Homework Problems

Green Engineering

(458.701)

Youn-Woo Lee
School of Chemical and Biological Engineering

155-741 San 56-1 Sillim, Gwanak, Seoul, Korea • ywlee@snu.ac.kr • http://sfpl.snu.ac.kr

Homework #1

Solve the Problems in Chapter 1:

5. Ozone Depletion Potential of Substitute Refrigerants
(hint: read page 12 carefully)

Due date: March 17, 2011

Homework #2

Problem 2-5 (a), (b), (c) and (d)

Choice of a Safe Solvent for Photo-resist which consists of an acrylate monomer, polymeric binder, and photo-initiator.

Due date: March 31, 2011

Homework #3

Problem

1. Provide definitions for the following terms
    a) pollution prevention
    b) source reduction
    c) in-process versus on-site versus off-site recycling
    d) waste treatment
    e) disposal
    f) direct release

Homework #4

Further Reading in Engineering Ethics

- *Process safety and environmental protection are not the only responsibilities of professional engineers. Engineers also have responsibilities to clients, to colleagues and to the professions*.

AIChE Web *http://www.aiche.org/membership/ethics.htm*

Problems 4-1 by April 6

Homework #5

Problems

5-1.
5-4.

Due date: April 21, 2011

Homework #6

Problem 7-1

Due on April 30, 2011

Homework #7

Problem 8-1

Due on May14, 2011

Homework Solution #1

Ozone Depletion Potential of Substitute Refrigerants

A discussed in chapter 1, bromine is a much more potent ozone depletion substance compared to chlorine on a per-atom basis. Fluorine is thought to have no adverse ozone depletion effects. Therefore, substituting fluorine for chlorine on alternative refrigerants would help solve the ozone depletion problem. On the other hand, fluorine on hydrocarbon refrigerants is a potent greenhouse gas and fluorinated compounds have been found to accumulate in the body fat of animals as far away as the arctic, well away from any known sources of these compounds. Apparently the persistence of these fluorinated compounds combined with atmospheric transport over long distances creates exposure to these remote creatures.

Homework solution #2

5. Choice of a Safe Solvent for a Photoresist

a) Rank solvents based on toxicity from higher to lower hazard

	PEL (ppm)
diethylemine	25
monomethyl ether	25
furfuryl alcohol	50
n-butyl acetate	150
methyl ethyl ketone	200
ethyl acetate	400

b) Rank from higher to lower exposure potential using vapor pressure

	Vapor Press. (kPa @ 25˚C)
diethylemine	30.1
ethyl acetate	12.6
methyl ethyl ketone	12.1
monomethyl ether	1.3
n-butyl acetate	1.3
furfuryl alcohol	0.1

c) Considering hazard and exposure, rank from higher to lower risk
If we take the inverse of the PEL as a measure of potential hazard and multiply by the vapor pressure (a measure of exposure), we could estimate the overall risk potential by inhalation.

	1/PEL • Vapor Press.
diethylemine	1/25 • 30.1 = 1.20
methyl ethyl ketone	1/200 • 12.1 = 0.06
monomethyl ether	1/25 • 1.3 = 0.05
ethyl acetate	1/400 • 12.6 = 0.03
n-butyl acetate	1/150 • 1.3 = 0.009
furfuryl alcohol	1/50 • 0.1 = 0.002

Furfural alcohol is the solvent with the lowest risk.

d) To lower the risk even more, process modifications could be placed on the integrated circuits fabrication process to reduce the amount of vapor generated and to collect and recover any vapors prior to exposure to workers.

Homework solution #3

a) pollution prevention: Any act of source reduction, in-process recycle, on-site recycle, and off-site recycle that reduces the amounts of releases and the hazardous characteristics of those releases which ultimately reach the environment.

b) source reduction: Any modification of a manufacturing process or of production procedures which reduces the amount of components entering a waste stream or the hazardous characteristics of those components entering waste streams prior to recycle, treatment, or disposal.

c) in-process versus on-site versus off-site recycle: In-process recycle is the recovery and return of components that would otherwise become waste to the process unit where these components were generated, usually immediately after they are generated. Examples would be unconverted reactants leaving a reactor that are separated and returned to the reactor inlet. On-site recycle is the recovery of valuable stream components using process units within the same facility where those components were generated. Off-site recycle is the recovery of valuable components at a remote location from waste streams generated at a facility and the return of the valuable components to the facility.

d) waste treatment: Any process that renders a waste stream less hazardous prior to disposal or direct release through physical, biological, or chemical means. Examples are primary, secondary, and tertiary wastewater treatment, adsorption of volatile organic compounds from air, and landtreatment of petroleum hydrocarbon sludges from tank bottoms.

e) disposal: Long-term isolation of raw or treated waste components in a secured landfill. Examples include landfills for domestic and industrial hazardous and non-hazardous waste.

