

Contents

<i>Syllabus</i>	7	
1	<i>Transforming Raw Materials into Useful Products</i>	15
1.1	<i>Summary</i>	15
1.2	<i>From Raw Materials to Useful Products</i>	15
1.2.1	<i>Example: Polylactide Production</i>	15
1.2.2	<i>From Crude Oil to Plastic Bottles</i>	16
1.3	<i>Stoichiometry and Chemical Calculations</i>	17
1.3.1	<i>Balanced Chemical Reactions</i>	17
1.3.2	<i>Stoichiometric Coefficients</i>	18
1.3.3	<i>Molecular Matrix</i>	18
1.3.4	<i>Condition for a Balanced Reaction</i>	19
1.3.5	<i>Balancing Reactions</i>	19
1.3.6	<i>Molecular Matrix</i>	20
1.4	<i>Solved Problems</i>	21
P1.1	<i>Gasoline Combustion, Carbon Dioxide Production, and Mileage</i>	21
P1.2	<i>Combustion of Nitromethane</i>	23
P1.3	<i>Hypergolic Reaction – Apollo Lunar Module</i>	25
P1.4	<i>Oxidation of Sugar with Potassium Chlorate</i>	26
P1.5	<i>Dissolution of Gold</i>	27
P1.6	<i>Hot Air Balloon</i>	29
P1.7	<i>Leaching of Gold Ore</i>	30
P1.8	<i>Ostwald Process for Nitric Acid</i>	33
P1.9	<i>Synthesis of Methanol from Coal and Methane</i>	34
P1.10	<i>Airbag Pyrotechnic Device</i>	36

1.5 Exercises	39
<i>P1.11 Quick Answer Question</i>	39
<i>P1.12 Homemade Ant Killer</i>	39
<i>P1.13 Cleaning Rust with Coca-Cola</i>	39
<i>P1.14 Aluminum and Toilet Bowel Cleaner</i>	39
<i>P1.15 Hypergolic Reaction – Ethylene Glycol and Potassium Permanganate</i>	40
<i>P1.16 Conversion of ATP to ADP</i>	40
<i>P1.17 Chemistry of Fireworks</i>	41
<i>P1.18 Simple HDA: Generation-Consumption Analysis</i>	42
<i>P1.19 Biodiesel Production from Sugarcane</i>	42
<i>P1.20 Production of Nylon from Renewable Resources</i>	43
2 Chemical Processes and Flowsheets	45
2.1 Summary	45
2.2 Solved Problems	46
<i>P2.21 TNT Production</i>	46
<i>P2.22 Gasoline Blending</i>	50
<i>P2.23 Separating a Methanol/Ethanol Mixture</i>	52
<i>P2.24 Blending Pigments for White Paint</i>	54
<i>P2.25 Acrylonitrile Production</i>	55
<i>P2.26 Ethylene Production</i>	57
<i>P2.27 Drying Ethanol</i>	59
2.3 Exercises	63
<i>P2.28 Watershed Modeling</i>	63
<i>P2.29 Environmental Cleanup</i>	63
<i>P2.30 Selective Reduction Catalysis of Diesel Engine Exhaust</i>	64
<i>P2.31 Sulfur Burner</i>	64
3 Material Balances	67
3.1 Summary	67
3.2 Component Balances	67
3.2.1 Molar Component Balances	67
3.2.2 Mass Component Balances	68

3.3 Solved Problems	68
<i>P3.32 Reactor with Recycle</i>	68
<i>P3.33 Carbon Dioxide Scrubber</i>	70
<i>P3.34 Production of Formaldehyde from Methanol (needs formatting)</i>	72
<i>P3.35 DOF Analysis for an Ammonia Recycle Reactor</i>	78
<i>P3.36 Process Flowsheeting</i>	82
3.4 Exercises	85
<i>P3.37 Hydrodealkylation of Toluene</i>	85
4 Reactors	87
4.1 Summary	87
4.2 Chemical Equilibrium	88
4.2.1 Gibb's Free Energy	88
4.2.2 Spontaneous Change	89
4.2.3 Gibbs Free Energy of Reaction	90
4.2.4 Enthalpy of Reaction	90
4.2.5 Calculating the Equilibrium Constants	91
4.3 Measures of Reactor Performance	93
4.3.1 Limiting and Excess Reactants	93
4.3.2 Fractional Conversion	95
4.3.3 Conversion, Yield, and Selectivity	95
4.4 Solved Problems	96
<i>P4.38 Soyuz Spacecraft Soft-Landing Rockets</i>	96
<i>P4.39 Biodiesel Production (to be modified)</i>	98
<i>P4.40 Production of Methanol</i>	102
<i>P4.41 ATP/ADP Equilibrium at Standard Conditions (NEEDS WORK)</i>	107
<i>P4.42 Contact Process for Sulfuric Acid</i>	108
4.5 Exercises	111
<i>P4.43 Short Answer Questions</i>	111
<i>P4.44 Citric Acid Production</i>	112
<i>P4.45 HDA Reactor</i>	112
<i>P4.46 Equilibrium Reaction Problem</i>	113
<i>P4.47 Reaction Equilibrium</i>	113

5	<i>Separations</i>	115
5.1	<i>Summary</i>	115
5.2	<i>Txy Diagrams</i>	116
5.2.1	<i>Lever Rule</i>	116
5.3	<i>Binary Distillation</i>	117
5.3.1	<i>Enriching (Rectifying) Section</i>	117
5.4	<i>Solved Problems</i>	117
<i>P5.48 Quick Answer Questions</i>	117	
<i>P5.49 Quick Answer Question</i>	118	
<i>P5.50 Quick Answer Question</i>	118	
<i>P5.51 Flash Separation of n-Hexane and n-Octane</i>	119	
<i>P5.52 Vapor-Liquid Equilibrium Problem</i>	120	
<i>P5.53 Binary Distillation of an n-heptane/n-octane Mixture</i>	122	
5.5	<i>Exercises</i>	126
<i>P5.54 Txy Diagram for 1,4 Dioxane/Water</i>	126	
<i>P5.55 Solving Separation Problems</i>	127	
<i>P5.56 Isothermal Flash for a Four Component System</i>	127	
<i>P5.57 Binary Distillation Design</i>	128	
<i>P5.58 Txy Diagram from Experimental Data</i>	129	
6	<i>Energy Balances</i>	131
6.1	<i>Summary</i>	131
6.2	<i>Force, Work, and Power</i>	132
6.2.1	<i>Force</i>	132
6.2.2	<i>Mechanical Work</i>	132
6.2.3	<i>Power</i>	133
6.3	<i>Types of Energy</i>	133
6.4	<i>Specific Energy</i>	134
6.5	<i>Types of Energy</i>	134
6.6	<i>Energy Balances</i>	135
6.7	<i>Process Energy Balance</i>	135
6.8	<i>Steam Tables</i>	138
6.8.1	<i>Sources of Data</i>	138

6.9 Heat Capacity	141
6.10 Reference States	145
6.11 Heat of Vaporization	147
6.12 Energy Balances with Reactions	147
6.13 Enthalpy of Combustion $\Delta\hat{H}_c^\circ$	148
6.14 Higher and Lower Heating Values	148
6.15 Second Law	150
6.15.1 Thought Experiment	150
6.15.2 Introducing Entropy	151
6.15.3 The Second Law and Time's Arrow	151
6.15.4 Carnot Efficiency	152
6.15.5 Ocean Thermal Energy Conversion (OTEC)	153
6.15.6 Steam Turbines	154
6.15.7 Adiabatic Processes	155
6.15.8 PVT Diagrams	156
6.15.9 T-S Diagrams	157
6.15.10 Because Entropy is a State Function	157
6.15.11 Available Work	157
6.15.12 Extracting Useful Work from Internal Energy	158
6.15.13 Reversible Processes	158
6.15.14 Irreversible Process	159
6.15.15 Available Work	159
6.15.16 Hydrogen Economy	159
6.15.17 Hydrogen Economy	160
6.15.18 Three Big Ideas!	160
6.16 Solved Problems	160
P6.59 Reclaiming Freshwater from Seawater	160
P6.60 Energy Balance for Mixing Benzene Streams	161
P6.61 Steam Properties	163
P6.62 Energetics of a Monopropellant	164
P6.63 Steam Turbine Performance	166
P6.64 Acetaldehyde Production	167

