Solutions Manual

to accompany

Introduction to Chemical Processes
Principles, Analysis, Synthesis

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P1.1

$SiO_2 + 3C \rightarrow 2CO + SiC$

P1.2

$C_3H_5(NO_3)_3 \rightarrow \nu_2 CO_2 + \nu_3 H_2O + \nu_4 N_2 + \nu_5 O_2$

From element balances on N, C, H, and O, we write 4 equations:

$$3 = 2\nu_4$$
$$3 = \nu_2$$
$$5 = 2\nu_3$$
$$9 = 2\nu_2 + \nu_3 + 2\nu_5$$

Solving, we find

$$C_3H_5(NO_3)_3 \rightarrow 3CO_2 + \frac{5}{2}H_2O + \frac{3}{2}N_2 + \frac{1}{4}O_2$$

P1.3

$(NH_4)_2PtCl_6 \rightarrow \nu_2 Pt + \nu_3 NH_4Cl + \nu_4 N_2 + \nu_5 HCl$

Pt: $\nu_2 = 1$

N: $\nu_3 + 2\nu_4 = 2$

H: $4\nu_3 + \nu_5 = 8$

Cl: $\nu_3 + \nu_5 = 6$

Combine H and Cl balances and solve, than solve N balance:

$$\nu_3 = \frac{2}{3},\ \nu_5 = 5\frac{1}{3},\ \nu_4 = \frac{2}{3}$$

$$(NH_4)_2PtCl_6 \rightarrow Pt + \frac{2}{3}NH_4Cl + \frac{2}{3}N_2 + 5\frac{1}{3}HCl$$

P1.4

The three balanced equations are

$$NaHCO_3 + HCl \rightarrow NaCl + CO_2 + H_2O$$
$$CaCO_3 + 2HCl \rightarrow CaCl_2 + CO_2 + H_2O$$
$$MgCO_3 + 2HCl \rightarrow MgCl_2 + CO_2 + H_2O$$

To calculate the grams HCl neutralized per gram of each compound, we need the molar masses: 84 g/gmol for sodium bicarbonate, 100 g/gmol for calcium carbonate, and 84 g/gmol for magnesium carbonate.

$$NaHCO_3\text{:}\ \frac{1\text{ gmol HCl}}{\text{gmol NaHCO}_3} \times \frac{\text{gmol NaHCO}_3}{84\text{ g NaHCO}_3} \times \frac{36.5\text{ g HCl}}{\text{gmol HCl}} = \frac{0.435\text{g HCl}}{\text{g NaHCO}_3}$$

$CaCO_3$: $\dfrac{2 \text{ gmol HCl}}{\text{gmol CaCO}_3} \times \dfrac{\text{gmol CaCO}_3}{100 \text{ g CaCO}_3} \times \dfrac{36.5 \text{ g HCl}}{\text{gmol HCl}} = \dfrac{0.73\text{g HCl}}{\text{g CaCO}_3}$

$MgCO_3$: $\dfrac{2 \text{ gmol HCl}}{\text{gmol MgCO}_3} \times \dfrac{\text{gmol MgCO}_3}{84 \text{ g MgCO}_3} \times \dfrac{36.5 \text{ g HCl}}{\text{gmol HCl}} = \dfrac{0.869\text{g HCl}}{\text{g MgCO}_3}$

$MgCO_3$ has the best neutralizing ability, gram for gram.

P1.5

Molar mass of urea $(NH_2)_2CO$ = $2 \times 14 + 4 \times 1 + 12 + 16 = 60 \text{ g/gmol}$.

$$10 \text{ gmol} \times 60 \ \frac{\text{g}}{\text{gmol}} \times \frac{1 \text{ lb}}{454 \text{ g}} = 1.3 \text{ lb}$$

$$10 \text{ lbmol} \times 60 \ \frac{\text{lb}}{\text{lbmol}} \times \frac{454 \text{ g}}{\text{lb}} = 272{,}000 \text{ g}$$

P1.6

Water is required to decompose the urea:

$$(NH_2)_2CO + H_2O \rightarrow 2NH_3 + CO_2$$

$$\text{Fractional atom economy} = \frac{2 \text{ gmol NH}_3 \times (17\text{g/gmol})}{1 \text{ gmol urea} \times (60\text{g/gmol}) + 1 \text{ gmol H}_2\text{O} \times (18\text{g/gmol})} = 0.44$$

(with only urea counted in the denominator, fractional atom economy is 0.57.)

P1.7

Hexane:

$$C_6H_{14} + 9.5O_2 \rightarrow 6CO_2 + 7H_2O$$

$$\frac{6 \text{ gmol CO}_2}{\text{gmol C}_6\text{H}_{14}} \times \frac{44 \text{ g CO}_2/\text{gmol CO}_2}{86 \text{ g C}_6\text{H}_{14}/\text{gmol C}_6\text{H}_{14}} = 3.1\text{g CO}_2/\text{g C}_6\text{H}_{14}$$

$$\frac{7 \text{ gmol H}_2\text{O}}{\text{gmol C}_6\text{H}_{14}} \times \frac{18 \text{ g H}_2\text{O}/\text{gmol H}_2\text{O}}{86 \text{ g C}_6\text{H}_{14}/\text{gmol C}_6\text{H}_{14}} = 1.5\text{g H}_2\text{O}/\text{g C}_6\text{H}_{14}$$

Glucose: $C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$

$$\frac{6 \text{ gmol CO}_2}{\text{gmol C}_6\text{H}_{12}\text{O}_6} \times \frac{44 \text{ g CO}_2/\text{gmol CO}_2}{180 \text{ g C}_6\text{H}_{12}\text{O}_6/\text{gmol C}_6\text{H}_{12}\text{O}_6} = 1.5\text{g CO}_2/\text{g C}_6\text{H}_{12}\text{O}_6$$

$$\frac{6 \text{ gmol H}_2\text{O}}{\text{gmol C}_6\text{H}_{12}\text{O}_6} \times \frac{18 \text{ g H}_2\text{O}/\text{gmol H}_2\text{O}}{180 \text{ g C}_6\text{H}_{12}\text{O}_6/\text{gmol C}_6\text{H}_{12}\text{O}_6} = 0.6\text{g H}_2\text{O}/\text{g C}_6\text{H}_{12}\text{O}_6$$

P1.8

$$\left(10^9 \text{ lb NH}_3\right)\left(\frac{\text{lbmol NH}_3}{17 \text{ lb NH}_3}\right)\left(\frac{\text{lbmol N}_2}{2 \text{ lbmol NH}_3}\right)\left(\frac{28 \text{ lb N}_2}{\text{lbmol N}_2}\right) = 820 \text{ million lbs N}_2$$

$$\left(10^9 \text{ lb NH}_3\right)\left(\frac{\text{lbmol NH}_3}{17 \text{ lb NH}_3}\right)\left(\frac{3 \text{ lbmol H}_2}{2 \text{ lbmol NH}_3}\right)\left(\frac{2 \text{ lb H}_2}{\text{lbmol H}_2}\right) = 180 \text{ million lbs H}_2$$

P1.9

$$Cl_2\text{:}\ \frac{\$0.016}{\text{gmol}} \times \frac{1\ \text{gmol}}{71\ \text{g}} \times \frac{454\ \text{g}}{\text{lb}} \times \frac{2000\ \text{lb}}{\text{ton}} = \frac{\$205}{\text{ton}}$$

$$NH_3\text{:}\ \frac{\$0.0045}{\text{gmol}} \times \frac{1\ \text{gmol}}{17\ \text{g}} \times \frac{454\ \text{g}}{\text{lb}} \times \frac{2000\ \text{lb}}{\text{ton}} = \frac{\$240}{\text{ton}}$$

P1.10

The conventional process has an atom economy of 0.45, which means that 0.55 lb reactants are shunted to waste per 0.45 lb of product made. At 300 million lb/yr 4-ADPA production, this amounts 367 million lb/yr waste.

