CIVE 3331 - ENVIRONMENTAL ENGINEERING
Spring 2003

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Purpose: Exercises related to Lecture # 4. These exercises develop skills in selected environmental chemistry problems. Critical thinking is exercised in determination of analogies between lecture examples and the problems in this exercise set. Direct relationships to various accreditation objectives are highlighted in **Bold** type in the following sections. The exercises start on the next page.

Relevant ABET EC 2000 Criteria: Criterion 3 Program Outcomes and Assessment

(3-a) an ability to **apply knowledge of mathematics, science, and engineering**.
(3-e) an ability to identify, **formulate, and solve engineering problems**.
(3-k) **an ability to use the techniques, skills, and modern engineering tools necessary for engineering practice.**

Relevant CEE Educational Objectives:

(3) Emphasize **problem-identification**, **problem-formulation** and communication skills, **problem-solving techniques** and the many facets of engineering design throughout the curriculum.

(5) **Prepare every student to develop the skills for critical thinking and lifelong learning.**

Relevant CEE Program Outcomes:

ii. **Students should acquire the ability to solve practical civil engineering problems by applying the knowledge of mathematics, science**, **engineering**, **modern techniques**, **skills and practical tools** they **gained in their courses.**

Exercise_004-1

Consider the following reaction representing the combustion of propane:

$$C_3H_8 \quad + \quad O_2 \quad => \quad CO_2 \quad + \quad H_2O$$

a) Balance the equation.
b) How many moles of oxygen are required to burn one mole of propane?
c) How many grams of oxygen are required to burn 100g of propane?
d) At STP (standard temperature and pressure) what volume of oxygen would be required to burn 100g propane?
e) If air is 21% oxygen, what volume of air at STP is required?
f) At STP what volume of CO_2 would be produced when 100g of propane is burned?

Consider $C_3H_8 + O_2 \rightarrow CO_2 + H_2O$ (propane combustion)

a) balance the equation

(i) balance C (add $2CO_2$, for total $3CO_2$ on right)

$$C_3H_8 + O_2 \rightarrow 3CO_2 + H_2O$$

(ii) balance H (add $3H_2O$ for total $4H_2O$ on right)

$$C_3H_8 + O_2 \rightarrow 3CO_2 + 4H_2O$$

(iii) balance O (10-O on right, so make $5O_2$ on left

$$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$$

(b) How many mol of oxygen to burn 1 mol of propane?

1 mol propane needs 5 mol of $O_2(g)$ or 10 mol of O

(c) How many grams of O to burn 100g propane

$$100g\,C_3H_8 \cdot \frac{1\ mol}{44\ g} \cdot \frac{5\ mol\,O_2}{1\ mol\,C_3H_8} \cdot \frac{32\ g\,O_2}{1\ mol\,O_2} = 363\ grams\ O_2$$

(d) At STP (25°C, 1atm) what volume of O_2 is required
If air is 21% O_2 by volume, what volume of air?

V_{O_2}: $363 g\ O_2 \frac{1 mol}{32 g} \cdot \frac{22.4 L}{1 mol} = 254.5 L \frac{m^3}{1000 L} = 0.25 m^3$

V_{AIR}: $0.21(V_{AIR}) = V_{O_2}$ (partial pressures $\Rightarrow V \propto$ mole fraction)

$V_{AIR} = \frac{254.5 L}{0.21} = 1212 L \frac{m^3}{1000 L} = 1.21 m^3$ air

f) At STP what volume of CO_2 is produced when 100g of propane is burned?

$100 g\ C_3H_8 \frac{1 mol}{44 g} \cdot \frac{3 mol\ CO_2}{1 mol\ C_3H_8} \cdot \frac{22.4 L}{1 mol} = 152.7\ L\ CO_2$

$= \frac{152.7 L}{1000 L} = 0.15 m^3 CO_2$

Exercise_004-2

An unknown substance is empirically determined to be 40.00 percent carbon by weight, 6.67 percent hydrogen, and 53.33 percent oxygen. Its molecular weight is roughly 55 g/mol. Determine the molecular formula and the correct molecular weight.