<i>6.17 Exercises</i>	169
<i>P6.65 Short Answer Questions</i>	169
<i>P6.66 Short Answer Questions</i>	170
<i>P6.67 Short Answer Questions</i>	170
<i>P6.68 Kinetic Energy Comparisons</i>	170
<i>P6.69 Energy Transfer by Gasoline</i>	170
<i>P6.70 Diesel Engine Efficiency</i>	170
<i>P6.71 Automobile Energy Balance</i>	170
<i>P6.72 Steam Conditions for an Aircraft Catapult</i>	171
<i>P6.73 Free Energy of Reaction of Nitromethane</i>	171
<i>P6.74 Sublimation of Ice</i>	172
<i>P6.75 Condenser Heat Duty</i>	173
<i>P6.76 Flash Separation of n-Hexane and n-Octane</i>	173
<i>P6.77 Thermite Reaction</i>	173
<i>P6.78 Reactor Analysis for the Production of Ketene from Acetic Acid</i>	174
<i>P6.79 Adiabatic Flame Temperature for a Sulfur Burner</i>	174
<i>P6.80 Rocket Motors from Sugar, Stump Remover, and Kitty Litter</i>	174
<i>P6.81 Coke Gasification with CO₂</i>	175
7 Projects	177
<i>7.1 The Stoichiometry of NOx Emissions Control in Diesel Engines using Urea/SCR - Combine with Next Problem</i>	177
<i>7.2 NOx Emissions Control in Diesel Engines</i>	179
<i>P7.82 Exhaust Flowrate</i>	179
<i>P7.83 Catalytic Decomposition of Urea</i>	181
<i>P7.84 Selective Catalytic Reduction of NO_x</i>	182
<i>P7.85 Production of Urea from Natural Gas</i>	183
<i>P7.86 DEF Consumption Rate</i>	186
<i>P7.87 Cost of Raw Materials for DEF</i>	187
<i>7.3 Regeneration of Spent Pickling Liquor</i>	188
<i>P7.88 Estimating Iron Loss</i>	188
<i>P7.89 Neutralization and Disposal of SPL</i>	188
<i>P7.90 PORI Process</i>	189
<i>P7.91 By-Products of the PORI Process</i>	190
<i>P7.92 Optimal Waste Reduction</i>	190

7.4 <i>Battery Technologies for the Electricity Grid</i>	190
<i>P7.93 Liquid Metal Batteries</i>	190
<i>P7.94 Vanadium Flow Batteries</i>	191
<i>P7.95 Evaluating Commercial Technologies for Grid Electricity Storage</i>	192
7.5 <i>Production of Biodiesel from Waste Coffee Grounds</i>	192
7.6 <i>PHA Biopolymers</i>	192

List of Figures

- 1.1 Different representations of the chemical structure for lactic acid. 16
- 1.2 Nitromethane packaged for use as a racing fuel. Photo Source 23
- 1.3 Chemical structure of nitromethane. Source: Wikimedia Commons 23
- 1.4 Apollo lunar module moments after lunar liftoff. Note the lack of a visible plume. 25
- 1.5 Unsymmetrical dimethylhydrazine (UMDH). The actual fuel used on the Apollo lunar module was a 50 wt% mix of UMDH and hydrazine. 25
- 1.6 Oxidation of sugar with potassium chloride. Source: <http://www.thedailysheep.com> 26
- 1.7 Propane fired hot air balloon. Source: <https://www.flickr.com/> 29
- 1.8 Photo Source 33
- 1.9 Airbags deployed in a car. Source: Wikimedia Commons 36
- 1.10 Cast iron skillets, the right hand side showing rust in an unseasoned skillet. Source: Wikimedia Commons 39
- 1.11 *Ricinus communis* Castor beans. Source: Wikimedia Commons 43
- 1.12 The triglyceride that is of the major component of Castor oil. Source: Wikimedia Commons 43

- 2.1 TNT Explosive 46
- 2.2 White paint. Source: 54
- 2.3 Zinc oxide packaged for shipment as paint pigment. Source: 54
- 2.4 Flowsheet for ethanol dehydration using an adsorbant. 60
- 2.5 Rainy Lake, Minnesota. Note the flooding of shoreline vegetation. Also note the lower limbs of conifers are well below the grazing height of deer, which is another indication of flooding. Source: jckphotos. 63
- 2.6 Trichloroethylene molecule. Source: Wikimedia Commons 63

- 3.1 Ammonia Synthesis Flow-sheet 79

- 4.1 Josiah Willard Gibbs 88
- 4.2 Jacobus van't Hoff 92
- 4.3 Relationship among primary measures of reactor performance. Each of the measures (Conversion, Yield, Selectivity) can be expressed as a product or ratio of the other two. 95

- 4.4 Soyuz spacecraft. Source: Wikimedia Commons 96
- 4.5 Landing sequence for the Soyuz descent module. Source: Wikimedia Commons 96
- 4.6 The 17 by 20 cm Soyuz soft landing thruster. Source: Steve Jurvetson 96
- 4.7 Soybeans ready for harvesting. Source: Accuweather 98
- 4.8 Flowsheet for the production of methanol from synthesis gas. 102

- 5.1 Binary Distillation 117
- 5.2 Txy diagram for binary 1,4 dioxane/water system at 1 atm. Source: Wikimedia Commons 126

- 6.1 General configuration for energy balances. 135
- 6.2 For most chemical processes the kinetic and potential energy of the input and output flows will be negligible. Accounting for flow work, and neglecting kinetic and potential energy, results in 136
- 6.3 Generic Energy Balance Equations. 136
- 6.4 Scuba tank and compressor. 136
- 6.5 The Conair Model 259NP hair dryer is rated at 1875 watts. 141
- 6.6 LNG Tanker. 142
- 6.7 Surface Condenser. 143
- 6.8 Demonstration of a fire piston. 144
- 6.9 Eccotemp Model L-10 tankless propane water heater. The water heater has a output of 78,000 BTU delivering 2.65 gallons per minute of hot water. 146
- 6.10 Sadi Carnot 152
- 6.11 An F-14 Tomcat launches from the waist catapult as four F/A-18 Hornets wait to launch from the bow catapults on USS Enterprise (CVN 65) during operations in the Adriatic Sea on Feb. 23, 1999. 171
- 6.12 Iron thermite welding for joining railroad sections. Source: Wikimedia Commons. 173

- 7.1 Adblue is a tradename for Diesel Exhaust Fluid (DEF) consisting of 32.5 wt% urea in deionized water. 179
- 7.2 A steel pickling line. Source: <http://xcelsteel.com/> 188
- 7.3 Schematic diagram of a liquid metal battery. Source: Figure 15a from Kim, et. al., 2013. 191
- 7.4 Schematic diagram of a redox flow battery. Source: Wikimedia Commons 191
- 7.5 Vanadium can exist in solution in four common oxidation states. From left-to-right, VO_2^+ (yellow), VO^{2+} (blue), V^{3+} (green), and V^{2+} (purple). Source: Wikimedia Commons 191

List of Tables

1.1 Conversion Factors	23
2.1 10 Steps for Material Balances	46
2.2 10 Steps for Material Balances	50
5.2 Experimental Txy data for binary 1,4 dioxane/water system at 1 atm.	129
6.1 Properties of Water	146
6.2 Data	172

Syllabus

Catalog Description

INTRODUCTION TO CHEMICAL ENGINEERING ANALYSIS introduces students to mass and energy balances for chemical processes. Students will learn how to prepare and analyze flowsheets for chemical processes, perform generation-consumption analysis, and perform basic engineering calculations for stoichiometry, reactor performance, separations, and energy analysis. This course prepares students for further coursework in Chemical and Biomolecular Engineering.

Meeting Schedule and Locations

Lectures: MWF 9:25–10:15am in 155 DeBartolo Hall

Recitations: Students are required to register for one of the small group weekly recitation sessions (CBE 22255):

Section 01: Monday 3:30–4:20pm in 317 DeBartolo Hall

Section 02: Monday 4:30–5:20pm in 129 DeBartolo Hall

Section 03: Tuesday 3:30–4:20pm in 318 DeBartolo Hall

Section 04: Tuesday 4:30–5:20pm in 318 DeBartolo Hall

Instructors

Jeffrey Kantor Department of Chemical & Biomolecular Engineering

Office: 176 Fitzpatrick Hall.

Office Hours: Thursday Afternoons. These are the regularly scheduled office hours for the course. Otherwise I'm generally available during regular hours if you make an appointment by email, phone, or text.

Email: Kantor.1@nd.edu – this is the best way to reach me.

- Alternatively you can call or text my cell 574-532-4233. As a last resort, you might try my office number 574-631-5797.

Davide Hill Department of Chemical & Biomolecular Engineering

Office: 173 Fitzpatrick Hall.

Office Hours:

Email: Hill.1@nd.edu – this is the best way to reach me.

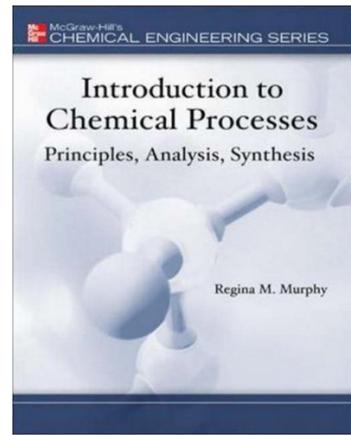
Phone: Office number 574-631-8487.

Textbook and Software

Required Textbook: Regina Murphy, "Introduction to Chemical Processes: Principles, Analysis, Synthesis," McGraw-Hill, 2005.

Learning Management System: CBE 20255 uses the 'Concourse in Sakai' learning management system to distribute lecture notes, homework assignments, and grades.

Software: Some of the problems and exercises will require computational solutions. Students are welcome to use either Matlab or Python. Students are expected to have a working knowledge of Matlab from earlier courses, and the University maintains a site license to Matlab for students and faculty. Free, open source IPython packages can be downloaded from various sources.