The new process, with an atom economy of 0.84, produces 0.16 lb waste per 0.84 lb product. At 300 million lb/yr 4-ADPA production, this amounts 57 million lb/yr waste, or only 15% of the waste production of the conventional process.

P1.11

Molar mass = 2 + 32 + 4(16) = 98 tons/tonmol

$$\frac{45 \times 10^6 \text{ tons}}{\text{yr}} \times \frac{1 \text{ tonmol}}{98 \text{ tons}} = 4.6 \times 10^5 \text{tonmol/yr}$$

$$\frac{45 \times 10^6 \text{ tons}}{\text{yr}} \times \frac{2000 \text{ lb}}{\text{ton}} \times \frac{454 \text{ g}}{\text{lb}} = 4.09 \times 10^{13} \text{g/yr}$$

$$\frac{\dfrac{45 \times 10^6 \text{ tons}}{\text{yr}} \times \dfrac{2000 \text{ lb}}{\text{ton}}}{6 \times 10^9 \text{people}} = 15 \text{ lb/person/yr}$$

$$\frac{45 \times 10^6 \text{ tons}}{\text{yr}} \times \frac{\$75}{\text{ton}} = \$3.4 \text{ billion/yr}$$

P1.12

The glucose-to-adipic acid process loses $5400/day while the benzene to adipic acid process makes $27,100. For the glucose process to be competitive, the cost for the glucose needs to drop by 27,100+5400 or by $32,500. The current cost is $48,500/day, so

the cost would have to drop to $16,000. At 80,850 kg/day consumption of glucose, this converts to a glucose price of $0.198/kg.

The glucose-to-catechol process makes $49,200/day, but the benzene-to-catechol process nets $89,300. The difference is $40,100. The glucose price would have to drop to $0.104/kg to be competitive with benzene.

P1.13
Some possible explanations: greater number of reactions in pathway, more stringent product purity requirements, less pressure to trim costs by reducing wastes.

P1.14

$$\left(\frac{\$2.89}{\text{gal}}\right)\left(\frac{\text{gal}}{8\text{ lb}}\right) = \$0.36/\text{lb} \text{ : milk is a commodity chemical}$$

$$\left(\frac{\$1.75}{12\text{ oz}}\right)\left(\frac{16\text{ oz}}{\text{lb}}\right) = \$2.33/\text{lb} \text{ : at this price, water is a specialty chemical!}$$

P1.15

$$HNO_3 + \nu_2 CH_3OH \rightarrow \nu_3 C_3H_7NO_2 + \nu_4 CO_2 + \nu_5 H_2O$$

The element balance equations for N, C, H and O are

$$1 = \nu_3$$
$$\nu_2 = 3\nu_3 + \nu_4$$
$$1 + 4\nu_2 = 7\nu_3 + 2\nu_5$$
$$3 + \nu_2 = 2\nu_3 + 2\nu_4 + \nu_5$$

This is a set of 4 equations in 4 unknowns that we solve by substitution and elimination to find the balanced reaction:

$$HNO_3 + 3\frac{1}{3}CH_3OH \rightarrow C_3H_7NO_2 + \frac{1}{3}CO_2 + 3\frac{2}{3}H_2O$$

We want to react (54-10 mg/L) x 10 L of nitric acid, or 0.44 g. The molar mass of HNO_3 is 63 g/gmol, while that of CH_3OH is 32 g/gmol. Therefore:

$$0.44\text{ g }HNO_3 \times \frac{\text{gmol }HNO_3}{63\text{g }HNO_3} \times \frac{3\frac{1}{3}\text{ gmol }CH_3OH}{\text{gmol }HNO_3} \times \frac{32\text{ g }CH_3OH}{\text{gmol }CH_3OH} = 0.75\ g\ CH_3OH$$

P1.16
The stoichiometrically balanced equation is found by balancing elements:

$$CF_2Cl_2 + 2Na_2C_2O_4 \rightarrow 2NaCl + 2NaF + 1C + 4CO_2$$

Grams of sodium oxalate required per gram of Freon-12 destroyed:

$$\frac{2\text{ gmol Na}_2\text{C}_2\text{O}_4}{\text{gmol CF}_2\text{Cl}_2}\times\frac{\text{gmol CF}_2\text{Cl}_2}{121\text{ g CF}_2\text{Cl}_2}\times\frac{134\text{ g Na}_2\text{C}_2\text{O}_4}{\text{gmol Na}_2\text{C}_2\text{O}_4}=2.21\ g\text{ Na}_2\text{C}_2\text{O}_4/\text{g CF}_2\text{Cl}_2$$

Grams of solid products produced (includes NaF, NaCl and C):

$$\left(\frac{2\text{ gmol NaCl}}{\text{gmol CF}_2\text{Cl}_2}\times\frac{58.5\text{ g NaCl}}{\text{gmol NaCl}}\right)+\left(\frac{2\text{ gmol NaF}}{\text{gmol CF}_2\text{Cl}_2}\times\frac{42\text{ g NaF}}{\text{gmol NaF}}\right)+\left(\frac{1\text{ gmol C}}{\text{gmol CF}_2\text{Cl}_2}\times\frac{12\text{ g C}}{\text{gmol C}}\right)$$
$$\times\frac{\text{gmol CF}_2\text{Cl}_2}{121\text{ g CF}_2\text{Cl}_2}=1.76\ g\text{ solid products/g CF}_2\text{Cl}_2$$

P1.17

Ethanol: $$\frac{6\text{ gmol H}}{\text{gmol C}_2\text{H}_5\text{OH}}\times\frac{\text{gmol C}_2\text{H}_5\text{OH}}{46\text{ g C}_2\text{H}_5\text{OH}}\times\frac{1\text{ g H}}{\text{gmol H}}\times100\%=13\text{wt\% H}$$

Water: $$\frac{2\text{ gmol H}}{\text{gmol H}_2\text{O}}\times\frac{\text{gmol H}_2\text{O}}{18\text{ g H}_2\text{O}}\times\frac{1\text{ g H}}{\text{gmol H}}\times100\%=11\text{wt\% H}$$

Glucose: $$\frac{12\text{ gmol H}}{\text{gmol C}_6\text{H}_{12}\text{O}_6}\times\frac{\text{gmol C}_6\text{H}_{12}\text{O}_6}{180\text{ g C}_6\text{H}_{12}\text{O}_6}\times\frac{1\text{ g H}}{\text{gmol H}}\times100\%=6.7\text{wt\% H}$$

Methane: $$\frac{4\text{ gmol H}}{\text{gmol CH}_4}\times\frac{\text{gmol CH}_4}{16\text{ g CH}_4}\times\frac{1\text{ g H}}{\text{gmol H}}\times100\%=25\text{wt\% H}$$

It does seem hard to believe that they achieved 50 wt% H.

