



Introduction to
Chemical Processes
Principles, Analysis, Synthesis

Regina M. Murphy

McGraw-Hill International Edition



Contents

Preface	xvi
List of Nomenclature	xxvi
List of Important Equations	xxix

CHAPTER 1	Converting the Earth's Resources into Useful Products	1
1.1	Introduction	2
1.2	Raw Materials	3
1.3	Balanced Chemical Reaction Equations	6
	Example 1.1 Balanced Chemical Reaction Equation: Nitric Acid Synthesis	
	Example 1.2 Balanced Chemical Reaction Equations: Adipic Acid Synthesis	
1.4	Generation-Consumption Analysis	11
	Example 1.3 Generation-Consumption Analysis: The LeBlanc Process	
	Example 1.4 Generation-Consumption Analysis: The Solvay Process	
	Example 1.5 Generation-Consumption Analysis: Ammonia Synthesis	
1.5	A First Look at Material Balances and Process Economics	18
	1.5.1 Mass, Moles, and Molar Mass	19
	1.5.2 Atom Economy	20
	Example 1.6 Atom Economy: LeBlanc versus Solvay	
	Example 1.7 Atom Economy: Improved Synthesis of 4-ADPA	
	1.5.3 Process Economy	24
	Example 1.8 Process Economy: The Solvay Process	
	1.5.4 Process Capacities and Product Values	26
	Case Study: Six-Carbon Chemistry	27
	Summary	37
	ChemiStory: Changing Salt into Soap	39
	Quick Quiz Answers	40
	References and Recommended Readings	41
	Chapter 1 Problems	41

CHAPTER 2	Process Flows: Variables, Diagrams, Balances	57
2.1	Introduction	58
2.2	Process Variables	59
2.2.1	A Brief Review of Dimensions and Units	59
2.2.2	Mass, Moles, and Composition	61
2.2.3	Temperature and Pressure	63
2.2.4	Volume, Density, and Concentration	64
2.2.5	Flowrates	66
2.3	Chemical Process Flow Sheets	67
2.3.1	Input-Output Flow Diagrams	68
2.3.2	Block Flow Diagrams	69
2.3.3	Process Flow Diagrams (PFD)	71
2.3.4	Modes of Process Operation	74
2.4	Process Flow Calculations	75
2.4.1	Definitions	76
2.4.2	Material Balance Equations	78
2.4.3	A Systematic Procedure for Process Flow Calculations	81
2.4.4	Helpful Hints for Process Flow Calculations	82
2.4.5	A Plethora of Problems	84
	Example 2.1 Mixers: Battery Acid Production	
	Example 2.2 Reactors: Ammonia Synthesis	
	Example 2.3 Separators: Fruit Juice Concentration	
	Example 2.4 Splitters: Fruit Juice Processing	
	Example 2.5 Elements as Components: Ibuprofen Analysis	
	Example 2.6 Separation with Accumulation: Air Drying	
	Example 2.7 Reaction with Accumulation: Light from a Chip	
2.5	Degree of Freedom Analysis	104
	Example 2.8 DOF Analysis: Ammonia Synthesis	
	Example 2.9 DOF Analysis: Light from a Chip	
	Example 2.10 DOF Analysis: Battery Acid Production	
	Example 2.11 DOF Analysis: Eat Your Greens!	
2.6	Process Flow Calculations with Multiple Process Units	112
	Example 2.12 Multiple Process Units: Toxin Accumulation	
	Example 2.13 Multiple Process Units: Adipic Acid Manufacture from Glucose	
2.6.1	Synthesizing Block Flow Diagrams	121
	Example 2.14 Synthesizing Block Flow Diagrams: Adipic Acid Process	

2.6.2	The Art of Approximating	124
2.6.3	Degree of Freedom Analysis for Block Flow Diagrams with Multiple Process Units	125
	Example 2.15 DOF Analysis: Adipic Acid Production	
	Case Study: Evolution of a Greener Process	127
	Summary	136
	ChemiStory: Guano and the Guns of August	137
	Quick Quiz Answers	141
	References and Recommended Readings	141
	Chapter 2 Problems	142

CHAPTER 3 Mathematical Analysis of Material Balance Equations and Process Flow Sheets **169**