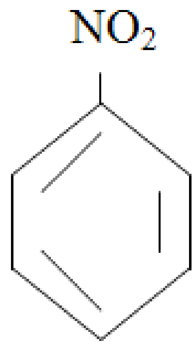
f) direct release: The direct release of components from processes to the air, land, or water. An example of this includes the release of volatile organic compounds from fugitive emission sources in chemical or petroleum refinery processes (from valves, fittings, pumps, flanges, connectors, etc.).

Homework solution #4

Inherently Safer Design Concepts	Pollution Prevention Concepts
Intent: reduce catastrophic releases of hazardous chemicals and the hazards of those releases by modifying the process to eliminate the source of those hazards within the process.	**Intent**: reduce chronic releases of hazardous chemicals and the hazards of those releases by modifying the process to make them more efficient at using energy and mass.
Minimize: reduce the inventory of hazardous chemicals within the process.	Source Reduction: reduce the generation and release of hazardous wastes from a process.
Substitute: replace hazardous materials with safer chemicals to reduce impacts of catastrophic releases.	Material Substitution: replace hazardous materials or materials that use excessive energy with more benign materials.
Moderate: Use less hazardous conditions to lessen the impacts of any catastrophic releases.	Process/Procedure Modifications: change process conditions to reduce waste generation and energy consumption.
Simplify: design facilities to be less complex and less error prone, and forgiving of any errors that are made.	Process Modification: change the process control strategy to more precisely achieve the desired operating conditions.

Homework solution #5

1. Estimate properties for nitrobenzene.
Nitrobenzene has the molecular formula



Boiling Pt., from eqn. 5-1,

$T_b\,(K) = 198.2 + \Sigma\, n_i\, g_i$

group	g_i contribution
NO_2	113.99
1 aaC	30.76 (a substituted carbon bound to 2 aromatic carbons)
5 aaCH	5(28.53)

$T_b(K) = 198.2 + 113.99 + 30.76 + 5(28.53)$ = 485.60 K ▲ estimated
= 484.12 K ▲ actual

$T_b\,(\text{corrected}) = T_b - 94.84 + 0.5577T_b - 0.0007705(T_b)^2 \quad [T_b \le 700K]$ (Eqn. 5-2)
$= 485.6 - 94.84 + 0.5577(485.6) - 0.0007705(485.6)^2 = 479.9\ K$

T_b (corrected) is in error by 0.87% compared to the actual value.

Homework solution #5

Vapor pressure (P_{vp}):

$\ln P_{vp} = \frac{[A(T_b - C)^2]}{[0.97\ R\ T_b\ ]} * [1/(T_b - C) - 1/(T - C)]$ (Eqn. 5-7)

$A = K_F\ (8.75 + R \ln T_b\ ) = 1.05(8.75 + 1.987 \ln(485.6)) = 22.09$

$C = -18 + 0.19\ T_b = -18 + 0.19(485.6) = 74.26$

$\ln P_{vp} = \frac{[22.09(485.6 - 74.26)^2]}{[0.97\ (1.987)\ (485.6)\ ]} * [1/(485.6 - 74.26) - 1/(298 - 74.26)] = -8.139$

$P_{vp} = \exp(-8.13) = 2.92\text{x}10^{-4}$ atm = 0.22 mm Hg.

Henry's Law constant (H)

$-\log H = \log$ (air-water partition coefficient) $= \Sigma\ n_i\ h_i + \Sigma\ n_j\ c_j$ (H unitless)

1 $C_{aromatic}$-NO_2 $n_i\ h_i = 2.496$

6 $C_{aromatic}$ - $C_{aromatic}$ $n_i\ h_i = 6(0.2638)$

5 $C_{aromatic}$-H $n_i\ h_i = 5(-0.1543)$

No corrections factors

$-\log H = 2.2496 + 6(0.\ 2638) + 5(-0.1543) = 3.06$

$H = 10^{-3.06} = 8.69\text{x}10^{-4}$ unitless $= 2.13\text{x}10^{-4}$ atm-m^3/mole

H (experimental) $= 2.40\text{x}10^{-4}$ atm-m^3/mole

Homework solution #5

<u>Water solubility (S):</u> (S in mole/L)

$\log S = 0.796 - 0.854 \log K_{ow} - 0.00728(MW) + \Sigma h_j$ (used when melting pt. not available)

Corrections factors $h_j = -.390$ (aromatic nitro group)