P1.18

The reactions are balanced by writing element balance equations and solving them simultaneously. The balanced equations are given, along with a calculation of atom economy.

<u>Hydrogenation:</u>

(a) conventional

$$C_6H_5COCH_3+\frac{1}{4}NaBH_4+H_2O\rightarrow C_6H_5CH(OH)CH_3+\frac{1}{4}NaB(OH)_4$$

	ν_i	M_i	$\nu_i M_i$
$C_6H_5COCH_3$	-1	120	-120
$NaBH_4$	-0.25	38	-9.5
H_2O	-1	18	-18
$C_6H_5CH(OH)CH_3$	+1	122	122

Atom economy = 122/(120+9.5+18) = 0.83

(b) catalytic

$$C_6H_5COCH_3+H_2\rightarrow C_6H_5CH(OH)CH_3$$

Atom economy = 1.0!

<u>Oxidation</u>:
(a) conventional

$$C_6H_5CH(OH)CH_3 + \frac{2}{3}CrO_3 + H_2SO_4 \rightarrow C_6H_5COCH_3 + \frac{1}{3}Cr_2(SO_4)_3 + 2H_2O$$

	ν_i	M_i	$\nu_i M_i$
$C_6H_5CH(OH)CH_3$	-1	122	-122
CrO_3	-0.667	100	-66.7
H_2SO_4	-1	98	-98
C_6H_5 $COCH_3$	+1	120	120

Atom economy = 120/(122+66.7+98) = 0.42

(b) catalytic

$$C_6H_5CH(OH)CH_3 + H_2O_2 \rightarrow C_6H_5COCH_3 + 2H_2O$$

Atom economy = 120/(122+34) = 0.77

<u>C-C bond formation</u>
(a) conventional

$$C_6H_5CH(OH)CH_3 + Mg + CO_2 + 2HCl \rightarrow C_6H_5CHCH_3COOH + MgCl_2 + H_2O$$

	ν_i	M_i	$\nu_i M_i$
$C_6H_5CH(OH)CH_3$	-1	122	-122
Mg	-1	24	-24
CO_2	-1	44	-44
HCl	-2	36.5	-73
C_6H_5 $CHCH_3COOH$	+1	150	150

Atom economy = 150/(122+24+44+73) = 0.57

(b) catalytic

$$C_6H_5CH(OH)CH_3 + CO \rightarrow C_6H_5CHCH_3COOH$$

Atom economy = 1.00!

P1.19
We are told that there may be some water or carbon dioxide made as byproducts in addition to the products shown. To find out if they are, we include them in the reaction,

solve for stoichiometric coefficients – and check to see whether the coefficients for water and/or carbon dioxide are nonzero. To balance the first reaction, we write

$$C_6H_5OH + \nu_2 CH_3COCH_3 \rightarrow \nu_3 C_{15}H_{16}O_2 + \nu_4 CO_2 + \nu_5 H_2O$$

The element balance equations for C, O and H are:

$$6 + 3\nu_2 = 15\nu_3 + \nu_4$$
$$6 + 6\nu_2 = 16\nu_3 + 2\nu_5$$
$$1 + \nu_2 = 2\nu_3 + 2\nu_4 + \nu_5$$

There are 3 equations and 4 stoichiometric coefficients. Thus, one of them is zero (in other words, that compound is NOT a byproduct.) We find a solution if we set $\nu_4 = 0$: $\nu_2 = 1/2$, $\nu_3 = 1/2$, $\nu_5 = 1/2$. (There is not a reasonable solution if we assume no water is made.)

We balance the remaining reactions in a similar fashion and find 4 balanced equations

$$C_6H_5OH + \frac{1}{2}CH_3COCH_3 \rightarrow \frac{1}{2}C_{15}H_{16}O_2 + \frac{1}{2}H_2O$$
$$CH_4 + H_2O \rightarrow CO + 3H_2$$
$$Cl_2 + CO \rightarrow COCl_2$$
$$C_{15}H_{16}O_2 + COCl_2 + 2NaOH \rightarrow$$
$$\frac{1}{50}\left[-OC_6H_4C(CH_3)_2C_6H_4OCO-\right]_n + 2NaCl + 2H_2O$$

To put together the generation-consumption analysis per mole of polycarbonate, we (a) multiply the 4th reaction by 50, (b) match phosgene consumption to phosgene generation by multiplying reaction 3 by 50, (c) match CO consumption to CO generation by multiplying reaction 2 by 50 and (d) match bisphenol A consumption to bisphenol A generation by multiplying reaction 1 by 100. The result is summarized in table form.

Generation-consumption analysis for production of polycarbonate

	R1	R2	R3	R4	net
C_6H_5OH	-100				-100
CH_3COCH_3	-50				-50
$C_{15}H_{16}O_2$	50			-50	
H_2O	50	-50		100	+100
CH_4		-50			-50
CO		50	-50		
H_2		150			+150
Cl_2			-50		-50
$COCl_2$			50	-50	
NaOH				-100	-100
polycarbonate				1	+1

NaCl				100	+100

P1.20

The balanced reactions are found from element balances on C, H, O and N. To determine if water is required as a reactant or product, we postulate that water is a product and then try to balance the equations. If the stoichiometric coefficient for water is zero, it is not a reactant or a product. If it is negative, water is a reactant, if positive, it is a product.

The balanced chemical reactions are

$$HCO_3^- + NH_4^+ + C_5H_{12}O_2N_2 \rightarrow C_6H_{13}O_3N_3 + 2H_2O$$

$$C_6H_{13}O_3N_3 + C_4H_7O_4N \rightarrow C_{10}H_{18}O_6N_4 + H_2O$$

$$C_{10}H_{18}O_6N_4 \rightarrow C_4H_4O_4 + C_6H_{14}O_2N_4$$

$$C_6H_{14}O_2N_4 + H_2O \rightarrow CH_4ON_2 + C_5H_{12}O_2N_2$$

The generation-consumption table for this set of reactions is:

	R1	R2	R3	R4	net
bicarbonate	-1				-1
ammonium	-1				-1
ornithine	-1			+1	0
citrulline	+1	-1			0
water	+2	+1		-1	+2
aspartic acid		-1			-1
arginosuccinate		+1	-1		0
fumarate			+1		+1
arginine			+1	-1	0
urea				+1	+1

The overall reaction is:

$$HCO_3^- + NH_4^+ + C_4H_7O_4N \rightarrow C_4H_4O_4 + CH_4ON_2 + 2H_2O$$

There is net generation of urea, fumarate and water. The urea and water are eliminated in the urine. Fumarate can be used for new amino acid synthesis, or further broken down into CO_2 and water.

