

Solutions Manual

to accompany

Introduction to Chemical Processes

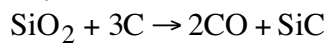
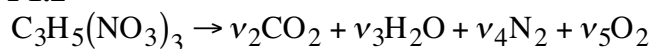
Principles, Analysis, Synthesis

Prepared by

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P1.1**P1.2**

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

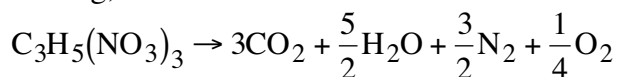
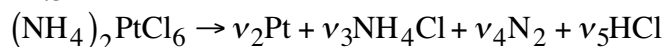
$$3 = 2\nu_4$$

$$3 = \nu_2$$

$$5 = 2\nu_3$$

$$9 = 2\nu_2 + \nu_3 + 2\nu_5$$

Solving, we find

**P1.3**

$$\text{Pt: } \nu_2 = 1$$

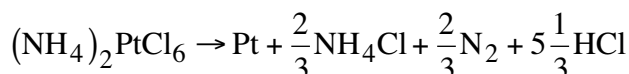
$$\text{N: } \nu_3 + 2\nu_4 = 2$$

$$\text{H: } 4\nu_3 + \nu_5 = 8$$

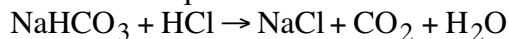
$$\text{Cl: } \nu_3 + \nu_5 = 6$$

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

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

**P1.4**

The three balanced equations are



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.

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

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

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

MgCO₃ has the best neutralizing ability, gram for gram.

P1.5

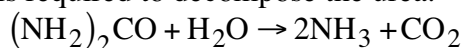
Molar mass of urea (NH₂)₂CO = 2 × 14 + 4 × 1 + 12 + 16 = 60 g/gmol.

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

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

P1.6

Water is required to decompose the urea:

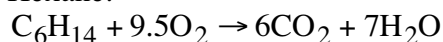


$$\text{Fractional atom economy} = \frac{2 \text{ gmol NH}_3 \times (17 \text{ g/gmol})}{1 \text{ gmol urea} \times (60 \text{ g/gmol}) + 1 \text{ gmol H}_2\text{O} \times (18 \text{ g/gmol})} = 0.44$$

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

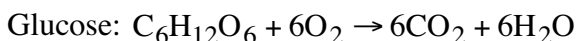
P1.7

Hexane:



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

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



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

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

P1.8

$$\left(10^9 \text{ lb NH}_3\right) \left(\frac{1 \text{ lbmol NH}_3}{17 \text{ lb NH}_3}\right) \left(\frac{1 \text{ lbmol N}_2}{2 \text{ lbmol NH}_3}\right) \left(\frac{28 \text{ lb N}_2}{1 \text{ lbmol N}_2}\right) = 820 \text{ million lbs N}_2$$

$$\left(10^9 \text{ lb NH}_3\right) \left(\frac{1 \text{ lbmol NH}_3}{17 \text{ lb NH}_3}\right) \left(\frac{3 \text{ lbmol H}_2}{2 \text{ lbmol NH}_3}\right) \left(\frac{2 \text{ lb H}_2}{1 \text{ lbmol H}_2}\right) = 180 \text{ million lbs H}_2$$

P1.9

$$\text{Cl}_2: \frac{\$0.016}{\text{gmol}} \times \frac{1 \text{ gmol}}{71 \text{ g}} \times \frac{454 \text{ g}}{\text{lb}} \times \frac{2000 \text{ lb}}{\text{ton}} = \frac{\$205}{\text{ton}}$$

$$\text{NH}_3: \frac{\$0.0045}{\text{gmol}} \times \frac{1 \text{ gmol}}{17 \text{ g}} \times \frac{454 \text{ g}}{\text{lb}} \times \frac{2000 \text{ lb}}{\text{ton}} = \frac{\$240}{\text{ton}}$$