$C_x H_y O_z \approx 55 g/mol$

$C_x \approx 0.40 \; 55 g/mol = 22 g/mol$

$H_y \approx 0.0667 \; 55 g/mol = 3.66 g/mol$

$O_z \approx 0.5333 \; 55 g/mol = 29.33 g/mol$

MW-C = 12 $\quad x = \frac{22}{12} = 1.8333$

MW-H = 1 $\quad y = \frac{3.66}{1} = 3.66$

MW-O = 16 $\quad z = \frac{29.33}{16} = 1.833$

Empirical formula is $C_{1.833} H_{3.66} O_{1.833}$

Observe $\frac{3.66}{1.833} = 1.996$ (2 for all practical purposes)

∴ Atomic ratios are $C_x H_{2x} O_x$

Now choose x so that MW ≈ 55

MW in terms of x.

$12(x) + 2(x) + 16(x) = 30x$

x is probably 2

∴ Formula is $C_2 H_4 O_2$, MW = 60 g/mol

Exercise_004-3

What is the molarity of 10g glucose dissolved into 1 liter of water?

Glucose $C_6H_{12}O_6$

MW = 6x12 + 12x1 + 6x16 = 180 g/mol

(10 g-Gluclose/L) / (180 g/mol) = 0.0555 mol/L

Report as : 0.0555 M

Exercise_004-4

For the following possible automobile fuels, express their higher heating value (HHV) in Btu/gallon.

a) Methanol (CH_3OH), density 6.7lbs/gallon, H^o = -238.6 kJ/mol
b) Ethanol (C_2H_5OH), density 6.6 lbs/gallon, H^o = -277.6 kJ/mol
c) Propane (C_3H_8), density 4.1 lbs/gallon, H^o = -103.8 kJ/mol

a) Methanol CH_3OH, $\rho = 6.1$ lb/gal

$$2CH_3OH + 3O_2 \rightarrow 2CO_2 + 4H_2O$$

$$2(-238.6) + 3(0) \qquad 2(-393.5) + 4(-285.8)$$

$$\Delta H = -1453 \text{ kJ/mol}$$

Need gallons/mol

$$1 \text{ mol} = (12) + (16) + 4) = 32 \text{ grams} \cdot \frac{2.2046 \text{ lbs}}{10^3 \text{ grams}}$$

$$= 0.0705 \text{ lbs} * \frac{1 \text{ gal}}{6.7 \text{ lbs}} = 0.01156 \text{ gal}$$

$$1453 \cdot \text{kJ} \cdot \frac{0.9478 \text{ Btu}}{1 \text{ kJ}} = 1377.15 \text{ Btu}$$

$$\therefore \Delta H = - \frac{1377.15 \text{ Btu}}{0.01156 \text{ gal}} = -130,790 \text{ Btu/gal}$$

b) Ethanol

$$C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$$
$$(-277.6) + 3(0) \rightarrow 2(-393.5) + 3(-285.8)$$

$\Delta H = -1366.8$ kJ/mol

$2(12) + 6 + 16 = 46$ g/mol

$46\text{ grams} \cdot \frac{2.2046}{10^3} = 0.1014\text{ lbs} \cdot \frac{1}{6.6} = 0.0153\text{ gal}$

$-1366.8 \cdot 0.9478 = -1295\text{ Btu}/$

$\therefore \Delta H = \frac{-1295\text{ Btu}}{0.0153\text{ gal}} = -84309\text{ Btu/gal}$

c) Propane

$$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$$
$$(-103.8) \quad 5(0) \quad 3(-393.5) + 4(-285.8)$$

$\Delta H = -2219.9$ kJ/mol

$3(12) + 8 = 44\text{ g/mol} \cdot \frac{2.2046}{10^3} = 0.097\text{ lbs/mol} \cdot \frac{1\text{ gal}}{4.1\text{ lbs}} = 0.0236\text{ gal}$

$-2219.9\text{ kJ} \cdot 0.9478 = -2104\text{ Btu}$

$\therefore \Delta H = \frac{-2104\text{ Btu}}{0.0236\text{ gal}} = -88930\text{ Btu/gal}$

Exercise_004-5

Find the ThOD for the following solutions:

a) 200 mg/L of acetic acid (CH_3COOH)
b) 30 mg/L ethanol
c) 50 mg/L sucrose ($C_2H_{12}O_6$)