P1.21

If all the Fe is incorporated into the nanoparticles, there are (1.52/2) or 0.76 mmol Fe_2O_3 produced, or, at a molar mass of 160 g/gmol, 0.121 g. The molar mass of $Fe(CO)_5$ is 196 g/gmol. 1.52 mmol of $Fe(CO_5)$ is therefore equal to (1.52 x 196 x 0.001) = 0.298 g. Thus, the atom economy is 0.121/(0.298+1.28+0.34) = 0.063.

P1.22
The LeBlanc chemistry is given in Example 1.3. At a sodium carbonate production rate of 1000 ton/day, we complete the following process economy calculations.

Compound	ν_i	M_i	$\nu_i M_i$	tons/day (SF = 1000/106)	\$/ton	\$/day
NaCl	-2	58.5	-117	-1104	95	-104,860
H_2SO_4	-1	98	-98	-927	80	-74,160
HCl	+2	36.5	+73	+689		
C	-2	12	-24	-226		
CO_2	+2	44	+88	+830		
$CaCO_3$	-1	100	-100	-943	87	-82,040
Na_2CO_3	+1	106	+106	+1000	105	+105,000
CaS	+1	72	+72	+679		
sum				-2 (close enough to zero)		-156,000

The LeBlanc process looks atrociously bad, at current prices.

P1.23
The reactions are

$$C_2H_5OH + \frac{1}{2}O_2 \rightarrow CH_3CHO + H_2O \qquad (R1)$$

$$CH_3CHO + \frac{1}{2}O_2 \rightarrow CH_3COOH \qquad (R2)$$

Water is the only byproduct.

The generation-consumption analysis is shown in the table.

Compound	ν_1	ν_2	ν_{net}	M_i	$\nu_i M_i$	kg (SF = 1/60)
C_2H_5OH	-1		-1	46	-46	-0.77
O_2	-1/2	-1/2	-1	32	-32	-0.53
CH_3CHO	+1	-1	0			
H_2O	+1		+1	18	+18	+0.30
CH_3COOH		+1	+1	60	+60	+1.0
sum						0

At 0.77 kg ethanol consumed per kg acetic acid generated, and \$0.29/kg ethanol, the minimum selling price for acetic acid is 0.77(\$0.29) = \$0.22/kg.

P1.24
The balanced chemical equations are:

$$SiO_2 + 2C \rightarrow Si + 2CO \qquad (R1)$$
$$Si + 2Cl_2 \rightarrow SiCl_4 \qquad (R2)$$
$$SiCl_4 + 2H_2 \rightarrow Si + 4HCl \qquad (R3)$$

Compound	ν_1	ν_2	ν_3	ν_{net}	M_i	$\nu_i M_i$	Grams (SF = 3.57)
SiO_2	-1			-1	60	-60	-214
C	-2			-2	12	-24	-86
Si	+1	-1	+1	+1	28	+28	+100
CO	+2			+2	28	+56	+200
Cl_2		-2		-2	71	-142	-507
$SiCl_4$		+1	-1		170		
H_2			-2	-2	2	-4	-14
HCl			+4	+4	36.5	+146	+521
sum							0

Reactant and byproduct quantities per 100 g Si produced are shown in the last column.

The atom economy is 28/(60+24+142+4) = 0.12.

P1.25

Water is a required byproduct in (R2) and (R3). The balanced reactions are:

$$C_4H_8 + CH_2O \rightarrow C_5H_{10}O \qquad (R1)$$
$$C_5H_{10}O + \frac{1}{2}O_2 \rightarrow C_5H_8O + H_2O \qquad (R2)$$
$$C_5H_{10}O + C_5H_8O \rightarrow C_{10}H_{16}O + H_2O \qquad (R3)$$

We need to multiply (R1) by 2 to avoid making unwanted intermediates. The generation-consumption analysis is:

Compound	ν_1	ν_2	ν_3	ν_{net}	M_i	$\nu_i M_i$	Grams (SF = 1000/152)
C_4H_8	-2			-2	56	-112	-737
CH_2O	-2			-2	30	-60	-395
$C_5H_{10}O$	+2	-1	-1	0			
O_2		-1/2		-1/2	32	-16	-105
C_5H_8O		+1	-1	0			
H_2O		+1	+1	+2	18	+36	+237
$C_{10}H_{16}O$			+1	+1	152	+152	+1000
sum							0

Per kg of citral, 0.737 kg butene, 0.395 kg formaldehyde, and 0.105 kg oxygen are required, with 0.237 kg water as the only byproduct.

P1.26
The reaction, written with unknown stoichiometric coefficients, is

$$(CaF)Ca_4(PO_4)_3 + \nu_2 H_2SO_4 + \nu_3 H_2O \rightarrow \nu_4 CaH_4(PO_4)_2 H_2O + \nu_5 CaSO_4 + \nu_6 HF$$

We write the element balance equations to find the stoichiomeric coefficients:

Ca: $5 = \nu_4 + \nu_5$
F: $1 = \nu_6$
P: $3 = 2\nu_4$
O: $12 + 4\nu_2 + \nu_3 = 9\nu_4 + 4\nu_5$
H: $2\nu_2 + 2\nu_3 = 6\nu_4 + \nu_6$

Balances on F and P are readily solved, followed by the balance on Ca. Finally, H and O balances are solved.

$$(CaF)Ca_4(PO_4)_3 + 3\frac{1}{2}H_2SO_4 + \frac{3}{2}H_2O \rightarrow \frac{3}{2}CaH_4(PO_4)_2 H_2O + 3\frac{1}{2}CaSO_4 + HF$$

The process economy calculations are summarized in the table, per ton of monocalcium phosphate.

Compound	ν_i	M_i	$\nu_i\ M_i$	Tons (SF = 1/378)	$/ton	$
Phosphate rock	-1	504	-504	-1.33	128	-170
Sulfuric acid	-3.5	98	-343	-0.91	80	-73
water	-1.5	18	-27	-0.0714		
Monocalcium phosphate	+1.5	252	+378	+1	320	+320
Calcium sulfate	+3.5	136	+476	+1.26	320	+403
Hydrogen fluoride	+1	20	+20	+0.053		
sum						+480

Required raw materials and byproducts are listed in the "tons" column. The fertilizer is a mix of monocalcium phosphate and calcium sulfate, per ton of mcp, we make 2.26 tons fertilizer. Therefore the net profit is $480/2.26 tons fertilizer, or $212/ton.

P1.27
100 grams of yeast contain

50 g C, or 4.167 gmol C
6.94 g H, or 6.94 gmol H
9.72 g N, or 0.69 gmol N
33.33 g O, or 2.08 gmol O

To normalize to one mole C per mole yeast, we divide all numbers by 4.167. Therefore the "molecular formula" for yeast is $CH_{1.66}O_{0.5}N_{0.166}$.