3.1	Introduction	170
3.2	The Material Balance Equation—Again	170
3.2.1	Conservation of Mass and the Material Balance Equation	171
	Example 3.1 Decomposition Reactions	
3.2.2	General Forms of the Differential Material Balance Equations	176
	Example 3.2 Mass Balances: Sugar Dissolution	
	Example 3.3 Mass Balances: Glucose Consumption in a Fermentor	
	Example 3.4 Mole Balances: Manufacture of Urea	
	Example 3.5 Mole Balances: Urea Manufacture from Cheaper Reactants	
3.2.3	Degree of Freedom Analysis	182
	Example 3.6 DOF Analysis: Urea Synthesis from Cheaper Reactants	
	Example 3.7 Differential Material Balance Equation with Multiple Chemical Reactions at Steady State: Benzene into Catechol	
3.2.4	General Forms of the Integral Material Balance Equations	186
	Example 3.8 Integral Equation: Blending and Shipping	
	Example 3.9 Integral Equation with Unsteady Flow: Jammin' with Cherries	
3.2.5	A Few More Problems	193
	Example 3.10 Integral Equation with Unsteady Flow and Chemical Reaction: Controlled Drug Release	

	Example 3.11	Differential Equation with Unsteady Flow and Chemical Reaction: Glucose Utilization in a Fermentor	
3.3		Linear Equations and Chemical Reactions (Optional Section)	200
3.3.1		Linear Equations, Linear Independence, Solution Existence, and Solution Uniqueness	201
3.3.2		Using Matrices to Balance Chemical Reactions	204
	Example 3.12	Balancing Chemical Equations with Matrix Math: Adipic Acid	
3.3.3		Using Matrices in Generation-Consumption Analysis	207
	Example 3.13	Generation-Consumption Analysis Using Matrix Math: Nitric Acid Synthesis	
3.3.4		Using Matrices to Find Linearly Independent Chemical Equations	210
3.4		Linear Models of Process Flow Sheets (Optional Section)	213
3.4.1		Linear Models of Single Process Units	214
	Example 3.14	Linear Model of a Mixer: Sweet Mix	
	Example 3.15	Linear Model of a Splitter: Sweet Split	
	Example 3.16	Linear Model of a Reactor: Glucose-Fructose Isomerization	
	Example 3.17	Linear Model of a Reactor: Multiple Reactions	
	Example 3.18	Linear Model of a Separator: Sweet Solutions	
3.4.2		Process Topology	226
	Example 3.19	Linear Models with Multiple Process Units and Recycle: Taking an old Plant out of Mothballs	
		Case Study: Manufacture of Nylon-6,6	234
		Summary	244
		ChemiStory: Of Toothbrushes and Hosiery	246
		Quick Quiz Answers	249
		References & Recommended Reading	249
		Chapter 3 Problems	249

CHAPTER 4 **Synthesis of Reactor Flow Sheets and Selection of Reactor Process Conditions** **263**

4.1		Introduction	264
	4.1.1	Industrially Important Chemical Reactions	264
	4.1.2	Heuristics for Selecting Chemical Reactions	266

4.1.3	A Brief Review: Generation-Consumption Analysis and Atom Economy	266
Example 4.1	Generation-Consumption and Atom Economy: Improved Synthesis of Ibuprofen	
4.1.4	Reactor Design Variables	269
4.2	Reactor Material Balance Equations	271
4.2.1	Reactors with Known Reaction Stoichiometry	271
Example 4.2	Continuous-Flow Steady-State Reactor with Known Stoichiometry: Combustion of Natural Gas	
Example 4.3	Batch Reactor with Known Reaction Stoichiometry: Ibuprofen Synthesis	
Example 4.4	Semibatch Reactor with Known Reaction Stoichiometry: Ibuprofen Synthesis	
4.2.2	Reactors with Unknown Reaction Stoichiometry	278
Example 4.5	Material Balance Equation with Elements: Combustion of Natural Gas	
Example 4.6	Mass Rates of Reaction: Microbial Degradation of Soil Contaminants	
4.3	Stream Composition and System Performance Specifications for Reactors	282
4.3.1	Stream Composition Specification: Excess and Limiting Reactants	284
Example 4.7	Excess Reactants: A Badly Maintained Furnace	
4.3.2	System Performance Specification: Fractional Conversion	287
Example 4.8	Fractional Conversion: Ammonia Synthesis	
Example 4.9	Effect of Conversion on Reactor Flows: Ammonia Synthesis	
4.3.3	Fractional Conversion and Its Effect on Reactor Flow Sheet Synthesis: Recycle	290
Example 4.10	Low Conversion and Recycle: Ammonia Synthesis	
4.3.4	Fractional Conversion and Its Effect on Reactor Flow Sheet Synthesis: Recycle and Purge	294
Example 4.11	Recycle with Purge: Ammonia Synthesis	
4.3.5	System Performance Specifications: Selectivity and Yield	298
Example 4.12	Selectivity and Yield Definitions: Acetaldehyde Synthesis	