Corrections to the textbook are available at this link ([click here](#)).

Links to booksellers

- Notre Dame Hammes Bookstore
- Amazon

Important Course Links

Course pages	https://sakailogin.nd.edu
IPython/Matlab notebooks	http://jckantor.github.io/CBE20255/
Matlab download	http://oit.nd.edu/software
IPython download	https://store.continuum.io/cshop/anaconda/

Course Topics

Weeks 1–2: Converting Raw Materials to Useful Products

Stoichiometry Analyze and balance one or more chemical reactions.

Generation/Consumption Analysis Combine reactions for the production of useful products from available raw materials.

Atom and Process Economy Measure the resources and economic efficiency of process alternatives.

Process Variables and Engineering Units Quantify and communicating chemical and process data.

Weeks 3–4: Chemical Processes

Flowsheets A basic toolkit of mixers, reactors, splitters, and separators for the synthesis and analysis of chemical processes.

Flow Calculations Apply the conservation of mass principle to write equations for process variables.

Degrees of Freedom Analysis Establish the information needed to fully specify a chemical process.

Multiple Process Units Work with multiple process units.

Flowsheet Synthesis Synthesis flowsheets to accomplish multi-step chemical transformations.

Weeks 4–6: Material Balances

Mathematical Formulation Describe material balances in a formal and structured fashion, in molar and mass units.

Solution Solve material balances by hand, by spreadsheet, and in Matlab/Python.

Linear Equations Formulate and solve complex material balances, including systems with material recycling, using linear algebra.

Un

Applications Analyze complex chemical and biomolecular systems using material balances.

Weeks 7–8: Reactors

Reactions Survey the wide range of reactions available for the transformation of raw materials.

Extents of Reaction, Conversion, Yield, and Selectivity Specify the performance of chemical reactors.

Equilibrium Calculations Use the principles of chemical equilibrium to determine the performance of chemical reactors. Use Gibb's free energy, enthalpy, and Van't Hoff law to compute equilibrium constants.

Reaction Kinetics Model and solve for the dynamic behavior of kinetically limited reactions.

Case Study Examine one or more examples in depth.

Weeks 9–10: Chemical Separations

Physical and Chemical Bases for Separation Identify means for accomplishing chemical and physical separations.

Phase Diagram for a Pure Component Identify the relationships among the solid, liquid, and vapor phases of a pure component. Use Antoine's equation to model vapor-liquid equilibrium.

Vapor-Liquid Equilibria for Real Mixtures Examine Txy and Pxy diagrams for common binary mixtures, identify azeotropes. Learn and use the 'lever rule' to solve material balances for flash units.

Vapor-Liquid Equilibria for Ideal Mixtures Model ideal mixtures with Raoult's and Henry's laws, compute the bubble and dew points of mixture, use Rachford-Rice equation to solve material balances for flash units.

Equilibrium Stage Operations Describe the basic elements of single equilibrium stage for chemical separations, and how they can be organized into co-current and counter-current operations.

Binary Distillation Solve binary distillation problems for ideal mixtures using the McCabe-Thiele technique.

Weeks 11–12: Energy Balances - Effective Use of a Limited Resource

Forms of Energy Describe kinetic, potential, and internal energy, and estimate the work necessary to change the state of a system.

Process Energy Balances Define differences among heat, shaft, and flow work, and internal energy and enthalpy.

Steam Table Use the steam table for process energy calculations where steam is used to provide or store energy.

State Functions Understand internal energy and enthalpy as state functions, and the role of the reference state. Calculate energy required for complex state transformations, heats of combustion, adiabatic flame temperatures, higher and lower heating values.

Limits on the Conversion of Heat to Work Understand the role of entropy, and the use of Gibb's free energy in engineering systems.

Heat and Energy Integration Making the most of a limited resource through reuse. Multi-effect evaporators and heat recovery networks.

Weeks 13–14: Putting it all Together - Project

The final component of the course will be in-depth look at one or more chemical operations. Students will work in groups to develop and explore an open-ended project, and present posters showing their work.

Grading

Course grades will be determined from an assessment of submitted homework, the best two out of three mid-semester examinations, a

portfolio project, and a final examination. These elements will be graded and assigned points as listed on the accompanying table. Relief for a poor result in one of the three mid-semester examinations is provided by deleting the lowest of the three scores.

The grading scale places no upper limit on the number of A's and A-'s that can be earned in the course. The intention is to reward students who study and master the course material. Students earning 90% of the possible points can expect to receive an "A" or "A-" for the semester, 80% a "B-" or better, and 70% a "C-" or better. The instructor retains discretion to extend the grade ranges.

Students have the responsibility for tracking their progress in the course. Up to date grades for homework and exams will be maintained on Concourse. Issues of missing homework, requests for regrading, and the like, must be in writing and will be allowed for one week after a grade has been posted.

Exams

Examinations will be the primary means for student assessment. The knowledge and skills you develop in this course are keys to your success in subsequent courses and your engineering career. Therefore there will be a strong emphasis on testing for knowledge and skill development.

1. Exams will be closed book unless stated otherwise. You may bring one page of notes (8.5 by 11, you can write on both sides).
2. There will be three mid-semester exams and a final exam. Makeup exams will be permitted for excused university absences.
3. Students with special testing needs should notify the instructor at start of the course so appropriate arrangements can be made.
4. The University 'Academic Code of Honor' regarding examinations is in effect for all examinations. Any perceived violations will be referred to the adjudication process outlined in the Code.

Homework

Homework is an essential component of the course. Doing the homework exercises develops the skills and insights needed to succeed in the course and major.

1. Homework is required. Missing two or more homework assignments will result in an 'Incomplete' for the course.

Course Points	Points
Homework (12)	120
Hour Exams (best 2 of 3)	200
Project	50
Final Exam	200
Total Possible Points	570

Grading Scale

Points Earned	Grade
above 90%	A- or better
above 80%	B- or better
above 70%	C- or better
above 60%	D or better

2. Homework is due at the beginning of the class period on the stated due date (normally Wednesday's). Late homework will be noted only for the purpose of avoiding an 'Incomplete'.
3. Solutions will be posted on the course web site. Graded homework will be returned normally on Monday of the following week.
4. Each student is individually responsible for all homework. The instructor may regrade homework if there are obvious disparities between a student's written solution and their ability to explain the solution.
5. Homework must be prepared consistent the "Guidelines for Homework Submission." (See Table of Contents).

Electronic Etiquette Policy

The purpose of this policy is to maintain a high quality classroom learning experience by managing the use of personal electronics. In short, personal electronics are welcome in the classroom, but only to the extent their use directly augments your learning.

Phone calls, texting, and the use of personal electronics for outside social interaction is strictly banned during classroom time. If you have a personal situation requiring your attention, please go out to the hallway and take care of business where you won't be a distraction to others.

Using laptops or tablets for note taking, or using phones to take photographs of the chalkboard, is fine and welcomed. So-called 'multi-tasking', however, is not. Objective research shows students don't multi-task nearly as well as they think they do, and laptop use, even for simple note taking, correlates with poorer recall and exam scores.¹ From a well-known study done at Cornell² –

The effects of multitasking in the classroom were investigated in students in an upper level Communications course. Two groups of students heard the same exact lecture and tested immediately following the lecture. One group of students was allowed to use their laptops to engage in browsing, search, and/or social computing behaviors during the lecture. Students in the second condition were asked to keep their laptops closed for the duration of the lecture. Students in the open laptop condition suffered decrements on traditional measures of memory for lecture content.

For many situations the most productive approach to the classroom is to stay alert, take notes by hand for later review and revision, and ask questions to clarify your understanding of the material being presented.



Photo Source

¹ Pam A. Mueller and Daniel M. Oppenheimer. The pen is mightier than the keyboard: Advantages of longhand over laptop note taking. *Psychological Science*, 04 2014

² Helene Hembrooke and Geri Gay. The laptop and the lecture: The effects of multitasking in learning environments. *Journal of Computing in Higher Education*, 15(1):46–64, 2003

Engineering lectures often include numerical examples. For these situations it is often useful to have a calculator handy to check calculations and your understanding by working through the example in parallel with the instructor's explanation. There will also be in-class computational exercises for which a laptop will be needed. You will be notified in advance of class sessions for which a laptop may be needed.

This policy reflects my experience as an engineering educator. I welcome any and all advice or suggestions on how it can be improved.

Academic Integrity and the Academic Code of Honor

One responsibility for engineering educators is to prepare students for modern engineering practice that values collaboration, teamwork, and shared responsibility for the end results. At the same time, education is concerned with the development and assessment of individual knowledge. These challenging goals require scrupulous attention to academic honesty and integrity, and the inculcation of ethical behavior as a professional norm.

The University "Academic Code of Honor"³ is the operative policy regarding academic honesty and integrity for this course. Students in this course are required to understand and abide by the norms outlined in the "Student Guide to the Academic Code of Honor."⁴

Regarding homework assignments –

- When doing assignments, students are welcome to discuss the problem formulation and solution strategies. Written work submitted for a grade, however, must represent a student's individual work. For example, using another student's written homework or computer codes in the preparation of your assignment is strictly unacceptable.
- It is expected that students are able to discuss in depth any work submitted under their name. The instructor and teaching assistants will use one-on-one discussion as an additional means of assessing homework submissions. An inability to reasonably explain work submitted in your own name will result in a loss of grade for that assignment.
- Homework is to be submitted no later than the start of the class period on the date which it is due. Late homework can not be accepted. Exceptions for extenuating circumstances must be made in advance with the instructor or teaching assistant.