An overall reaction for reaction of glucose, oxygen, and ammonia to yeast, CO_2 and water is:

$$\nu_1 C_6H_{12}O_6 + \nu_2 O_2 + \nu_3 NH_3 \rightarrow \nu_4 CH_{1.66}O_{0.5}N_{0.166} + \nu_5 CO_2 + \nu_6 H_2O$$

We know that 3.9 g CO_2 are produced per gram of yeast. The molar mass of CO_2 is 44, and that of "yeast" is (12+1.66+0.5(16)+0.166(14)) = 23.98 g/gmol. Therefore, 3.9(23.98/44) or 2.1255 gmol CO_2 are produced per gmol yeast. We will set $\nu_4 = 1$ as our basis, and $\nu_5 = 2.1255$ from these data. Now we can complete the remaining element balances.

$$\begin{aligned}
&C:\ 6\nu_1 = 1 + 2.1255\\
&H:\ 12\nu_1 + 3\nu_3 = 1.66 + 2\nu_6\\
&O:\ 6\nu_1 + 2\nu_2 = 0.5 + 2(2.1255) + \nu_6\\
&N:\ \nu_3 = 0.166
\end{aligned}$$

The balanced reaction is:

$$0.521 C_6H_{12}O_6 + 2.085 O_2 + 0.166 NH_3 \rightarrow CH_{1.66}O_{0.5}N_{0.166} + 2.1255 CO_2 + 2.545 H_2O$$

Of the 3.126 gmol C in glucose, 1 gmol is used to make yeast (or about 32%) and about 68% is used to make CO_2. (This is probably the best measure of relative utilization of glucose for yeast vs. for CO_2.) About 20% of the mass of carbon containing compounds is yeast, with the remainder as CO_2.

P1.28

A close examination of the first 3 reactions shows that only 2 are independent – if we add reaction 1 and reaction 3 together, we get reaction 2. Therefore, we need to consider only 2 of these 3 reactions. A generation-consumption table for reactions 1, 3, and 4 is shown (trial 1):

	ν_{i1}	ν_{i3}	ν_{i4}	$\nu_{I,net}$
Cu_2S	-1			-1
$Fe_2(SO_4)_3$	-1	-1		-2
CuS	+1	-1		0
$CuSO_4$	+1	+1	-1	+1
$FeSO_4$	+2	+2	+1	+5
S		+1		+1
Fe			-1	-1
Cu			+1	+1

To maximize Cu per ton chalcocite, we want to have no net generation of Cu-containing compounds (only metallic Cu). In other words, we want to find multiplying factors such that

$$\sum_k \nu_{CuS,k}\chi_k = 0$$

and

$$\sum_k \nu_{CuSO_4,k}\chi_k = 0$$

From these restrictions, we find:

$$\chi_1 = \chi_3$$

$$\chi_1 + \chi_3 - \chi_4 = 0$$

We can arbitrarily choose one multiplying factor, so we'll set $\chi_1 = 1 = \chi_3$, which leaves us with $\chi_4 = 2$. The revised generation-consumption table, along with calculations of mass requirements, is shown.

	ν_{i1}	ν_{i3}	ν_{i4}	$\nu_{I,net}$	M_ι	$\nu_{I,net}M_\iota$	Tons (SF=1/127)
Cu_2S	-1			-1	159	-159	-1.25
$Fe_2(SO_4)_3$	-1	-1		-2	400	-800	-6.3
CuS	+1	-1		0			
$CuSO_4$	+1	+1	-2	0			
$FeSO_4$	+2	+2	+2	+6	152	+912	+7.18
S		+1		+1	32	+32	+0.25
Fe			-2	-2	56	-112	-0.88
Cu			+2	+2	63.5	+127	+1

Per ton of metallic Cu, we need 1.25 tons chalcocite, but also 0.88 tons metallic Fe and an enormous 6.3 tons $Fe_2(SO_4)_3$. 7.43 tons of byproducts are generated.

P1.29

In the first process, we use lactose to produce glucose with the byproduct galactose. The economic evaluation is summarized in tabular form.

Compound	ν_i	M_i	$\nu_i M_i$	kg (SF = 1/342)	$/kg	$
Lactose	-1	342	-342	-1	0.484	-0.484
H_2O	-1	18	-18	-0.053		
Glucose	+1	180	+180	+0.526	0.60	+0.316
Galactose	+1	180	+180	+0.526		
sum						-0.17

We lose 17 cents per kg lactose processed on this deal. If we convert galactose to glucose, we add another $0.316 to the last column. With that process modification, we can make about $0.15/kg lactose processed.

P1.30

Sulfuric acid process

Three reactions

$$S + O_2 \rightarrow SO_2 \qquad \text{(R1)}$$

$$SO_2 + \frac{1}{2}O_2 \rightarrow SO_3 \qquad \text{(R2)}$$

$$SO_3 + H_2O \rightarrow H_2SO_4 \qquad \text{(R3)}$$

These reactions combine easily to an overall reaction of

$$S + 1.5O_2 + H_2O \rightarrow H_2SO_4$$

Nitric acid process:

Three balanced reactions are

$$2NH_3 + \frac{5}{2}O_2 \rightarrow 2NO + 3H_2O \qquad \text{(R1)}$$

$$NO + \frac{1}{2}O_2 \rightarrow NO_2 \qquad \text{(R2)}$$

$$3NO_2 + H_2O \rightarrow 2HNO_3 + NO \qquad \text{(R3)}$$

The generation-consumption table gives:

Compound	R1	R2	R3	net
NH_3	-2			-2
O_2	-5/2	-1/2		-3
NO	+2	-1	+1	+2
H_2O	+3		-1	+2
NO_2		+1	-3	-2
HNO_3			+2	+2

This doesn't satisfy the restrictions on the solution, e.g., we have NO generated and NO_2 consumed, which are not allowed. To have no net generation or consumption of these two intermediates, we find multiplying factors such that

$$2\chi_1 - \chi_2 + \chi_3 = 0$$

$$\chi_2 - 3\chi_3 = 0$$

Choosing arbitrarily $\chi_1 = 1$, we find the solution is $\chi_2 = 3$ and $\chi_3 = 1$. The new generation-consumption table is

Compound	R1	R2	R3	net
NH_3	-2			-2
O_2	-5/2	-3/2		-4

NO	+2	-3	+1	
H_2O	+3		-1	+2
NO_2		+3	-3	
HNO_3			+2	+2

For an overall reaction of

$$NH_3 + 2O_2 \rightarrow HNO_3 + H_2O$$

The difference in value of nitric vs sulfuric acid is likely due to the difference in cost of ammonia vs sulfur. Sulfur is a byproduct of oil refining (desulfurization) and is available in very large quantities. Ammonia, on the other hand, is synthesized from nitrogen and methane in a high pressure, high temperature process.