$\log S = 0.796 - 0.854(1.85) - 0.00728(123.11) + -.390 = -2.07$

$S = 10^{-2.07} = 8.51\text{x}10^{-3}$ moles/L = 1.05 g/L = 1,047.5 mg/L

<u>Soil sorption coefficient (K_{oc}):</u>

$\log K_{oc} = 0.53\,{}^{1}\chi + 0.62 + \Sigma n_j P_j$ (K_{oc} is ratio of µg/g carbon to µg/ml solution)

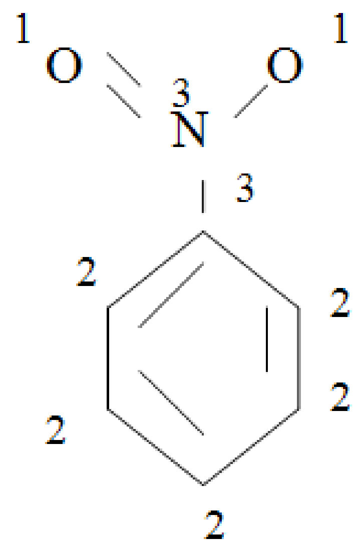
${}^{1}\chi = \Sigma(\delta_i * \delta_j)^{-0.5}$, the first order molecular connectivity index

δ_i ,the connectedness of carbon or other heteroatom i)

Bond connectedness ($\delta_i * \delta_j$)

(N-O) (N=O) (N-C) 2(C-C) 4(C-C)

(3,1) (3,1) (3,3) 2(3,2) 4(2,2)



$${}^{1}\chi = \Sigma(\delta_i * \delta_j)^{-0.5}$$

$${}^{1}\chi = \frac{1}{\sqrt{3}} + \frac{1}{\sqrt{3}} + \frac{1}{\sqrt{9}} + 2\frac{1}{\sqrt{6}} + 4\frac{1}{\sqrt{4}} = 4.305$$

$\log K_{oc} = 0.53(4.305) + 0.62 - 0.632 = 2.27$

$K_{oc} = 10^{2.27} = 186$

Homework solution #5

Octanol-water partition coefficient (K_{ow}):

$\log K_{ow} = 0.229 + \Sigma n_i f_i + \Sigma n_j c_j$

6 $C_{aromatic}$ $n_i h_i = 6(0.2940)$

$-NO_2$ (aromatic attach.) $n_i h_i = -0.1823$

No corrections factors

$\log K_{ow} = 0.229 + 6(0.2940) + -0.1823 = 1.81$

$K_{ow} = 10^{1.81} = 64.67$

$\log K_{ow}$ (experimental) = 1.85

Atmospheric half life:

The only significant reaction is addition to aromatic ring = 0.2437×10^{-12} cm^3/molecule-sec.

$t_{1/2½} = \ln(2) / (k\,[OH\cdot]) = 0.693/((0.2437 \times 10^{-12}$ cm^3/molecule-sec)$(1.5 \times 10^6$ molecules/ cm^3))

$t_{1/2½} = 1.896 \times 10^6$ sec = 22 days.

Biodegradability:

$I = 3.199 + a_1 f_1 + a_2 f_2 + \ldots\ldots + a_n f_n + a_m MW$

Unsubstituted phenyl group a = 0.022

Aromatic (NO_2) a = -.134 (used aromatic amine as substitute)

Molecular weight a = -0.00221

$I = 3.199 + 0.022 - .134 + 123.11(-0.00221) = 2.81$ (weeks to a month)