Example 4.13	Using Selectivity in Process Flow Calculations: Acetaldehyde Synthesis	
4.4	Why Reactors Aren't Perfect: Chemical Equilibrium and Chemical Kinetics	304
4.4.1	The Chemical Reaction Equilibrium Constant K_a	304
Example 4.14	Deriving Equations for K_a : Three Cases	
4.4.2	Calculating K_a	307
Example 4.15	Calculating K_a : Ethyl Acetate Synthesis	
Example 4.16	Chemical Equilibrium Considerations in Selection of Reaction Pathway: Safer Routes to Dimethyl Carbonate	
4.4.3	Chemical Reaction Equilibrium and Reactor Performance	314
Example 4.17	Reactor Performance and K_a : Ammonia Synthesis	
Example 4.18	Equilibrium Conversion as a Function of T and P : Ammonia Synthesis	
Example 4.19	Multiple Chemical Equilibria and Reactor T : NO _x Formation.	
4.4.4	Chemical Reaction Kinetics and Reactor Performance (Optional Section)	323
Example 4.20	Reaction Kinetics and Reactor Performance: Vegetable Processing	
	Case Study: Hydrogen and Methanol	327
	Summary	335
	ChemiStory: Quit Bugging Me	337
	Quick Quiz Answers	340
	References and Recommended Readings	340
	Chapter 4 Problems	341

CHAPTER 5 Selection of Separation Technologies and Synthesis of Separation Flow Sheets 365

5.1	Introduction	366
5.1.1	Physical Property Differences: The Basis for All Separations	366
Example 5.1	Physical Property Differences: Separating Salt From Sugar	
5.1.2	Mixtures and Phases	367
5.1.3	Classification of Separation Technologies	369
5.1.4	Heuristics for Selecting and Sequencing Separation Technologies	373

Example 5.2	Selection of Separation Technology: Separating Benzene from Toluene	
Example 5.3	Selection of Separation Technology: Cleaning up Off-Gas from a Printing Press	
Example 5.4	Sequencing of Separation Technologies: Aromatics and Acid	
5.2	Separator Material Balance Equations	379
Example 5.5	Semibatch Mechanical Separation: Filtration of Beer Solids	
Example 5.6	Rate-Based Separation: Membranes for Kidney Dialysis	
5.3	Stream Composition and System Performance Specifications for Separators	386
Example 5.7	Defining Separator Performance Specifications: Separating Benzene from Toluene	
Example 5.8	Purity and Recovery Specifications in Process Flow Calculations: Separating Benzene and Toluene	
Example 5.9	Fractional Recovery in Rate-Based Separations: Membranes for Kidney Dialysis	
5.3.1	Recycling in Separation Flow Sheets	394
Example 5.10	Separation with Recycle: Separating Sugar Isomers	
5.4	Why Separators Aren't Perfect: Entrainment and Equilibrium	398
5.4.1	Entrainment: Incomplete Mechanical Separation	398
Example 5.11	Accounting for Entrainment: Coffee Making	
5.4.2	Phase Equilibrium and the Equilibrium Stage	401
5.5	An Exhausting (but Not Exhaustive) Look at Phase Equilibrium	403
5.5.1	The Gibbs Phase Rule	404
5.5.2	Single-Component Phase Equilibrium	405
5.5.3	Multicomponent Phase Equilibrium	408
Example 5.12	Using Raoult's Law: Dew Point and Bubble Point Temperatures of Hexane-Heptane Mixtures	
5.6	Equilibrium-Based Separations	423
5.6.1	Crystallization	425
Example 5.13	Process Flow Calculations with Liquid-Solid Equilibrium Data: Potassium Nitrate Crystallization	

Example 5.14	Entrainment Effects in Equilibrium-Based Separations: Separation of Benzene and Naphthalene by Crystallization	
5.6.2	Evaporation, Condensation, and Equilibrium Flash	429
Example 5.15	Process Flow Calculations with Raoult's Law: Dehumidification of Air by Condensation	
Example 5.16	Process Flow Calculations with Raoult's Law: Equilibrium Flash of a Hexane/Heptane Mixture	
Example 5.17	Vapor-Liquid Separations with Nonideal Solutions: Equilibrium Flash Separation of Ethanol-Water Mixture	
5.6.3	Distillation (Optional)	434
Example 5.18	The Power of Multistaging: Distillation versus Equilibrium Flash for Hexane/Heptane Separation	
5.6.4	Absorption, Adsorption, and Extraction	437
Example 5.19	Process Flow Calculations Using Gas-Liquid Equilibrium Data: Cleaning up Dirty Air by Absorption	
Example 5.20	Process Flow Calculations Using Adsorption Isotherms: Monoclonal Antibody Purification	
Example 5.21	Process Flow Calculations Using Liquid-Liquid Distribution Coefficients: Cleanup of Wastewater Stream by Solvent Extraction	
Example 5.22	Process Flow Calculations Using Triangular Phase Diagrams: Separating Acetic Acid from Water	
5.6.5	Multistaged Separations Using Material Separating Agents (Optional)	446
Example 5.23	The Power of Multistaging: Recovery of Acetic Acid from Wastewater	
	Case Study: Scrubbing Sour Gas	451
	Summary	457
	ChemiStory: How Sweet It Is	458
	Quick Quiz Answers	461
	References and Recommended Readings	462
	Chapter 5 Problems	462