200 mg/L of acetic acid; CH_3COOH

$$CH_3COOH + 2O_2 \rightarrow 2CO_2 + 2H_2O$$

balance C 2 ✓ $CH_3COOH = 12+3+12+32+1 = 60 g/mol$
balance H 4 ✓ $2O_2 = 64 g/mol$
balance O 6 ✓ $2CO_2 = 2(44) = 88 g/mol$
Convert to masses $2H_2O = 2(18) = 36 g/mol$

60 g CH_3COOH required 64 g O_2 for complete oxidization

$$200 mg/L - CH_3COOH \cdot \frac{64 g\ O_2}{60 g\ CH_3COOH} = \underline{\underline{213 mg/L}}\ O_2 \text{ required}$$

30mg/L ethanol C_2H_5OH

$C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$

24+16+6 3(32) 2(44) 3(18)

46g/mol

$30\text{ mg/L EtOH} \cdot \frac{96\text{g } O_2}{46\text{g EtOH}} = \underline{\underline{62.6\text{ g/L}}}\ O_2$ required

50mg/L sucrose $C_2H_{12}O_6$

$C_2H_{12}O_6 + 2O_2 \rightarrow 2CO_2 + 6H_2O$

24+12+6(16) 2(32)

132g/mol 64g/mol

$50\text{ mg/L sugar} \cdot \frac{64\text{g } O_2}{132\text{g sugar}} = 24.2\text{ mg/L}$ Oxygen.

Exercise_004-6

Water is usually disinfected with chlorine gas, forming hypochlorous acid (HOCl), which partially ionizes into hypochlorite and hydrogen ions:

$HOCl \Leftrightarrow H^+ + OCl^- \quad K_{HOCl} = 2.9 \times 10^{-8}$

The amount of [HOCl], which is the desired disinfectant, depends on the pH. Develop a design curve that relates the fraction of hypochlorous acid in solution to the pH (i.e. [HOCl]/{[HOCl] + [OCl⁻]}. What would be the hypochlorous fraction at pH = 4.0, 6.0, 8.0, and 10.0?

$$HOCl \rightleftharpoons H^+ + OCl^- \qquad K_{eq} = 2.9 \cdot 10^{-8}$$

[HOCl] is pH dependent. Find the fraction of [HOCl]/([HOCl] + [OCl⁻]) as a function of pH.

$$\frac{[H^+][OCl^-]}{[HOCl]} = 2.9 \cdot 10^{-8}$$

$$\frac{[OCl^-]}{[HOCl]} = \frac{2.9 \cdot 10^{-8}}{10^{-pH}}$$

$$\frac{[HOCl]}{[HOCl]+[OCl^-]} = \frac{1}{1 + \frac{[OCl^-]}{[HOCl]}} = \frac{1}{1 + \frac{2.9 \cdot 10^{-8}}{10^{-pH}}}$$

pH	H^+	$\frac{[OCl^-]}{[HOCl]} = \frac{2.9 \cdot 10^{-8}}{10^{-pH}}$	$\frac{[HOCl]}{[HOCl]+[OCl^-]}$	%HOCl
10	$1 \cdot 10^{-10}$	290	0.003	.3%
9	$1 \cdot 10^{-9}$	29	0.033	3.3%
8	$1 \cdot 10^{-8}$	2.9	0.256	25.6%
7	$1 \cdot 10^{-7}$	0.29	0.775	77.5%
6	$1 \cdot 10^{-6}$	0.029	0.971	97.1%
5	$1 \cdot 10^{-5}$	0.0029	0.997	99.7%

Exercise_004-7

Hydrogen sulfide (H_2S) is an odorous gas that can be stripped from solution in a process similar to ammonia stripping. The reaction is

$H_2S \Leftrightarrow H^+ + HS^-$ $K_1 = 0.86 \times 10^{-7}$

Develop a design curve that relates the fraction of H_2S in solution as a function of pH. What are the fractions at ph = 4, 6, and 8?