Regarding examinations –



³ The University Academic Code of Honor is available on-line at <http://www.nd.edu/~hnrcode/index.htm>

⁴ Student Guide to the Academic Code of Honor (pdf)

- Mid-semester and final examinations will be based on original problems developed by the instructor. Students are welcome to use past examinations and solution keys as study guides.
- Examination dates will be set at the beginning of the course and confirmed several weeks in advance. Makeup exams will be provided only for extenuating circumstances such as personal medical or family emergencies.
- Any cheating or unauthorized assistance on examinations will subject to the procedures outlined in the “Academic Code of Honor.” *This is a zero tolerance policy with a he minimum penalty of one full semester grade.*

1

Transforming Raw Materials into Useful Products

1.1 Summary

Concepts	Skills	Practice Problems
Units, etc.	<ul style="list-style-type: none">- convert among mass and molar flow rates- compute mass and mole fractions- convert among temperature scales- use proper number of significant digits	P1.5, P1.11
Moles	<ul style="list-style-type: none">- understand and explain the concept of mole- work with g-mol, lb-mol, kg-mol	Explain the concept of mole to a room-mate (seriously, try it)
Atomic Matrix	<ul style="list-style-type: none">- Construct the atomic matrix- Find the stoichiometric coefficients- Balance a chemical reaction	P1.7, P1.15, P3.35
Generation/Consumption	<ul style="list-style-type: none">- Construct problem solving table- Choose basis- Identify raw materials, products, by-products- Solve for plausible process stoichiometries- Scale-up to specified process capacity	P1.39, P1.41, P2.55
Atom Efficiency	<ul style="list-style-type: none">- Compute atom efficiency from stoichiometry- Compare alternative processes	P 1.41

1.2 From Raw Materials to Useful Products

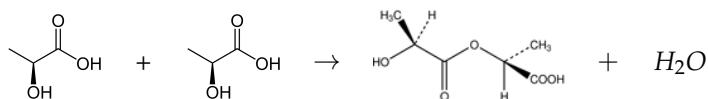
1.2.1 Example: Polylactide Production

Lactic acid is produced in your body through a fermentation reaction that occurs during normal metabolism and exercise. During

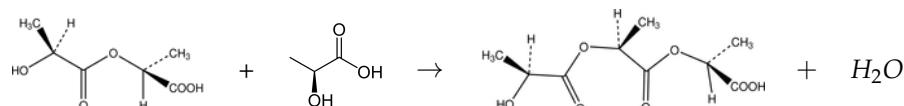
strenuous anaerobic exercise the rate of generation exceeds the rate of removal causing a buildup of lactic acid. This is what causes the ‘muscle burn’ familiar to athletes.

Lactic acid has a number of commercial uses that include food flavoring and preservation, use a mordant for textiles and leather dyeing, and some pharmaceutical and cosmetic applications. On an industrial scale, lactic acid generally produced from renewable resources through the fermentation of corn starch or sugarcane using the microorganism *Lactobacillus*.

Chemically, lactic acid consists of a three carbon chain with a carboxylic acid group ($-COOH$) on one end of the molecule, and an alcohol group ($-OH$) appearing on the central carbon atom. Two lactic acid molecules can combine through a ‘condensation’ reaction where the acid group of one molecule reacts with the alcohol group from the other to release one water molecule.



The product of the reaction is also has a carboxylic acid group at one end and, at the other end an alcohol group on the next to last carbon atom. This configuration enables the product to react with another lactic acid molecule.



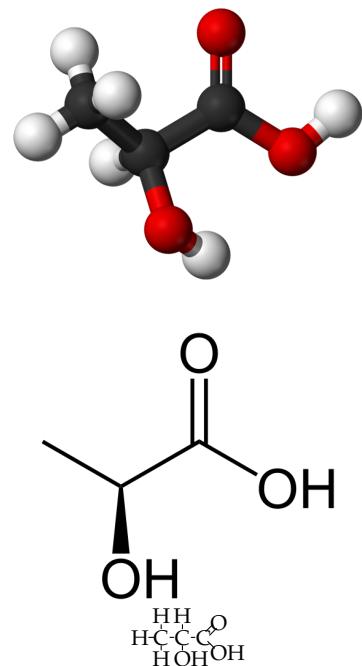
The process can continue indefinitely, resulting in a long polyester molecule that could potentially be used in a variety of commercial applications.

The problem with this approach is that a water molecule is released in each step of the polymerization. Without an effective means of removing the water during the course of the reaction, the water accumulation destroys useful product properties.

1.2.2 From Crude Oil to Plastic Bottles

- Crude oil typically has 0.5–1% (by mass) of xylenes. Xylenes are a very useful chemical for the production of plastics. So additional xylene must be manufactured from other raw materials.
- Additional xylenes can be produced by catalytic reforming, and coal carbonization when manufacturing coke.

Figure 1.1: Different representations of the chemical structure for lactic acid.



1.3 Stoichiometry and Chemical Calculations

1.3.1 Balanced Chemical Reactions

A chemical reaction can be expressed as a formula of the type



where A, B, C, and D are the molecular species involved in the reaction, and the numbers a , b , c , and d indicate the molar quantities of each species on the reactant and product sides of the reaction.

Balanced chemical reactions are the foundation for performing mass balances for chemical processes with reacting systems. A *balanced chemical reaction*

1. shows the *molecular identity* of compounds involved in the reaction,
2. shows the *molar quantity* of the compounds in the reaction,
3. conserves the total number of each type of atom between reactants and products,
4. conserves total electrical charge, and
5. conserves mass.

The last property, the conservation of mass in a balanced chemical reaction, is a consequence of the conservation of atomic species.

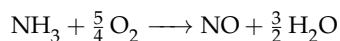
Example: Balanced Chemical Reactions

Are these reactions balanced?

a.



b.



c.



Solution

Part a. The reaction is not balanced because the number of hydrogen and chlorine atoms are not conserved between reactants and products.

Part b. This reaction is balanced.

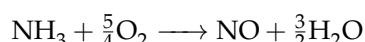
Part c. The reaction is not balanced because the total charge on the reactant side, +7, is not equal to the total charge on the product side, +2.

1.3.2 Stoichiometric Coefficients

The *stoichiometric coefficients* v_j represent the number of molecules of each type that participate in a chemical reaction. The subscript j refers to the molecule type.

If molecule type j is a product of the reaction, then the stoichiometric coefficient is a positive number $v_j > 0$. Otherwise, if the molecule type is consumed as a reactant then the stoichiometric coefficient is negative $v_j < 0$.

For example, the stoichiometric coefficients for the reaction



are

$$\begin{bmatrix} v_{\text{NH}_3} \\ v_{\text{O}_2} \\ v_{\text{NO}} \\ v_{\text{H}_2\text{O}} \end{bmatrix} = \begin{bmatrix} -1 \\ -\frac{5}{4} \\ +1 \\ +\frac{3}{2} \end{bmatrix}$$

Later on we'll see that allowing stoichiometric coefficients to take both positive and negative values simplifies the algebra for material and energy balances for reacting systems.

1.3.3 Molecular Matrix

The *molecular matrix* shows the number of atoms of each type appearing in each molecule participating in a set of one or more reactions.

The molecular matrix for the molecules NH_3 , O_2 , NO , H_2O , for example, is given by

Elements	Molecules			
	NH_3	O_2	NO	H_2O
N	1	0	1	0
H	3	0	0	2
O	0	2	1	1

In general, if we let i represent the row index corresponding to specific elements, and let j represent the column index corresponding to specific molecules, then the coefficients of the molecular matrix can be organized as a matrix $[a_{ij}]$. For the above example,

$$A = [a_{ij}] = \begin{bmatrix} 1 & 0 & 1 & 0 \\ 3 & 0 & 0 & 2 \\ 0 & 2 & 1 & 1 \end{bmatrix}$$

That's the Greek letter Nu denoted by the symbol ν , not the letter 'v' from the English alphabet. If you need to represent the symbol on a system without the ν symbol, such as Python or Matlab programming, don't hesitate to use 'v' as a substitute. But do be aware of the use of Greek symbols in chemical engineering analysis.

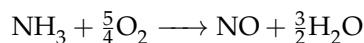
1.3.4 Condition for a Balanced Reaction

Chemical reactions restructure molecules but do not change the identity of the atoms that make up the molecules. For each type of atom, the total number of atoms of that type appearing on the reactant of the reaction must equal the number appearing on the product side.