CHAPTER 6 Process Energy Calculations and Synthesis of Safe and Efficient Energy Flow Sheets 495

6.1	Introduction	496
6.1.1	Energy Sources	496
6.1.2	Energy Distribution: Electricity, Heating Fluids, and Cooling Fluids	499
6.1.3	Energy Transfer Equipment	500
6.1.4	A Brief Review of Energy-Related Dimensions and Units	502
6.2	Process Energy Calculations: The Basics	504
6.2.1	The Energy Balance Equation	504
6.2.2	System Energy, Energy Flows, Specific Energy	505
6.3	Putting a Number on Energy: Energy Data and Model Equations	507
6.3.1	Two Forms of Energy: Kinetic and Potential	508
	Example 6.1 Kinetic and Potential Energy: Toddler Troubles	
	Example 6.2 Change in Potential Energy: Snow Melt	
	Example 6.3 Change in Kinetic Energy of a Stream: Thomas Edison or Rube Goldberg?	
6.3.2	A Third Kind of Energy and a Convenience Function: Internal Energy and Enthalpy	511
6.3.3	Using Tables and Graphs to Find \hat{U} and \hat{H}	512
	Example 6.4 Using Steam Tables to Find \hat{H} : Several Cases	
	Example 6.5 Using Steam Tables: Pumping Water, Compressing Steam	
	Example 6.6 Comparing Kinetic, Potential, and Internal Energy: Frequent Flyer	
	Example 6.7 Using Enthalpy-Composition Graphs: Ammonia-Water Mixtures	
6.3.4	Using Model Equations to Find \hat{U} and \hat{H}	521
	Example 6.8 Enthalpy Calculations: Enthalpy of Vaporization of Water at High Pressure	
	Example 6.9 Enthalpy Calculations: Enthalpy of Reaction at High Temperature	
6.3.5	Minisummary	535
6.4	Energy Flows: Heat and Work	536
6.5	The Energy Balance Equation—Again	538
6.6	Process Energy Calculations	540
6.6.1	A Systematic Procedure for Process Energy Calculations	540
6.6.2	Helpful Hints for Process Energy Calculations	541
6.6.3	A Plethora of Problems	542

Example 6.10	Potential Energy into Work: Water over the Dam	
Example 6.11	Integral Energy Balance with a Closed System: Unplugging the Frozen Pipes	
Example 6.12	Temperature Change with Dissolution: Caustic Tank Safety	
Example 6.13	Simultaneous Energy and Material Balances: Mel and Dan's Lemonade Stand	
Example 6.14	Energy Balance with Equilibrium Flash: Separation of Hexane and Heptane	
Example 6.15	Energy Balance with Chemical Reaction: Adiabatic Flame Temperature	
Example 6.16	Energy Balance with Multiple Reactions: Synthesis of Acetaldehyde	
Example 6.17	Unsteady-State Heat Loss: Cooling a Batch of Sterilized Broth	
6.7	A Process Energy Sampler (Optional Section)	560
6.7.1	Work and the Engineering Bernoulli Equation	560
Example 6.18	The Engineering Bernoulli Equation: Sizing a Pump	
6.7.2	Heat and the Synthesis of Heat Exchange Networks	563
Example 6.19	Heat Exchanger Sizing: Steam Heating of Methanol Vapor	
6.7.3	Energy Conversion Processes	567
Example 6.20	Converting Reaction Energy to Heat: Furnace Efficiency	
Example 6.21	Converting Reaction Energy to Work: Heat Engine Analysis	
Example 6.22	Converting Reaction Energy to Work: Hydrogen Fuel Cells	
6.7.4	Chemical Energy and Chemical Safety: Explosions	579
Example 6.23	Estimating Explosive Potential: Trinitrotoluene	
	Case Study: Energy Management in a Chemical Reactor	584
	Summary	589
	ChemiStory: Get the Lead Out!	591
	Quick Quiz Answers	595
	References and Recommended Readings	595
	Chapter 6 Problems	596
APPENDIX A	Mathematical Methods	621
APPENDIX B	Physical Properties	641
APPENDIX C	Answers to Select Problems	673
	Glossary	681
	Index	I-1