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

$$\text{Molar mass} = 2 + 32 + 4(16) = 98 \text{ tons/tonmol}$$

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

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

$$\frac{45 \times 10^6 \text{ tons}}{\text{yr}} \times \frac{2000 \text{ lb}}{\text{ton}} = \frac{180 \times 10^6 \text{ lb}}{\text{yr}}$$

$$\frac{180 \times 10^6 \text{ lb}}{6 \times 10^9 \text{ people}} = 15 \text{ lb/person/yr}$$

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

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

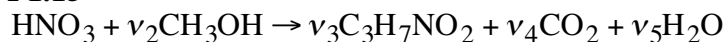
Some possible explanations: greater number of reactions in pathway, more stringent product purity requirements, less pressure to trim costs by reducing wastes.

P1.14

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

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

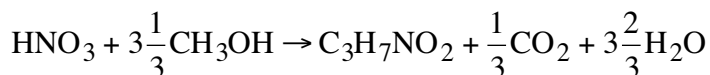
P1.15



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

$$\begin{aligned} 1 &= \nu_3 \\ \nu_2 &= 3\nu_3 + \nu_4 \\ 1 + 4\nu_2 &= 7\nu_3 + 2\nu_5 \\ 3 + \nu_2 &= 2\nu_3 + 2\nu_4 + \nu_5 \end{aligned}$$

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



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:



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

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

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

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

P1.17

Ethanol: $\frac{6 \text{ gmol H}}{\text{gmol C}_2\text{H}_5\text{OH}} \times \frac{\text{gmol C}_2\text{H}_5\text{OH}}{46 \text{ g C}_2\text{H}_5\text{OH}} \times \frac{1 \text{ g H}}{\text{gmol H}} \times 100\% = 13\text{wt}\% \text{ H}$

Water: $\frac{2 \text{ gmol H}}{\text{gmol H}_2\text{O}} \times \frac{\text{gmol H}_2\text{O}}{18 \text{ g H}_2\text{O}} \times \frac{1 \text{ g H}}{\text{gmol H}} \times 100\% = 11\text{wt}\% \text{ H}$

Glucose: $\frac{12 \text{ gmol H}}{\text{gmol C}_6\text{H}_{12}\text{O}_6} \times \frac{\text{gmol C}_6\text{H}_{12}\text{O}_6}{180 \text{ g C}_6\text{H}_{12}\text{O}_6} \times \frac{1 \text{ g H}}{\text{gmol H}} \times 100\% = 6.7\text{wt}\% \text{ H}$

Methane: $\frac{4 \text{ gmol H}}{\text{gmol CH}_4} \times \frac{\text{gmol CH}_4}{16 \text{ g CH}_4} \times \frac{1 \text{ g H}}{\text{gmol H}} \times 100\% = 25\text{wt}\% \text{ H}$

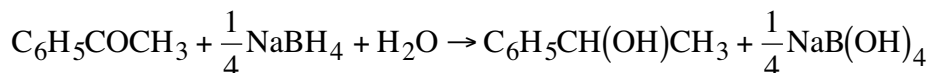
It does seem hard to believe that they achieved 50 wt% H.

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:

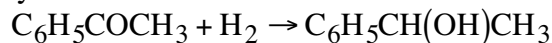
(a) conventional



	v_i	M_i	$v_i M_i$
$\text{C}_6\text{H}_5\text{COCH}_3$	-1	120	-120
NaBH_4	-0.25	38	-9.5
H_2O	-1	18	-18
$\text{C}_6\text{H}_5\text{CH(OH)CH}_3$	+1	122	122

$$\text{Atom economy} = 122 / (120 + 9.5 + 18) = 0.83$$

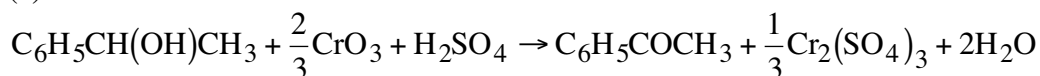
(b) catalytic



Atom economy = 1.0!