$H_2S \rightleftharpoons H^+ + HS^-$ $K_{eq} = 0.86 \cdot 10^{-7}$

Find fraction of H_2S in water at pH6 and pH8.

$$\frac{[H^+][HS^-]}{[H_2S]} = 0.86 \cdot 10^{-7}$$

$$\frac{[H_2S]}{[HS^-]} = \frac{[H^+]}{0.86 \cdot 10^{-7}} \qquad pH = -\log[H^+]$$

$$\frac{[H_2S]}{[H_2S] + [HS^-]} = \frac{1}{1 + \frac{HS^-}{H_2S}}$$

pH	$[H^+]$	$\frac{[H^+]}{0.86 \cdot 10^{-7}} = \frac{H_2S}{HS^-}$	$\frac{1}{1 + \frac{HS^-}{H_2S}}$	% H_2S
9	$1 \cdot 10^{-9}$	0.0011627	0.011	1.1%
8	$1 \cdot 10^{-8}$	0.11627	0.104	10.4%
7	$1 \cdot 10^{-7}$	1.16279	0.537	53.7%
6	$1 \cdot 10^{-6}$	11.6279	0.920	92.0%
5	$1 \cdot 10^{-5}$	116.279	0.991	99.1%
4	$1 \cdot 10^{-4}$	1162.79	0.999	99.9%
3	$1 \cdot 10^{-3}$	11627.9	0.999	99.99%

Exercise_004-8

Calculate the equilibrium concentration of dissolved oxygen in 15°C water at 1 atm., and again at an elevation of 2000 meters above sea level.

$DO_{sat} = K_H P_g$ @ 15°C $K_H = 0.0015236$

$DO_{sat} = (0.0015236)(0.22)(1\,atm) = 0.00031996\ mol/L \cdot \frac{32{,}000\,mg}{1\,mol\ O_2} = \underline{\underline{10.2\ mg/L}}$ ←

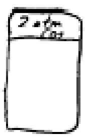
@ 2000 m

$P_g = 1 - 1.15\cdot10^{-4}(2000) = 0.77\ atm$

$DO_{sat} = (0.0015236)(0.22)(0.77) = 0.0002464\ \frac{mol}{L} \cdot \frac{32{,}000\,mg}{1\,mol} = \underline{\underline{7.9\ mg/L}}$ ←

Exercise_004-9

Suppose the gas above the soda in a bottle of soft drink is pure CO_2 at a pressure of 2 atm. Calculate the pH of the soft drink.



$$CO_{2(aq)} = K_H P_g$$
$$= 0.033363(2) = 0.066676\ mol/L \times \frac{44{,}000\ mg}{mol} = 2900\ mg/L = 2.9\ g/L$$

Exercise_004-10

It is estimated that the concentration of CO_2 in the atmosphere before the industrial revolution was 275 ppm. If CO_2 accumulation in the atmosphere continues at current rates it may be around 600 ppm by the next century. Calculate the *pH* of rainfall in these two periods (pre-industrialization and next century).

@ 275 ppm

$[CO_2] = K_H P_g = 0.033363 \cdot 275 \cdot 10^{-6} = 9.17 \cdot 10^{-6}$ mol/L

$[H^+]^2 \approx (4.47 \cdot 10^{-7})(9.17 \cdot 10^{-6}) + 10^{-14} = 4.11 \cdot 10^{-12}$ $\therefore [H^+] \approx 2.0 \cdot 10^{-6}$

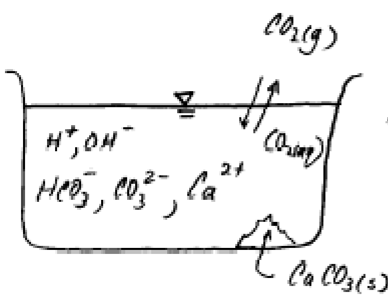
$pH = -\log(2.0 \cdot 10^{-6}) = 5.69$

Repeat for $P_g = 600 \cdot 10^{-6}$ $pH = 5.52$

Exercise_004-11

One strategy for controlling acidification of lakes is to periodically add excess lime ($CaCO_3$) into the lake. Calculate the *pH* of a lake that has enough excess lime so that the lake is saturated with calcium and carbonate ions. This calculation is identical to that one would make to estimate the pH of the oceans, which are saturated with $CaCO_3$.

Acid lakes can be periodically limed ($CaCO_3$) to increase the pH. Calculate pH of a lake with excess lime.