A chemical reaction is balanced if and only if for every atomic species

$$\sum_j a_{ij}v_j = 0$$

Given a molecular matrix A and a vector of stoichiometric coefficients v , a simple way to test for a balanced reaction is to check if the matrix/vector product $A \cdot v = 0$. For example, for the reaction



we have

$$\underbrace{\begin{bmatrix} 1 & 0 & 1 & 0 \\ 3 & 0 & 0 & 2 \\ 0 & 2 & 1 & 1 \end{bmatrix}}_A \cdot \underbrace{\begin{bmatrix} -1 \\ -\frac{5}{4} \\ +1 \\ +\frac{3}{2} \end{bmatrix}}_v = \underbrace{\begin{bmatrix} 0 \\ 0 \\ 0 \end{bmatrix}}_0$$

1.3.5 Balancing Reactions

To balance a chemical reaction,

1. choose one compound as the 'basis'
2. set the basis stoichiometric coefficient to 1 (if product), or -1 (if reactant)
3. use conditions $\sum_j a_{ij}v_j = 0$ to solve for the other stoichiometric coefficients.

Example: Balance an unbalanced reaction.

Given the unbalanced reaction



what are the stoichiometric coefficients that balance the reaction?

Solution

Assuming all of the stoichiometric coefficients are unknown, the conditions for a balanced reaction can be written as a matrix/vector

product

$$A \cdot v = \underbrace{\begin{bmatrix} 1 & 0 & 1 & 0 \\ 3 & 0 & 0 & 2 \\ 0 & 2 & 1 & 1 \end{bmatrix}}_A \cdot \underbrace{\begin{bmatrix} v_{\text{NH}_3} \\ v_{\text{O}_2} \\ v_{\text{NO}} \\ v_{\text{H}_2\text{O}} \end{bmatrix}}_v = \begin{bmatrix} 0 \\ 0 \\ 0 \end{bmatrix}$$

which gives three equations for the four stoichiometric coefficients

$$\begin{aligned} v_{\text{NH}_3} + v_{\text{NO}} &= 0 \\ 3v_{\text{NH}_3} + 2v_{\text{H}_2\text{O}} &= 0 \\ 2v_{\text{O}_2} + v_{\text{NO}} + v_{\text{H}_2\text{O}} &= 0 \end{aligned}$$

The principle reactant appears to be ammonia (NH_3), so we set its stoichiometric coefficient

$$v_{\text{NH}_3} = \boxed{-1}$$

Substituting this value into the equations and arranging so the constant values are on the right-hand sides gives

$$\begin{aligned} v_{\text{NO}} &= \boxed{1} \\ 2v_{\text{H}_2\text{O}} &= 3 \\ 2v_{\text{O}_2} + v_{\text{NO}} + v_{\text{H}_2\text{O}} &= 0 \end{aligned}$$

Solving the second equation yields

$$v_{\text{H}_2\text{O}} = \boxed{\frac{3}{2}}$$

Finally, substituting all of the known values into the last equation gives us the last stoichiometric coefficient

$$v_{\text{O}_2} = -\frac{1}{2}(v_{\text{NO}} + v_{\text{H}_2\text{O}}) = \boxed{\frac{5}{4}}$$

1.3.6 Molecular Matrix

The *molecular matrix* shows the number of atoms of each type appearing in each molecule participating in a set of one or more reactions.

For example, the molecular matrix for the molecules SiCl_4 , H_2 , Si , and HCl is given by

Elements	Molecules			
	SiCl_4	H_2	Si	HCl
Si	1	0	1	0
Cl	4	0	0	1
H	0	2	0	1

In general, if we let i represent the row index corresponding to specific elements, and let j represent the column index corresponding to specific molecules, then the coefficients of the molecular matrix can be organized as a matrix $[a_{ij}]$. For the above example,

$$A = [a_{ij}] = \begin{bmatrix} 1 & 0 & 1 & 0 \\ 4 & 0 & 0 & 1 \\ 0 & 2 & 0 & 1 \end{bmatrix}$$

1.4 Solved Problems

P1.1 Gasoline Combustion, Carbon Dioxide Production, and Mileage

A question that occasionally appears in the popular press

¹ is “how can each gallon of gasoline burned in a car produce 19 pounds of carbon dioxide”? Assume gasoline is made up of pure octane (C_8H_{18}) and completely burns to carbon dioxide and water. Use the data in the accompanying table to answer the following questions:

- a. Provide a descriptive, one sentence answer to the question “how can each gallon of gasoline burned in a car produce 19 pounds of carbon dioxide”?

Solution

The carbon dioxide produced in the combustion of gasoline includes two atoms of oxygen from the atmosphere for every atom of carbon burned.

- b. Calculate the molar density of gasoline in units of lb-mol/gal.

Solution

The molar density is the number of moles per unit volume. For the desired units

$$\rho = 6 \text{ lb/gal} \times 1 \text{ lb-mol}/114 \text{ lb} = 0.0526 \text{ lb-mol/gal}$$

- c. Write a balanced reaction for the oxidation of octane to carbon dioxide and water.

Solution

The combustion of octane consumes oxygen to produce car-

¹ Engber, Daniel. "How Gasoline Becomes CO₂." *Slate*. 1 Nov 2006. <<http://www.slate.com/id/2152685/>>.

Compound	Property	Value
Gasoline	Density	6 $\frac{\text{lb}}{\text{gal}}$
Octane	Molar Mass	114
Carbon Dioxide	Molar Mass	44
Water	Molar Mass	18

bon dioxide and water through the unbalanced reaction



The unbalanced reaction is simple enough that it can be balanced by inspection. Starting with octane, each carbon atom produces a corresponding molecule of carbon dioxide, and every pair of hydrogen atoms produces a molecule of water. To complete the balance we note the number of required oxygen molecules to produce the indicated carbon dioxide and water.



Though not necessary to solve this problem, the molecular matrix provides a simple means of verifying the solution.

	C_8H_{18}	O_2	CO_2	H_2O
C	8	0	1	0
H	18	0	0	2
O	0	2	2	1

Multiplying the molecular matrix by the vector of stoichiometric coefficients produces zero which verifies that the reaction is balanced.

- d. How many lb-mol's of carbon dioxide are produced per gallon of gasoline consumed?

Solution

The molar density of gasoline is $\rho = 0.0526 \text{ lb-mol/gal}$. From the reaction stoichiometry, each mole of octane consumed produces 8 moles of carbon dioxide. Therefore

$$8 \text{ mol CO}_2 / \text{mol C}_8\text{H}_{18} \times 0.0526 \text{ lb-mol C}_8\text{H}_{18}/\text{gal} = 0.421 \text{ lb-mol CO}_2/\text{gal}$$

of carbon dioxide are produced per gallon of gasoline.

- e. How many pounds of carbon dioxide are produced per gallon of gasoline?

Solution

The molar mass of carbon dioxide is 44 lb/lb-mol. The mass of

carbon dioxide produced by one gallon of gasoline

$$44 \text{ lb CO}_2/\text{lb-mol CO}_2 \times 0.421 \text{ lb-mol CO}_2/\text{gal} = 18.53 \text{ lb CO}_2/\text{gal}$$

- f. By 2016, EPA standards will require passenger cars to emit less than 225 g/mile of carbon dioxide and have a fuel efficiency greater than 39.5 miles/gal. Can a gasoline burning car meet with a mileage of 39.5 miles/gal meet the carbon dioxide standard?

Solution

We've already determined a gasoline burning car will generate 18.53 lb/gal of carbon dioxide. Using the mileage of 39.5 miles/gal, we compute that 212.8 g/miles of carbon dioxide is generated per mile.

$$18.53 \text{ lb CO}_2/\text{gal} \times 1 \text{ gal}/39.5 \text{ mi} \times 453.59 \text{ g/lb} = 212.8 \text{ g CO}_2/\text{mile}$$

Since this is less than the standard 225 g/mile, it is possible for a gasoline burning car to meet the 2016 EPA standard for CO_2 emissions.

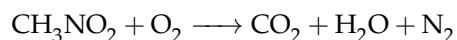
Table 1.1: Conversion Factors

$$1 \text{ lb} = 453.59 \text{ g}$$



P1.2 Combustion of Nitromethane

Nitromethane (CH_3NO_2) is commonly used as a solvent in the semiconductor industry, and as a fuel ('nitro') for rockets, model airplanes and car racing. The *unbalanced* combustion reaction reaction for nitromethane in air is



Using one mole of reacting nitromethane as the basis, find stoichiometric coefficients for this reaction using the molecular matrix approach.

Solution

The atomic matrix is constructed from the chemical formulas of the species participating in the reaction.