P1.31

Analysis of the process economy is summarized in the table. A multiplying factor of 3 was use in reaction R2 to eliminate generation/consumption of intermediates.

compound	ν_1	ν_2	ν_{net}	M_i	$\nu_{net} M_i$	Lb (SF = 1/918)	\$/lb	\$
Glycerol stearate	-1		-1	890	-890	-0.97	1.00	-0.97
H_2O	-3	+3		18				
Stearic acid	+3	-3		284				
glycerol	+1		+1	92	+92	0.100	1.10	+0.11
NaOH		-3	-3	40	-120	-0.13	0.50	-0.065
Sodium stearate		+3	+3	306	+918	+1	x	x

To just break even, we need x - 0.97 + 0.11 - 0.065 = 0, or x = \$0.925/lb soap. I found soap available in 18 lb quantities for about \$2/pound on an internet site. You'll spend about \$2 for a 4 oz bar of soap at the drugstore.

P1.32

This problem is designed to encourage students to learn how to find and to use Kirk-Othmer and other reference books.

P1.33

<u>Reaction pathway 1:</u>

The balanced chemical reactions are

$$C_4H_6 + 2HCN \rightarrow C_6H_8N_2 \qquad (R1)$$

$$C_6H_8N_2 + 4H_2 \rightarrow C_6H_{16}N_2 \qquad (R2)$$

The process economy evaluation, at 116,000 lb/day, is summarized in a table.

compound	ν_1	ν_2	ν_{net}	M_i	$\nu_{net} M_i$	Lb (SF = 1000)	\$/lb	\$
C_4H_6	-1		-1	54	-54	-54000	0.21	-11,340

HCN	-2		-2	27	-54	-54000	0.93	-50,220
$C_6H_8N_2$	+1	-1						
H_2		-4	-4	2	-8	-8000	0.09	-720
$C_6H_{16}N_2$		+1	+1	116	+116	+116,000		
sum						0		-62,280

Raw material costs are $62,280/day at the desired production rate.

Reaction pathway 2:
The balanced chemical reactions are

$$2C_3H_3N + H_2 \rightarrow C_6H_8N_2 \qquad (R1)$$
$$C_6H_8N_2 + 4H_2 \rightarrow C_6H_{16}N_2 \qquad (R2)$$

The process economy evaluation, at 116,000 lb/day, is summarized in a table.

compound	ν_1	ν_2	ν_{net}	M_i	$\nu_{net} M_i$	Lb (SF = 1000)	$/lb	$
C_3H_3N	-2		-2	53	-106	-106000	0.65	-68,900
$C_6H_8N_2$	+1	-1						
H_2	-1	-4	-5	2	-10	-10000	0.09	-900
$C_6H_{16}N_2$		+1	+1	116	+116	+116,000		
sum						0		-69,800

Raw material costs are $69,800/day at the desired production rate, or roughly 10% higher than in reaction pathway 1. However, no HCN is required, increasing the safety of the process. The cost differential is insufficient to justify the increased risks associated with process 1.

P1.34
This problem requires students to consider their own consumption patterns and to estimate market size based on their own consumption, and to look up information on market size in several common reference materials.

P1.35
I used values of $1.80/lb for ethylene, $0.60/lb for hydrogen cyanide, $0.075/lb for ammonia, $0.015/lb for oxygen, $0.56/lb for ethylene oxide, and $1.12/lb for acrylonitrile. Results may vary depending on the current prices.

Pathway 1

	ν_i	M_i	$\nu_i M_i$	lb/day (SF = 100/53)	$/lb	$/day
C_2H_2	-1	26	-26	-49	1.80	-88.2
HCN	-1	27	-27	-51	0.60	-30.6

C_3H_3N	+1	53	+53	+100	1.12	+112
sum						-6.8

Pathway 1 loses money, and requires a highly toxic raw material (HCN). However, the atom economy is great (100%), and there are no byproducts to deal with.

Pathway 2

	ν_i	M_i	$\nu_i M_i$	lb/day (SF = 100/53)	\$/lb	\$/day
C_3H_6	-1	42	-42	-79	0.19	-15
NH_3	-1	17	-17	-32	0.075	-2.4
O_2	-1.5	32	-48	-90.6	0.015	-1.4
H_2O	+3	18	+54	+102		
C_3H_3N	+1	53	+53	+100	1.12	+112
sum						+93.2

Pathway 2 has very favorable economics! Furthermore, the only byproduct is water, and ammonia and oxygen are relatively safe raw materials. However, the atom economy is poor (~50%).

Pathway 3

	ν_i	M_i	$\nu_i M_i$	lb/day (SF = 100/53)	\$/lb	\$/day
C_2H_4O	-1	44	-44	-83	0.56	-46.5
HCN	-1	27	-27	-51	0.60	-30.6
H_2O	+1	18	+18	+34		
C_3H_3N	+1	53	+53	+100	1.12	+112
sum						+34.9

The process economics are pretty attractive, although not quite as much as Pathway 2. The atom economy is better (75%) than Pathway 2 but not as good as Pathway 1. However, pathway 3 does not avoid the use of the toxic reactant HCN.

Given the process economics and safety concerns, the pathway with the worst atom economy looks like the overall best choice.

P1.36
This is another problem encouraging students to use various library and internet resources.

P1.37
Strecher synthesis
The 3 balanced chemical reactions for synthesis of alanine are:

$$CH_3CHO + NH_3 \rightarrow H_2NCHCH_3OH \qquad \text{(R1)}$$

$$H_2NCHCH_3OH + HCN \rightarrow H_2NCHCH_3CN + H_2O \qquad (R2)$$
$$H_2NCHCH_3CN + 2H_2O \rightarrow H_2NCHCH_3COOH + NH_3 \qquad (R3)$$

The process economy calculations are summarized in the table. I used values of \$0.60/lb for HCN, and \$0.455/lb for acetaldehyde.

compound	ν_1	ν_2	ν_3	ν_{net}	M_i	$\nu_{net}\, M_i$	Metric tons/yr (SF = 200/89)	\$/ton	\$
CH_3CHO	-1			-1	44	-44	-98.9	1001	-99,000
NH_3	-1		+1						
C_2H_7NO	+1	-1							
HCN		-1		-1	27	-27	-60.7	1320	-80,100
$C_3H_6N_2$		+1	-1						
H_2O		+1	-2	-1	18	-18	-40.5		
$C_3H_7O_2N$			+1	+1	89	+89	+200	4750	+950,000
sum							0		+770,000

The atom economy is 100%, and the process economy is quite attractive. One disadvantage is the requirement for a highly toxic reactant, hydrogen cyanide.