Assume: system at STP (25°C, 1 atm)

① System is in equilibrium with atmosphere
② System is in equilibrium with $CaCO_3$ precipitate
③ Charge balance is neutral (no excess charge)

(a) $CO_{2(aq)} = K_H P_{CO_{2(g)}} = (0.033363 \frac{m}{L \cdot atm})(360 \cdot 10^{-6} atm)$

$= 1.2011 \cdot 10^{-5} \frac{mol}{L}$ (dissolution)

(b) $CO_{2(aq)} + H_2O \rightleftharpoons H_2CO_3^* \rightleftharpoons H^+ + HCO_3^-$ (carbonic acid, bicarbonate eq.)

(c) $HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$ (bicarbonate - carbonate eq.)

(d) $CaCO_3 \rightleftharpoons Ca^{2+} + CO_3^{2-}$ (solid-liquid equilibrium)

(e) $H^+ + 2Ca^{2+} = HCO_3^- + 2CO_3^{2-} + OH^-$ (charge balance)

(f) $[H^+][OH^-] = 1 \cdot 10^{-14}$

(4) All "equilibria" & charge balance must be satisfied

(b) $\frac{[H^+][HCO_3^-]}{[CO_{2aq}]} = K_1 = 4.47 \cdot 10^{-7} m/L$

(c) $\frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} = K_2 = 4.68 \cdot 10^{-11}$

(d) $[Ca^{2+}][CO_3^{2-}] = K_{sp} = 4.57 \cdot 10^{-9}$

(f) $[H^+][OH^-] = 1 \cdot 10^{-14}$

(e) $H^+ + 2Ca^{2+} = HCO_3^- + 2CO_3^{2-} + OH^-$

known: $CO_{2(aq)}$, if we pick H^+ we can determine values for HCO_3^-, CO_3^{2-}, Ca^{2+}, OH^-

by trial & error, pick H^+ that satisfies all the equations!

1) $HCO_3^- = \frac{4.47\cdot10^{-7}[CO_{2aq}]}{H^+}$

2) $CO_3^{2-} = \frac{4.68\cdot10^{-11}[HCO_3^-]}{H^+} = \frac{4.68\cdot10^{-11}\times4.47\cdot10^{-7}[CO_{2aq}]}{[H^+]^2}$

3) $Ca^{2+} = \frac{4.57\cdot10^{-9}}{CO_3^{2-}} = \frac{4.57\cdot10^{-9}\ [H^+]^2}{4.68\cdot10^{-11}\times4.47\cdot10^{-7}[CO_{2aq}]}$

4) $OH^- = \frac{1\cdot10^{-14}}{H^+}$

5) Charge balance — best to do this with Excel or use algebra

$$[H^+] + 2\left[\frac{4.57\cdot10^{-9}[H^+]^2}{4.68\cdot10^{-11}\times4.47\cdot10^{-7}[CO_{2aq}]}\right] - \frac{4.47\cdot10^{-7}[CO_2(aq)]}{[H^+]}$$

$$- 2\left[\frac{4.68\cdot10^{-11}\times4.47\cdot10^{-7}[CO_{2aq}]}{[H^+]^2}\right] - \frac{1\cdot10^{-14}}{[H^+]} = 0$$

solve for H^+

by trial & error pH is somewhere between 8 & 9

pH = 8.27415 (too many sig. figs should be close)

$H^+ = 10^{-8.2745} = 5.3192 \cdot 10^{-9}$

$HCO_3^- = 1.0093 \cdot 10^{-3}$

$CO_3^{2-} = 8.8806 \cdot 10^{-6}$

$Ca^{2+} = 5.1461 \cdot 10^{-4}$

$OH^- = 1.88 \cdot 10^{-6}$

charge balance

$[H^+] + 2[Ca^{2+}]$

$5.3192 \cdot 10^{-9} + 2(5.1461 \cdot 10^{-4}) = 1.0292 \cdot 10^{-3}$

$[HCO_3^-] + 2[CO_3^{2-}] + [OH^-]$

$1.0093 \cdot 10^{-3} + 2(8.8806 \cdot 10^{-6}) + (1.88 \cdot 10^{-6}) = 1.0289 \cdot 10^{-3}$

difference

$$\begin{array}{r} 1.0292 \cdot 10^{-3} \\ -1.0289 \cdot 10^{-3} \\ \hline 2.588 \cdot 10^{-7} \end{array}$$

practically zero

∴ pH ≈ 8.27 for open system with excess solid present.

(Compare to open system, no solid (no Ca) pH = 5.63)

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