Figure 1.2: Nitromethane packaged for use as a racing fuel.
Photo Source

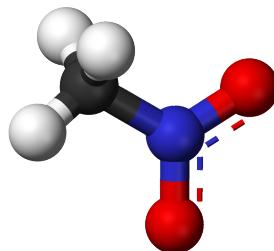


Figure 1.3: Chemical structure of nitromethane. Source: Wikimedia Commons

	CH_3NO_2	O_2	CO_2	H_2O	N_2
C	1		1		
H	3			2	
O	2	2	2	1	
N	1				2

The stoichiometric coefficients are $v_{\text{CH}_3\text{NO}_2}$, v_{O_2} , v_{CO_2} , $v_{\text{H}_2\text{O}}$, and v_{N_2} .

$$\begin{aligned}v_{\text{CH}_3\text{NO}_2} + v_{\text{CO}_2} &= 0 \\3v_{\text{CH}_3\text{NO}_2} + 2v_{\text{H}_2\text{O}} &= 0 \\2v_{\text{CH}_3\text{NO}_2} + 2v_{\text{O}_2} + 2v_{\text{CO}_2} + v_{\text{H}_2\text{O}} &= 0 \\v_{\text{CH}_3\text{NO}_2} + 2v_{\text{N}_2} &= 0\end{aligned}$$

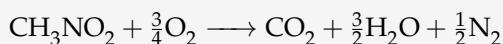
Choosing nitromethane as a reactant and a basis, we set $v_{\text{CH}_3\text{NO}_2} = -1$. Then from the first equation we get $v_{\text{CO}_2} = 1$, from the second we get $v_{\text{H}_2\text{O}} = \frac{3}{2}$, and from the fourth we get $v_{\text{N}_2} = \frac{1}{2}$. The remaining equation is third which we use to solve the last unknown coefficient v_{O_2}

$$\begin{aligned}v_{\text{O}_2} &= -v_{\text{CH}_3\text{NO}_2} - v_{\text{CO}_2} - \frac{1}{2}v_{\text{H}_2\text{O}} \\&= -(-1) - 1 - \frac{1}{2} \cdot \frac{3}{2} \\&= -\frac{3}{4}\end{aligned}$$

Summarizing

$$\begin{bmatrix} v_{\text{CH}_3\text{NO}_2} \\ v_{\text{O}_2} \\ v_{\text{CO}_2} \\ v_{\text{H}_2\text{O}} \\ v_{\text{N}_2} \end{bmatrix} = \begin{bmatrix} -1 \\ -\frac{3}{4} \\ 1 \\ \frac{3}{2} \\ \frac{1}{2} \end{bmatrix}$$

The balanced reaction can be written using the stoichiometric coefficients.

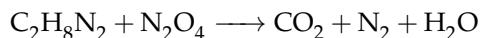


A simple check on the calculation is to compute the matrix/vector product of the molecular matrix M and stoichiometric coefficients v . The product $M \cdot v = 0$ which verifies the solution.

P1.3 Hypergolic Reaction – Apollo Lunar Module

Hypergolic reactions occur spontaneously upon mixing of the reactants. As such, they are easy to regulate and therefore widely used in steering rockets for satellites and other spacecraft. The main engines of the Apollo lunar module, for example, used a 50/50 mixture of unsymmetrical dimethylhydrazine (UDMH) ($C_2H_8N_2$) and hydrazine (N_2H_4) with nitrogen tetroxide (N_2O_4).

The *unbalanced* reaction is given by



Find the stoichiometric coefficients to balance this reaction. Show the atomic matrix, the equations that must be satisfied by the stoichiometric coefficients, and the final balanced reaction.

Solution

There are five compounds involving four atomic species. The atomic matrix is given by

	$C_2H_8N_2$	N_2O_4	CO_2	N_2	H_2O
C	2		1		
H	8			2	
O		4	2		1
N	2	2		2	

Associating stoichiometric coefficients with the columns of the atomic matrix, we have four atom balances that must be satisfied

$$\begin{aligned} 2\nu_1 + \nu_3 &= 0 \\ 8\nu_1 + 2\nu_5 &= 0 \\ 4\nu_2 + 2\nu_3 + \nu_5 &= 0 \\ 2\nu_1 + 2\nu_2 + 2\nu_4 &= 0 \end{aligned}$$

We'll choose the basis one mole of the reactant UMDH, so $\nu_1 = -1$. That results in the equations

$$\begin{aligned} \nu_3 &= 2 \\ 2\nu_5 &= 8 \\ 4\nu_2 + 2\nu_3 + \nu_5 &= 0 \\ 2\nu_2 + 2\nu_4 &= 2 \end{aligned}$$



Figure 1.4: Apollo lunar module moments after lunar liftoff. Note the lack of a visible plume.

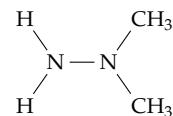
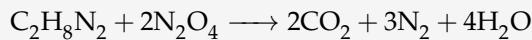


Figure 1.5: Unsymmetrical dimethylhydrazine (UDMH). The actual fuel used on the Apollo lunar module was a 50 wt% mix of UMDH and hydrazine.

The first two equations tell us $\nu_3 = 2$ and $\nu_5 = 4$. Substituting in the second pair of equations gives us solutions for ν_2 and ν_4 . The final balanced equation is



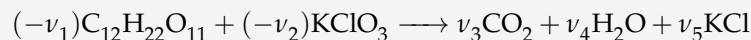
P1.4 Oxidation of Sugar with Potassium Chlorate

A common classroom demonstration is the oxidation of table sugar (i.e., sucrose, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$, or gummy bears) with potassium chlorate (KClO_3). Mix these two compounds together, initiate with a drop of sulfuric acid (H_2SO_4), and you will observe a very vigorous combustion. (Note, the sulfuric acid is only an initiator, it is neither consumed nor produced in the chemical reaction).

Assuming the combustion products are carbon dioxide (CO_2), water (H_2O), and potassium chloride (KCl), set up and solve the equations for the stoichiometric coefficients of the oxidation reaction.

Solution

The chemical reaction may be written as



where the negative signs are inserted because the coefficients are appearing on the reactant side of the reaction. The atomic matrix is

	$\text{C}_{12}\text{H}_{22}\text{O}_{11}$	KClO_3	CO_2	H_2O	KCl
C	12		1		
H	22			2	
O	11	3	2	1	
K		1			1
Cl		1			1

Note that the last row is identical to the row above, and therefore does not yield an extra independent equation for the sto-



Figure 1.6: Oxidation of sugar with potassium chloride. Source: <http://www.thedailysheep.com>

ichiometric coefficients. The equations to solve are

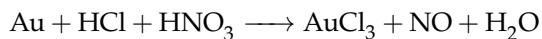
$$\begin{aligned} 12\nu_1 + \nu_3 &= 0 \\ 22\nu_1 + 2\nu_4 &= 0 \\ 11\nu_1 + 3\nu_2 + 2\nu_3 + \nu_4 &= 0 \\ \nu_2 + \nu_5 &= 0 \end{aligned}$$

The numerical solutions was not required, but these equations could be solved by inspection. Choosing $\nu_1 = -1$ as the basis, the first equation can be solved for $\nu_3 = 12$, and the second equation for $\nu_4 = 11$. Plugging those into the third equation gives $\nu_2 = -8$ and finally $\nu_5 = 8$ from the last equation. The result is a balanced reaction



P1.5 Dissolution of Gold

The dissolution of gold (Au) in *aqua regia* (a mixture of concentrated nitric (HNO_3) and hydrochloric (HCl) acids) occurs by way of the **unbalanced** reaction



to form gold(III) chloride (AuCl_3), nitric oxide (NO) and water (H_2O).

- a. Use the atomic matrix approach to write a system of algebraic equations for the stoichiometric coefficients of this reaction. How many equations are there? How many unknowns?

Solution

The atomic matrix is

	Au	HCl	HNO_3	AuCl_3	NO	H_2O
Au	1	0	0	1	0	0
Cl	0	1	0	3	0	0
H	0	1	1	0	0	2
N	0	0	1	0	1	0
O	0	0	3	0	1	1

Using stoichiometric coefficients ν_{Au} , ν_{HCl} , ν_{HNO_3} , ν_{AuCl_3} , ν_{NO} ,

v_{H_2O} , we obtain the atomic balances

$$v_{Au} + v_{AuCl_3} = 0 \quad (1.1)$$

$$v_{HCl} + 3 v_{AuCl_3} = 0 \quad (1.2)$$

$$v_{HCl} + v_{HNO_3} + 2 v_{H_2O} = 0 \quad (1.3)$$

$$v_{HNO_3} + v_{NO} = 0 \quad (1.4)$$

$$3 v_{HNO_3} + v_{NO} + v_{H_2O} = 0 \quad (1.5)$$

There are 5 equations in 6 unknowns.

- b. Solve for the stoichiometric coefficients and write the balanced reaction.

Solution

We will use Au as the basis for this reaction, and set $v_{Au} = -1$. From the first equation

$$v_{AuCl_3} = -v_{Au} = 1$$

Putting this into the second equation,

$$v_{HCl} = -3 v_{AuCl_3} = -3$$

Inserting these results into the remaining three equations

$$v_{HNO_3} + 2 v_{H_2O} = 3$$

$$v_{HNO_3} + v_{NO} = 0$$

$$3 v_{HNO_3} + v_{NO} + v_{H_2O} = 0$$

From the second of these, $v_{NO} = -v_{HNO_3}$, plugging that into the third gives a pair of equations in two unknowns

$$v_{HNO_3} + 2 v_{H_2O} = 3$$

$$2 v_{HNO_3} + v_{H_2O} = 0$$

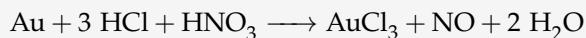
Subtracting the second equation to eliminate v_{H_2O} from the first gives

$$-3 v_{HNO_3} = 3$$

So that $\nu_{\text{HNO}_3} = -1$. Backtracking we have

$$\begin{aligned}\nu_{\text{HNO}_3} &= -1 \\ \nu_{\text{NO}} &= -\nu_{\text{HNO}_3} = +1 \\ \nu_{\text{H}_2\text{O}} &= -2 \nu_{\text{HNO}_3} = +2 \\ \nu_{\text{HCl}} &= -3 \\ \nu_{\text{AuCl}_3} &= -1\end{aligned}$$

yielding the balanced reaction



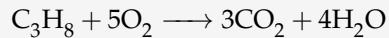
P1.6 Hot Air Balloon

A hot-air balloon is operated using liquid propane (C_3H_8) as a fuel. A typical private-class balloon may carry 2 20-gallon propane tanks each connected to the burner apparatus. The pilot intermittently burns the fuel to control the temperature of the air within the balloon. A typical hot-air balloon has a gas capacity of $2,800 \text{ m}^3$ and carries a total load (balloon, all equipment, and passengers) of 720 kg.