Homework solution #6

1. Atom and Mass Efficiency Calculations: Calculate mass and atom efficiencies

a) (Addition reaction) Isobutylene + methanol → methyl,tert-butyl ether

$C_4H_8 + CH_3OH \rightarrow (C_4H_9)\text{-O-}CH_3$

Mass efficiency: Feedstocks – 5(12) + 12(1) + 1(16) = 88

Product – 5(12) + 12(1) + 1(16) = 88 …….. efficiency = 100%

Carbon efficiency: Feedstocks – 5(12) = 60

Product – 5(12) = 60 …….. efficiency = 100%

Hydrogen efficiency: Feedstocks – 12(1) = 12

Product – 12(1) = 12 …….. efficiency = 100%

Oxygen efficiency: Feedstocks – 1(16) = 16

Product – 1(16) = 16 …….. efficiency = 100%

Homework solution #6

b) (Substitution reaction) Phenol + ammonia → aniline + water

$C_6H_5\text{-}OH + NH_3 \rightarrow C_6H_5\text{-}NH_2 + H_2O$

Mass efficiency: Feedstocks – 6(12) + 9(1) + 1(16) + 1(14) = 111

Product – 6(12) + 7(1) + 0(16) + 1(14) = 93 …….. efficiency = 83.8%

Carbon efficiency: Feedstocks – 6(12) = 72

Product – 6(12) = 72 …….. efficiency = 100%

Hydrogen efficiency: Feedstocks – 9(1) = 9

Product – 7(1) = 7 …….. efficiency = 77.8%

Oxygen efficiency: Feedstocks – 1(16) = 16

Product – 0(16) = 0 …….. efficiency = 0%

Nitrogen efficiency: Feedstocks – 1(14) = 14

Product – 1(14) = 14 …….. efficiency = 100%

Homework solution #6

c) (Elimination reaction) Ethylbenzene → styrene + hydrogen

$C_6H_5\text{-}C_2H_5 \rightarrow C_6H_5\text{-}C_2H_3 + H_2$

Mass efficiency: Feedstocks – 8(12) + 10(1) = 106

Product – 8(12) + 8(1) = 104 …….. efficiency = 98.1%

Carbon efficiency: Feedstocks – 8(12) = 96

Product – 8(12) = 96 …….. efficiency = 100%

Hydrogen efficiency: Feedstocks – 10(1) = 10

Product – 8(1) = 8 …….. efficiency = 80%

d) Other industrially important examples of additions, substitutions, and elimination reactions (see Wittkcoff, H.A. and Reuben, B.G. "Industrial Organic Chemicals", John Wiley & Sons, New York, 1996; and Weissermel, K. and Arpe, H.-J. "Industrial Organic Chemistry", VCH Verlagsgesellschaft mbH a Wiley company, Weinheim Germany, 1997).

Homework solution #7

1. Compare the carbonylation of dinitrotoluene and the amine-phosgene routes for the production of toluene diisocyanate (TDI) using a Tier 1 economic and environmental performance evaluation.

Amine - phosgene route:

$C_6H_3(CH_3)(NH_2)_2 + 2\ COCl_2 \rightarrow C_6H_3\ (CH_3)(\text{-N=C=O})_2 + 4\ HCl$

Carbonylation of nitrobenzene:

$C_6H_3\ (CH_3)(NO_2)_2 + 6\ CO \rightarrow C_6H_3\ (CH_3)(\text{-N=C=O})_2 + 4\ C\ O_2$

Table of stoichiometric and toxicity data for each reaction pathway

Compound	*Pounds produced or pounds of raw material required per pound of TDI**	*Cost ($/lb)***	*PEL ($\mu g/m^3$)*	*Overall inhalation toxicity factor*	*Overall oral toxicity factor*
Amine - phosgene route					
toluene diamine	-0.76	0.576	0.1 (est.)	NA	NA
chlorobenzene	-0.01	0.550	350	100	100
hydrochloric acid	0.4 (est.)	0.027	7	100	100
phosgene	-1.26	0.610	0.4	NA	NA
TDI	1.00	1.340	0.14	100,000	100
Carbonylation route					
dinitrotoluene	-1.04 (est.)	0.365	1.5	1,000	1,000
carbon monoxide	-1.0 (est.)	0.040	55	NA	NA
TDI	1.00	1.340	0.14	100,000	100
carbon dioxide	1.0 (est.)	-	9000	NA	NA

Homework solution #7

Environmental and Economic Evaluation

Environmental evaluation

$$\text{TLV Index} = \sum_i |v_i| \times TLV_i^{-1} \text{ (PEL can be used instead of TLV)} \quad \text{(Equation 8-2)}$$

$$\text{EPA Index} = \sum_i |v_i| \times (\text{maximum of oral and inhalation weighting factor})_i \quad \text{(Equation 8-3)}$$

Amine-phosgene route

TLV Index = (.76)(1/.1)+(.01)(1/350)+(.4)(1/7)+(1.26)(1/.4)+(1)(1/.14) = 17.95

EPA Index = (.01)(100)+(.4)(100)+(1)(100,000) = 100,041

Cost of Raw Materials = (.76)(.576)+(.01)(.550)+(1.26)(.610) = $1.21/lb TDI

Carbonylation Route

TLV Index = (1.04)(1/1.5)+(1)(1/55)+(1)(1/.14)+(1)(1/9000) = 7.85

EPA Index = (1.04)(1,000)+(1)(100,000) = 101,040

Cost of Raw Materials = (1.04)(.365)+(1)(.04) = $0.42/lb TDI

Discussion: The TLV Index indicates that the carbonylation route is superior to the amine-phosgene route. The EPA Index indicates that both routes are about the same, but data is lacking for this index, so we should rely less on this index. The cost analysis indicates that the carbonylation route is superior.