https://ebookyab.ir/solution-manual-introduction-to-chemical-processes-murphy/

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P1.1
$$SiO_2 + 3C \rightarrow 2CO + SiC$$

$$C_3H_5(NO_3)_3 \rightarrow v_2CO_2 + v_3H_2O + v_4N_2 + v_5O_2$$

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

$$3 = 2v_4$$

$$3 = v_2$$

$$5 = 2v_3$$

$$9 = 2v_2 + v_3 + 2v_5$$

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

$$(NH_4)_2$$
PtCl₆ $\rightarrow v_2$ Pt + v_3 NH₄Cl + v_4 N₂ + v_5 HCl

Pt:
$$v_2 = 1$$

N:
$$v_3 + 2v_4 = 2$$

H:
$$4v_3 + v_5 = 8$$

Cl:
$$v_3 + v_5 = 6$$

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

$$v_3 = \frac{2}{3}$$
, $v_5 = 5\frac{1}{3}$, $v_4 = \frac{2}{3}$

$$(NH_4)_2$$
PtCl₆ \rightarrow Pt + $\frac{2}{3}$ NH₄Cl + $\frac{2}{3}$ N₂ + $5\frac{1}{3}$ 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.

NaHCO₃:
$$\frac{1 \text{ gmol HCl}}{\text{gmol NaHCO}_3} \times \frac{\text{gmol NaHCO}_3}{84 \text{ g NaHCO}_3} \times \frac{36.5 \text{ g HCl}}{\text{gmol HCl}} = \frac{0.435 \text{g HCl}}{\text{g NaHCO}_3}$$

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CaCO₃:
$$\frac{2 \text{ gmol HCl}}{\text{gmol CaCO}_3} \times \frac{\text{gmol CaCO}_3}{100 \text{ g CaCO}_3} \times \frac{36.5 \text{ g HCl}}{\text{gmol HCl}} = \frac{0.73 \text{g HCl}}{\text{g CaCO}_3}$$

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

MgCO₃ has the best neutralizing ability, gram for gram.

P1.5

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

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

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

P1.6

Water is required to decompose the urea:

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

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

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

 $\frac{6 \text{ gmol } CO_2}{\text{gmol } C_6H_{12}O_6} \times \frac{44 \text{ g } CO_2/\text{gmol } CO_2}{180 \text{ g } C_6H_{12}O_6/\text{gmol } C_6H_{12}O_6} = 1.5 \text{ g } CO_2/\text{g } C_6H_{12}O_6$
 $\frac{6 \text{ gmol } H_2O}{\text{gmol } C_6H_{12}O_6} \times \frac{18 \text{ g } H_2O/\text{gmol } H_2O}{180 \text{ g } C_6H_{12}O_6/\text{gmol } C_6H_{12}O_6} = 0.6 \text{ g } H_2O/\text{g } C_6H_{12}O_6$

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

Cl₂:
$$\frac{\$0.016}{\text{gmol}} \times \frac{1 \text{ gmol}}{71 \text{ g}} \times \frac{454 \text{ g}}{\text{lb}} \times \frac{2000 \text{ lb}}{\text{ton}} = \frac{\$205}{\text{ton}}$$

NH₃:
$$\frac{\$0.0045}{\text{gmol}} \times \frac{1 \text{ gmol}}{17 \text{ g}} \times \frac{454 \text{ g}}{\text{lb}} \times \frac{2000 \text{ lb}}{\text{ton}} = \frac{\$240}{\text{ton}}$$

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

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

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

$$\frac{45 \times 10^6 \text{ tons}}{\text{vr}} \times \frac{875}{\text{ton}} = 3.4 \text{ billion/yr}$$

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

$$\text{HNO}_3 + v_2\text{CH}_3\text{OH} \rightarrow v_3\text{C}_3\text{H}_7\text{NO}_2 + v_4\text{CO}_2 + v_5\text{H}_2\text{O}$$

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

$$1 = v_3$$

$$v_2 = 3v_3 + v_4$$

$$1 + 4v_2 = 7v_3 + 2v_5$$

$$3 + v_2 = 2v_3 + 2v_4 + v_5$$

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

$$\text{HNO}_3 + 3\frac{1}{3}\text{CH}_3\text{OH} \rightarrow \text{C}_3\text{H}_7\text{NO}_2 + \frac{1}{3}\text{CO}_2 + 3\frac{2}{3}\text{H}_2\text{O}$$

We want to react (54-10 mg/L) x 10 L of nitric acid, or 0.44 g. The molar mass of HNO₃ is 63 g/gmol, while that of CH₃OH is 32 g/gmol. Therefore:

$$0.44 \text{ g HNO}_3 \times \frac{\text{gmol HNO}_3}{63 \text{g HNO}_3} \times \frac{3\frac{1}{3} \text{ gmol CH}_3 \text{OH}}{\text{gmol HNO}_3} \times \frac{32 \text{ g CH}_3 \text{OH}}{\text{gmol CH}_3 \text{OH}} = 0.75 \text{ g CH}_3 \text{OH}$$