Oxidation:

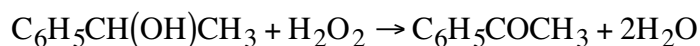
(a) conventional



	v_i	M_i	$v_i M_i$
$\text{C}_6\text{H}_5\text{CH}(\text{OH})\text{CH}_3$	-1	122	-122
CrO_3	-0.667	100	-66.7
H_2SO_4	-1	98	-98
$\text{C}_6\text{H}_5\text{COCH}_3$	+1	120	120

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

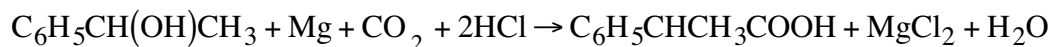
(b) catalytic



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

C-C bond formation

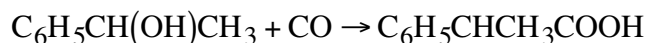
(a) conventional



	v_i	M_i	$v_i M_i$
$\text{C}_6\text{H}_5\text{CH}(\text{OH})\text{CH}_3$	-1	122	-122
Mg	-1	24	-24
CO_2	-1	44	-44
HCl	-2	36.5	-73
$\text{C}_6\text{H}_5\text{CHCH}_3\text{COOH}$	+1	150	150

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

(b) catalytic

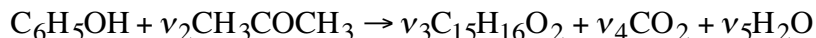


Atom economy = 1.00!

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



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

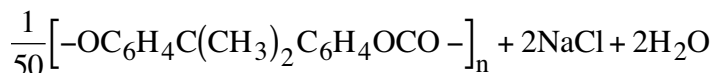
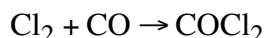
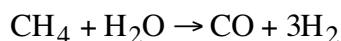
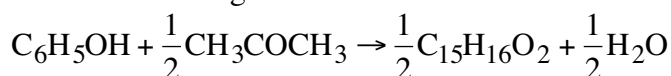
$$6 + 3\nu_2 = 15\nu_3 + \nu_4$$

$$6 + 6\nu_2 = 16\nu_3 + 2\nu_5$$

$$1 + \nu_2 = 2\nu_3 + 2\nu_4 + \nu_5$$

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



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

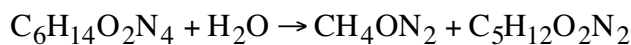
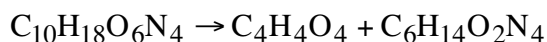
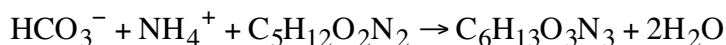
	R1	R2	R3	R4	net
$\text{C}_6\text{H}_5\text{OH}$	-100				-100
CH_3COCH_3	-50				-50
$\text{C}_{15}\text{H}_{16}\text{O}_2$	50			-50	
H_2O	50	-50		100	+100
CH_4		-50			-50
CO		50	-50		
H_2		150			+150
Cl_2			-50		-50
COCl_2			50	-50	
NaOH				-100	-100
polycarbonate				1	+1

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.

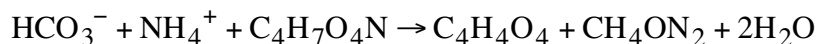
The balanced chemical reactions are



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:



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 $\text{Fe}(\text{CO})_5$ is 196 g/gmol. 1.52 mmol of $\text{Fe}(\text{CO})_5$ 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

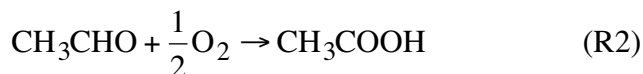
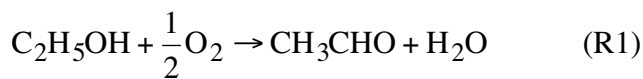
The LeBlanc chemistry is given in Example 1.3. At a sodium carbonate production rate of 1000 ton/day, we complete the following process economy calculations.