<u>Bucherer synthesis</u>
The 2 balanced chemical reactions for synthesis of alanine are:

$$CH_3CHO + NaCN + (NH_4)_2CO_3 \rightarrow C_4H_6O_2N_2 + NaOH + NH_3 + H_2O \qquad (R1)$$
$$C_4H_6O_2N_2 + 2H_2O \rightarrow H_2NCHCH_3COOH + CO_2 + NH_3 \qquad (R2)$$

The process economy calculations are summarized in the table. I used values of \$0.70/lb for NaCN, and \$0.29/lb for ammonium carbonate.

compound	ν_1	ν_2	ν_{net}	M_i	$\nu_{net}\, M_i$	Metric tons/yr (SF = 200/89)	\$/ton	\$
CH_3CHO	-1		-1	44	-44	-98.9	1001	-99,000
NaCN	-1		-1	49	-49	-110	1540	-169,000
$(NH_4)_2CO_3$	-1		-1	96	-96	-216	638	-138,000
$C_4H_6N_2O_2$	+1	-1						
NaOH	+1		+1	40	+40	+90		
NH_3	+1	+1	+2	17	+34	+76		
H_2O	+1	-2	-1	18	-18	-40		
$C_3H_7O_2N$		+1	+1	89	+89	+200	4750	+950,000
CO_2		+1	+1	44	+44	+98.9		
sum						0		+544,000

The atom economy is poor (43%). The process economy is quite attractive, although not as good as the Strecker synthesis. Handling all the byproducts would greatly increase the costs of running this process. Safety concerns are similar to the Strecker process.

P1.38

The aerobic decomposition of glucose to CO_2 is a well-known reaction:

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$$

The unbalanced reaction from glucose to lactic acid is (guessing that water is a byproduct):

$$C_6H_{12}O_6 + \nu_2 O_2 \rightarrow \nu_3 C_3H_6O_3 + \nu_4 H_2O$$

We can easily balance this: glucose-to-lactic acid conversion requires no oxygen (it is anaerobic – the reaction happens in the muscles during strenuous exercise).

$$C_6H_{12}O_6 \rightarrow 2C_3H_6O_3$$

Synthesis of bacteria from glucose will require ammonia and probably also oxygen. The unbalanced reaction is (guessing that water is a byproduct):

$$C_6H_{12}O_6 + \nu_2 O_2 + \nu_3 NH_3 \rightarrow \nu_4 CH_{1.666}O_{0.27}N_{0.20} + \nu_5 H_2O$$

We write element balances on C, H, O, and N. There are 4 equations in 4 unknowns:

$$6 = \nu_4$$
$$12 + 3\nu_3 = 1.666\nu_4 + 2\nu_5$$
$$6 + 2\nu_2 = 0.27\nu_4 + \nu_5$$
$$\nu_3 = 0.20\nu_4$$

We solve to find the stoichiometric coefficients

$$C_6H_{12}O_6 + 1.2NH_3 \rightarrow 6CH_{1.666}O_{0.27}N_{0.20} + 2.8H_2O + 0.79O_2$$

(Notice that oxygen must be a product to balance this reaction!)

In the fermentation, we generated 1.1 g bacteria. The "molar mass" of the bacteria is 20.786 g/gmol. Thus, we generated 0.0529 gmol bacteria which, from the above balanced reaction, must have consumed 0.088 gmol glucose, or (since glucose molar mass is 180 g/gmol) 1.588 g glucose. We also generated 3.6 g lactic acid, which, at 90 g/gmol, is 0.04 gmol lactic acid. This would require consumption of 0.02 gmol glucose, or, 3.6 g glucose.

The remaining glucose (18 – 1.588 – 3.6 = 12.812 g) must have been converted to CO_2. This mass of glucose consumed is equal to 0.0711 gmol; from the balanced reaction we know that this would generate 0.427 gmol CO_2, or 18.79 g CO_2.

8.8% of the glucose was consumed to grow bacteria, 20% was consumed to make lactic acid, and over 71% was oxidized to CO_2.

P1.39
Direct oxidation is the preferred method for converting ethylene-to-ethylene oxide. It would also be the preferred method for converting propylene-to-propylene oxide, but the reaction won't "go" under typical processing conditions. Oxidation with hydrogen peroxide is too expensive. This problem considers whether a new process, in which hydrogen peroxide is generated from oxygen "in situ", is economically attractive.

Ethylene oxide by conventional process:

$$C_2H_4 + \frac{1}{2}O_2 \rightarrow C_2H_4O$$

	ν_i	M_i	$\nu_i M_i$	kg (SF = 1000/44)	$/kg	$
C_2H_4	-1	28	-28	-636.4	0.57	-363
O_2	-1/2	32	-16	-363.6	0.033	-12
C_2H_4O	+1	44	+44	+1000	1.32	+1320
sum						+945

Propylene oxide by new process:

$$RAQ + O_2 \rightarrow RAHQ + H_2O_2 \quad (R1)$$
$$CH_4 + H_2O \rightarrow CO + 3H_2 \quad (R2)$$
$$RAHQ + H_2 \rightarrow RAQ \quad (R3)$$
$$C_3H_6 + H_2O_2 \rightarrow C_3H_6O + H_2O \quad (R4)$$

(Multiply stoichiometric coefficients for reaction R2 by 1/3 to avoid net generation/consumption of hydrogen.)

compound	ν_1	ν_2	ν_3	ν_4	ν_{net}	M_i	$\nu_{net} M_i$	kg (SF = 1000/58)	$/kg	$
RAQ	-1		+1							
O_2	-1				-1	32	-32	-552	0.033	-18.2
RAHQ	+1		-1							
H_2O_2	+1			-1						
CH_4		-1/3			-1/3	16	-5.33	-91.9	0.11	-10.1
CO		+1/3			+1/3	28	+9.3	+160		
H_2O		-1/3		+1	+2/3	18	+12	+207		
C_3H_6				-1	-1	42	-42	-724	0.42	-304
C_3H_6O				+1	+1	58	+58	+1000	1.32	+1320
H_2		+1	-1							
sum										+988

The new process to make propylene oxide has very attractive economics, because propylene is cheaper than ethylene. A downside is the production of CO, which is a health hazard; however, CO can easily be oxidized to CO_2.

P1.40

Process with hydrogen peroxide:

Balanced chemical equation is:

$$C_6H_{10} + 4H_2O_2 \rightarrow C_6H_{10}O_4 + 4H_2O$$

The process economy is summarized as follows:

	ν_i	M_i	$\nu_i\ M_i$	kg/day (SF = 28100/146)	$/kg	$/day
C_6H_{10}	-1	82	-82	-15,785	0.20	-3157
H_2O_2	-4	34	-136	-26,175	1.57	-41,095
$C_6H_{10}O_4$	+1	146	+146	+28,100	1.54	+43,274
H_2O	+4	18	+72	+13,860	0	
sum						-978

This is an attractive process based on environmental impact and on safety. Hydrogen peroxide is safer than nitric acid and produces no NO. Water is the only byproduct. However, the economics are unfavorable, because hydrogen peroxide is a very expensive oxidizing agent.

British process

Balanced chemical equation is:

$$C_6H_{14} + 3O_2 \rightarrow C_6H_{10}O_4 + 2H_2O$$

The process economy is summarized as follows:

	ν_i	M_i	$\nu_i\ M_i$	kg/day (SF = 28100/146)	$/kg	$/day
C_6H_{14}	-1	86	-86	-16,550	0.33	-5462
O_2	-3	32	-96	-18,480		
$C_6H_{10}O_4$	+1	146	+146	+28,100	1.54	+43,274
H_2O	+2	18	+36	+6930	0	
sum						+37,812

This is a very attractive process! The economics are very favorable – in fact, they are better than the benzene-to-adipic acid process. Water is the only byproduct, and oxygen is a safer oxidizer than nitric acid, particularly if air can be used as the source of oxygen.