- a. Write the balanced chemical formula for the combustion of propane. Assume complete combustion, so that all fuel is converted into carbon dioxide (CO_2) and water vapor (H_2O). What other compound is a reactant? Where does it come from?

Solution

Propane combusts with the oxygen in air. The reaction we care about is



which we can balance by inspection, but let's review the matrix solution. If the rows correspond to C, H, and O, respectively, and we take propane as the basis, we have

$$\left[\begin{array}{cccc} 3 & 0 & 1 & 0 \\ 8 & 0 & 0 & 2 \\ 0 & 2 & 2 & 1 \end{array} \right] \left[\begin{array}{c} -1 \\ \nu_2 \\ \nu_3 \\ \nu_4 \end{array} \right] = \left[\begin{array}{c} 0 \\ 0 \\ 0 \end{array} \right]$$



Figure 1.7: Propane fired hot air balloon. Source: <https://www.flickr.com/>

Multiplying out and recombining, we obtain

$$\begin{bmatrix} 0 & 1 & 0 \\ 0 & 0 & 2 \\ 2 & 2 & 1 \end{bmatrix} \begin{bmatrix} v_2 \\ v_3 \\ v_4 \end{bmatrix} = \begin{bmatrix} 3 \\ 8 \\ 0 \end{bmatrix}$$

If we left-multiply both sides by the inverse of the square matrix (or do A/b in MATLAB, or solve by substitution), we get [-5,3,4] as our coefficients, which matches the above result.

- b. The pilot burns 75% of her available fuel On a particular 90 minute flight. What is the average rate of carbon dioxide production in pounds per minute? The density of the propane fuel is about 6.8 lb/gal, and molecular weight is 44 lb/lb-mol.

Solution

While the problem asks for pounds/min of carbon dioxide, let's figure out all the molar flows. We were given a basis of 40 gallons of propane. Multiplying by density we have

$$(40 \text{ gallons propane})(6.8 \text{ lb/gal}) = 272 \text{ lb propane}$$

Using the atomic mass, we have $(272 \text{ lb})/(44 \text{ lb/lb-mol})=6.18 \text{ lbmol}$. We know 75% of that reacts, or 4.63 lbmol propane enters the burner. By stoichiometry, $5(4.63)=23.18 \text{ mol of oxygen reacts}$.

Likewise, by stoichiometry, we have produced $4(4.63) = 18.55 \text{ lbmol water}$ and $3(4.63)=13.91 \text{ lbmol carbon dioxide}$. Since there is none of these entering or accumulating, out = generation for both of these compounds. So we have 13.91 lbmol of carbon dioxide exiting. That's $(13.91 \text{ lbmol})(44 \text{ lb/lbmol}) = 612 \text{ lb of CO}_2$! The flight took 90 minutes, so we divide to get pounds per minute: $612 \text{ lb}/90 \text{ min} = 6.8 \text{ lb CO}_2/\text{min}$.

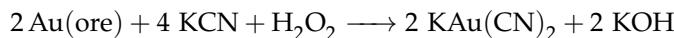
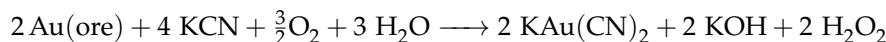
- c. Assume the balloon is operating at an altitude of 6000 ft where the air pressure is 791 millibar and at a temperature of 10°C . Further assume the balloon is filled with the hot exhaust products of combustion. If the temperature of gas within the balloon is 100°C , what is the maximum load that can be supported by the balloon?

P1.7 Leaching of Gold Ore

Gold (Au) is typically present in ores as a native metal in proportions of 20 to 50 ppm. One method for extracting gold from ore is

Species	MW
Au	197.0
KCN	65.1
O ₂	32.0
H ₂ O	18.0
KAu(CN) ₂	288.1
KOH	56.1
H ₂ O ₂	34.0
Zn	65.4
K ₂ Zn(CN) ₄	247.6

the 'cyanidation' process where gold is dissolved by contacting with a potassium cyanide (KCN) in the presence of oxygen. A chemical reactions take place:



The leachate is separated from the ore, and the gold precipitated by contacting with zinc (Zn):



Perform a generation-consumption analysis for the production of the gold precipitate. Hint: Because gold appears as a raw material in the ore and as a product of the process, regard them as different species. What are the required raw materials, and unavoidable by-products, and the atom efficiency of the process?

Solution

Using the reactions as written

Species	MW	R_1	R_2	R_3	Net
		χ_1	χ_2	χ_3	$\sum v_i \chi_i$
Au (ore)	197.0	-2	-2		
KCN	65.1	-4	-4		
O_2	32.0	$-\frac{3}{2}$			
H_2O	18.0	-3			
KAu(CN)_2	288.1	2	2	-2	0
KOH	56.1	2	2		
H_2O_2	34.0	2	-1		0
Zn	65.4			-1	
$\text{K}_2\text{Zn(CN)}_4$	247.6			1	
Au (product)	197.0			2	1

Setting the net stoichiometry of Au(product) to one gives $\chi_3 = \frac{1}{2}$. The remaining values χ_1 and χ_2 are determined by requiring that all KAu(CN)_2 produced in the process also be consumed, and that there be no net production of hydrogen peroxide H_2O_2 . This produces a set of three equations

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

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

$$2\chi_3 = 1$$

Solving the third equation $\chi_3 = \frac{1}{2}$ and substituting the result into the other two

$$\begin{aligned} 2\chi_1 + 2\chi_2 &= 1 \\ 2\chi_1 - \chi_2 &= 0 \end{aligned}$$

Subtracting the second equation from the first produces

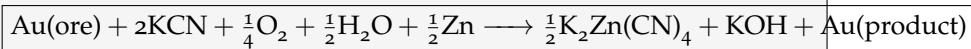
$$3\chi_2 = 1$$

The final solution is

$$\begin{aligned} \chi_1 &= \frac{1}{6} \\ \chi_2 &= \frac{1}{3} \\ \chi_3 &= \frac{1}{2} \end{aligned}$$

Species	MW	R_1	R_2	R_3	Net
		$\chi_1 = \frac{1}{6}$	$\chi_2 = \frac{1}{3}$	$\chi_3 = \frac{1}{2}$	$\sum v_i \chi_i$
Au (ore)	197.0	-2	-2		-1
KCN	65.1	-4	-4		-2
O ₂	32.0	− $\frac{3}{2}$			− $\frac{1}{4}$
H ₂ O	18.0	-3			− $\frac{1}{2}$
KAu(CN) ₂	288.1	2	2	-2	0
KOH	56.1	2	2		1
H ₂ O ₂	34.0	2	-1		0
Zn	65.4			-1	− $\frac{1}{2}$
K ₂ Zn(CN) ₄	247.6			1	$\frac{1}{2}$
Au (product)	197.0			2	1

The final process stoichiometry is given by



The required raw materials are:

- Au(ore)
- KCN potassium cyanide
- O₂ oxygen
- H₂O water
- Zn zinc

The unavoidable by-products are:

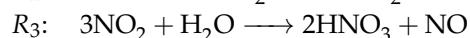
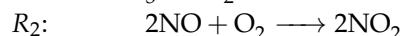
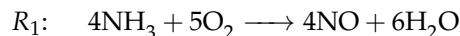
- $\text{KAu}(\text{CN})_2$
- KOH potassium hydroxide

The atom efficiency is the mass fraction of raw material that ends up in the desired product. In this problem

$$\text{eff} = \frac{1 \times 197.0}{\frac{1}{2}288.1 + 1 \times 56.1 + 1 \times 197.0} = \frac{197.0}{397.15} = 0.496 = \boxed{49.6\%}$$

P1.8 Ostwald Process for Nitric Acid

The Ostwald process for the commercial production of nitric acid consists of three reaction steps



- a. Construct the stoichiometric matrix for this system of three reactions.

Solution

The stoichiometric matrix by tabulating the reaction stoichiometric coefficients in a table where the rows correspond to chemical compounds, and the columns correspond to reactions.

	R_1	R_2	R_3	Net
$\chi_1 = \frac{5}{4}$	-4			$\sum_k \nu_{ik} \chi_k$
NH_3				-5
O_2	-5	-1		-10
NO	4	-2	1	0
H_2O	6		-1	5
NO_2		2	-3	0
HNO_3			2	5

The first three columns of the accompanying table constitute the stoichiometric matrix for this problem.