Compound	v_i	M_i	$v_i M_i$	tons/day (SF = 1000/106)	\$/ton	\$/day
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		
C	-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



Water is the only byproduct.

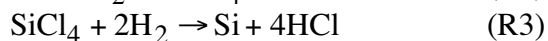
The generation-consumption analysis is shown in the table.

Compound	v_1	v_2	v_{net}	M_i	$v_i M_i$	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 $0.77(\$0.29) = \$0.22/\text{kg}$.

P1.24

The balanced chemical equations are:



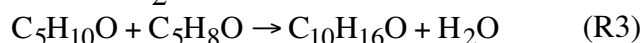
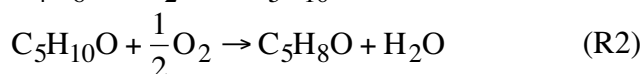
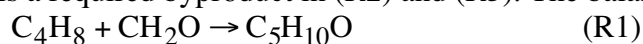
Compound	ν_1	ν_2	ν_3	ν_{net}	M_i	$\nu_i M_i$	Grams (SF = 3.57)
SiO ₂	-1			-1	60	-60	-214
C	-2			-2	12	-24	-86
Si	+1	-1	+1	+1	28	+28	+100
CO	+2			+2	28	+56	+200
Cl ₂		-2		-2	71	-142	-507
SiCl ₄		+1	-1		170		
H ₂			-2	-2	2	-4	-14
HCl			+4	+4	36.5	+146	+521
sum							0

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:



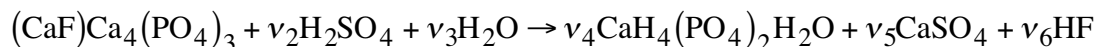
We need to multiply (R1) by 2 to avoid making unwanted intermediates. The generation-consumption analysis is:

Compound	ν_1	ν_2	ν_3	ν_{net}	M_i	$\nu_i M_i$	Grams (SF = 1000/152)
C ₄ H ₈	-2			-2	56	-112	-737
CH ₂ O	-2			-2	30	-60	-395
C ₅ H 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



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

$$\text{Ca: } 5 = \nu_4 + \nu_5$$

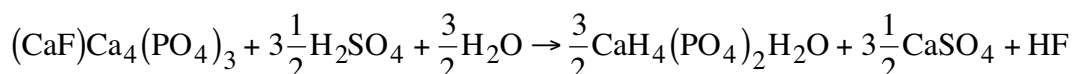
$$\text{F: } 1 = \nu_6$$

$$\text{P: } 3 = 2\nu_4$$

$$\text{O: } 12 + 4\nu_2 + \nu_3 = 9\nu_4 + 4\nu_5$$

$$\text{H: } 2\nu_2 + 2\nu_3 = 6\nu_4 + \nu_6$$

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



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 $\text{CH}_{1.66}\text{O}_{0.5}\text{N}_{0.166}$.

An overall reaction for reaction of glucose, oxygen, and ammonia to yeast, CO₂ and water is:



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.

$$\text{C: } 6\nu_1 = 1 + 2.1255$$

$$\text{H: } 12\nu_1 + 3\nu_3 = 1.66 + 2\nu_6$$

$$\text{O: } 6\nu_1 + 2\nu_2 = 0.5 + 2(2.1255) + \nu_6$$

$$\text{N: } \nu_3 = 0.166$$

The balanced reaction is:



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 CO₂. (This is probably the best measure of relative utilization of glucose for yeast vs. for CO₂.) About 20% of the mass of carbon containing compounds is yeast, with the remainder as CO₂.

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}	$\nu_{i,\text{net}}$
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

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

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.

	v_{i1}	v_{i3}	v_{i4}	$v_{i,net}$	M_i	$v_{i,net} M_i$	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

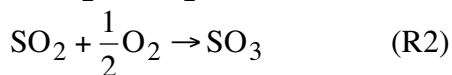
In the first process, we use lactose to produce glucose with the byproduct galactose. The economic evaluation is summarized in tabular form.