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:

$$\frac{2 \text{ gmol Na}_{2}C_{2}O_{4}}{\text{gmol CF}_{2}Cl_{2}} \times \frac{\text{gmol CF}_{2}Cl_{2}}{121 \text{ g CF}_{2}Cl_{2}} \times \frac{134 \text{ g Na}_{2}C_{2}O_{4}}{\text{gmol Na}_{2}C_{2}O_{4}} = 2.21 \text{ g Na}_{2}C_{2}O_{4} / \text{g CF}_{2}Cl_{2}$$

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

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

$$\times \frac{\text{gmol CF}_2\text{Cl}_2}{121 \text{ g CF}_2\text{Cl}_2} = 1.76 \text{ g solid products/g CF}_2\text{Cl}_2$$

P1.17

Ethanol:
$$\frac{6 \text{ gmol H}}{\text{gmol C}_{2}\text{H}_{5}\text{OH}} \times \frac{\text{gmol C}_{2}\text{H}_{5}\text{OH}}{46 \text{ g C}_{2}\text{H}_{5}\text{OH}} \times \frac{1 \text{ g H}}{\text{gmol H}} \times 100\% = 13\text{wt\% H}$$
Water:
$$\frac{2 \text{ gmol H}}{\text{gmol H}_{2}\text{O}} \times \frac{\text{gmol H}_{2}\text{O}}{18 \text{ g H}_{2}\text{O}} \times \frac{1 \text{ g H}}{\text{gmol H}} \times 100\% = 11\text{wt\% H}$$
Glucose:
$$\frac{12 \text{ gmol H}}{\text{gmol C}_{6}\text{H}_{12}\text{O}_{6}} \times \frac{\text{gmol C}_{6}\text{H}_{12}\text{O}_{6}}{180 \text{ g C}_{6}\text{H}_{12}\text{O}_{6}} \times \frac{1 \text{ g H}}{\text{gmol H}} \times 100\% = 6.7\text{wt\% H}$$
Methane:
$$\frac{4 \text{ gmol H}}{\text{gmol CH}_{4}} \times \frac{\text{gmol CH}_{4}}{16 \text{ g CH}_{4}} \times \frac{1 \text{ g H}}{\text{gmol H}} \times 100\% = 25\text{wt\% H}$$

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.

Hydrogenation:

(a) conventional

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

	$\nu_{\rm i}$	M_{i}	$v_i M_i$
C ₆ H ₅ COCH ₃	-1	120	-120
NaBH ₄	-0.25	38	-9.5
H ₂ O	-1	18	-18
C ₆ H ₅ CH(OH)CH ₃	+1	122	122

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

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

Atom economy = 1.0!

Oxidation:

(a) conventional

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

	$\nu_{\rm i}$	M_{i}	$\nu_i M_i$
C ₆ H ₅ CH(OH)CH ₃	-1	122	-122
CrO ₃	-0.667	100	-66.7
H ₂ SO ₄	-1	98	-98
C ₆ H 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

C-C bond formation

(a) conventional

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

	$\nu_{\rm i}$	M _i	$\nu_i M_i$
C ₆ H ₅ CH(OH)CH ₃	-1	122	-122
Mg	-1	24	-24
CO_2	-1	44	-44
HC1	-2	36.5	-73
C ₆ H ₅ CHCH ₃ COOH	+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

$$C_6H_5OH + v_2CH_3COCH_3 \rightarrow v_3C_{15}H_{16}O_2 + v_4CO_2 + v_5H_2O$$

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

$$6 + 3v_2 = 15v_3 + v_4$$

$$6 + 6v_2 = 16v_3 + 2v_5$$

$$1 + v_2 = 2v_3 + 2v_4 + v_5$$

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 $v_4 = 0$: $v_2 = 1/2$, $v_3 = 1/2$, $v_5 = 1/2$. (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 ₆ H ₅ OH	-100				-100
CH ₃ COCH 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:

$$HCO_3^- + NH_4^+ + C_4H_7O_4N \rightarrow C_4H_4O_4 + CH_4ON_2 + 2H_2O_4$$

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 Fe₂O₃ 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(CO₅) is therefore equal to $(1.52 \times 196 \times 0.001) = 0.298$ 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	$\nu_{\rm i}$	M _i	$\nu_{i} M_{i}$	tons/day	\$/ton	\$/day
				(SF = 1000/106)		
NaCl	-2	58.5	-117	-1104	95	-104,860
H ₂ SO ₄	-1	98	-98	-927	80	-74,160
HCl	+2	36.5	+73	+689		
С	-2	12	-24	-226		
CO_2	+2	44	+88	+830		
CaCO ₃	-1	100	-100	-943	87	-82,040
Na ₂ CO 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

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

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

Water is the only byproduct.

The generation-consumption analysis is shown in the table.

