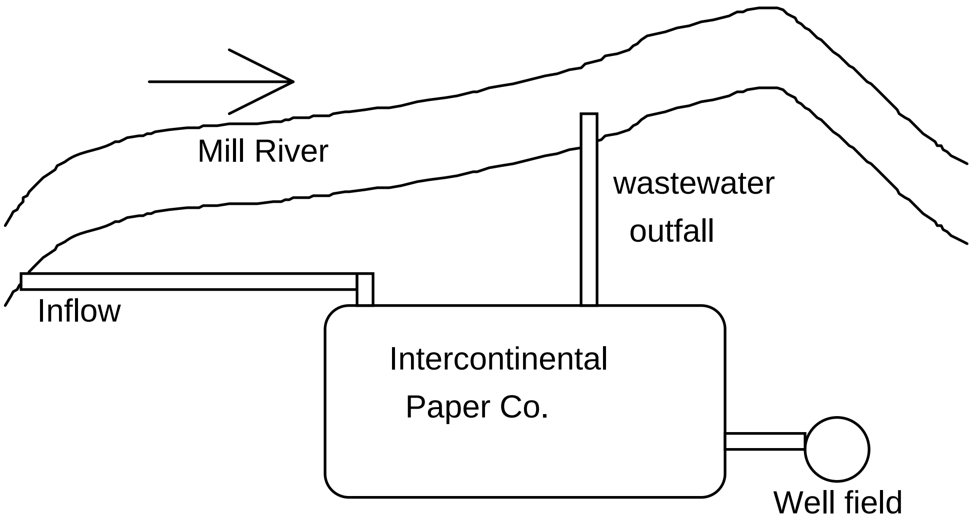
C. What would the fraction remaining be if you were doing this in a CMFR with a retention time of 5 hours

$$\frac{C}{C_o} = \frac{1}{1+\theta k} = \frac{1}{1 + 5hr(0.0077min^{-1})\,{}^{60min}/_{hr}} = \mathbf{0.302}$$

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 ft^3/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:

$$\begin{aligned} Q_d &= Q_u + Q_e \\ &= \left[12 - (0.5)3.8\right] + 3.8 \\ &= 13.9 cfs \end{aligned}$$

The solve for the effluent concentration using a mass balance:

$$\begin{aligned} C_e &= \frac{Q_d C_d - Q_u C_u}{Q_e} \\ &= \frac{13.9 cfs(15 mg/L) - 10.1(2.5 mg/L)}{3.8 cfs} \\ &= 48.2 \frac{mg}{L} \\ &\cong 48 \frac{mg}{L} \end{aligned}$$

6. <u>True/False</u>. 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 losses 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

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?

$$H_2CO_3 = HCO_3^- + H^+$$

First you need to recognize that bicarbonate is: HCO_3^-

The equilibrium expression for this reaction is:

$$K_{eq} = \frac{[H^+][HCO_3^-]}{[H_2CO_3]} = 10^{-6.3}$$

So:

$$\frac{[HCO_3^-]}{[H_2CO_3]} = \frac{10^{-6.3}}{[H^+]}$$

And therefore:

$$\frac{[HCO_3^-]}{[H_2CO_3]} = \frac{10^{-6.3}}{10^{-5.5}} = 10^{-0.8}$$

Thus:

$$\frac{[H_2CO_3]+[HCO_3^-]}{[H_2CO_3]} = 1 + 10^{-0.8}$$

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:

$$HCO_3^-/\text{total carbonate} \approx 1 - 0.863 = 0.137 = 13.7\%$$

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

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

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

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.

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

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.

Area Description	average runoff coefficient	acres	C*I*A (acre-ft/yr)
Urban Business	0.8	3000	9600
Urban single family	0.4	6000	9600
multifamily homes	0.5	6000	12000
Apartments	0.6	3000	7200
Parks & Cemeteries	0.15	2000	1200
	total	20000	39600

$$Q = \sum CIA = 39{,}600\ \frac{acre-ft}{yr}\left(\frac{43560ft^2}{acre}\right)\left(\frac{yr}{365.25d}\right)\left(\frac{d}{24hr}\right)\left(\frac{hr}{60min}\right)\left(\frac{min}{60s}\right)$$
$$= \mathbf{54.7\ cfs}$$

Appendix

Selected Chemical Constants

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

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

NAME	FORMULA	pK_a
Hydrochloric acid	$HCl = H^+ + Cl^-$	-3
Sulfuric acid	$H_2SO_4 = H^+ + HSO_4^-$	-3
Nitric acid	$HNO_3 = H^+ + NO_3^-$	-0
Bisulfate ion	$HSO_4^- = H^+ + SO_4^{-2}$	2
Phosphoric acid	$H_3PO_4 = H^+ + H_2PO_4^-$	2.15
Hydrofluoric acid	$HF = H^+ + F^-$	3.2
Nitrous acid	$HNO_2 = H^+ + NO_2^-$	4.5
Acetic acid	$CH_3COOH = H^+ + CH_3COO^-$	4.75
Propionic acid	$C_2H_5COOH = H^+ + C_2H_5COO^-$	4.87
Carbonic acid	$H_2CO_3 = H^+ + HCO_3^-$	6.35
Hydrogen sulfide	$H_2S = H^+ + HS^-$	7.02
Dihydrogen phosphate	$H_2PO_4^- = H^+ + HPO_4^{-2}$	7.2
Hypochlorous acid	$HOCl = H^+ + OCl^-$	7.5
Ammonium ion	$NH_4^+ = H^+ + NH_3$	9.24
Hydrocyanic acid	$HCN = H^+ + CN^-$	9.3
Phenol	$C_6H_5OH = H^+ + C_6H_5O^-$	9.9
Bicarbonate ion	$HCO_3^- = H^+ + CO_3^{-2}$	10.33
Monohydrogen phosphate	$HPO_4^{-2} = H^+ + PO_4^{-3}$	12.3
Bisulfide ion	$HS^- = H^+ + S^{-2}$	13.9

Conversions

7.48 gallon = 1.0 ft^3 1 gal = 3.7854×10^{-3} m^3

1 MGD = 694 gal/min = 1.547 ft^3/s = 43.8 L/s

1 ft^3/s = 449 gal/min

1 acre = 43,560 ft^2

g = 32 ft/s^2

W=γ = 62.4 lb/ft^3 = 9.8 N/L

1 hp = 550 ft-lbs/s = 0.75 kW

1 mile = 5280 feet 1 ft = 0.3048 m

1 watt = 1 N-m/s

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

At 60 ºF, $\nu = 1.217 \times 10^{-5}$ ft^2/s