Compound	v_i	M_i	$v_i M_i$	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

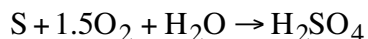
We lose 17 cents per kg lactose processed on this deal. If we convert galactose to glucose, we add another \$0.316 to the last column. With that process modification, we can make about \$0.15/kg lactose processed.

P1.30Sulfuric acid process

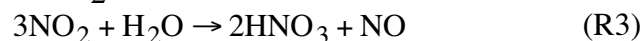
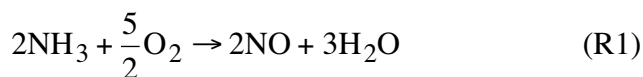
Three reactions



These reactions combine easily to an overall reaction of

Nitric acid process:

Three balanced reactions are



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

$$\text{NH}_3 + 2\text{O}_2 \rightarrow \text{HNO}_3 + \text{H}_2\text{O}$$

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 used in reaction R2 to eliminate generation/consumption of intermediates.

compound	v_1	v_2	v_{net}	M_i	$v_{\text{net}} M_i$	Lb (SF = 1/918)	\$/lb	\$
Glycerol stearate	-1		-1	890	-890	-0.97	1.00	-0.97
H ₂ O	-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 $x = \$0.925/\text{lb soap}$. 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.

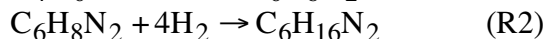
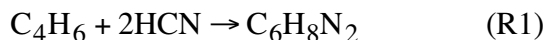
P1.32

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



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

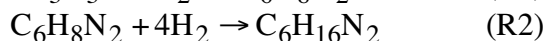
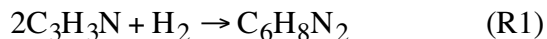
compound	v_1	v_2	v_{net}	M_i	$v_{\text{net}} M_i$	Lb (SF = 1000)	\$/lb	\$
C ₄ H ₆	-1		-1	54	-54	-54000	0.21	-11,340

HCN	-2		-2	27	-54	-54000	0.93	-50,220
C ₆ H ₈ N ₂	+1	-1						
H ₂		-4	-4	2	-8	-8000	0.09	-720
C ₆ H 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



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

compound	v_1	v_2	v_{net}	M_i	$v_{\text{net}} M_i$	Lb (SF = 1000)	\$/lb	\$
C ₃ H ₃ N	-2		-2	53	-106	-106000	0.65	-68,900
C ₆ H ₈ N ₂	+1	-1						
H ₂	-1	-4	-5	2	-10	-10000	0.09	-900
C ₆ H 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

	v_i	M_i	$v_i M_i$	lb/day (SF = 100/53)	\$/lb	\$/day
C ₂ H ₂	-1	26	-26	-49	1.80	-88.2
HCN	-1	27	-27	-51	0.60	-30.6

C ₃ H ₃ N	+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

	v_i	M_i	$v_i M_i$	lb/day (SF = 100/53)	\$/lb	\$/day
C ₃ H 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 ₂ O	+3	18	+54	+102		
C ₃ H ₃ N	+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

	v_i	M_i	$v_i M_i$	lb/day (SF = 100/53)	\$/lb	\$/day
C ₂ H ₄ O	-1	44	-44	-83	0.56	-46.5
HCN	-1	27	-27	-51	0.60	-30.6
H ₂ O	+1	18	+18	+34		
C ₃ H ₃ N	+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:





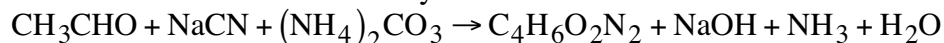
The process economy calculations are summarized in the table. I used values of \$0.60/lb for HCN, and \$0.455/lb for acetaldehyde.