Compound	ν_1	ν_2	$\nu_{ m net}$	M_{i}	$\nu_{i} M_{i}$	kg
						(SF = 1/60)
C ₂ H ₅ OH	-1		-1	46	-46	-0.77
O_2	-1/2	-1/2	-1	32	-32	-0.53
CH ₃ CHO	+1	-1	0			
H ₂ O	+1		+1	18	+18	+0.30
CH ₃ COOH		+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:

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

Compound	ν_1	ν_2	ν_3	$\nu_{ m net}$	M_{i}	$\nu_{i} M_{i}$	Grams
							(SF = 3.57)
SiO ₂	-1			-1	60	-60	-214
С	-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
HC1			+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:

$$C_4H_8 + CH_2O \rightarrow C_5H_{10}O$$
 (R1)

$$C_5H_{10}O + \frac{1}{2}O_2 \rightarrow C_5H_8O + H_2O$$
 (R2)

$$C_5H_{10}O + C_5H_8O \rightarrow C_{10}H_{16}O + H_2O$$
 (R3)

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

Compound	ν_1	v_2	ν_3	$\nu_{ m net}$	M_{i}	$\nu_{_{i}} M_{_{i}}$	Grams
							(SF = 1000/152)
C_4H_8	-2			-2	56	-112	-737
CH ₂ O	-2			-2	30	-60	-395
$C_5H_{10}O$	+2	-1	-1	0			
O_2		-1/2		-1/2	32	-16	-105
C ₅ H ₈ O		+1	-1	0			
H ₂ O		+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

$$(CaF)Ca_4(PO_4)_3 + v_2H_2SO_4 + v_3H_2O \rightarrow v_4CaH_4(PO_4)_2H_2O + v_5CaSO_4 + v_6HF$$

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

Ca:
$$5 = v_4 + v_5$$

F: $1 = v_6$

P: $3 = 2v_4$

O: $12 + 4v_2 + v_3 = 9v_4 + 4v_5$

H: $2v_2 + 2v_3 = 6v_4 + v_6$

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

$$(\text{CaF})\text{Ca}_4 (\text{PO}_4)_3 + 3\frac{1}{2}\text{H}_2\text{SO}_4 + \frac{3}{2}\text{H}_2\text{O} \rightarrow \frac{3}{2}\text{CaH}_4 (\text{PO}_4)_2\text{H}_2\text{O} + 3\frac{1}{2}\text{CaSO}_4 + \text{HF}$$

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

Compound	$\nu_{\rm i}$	M_{i}	$\nu_{i} M_{i}$	Tons	\$/ton	\$
				(SF = 1/378)		
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, CO₂ and water is:

$$v_1C_6H_{12}O_6 + v_2O_2 + v_3NH_3 \rightarrow v_4CH_{1.66}O_{0.5}N_{0.166} + v_5CO_2 + v_6H_2O_3$$

We know that 3.9 g CO₂ are produced per gram of yeast. The molar mass of CO₂ 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 CO₂ 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.

C:
$$6v_1 = 1 + 2.1255$$

H: $12v_1 + 3v_3 = 1.66 + 2v_6$
O: $6v_1 + 2v_2 = 0.5 + 2(2.1255) + v_6$
N: $v_3 = 0.166$

The balanced reaction is:

$$0.521 \text{C}_6\text{H}_{12}\text{O}_6 + 2.085\text{O}_2 + 0.166\text{NH}_3 \rightarrow \text{CH}_{1.66}\text{O}_{0.5}\text{N}_{0.166} + 2.1255\text{CO}_2 + 2.545\text{H}_2\text{O}_2 + 2.545\text{H}_2\text{O}_3 + 2.545\text{H}_2\text$$

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}	$\nu_{\mathrm{I},\mathrm{net}}$
Cu ₂ S	-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

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$$\sum_{k} v_{CuS,k} \chi_{k} = 0$$

$$\sum_{k} v_{CuSO_{4},k} \chi_{k} = 0$$

and

$$\sum_{k} v_{CuSO_4,k} \chi_k = 0$$

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}	$\nu_{\mathrm{I,net}}$	M_{ι}	$\nu_{I,net}M_{\iota}$	Tons
				·		·	(SF=1/127)
Cu ₂ S	-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	M _i	$\nu_{i} M_{i}$	kg	\$/kg	\$
				(SF =		
				1/342)		
Lactose	-1	342	-342	-1	0.484	-0.484
H ₂ O	-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

$$S + O_2 \rightarrow SO_2$$
 (R1)

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

$$SO_3 + H_2O \rightarrow H_2SO_4$$
 (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

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

$$NO + \frac{1}{2}O_2 \rightarrow NO_2 \tag{R2}$$

$$3NO_2 + H_2O \rightarrow 2HNO_3 + NO$$
 (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 ₂ O	+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 NO₂ 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 ₂ O	+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	v_2	$\nu_{ m net}$	M_{i}	$v_{\text{net}} M_{i}$	Lb	\$/lb	\$
						(SF = 1/918)		
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

Reaction pathway 1:

The balanced chemical reactions are

$$C_4H_6 + 2HCN \rightarrow C_6H_8N_2 \tag{R1}$$

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

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

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