In reality only about 1/3 of the hexane actually reacts via the desired pathway, and about 2/3 reacts to form unwanted byproducts. We need 3 times as much hexane, so the cost of the raw materials increases to $16,386/day, but there is still a profit of $26,885/day. However, we are making a lot of byproducts – roughly 2 lb of byproducts per lb of

desired product! We don't know whether these byproducts are safe or toxic, whether they are useful or must be disposed of, whether they can easily or only with difficulty be separated from the desired product. These issues make this process much less appealing, unless the catalyst can be greatly improved so that more of the hexane reacts via the desired path.

P1.41

Thinking about the raw material costs per mole is a useful way to begin this problem.

	\$/lb	lb/lbmol	\$/lbmol
C_2H_4	0.27	28	7.56
$C_2H_4Cl_2$	0.17	99	16.83
C_2H_2	1.22	26	31.72
Cl_2	0.1	71	7.10
HCl	0.72	36.5	26.28
NaOH	1.13	40	45.20
C_2H_3Cl	0.22	62.5	13.75

Observations: Cl_2 is cheaper per mole than HCl and would serve as a cheaper source of Cl. C_2H_2 and $C_2H_4Cl_2$ are pricey; the best source of C for vinyl chloride would be ethylene. The price of HCl and C_2H_2 makes reaction 1 unattractive. NaOH costs more than the desired product; besides, reaction 5 has very poor atom economy.

We could combine reactions 2 and 3, which uses our cheaper sources of C and Cl:

	ν_2	ν_3	ν_{net}	M_i	$\nu_{net}\, M_i$	\$/lbmol	\$
C_2H_4	-1		-1	28	-28	7.56	-7.56
Cl_2	-1		-1	71	-71	7.10	-7.10
$C_2H_4Cl_2$	+1	-1		99			
C_2H_3Cl		+1	+1	62.5	+62.5	13.75	+13.75
HCl		+1	+1	36.5	+36.5		
sum							-0.91

The fractional atom economy is 62.5/(28+71) = 0.63. There is a loss of \$0.91/lbmol of vinyl chloride – and that's before we consider operating costs or capital investment costs.

The HCl is just thrown away, thus wasting 1/2 of the Cl in the chlorine gas. This hurts our atom economy and our process economy. Is there a way to use the HCl? How about considering reaction R4 in combination with reactions R2 and R3?

	ν_2	ν_3	ν_4	ν_{net}
C_2H_4	-1		-1	-2
Cl_2	-1			-1
$C_2H_4Cl_2$	+1	-1	+1	+1
C_2H_3Cl		+1		+1

HCl		+1	-2	-1
O_2			-0.5	-0.5
H_2O				+1

This generation-consumption table would be greatly improved if we could find multiplying factors such that there was no net consumption of HCl, and no net generation of dichloroethane. By inspection (or by working through the math) we find that multiplying reaction R3 by 2 will do the trick.

	ν_2	ν_3	ν_4	ν_{net}	M_ι	$\nu_{net}M_\iota$	$/lbmol	$
C_2H_4	-1		-1	-2	28	-56	7.56	-15.12
Cl_2	-1			-1	71	-71	7.10	-7.10
$C_2H_4Cl_2$	+1	-2	+1					
C_2H_3Cl		+2		+2	62.5	+125	13.75	+27.50
HCl		+2	-2					
O_2			-0.5	-0.5	32	-16		
H_2O				+1	18	+18		

The atom economy is 125/(56+71+16) = 0.87, which is quite good and an improvement over the combination of reactions 2 and 3. The costs above are for making 2 lbmol of vinyl chloride; dividing by 2 shows that the profit is +$2.64/lbmol. Much more attractive than the earlier proposal!

Thus, the best pathway combines 3 reactions to take advantage of the cheaper raw materials, and to reduce byproduct generation. These steps improve both atom and process economy.

P1.42

The two reactions for production of DSIDA from ammonia, formaldehyde, hydrogen cyanide and sodium hydroxide are

$$NH_3 + 2CH_2O + 2HCN \rightarrow C_4H_5N_3 + 2H_2O \qquad (R1)$$
$$C_4H_5N_3 + 2NaOH + 2H_2O \rightarrow C_4H_5O_4NNa_2 + 2NH_3 \qquad (R2)$$

The generation-consumption and process economic analyses are summarized in the table.

	ν_1	ν_2	ν_{net}	M_ι	$\nu_{net}M_\iota$	lb/day (SF = 10)	$/lb	$/day
NH_3	-1	+2	+1	17	17	+170	0.0725	+12.325
CH_2O	-2		-2	30	-60	-600	0.324	-194.4
HCN	-2		-2	27	-54	-540	0.70	-378
$C_4H_5N_3$	+1	-1						
H_2O	+2	-2						
NaOH		-2	-2	40	-80	-800	0.32	-256

$C_4H_5O_4NNa_2$		+1	+1	177	+177	+1770		

The cost for the raw materials is $828/day at a DSIDA production rate of 1770 lb/day.

<u>Synthesis of DSIDA from DEA and NaOH</u> produces hydrogen as a byproduct:

$$C_4H_{11}O_2N + 2NaOH \rightarrow C_4H_5O_4NNa_2 + 4H_2 \qquad \text{(R3)}$$

	ν_3	M_ι	$\nu_3 M_\iota$	lb/day (SF = 10)	$/lb	$/day
$C_4H_{11}O_2N$	-1	105	-105	-1050	0.58	-609
NaOH	-2	40	-80	-800	0.32	-256
$C_4H_5O_4NNa_2$	+1	177	+177	+1770		
H_2	+4	2	+8	+80		

The cost for the raw materials is $865/day at a DSIDA production rate of 1770 lb/day. The cost is very similar to the conventional process; the environmental and safety advantages of the new process are significant. Overall the new process is quite attractive.

<u>Synthesis of DEA</u> from ethylene, oxygen and ammonia proceeds via two reactions:

$$C_2H_4 + \frac{1}{2}O_2 \rightarrow C_2H_4O \qquad \text{(R4)}$$

$$2C_2H_4O + NH_3 \rightarrow C_4H_{11}O_2N \qquad \text{(R5)}$$

Multiplication of reaction R4 by a multiplying factor of 2 results in no net generation or consumption of ethylene oxide.

	ν_4	ν_5	ν_{net}	M_ι	$\nu_{net}M_\iota$	lb (SF = 1/105)	$/lb	$
C_2H_4	-2		-2	28	-56	-0.533	0.38	-0.203
O_2	-1		-1	32	-32	-0.305	~0	
C_2H_4O	+2	-2						
NH_3		-1	-1	17	-17	-0.162	0.0725	-0.0117
$C_4H_{11}O_2N$		+1	+1	105	+105	1	0.58	+0.58
sum								+0.365

We can save $.365/lb DEA if we make it ourselves (neglecting all costs other than raw materials – which overestimates our savings). Still, this looks like a sufficiently attractive option to make it worth pursuing further.