compound	v_1	v_2	v_3	v_{net}	M_i	$v_{\text{net}} M_i$	Metric tons/yr (SF = 200/89)	\$/ton	\$
CH ₃ CHO	-1			-1	44	-44	-98.9	1001	-99,000
NH ₃	-1		+1						
C ₂ H ₇ NO	+1	-1							
HCN		-1		-1	27	-27	-60.7	1320	-80,100
C ₃ H ₆ N ₂		+1	-1						
H ₂ O		+1	-2	-1	18	-18	-40.5		
C ₃ H ₇ O ₂ N			+1	+1	89	+89	+200	4750	+950,000
sum							0		+770,000

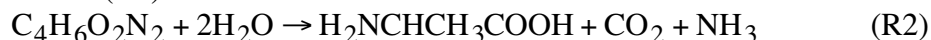
The atom economy is 100%, and the process economy is quite attractive. One disadvantage is the requirement for a highly toxic reactant, hydrogen cyanide.

Bucherer synthesis

The 2 balanced chemical reactions for synthesis of alanine are:



(R1)



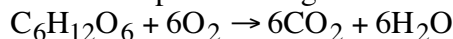
The process economy calculations are summarized in the table. I used values of \$0.70/lb for NaCN, and \$0.29/lb for ammonium carbonate.

compound	v_1	v_2	v_{net}	M_i	$v_{\text{net}} M_i$	Metric tons/yr (SF = 200/89)	\$/ton	\$
CH ₃ CHO	-1		-1	44	-44	-98.9	1001	-99,000
NaCN	-1		-1	49	-49	-110	1540	-169,000
(NH ₄) ₂ CO ₃	-1		-1	96	-96	-216	638	-138,000
C ₄ H ₆ N ₂ O ₂	+1	-1						
NaOH	+1		+1	40	+40	+90		
NH ₃	+1	+1	+2	17	+34	+76		
H ₂ O	+1	-2	-1	18	-18	-40		
C ₃ H ₇ O ₂ N		+1	+1	89	+89	+200	4750	+950,000
CO ₂		+1	+1	44	+44	+98.9		
sum						0		+544,000

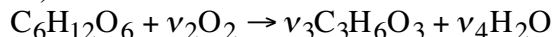
The atom economy is poor (43%). The process economy is quite attractive, although not as good as the Strecker synthesis. Handling all the byproducts would greatly increase the costs of running this process. Safety concerns are similar to the Strecker process.

P1.38

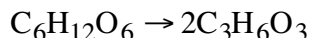
The aerobic decomposition of glucose to CO_2 is a well-known reaction:



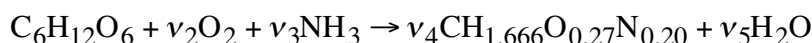
The unbalanced reaction from glucose to lactic acid is (guessing that water is a byproduct):



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).



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



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



(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.

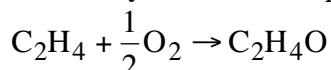
The remaining glucose ($18 - 1.588 - 3.6 = 12.812$ g) must have been converted to CO_2 . This mass of glucose consumed is equal to 0.0711 gmol; from the balanced reaction we know that this would generate 0.427 gmol CO_2 , or 18.79 g CO_2 .

8.8% of the glucose was consumed to grow bacteria, 20% was consumed to make lactic acid, and over 71% was oxidized to CO₂.

P1.39

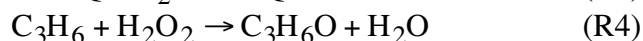
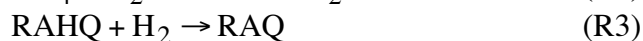
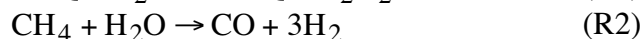
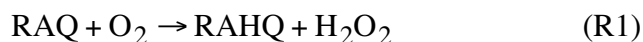
Direct oxidation is the preferred method for converting ethylene-to-ethylene oxide. It would also be the preferred method for converting propylene-to-propylene oxide, but the reaction won't "go" under typical processing conditions. Oxidation with hydrogen peroxide is too expensive. This problem considers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

Ethylene oxide by conventional process:



	v_i	M_i	$v_i M_i$	kg (SF = 1000/44)	\$/kg	\$
C ₂ H ₄	-1	28	-28	-636.4	0.57	-363
O ₂	-1/2	32	-16	-363.6	0.033	-12
C ₂ H ₄ O	+1	44	+44	+1000	1.32	+1320
sum						+945

Propylene oxide by new process:



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

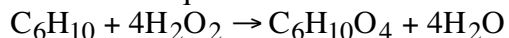
compound	v_1	v_2	v_3	v_4	v_{net}	M_i	$v_{\text{net}} M_i$	kg (SF = 1000/58)	\$/kg	\$
RAQ	-1		+1							
O ₂	-1				-1	32	-32	-552	0.033	-18.2
RAHQ	+1		-1							
H ₂ O ₂	+1			-1						
CH ₄		-1/3			-1/3	16	-5.33	-91.9	0.11	-10.1
CO		+1/3			+1/3	28	+9.3	+160		
H ₂ O		-1/3		+1	+2/3	18	+12	+207		
C ₃ H ₆				-1	-1	42	-42	-724	0.42	-304
C ₃ H ₆ O				+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 CO₂.

P1.40

Process with hydrogen peroxide:

Balanced chemical equation is:



The process economy is summarized as follows:

	v_i	M_i	$v_i M_i$	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
$\text{C}_6\text{H}_{10}\text{O}_4$	+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:



The process economy is summarized as follows:

	v_i	M_i	$v_i M_i$	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		
$\text{C}_6\text{H}_{10}\text{O}_4$	+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:

	v_2	v_3	v_{net}	M_i	$v_{net} M_i$	\$/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?

	v_2	v_3	v_4	v_{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 ₂ O				+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.

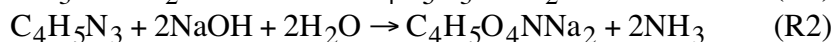
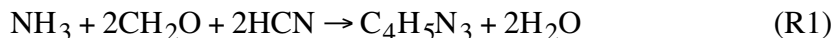
	v_2	v_3	v_4	v_{net}	M_t	$v_{\text{net}}M_t$	\$/lbmol	\$
C ₂ H ₄	-1		-1	-2	28	-56	7.56	-15.12
Cl ₂	-1			-1	71	-71	7.10	-7.10
C ₂ H ₄ Cl ₂	+1	-2	+1					
C ₂ H ₃ Cl		+2		+2	62.5	+125	13.75	+27.50
HCl		+2	-2					
O ₂			-0.5	-0.5	32	-16		
H ₂ O				+1	18	+18		

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



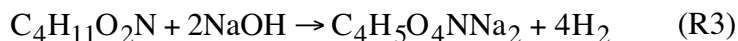
The generation-consumption and process economic analyses are summarized in the table.

	v_1	v_2	v_{net}	M_t	$v_{\text{net}}M_t$	lb/day (SF = 10)	\$/lb	\$/day
NH ₃	-1	+2	+1	17	17	+170	0.0725	+12.325
CH ₂ O	-2		-2	30	-60	-600	0.324	-194.4
HCN	-2		-2	27	-54	-540	0.70	-378
C ₄ H ₅ N ₃	+1	-1						
H ₂ O	+2	-2						
NaOH		-2	-2	40	-80	-800	0.32	-256

$C_4H_5O_4NNa_2$		+1	+1	177	+177	+1770		
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The cost for the raw materials is \$828/day at a DSIDA production rate of 1770 lb/day.

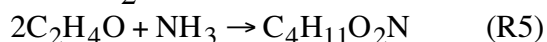
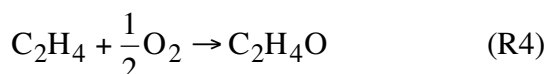
Synthesis of DSIDA from DEA and NaOH produces hydrogen as a byproduct:



	v_3	M_t	v_3M_t	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.

Synthesis of DEA from ethylene, oxygen and ammonia proceeds via two reactions:



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

	v_4	v_5	v_{net}	M_t	$v_{net}M_t$	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.