- b. Nitric oxide NO and nitric dioxide NO_2 are chemical intermediates in this process. If the basis is the production of 5 moles of

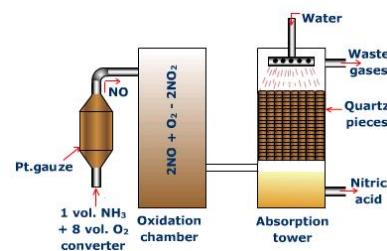


Figure 1.8: Photo Source

HNO_3 , find the reaction weights χ_1 , χ_2 , and χ_3 such that there is no net generation or consumption of these intermediates.

Solution

The solution to this problem is to find the coefficients χ_1 , χ_2 , and χ_3 such that the stoichiometry of the net reaction $\chi_1 R_1 + \chi_2 R_2 + \chi_3 R_3$ has the desired result. Examining the stoichiometric matrix, we find

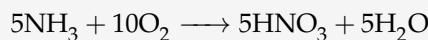
$$\begin{aligned} 4\chi_1 - 2\chi_2 + \chi_3 &= 0 \quad \text{NO} \\ 2\chi_2 - 3\chi_3 &= 0 \quad \text{NO}_2 \\ 2\chi_3 &= 5 \quad \text{HNO}_3 \end{aligned}$$

based on the rows corresponding to NO, NO_2 , and HNO_3 , respectively. These can be solved in order, starting with the last equation. The results are tabulated in the second row of the accompanying table.

- c. Assuming no net generation or consumption of NO or NO_2 , what is the overall process stoichiometry?

Solution

The net stoichiometry is found by computing the sum $\chi_1 R_1 + \chi_2 R_2 + \chi_3 R_3$ for the given solution.



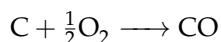
Note the basis is the production of five moles of nitric acid.

P1.9 Synthesis of Methanol from Coal and Methane

Methanol (CH_3OH) has been proposed as large scale liquid transportation fuel that could be synthesized from natural gas (assume it is pure methane, CH_4), coal (assume that is pure carbon, C), and water (H_2O). For this problem the relevant reactions are the steam reforming of methane



the partial oxidation of coal



and the catalytic hydrogenation of carbon monoxide



- Perform a generation/consumption analysis for the production of methanol. Your goal is to maximize the conversion of raw materials to the desired product.
- Sketch a process block diagram for the resulting process.

Solution

Part a. The starting point for the generation/consumption analysis is to prepare a table of stoichiometric coefficients for all reactions participating in the process.

	R_1	R_2	R_3	Net
	χ_1	χ_2	χ_3	
CH_4	-1			
H_2O	-1			
CO	+1	+1	-1	
H_2	+3		-2	
C		-1		
O_2		$-\frac{1}{2}$		
CH_3OH			+1	

Next we identify process constraints

	R_1	R_2	R_3	Net	Process Constraint
	χ_1	χ_2	χ_3		
CH_4	-1				≤ 0 because a raw material
H_2O	-1				≤ 0 because a raw material
CO	+1	+1	-1	0	\leftarrow avoid wasting carbon
H_2	+3		-2	0	\leftarrow don't waste hydrogen
C		-1			≤ 0 because a raw material
O_2		$-\frac{1}{2}$			≤ 0 because a raw material
CH_3OH			+1	+1	\leftarrow desired product

This gives us enough information to solve for χ_1 , χ_2 , and χ_3

	R_1 $\chi_1 = \frac{2}{3}$	R_2 $\chi_2 = \frac{1}{2}$	R_3 $\chi_3 = 1$	Net
CH ₄	-1			$-\frac{2}{3}$
H ₂ O	-1			$-\frac{2}{3}$
CO	+1	+1	-1	0
H ₂	+3		-2	0
C		-1		$-\frac{1}{3}$
O ₂		$-\frac{1}{2}$		$-\frac{1}{6}$
CH ₃ OH			+1	+1
				$\Rightarrow \chi_3 = 1$

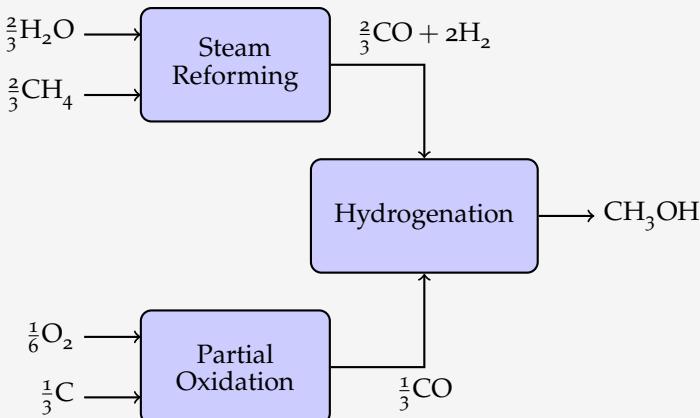
That yields an overall process stoichiometry



which is remarkable because there are absolutely no waste products. We'll return to this example later in the course when we take into account energy balances.

Part b.

The process could be implemented in a number of ways. This is perhaps the simplest diagram which only includes the essential reactors.



P1.10 Airbag Pyrotechnic Device

Automobile airbags are designed to protect occupants in the event of front and side impact crashes. The bags are inflated with nitrogen generated by the explosive decomposition of sodium azide.

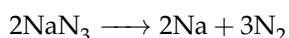
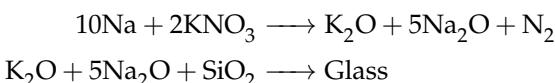


Figure 1.9: Airbags deployed in a car. Source: Wikimedia Commons

Highly reactive sodium would be a hazard at a crash site. To avoid the net production of sodium, a clever piece of chemical engineering is to add potassium nitrate (KNO_3) and silica (SiO_2). The balanced reactions are



which has the potential benefit of producing even more nitrogen.

- Perform a generation/consumption analysis to determine a process stoichiometry that avoids the net production of Na, Na_2O or K_2O . Show your work, including the stoichiometric matrix and the final net stoichiometry.
- Molecular weights of the compounds involved in the reactions are shown in the accompanying table. 98 grams of nitrogen are needed to fill a typical airbag. Specify, in grams, the required amount of sodium azide, potassium nitrate, and silica.

Molecular Weights

Species	MW
NaN_3	65
Na	23
N_2	28
KNO_3	101
K_2O	94
Na_2O	62
SiO_2	60
Glass	n/a

Solution

Part a.

Choosing NaN_3 as the basis, we set up the usual stoichiometric matrix for generation/consumption analysis

Species	MW	χ_1 $1/2$	χ_2 $1/10$	χ_3 $1/10$	Net	Objective
NaN_3	65	-2			-1	
Na	23	2	-10		0	← force to zero
N_2	28	3	1		1.6	
KNO_3	101		-2		-0.2	
K_2O	94		1	-1	0	← force to zero
Na_2O	62		5	-5	0	← force to zero
SiO_2	60			-1	-0.1	
Glass	n/a			1	0.1	

where the χ_i 's denote the relative weights of the each reaction in the overall stoichiometry. Choosing NaN_3 reactant as the basis gives us $\chi_1 = \frac{1}{2}$. The requirement that Na not be generated as a by-product gives us $\chi_2 = \frac{1}{10}$. Finally, both K_2O and Na_2O are removed from the stoichiometry if $\chi_3 = \frac{1}{10}$.

(The fact that both can be removed with just one parameter is a bit unusual, and results from the fact that K₂O and Na₂O appear in the same molar ratio in two different reactions.) The net stoichiometry is



Part b.

98 grams of N₂ corresponds to 98 grams \times 1 gmol/28g = 3.5 gmol of N₂. To generate 3.5 gmol we need $1 \times \frac{3.5}{1.6} = 2.1875$ gmol of NaN₃, $0.2 \times \frac{3.5}{1.6} = 0.4375$ gmol of KNO₃, and $0.1 \times \frac{3.5}{1.6} = 0.21875$ gmol of SiO₂. Another way of expressing this is to rescale the process stoichiometry to explicitly show the generation of 3.5 moles of N₂, that is



Tabulating the mass requirements

	MW	χ_1 1/2	χ_2 1/10	χ_3 1/10	ν_i^{net}	ν_i^{net} Rescaled	Mass [g]
NaN ₃	65	-2			-1	-2.19	-142.4
Na	23	2	-10		0	0	0
N ₂	28	3	1		1.6	3.5	98
KNO ₃	101		-2		-0.2	-0.438	-44.3
K ₂ O	94		1	-1	0	0	0
Na ₂ O	62		5	-5	0	0	0
SiO ₂	60			-1	-0.1	-0.219	-13.2
Glass					1	0.1	

The total mass of reactants required is 142 + 44.3 + 13.2 = 200 grams which will produce 98 grams of nitrogen to inflate the airbag. A total of 102 grams of glass is generated as a by-product of the reaction. If you've ever been in a car crash, this is part of the white powder dispersed around the car following airbag deployment.

1.5 Exercises

P1.11 Quick Answer Question

Give three examples of intensive process variables. Give two examples of extensive process variables.

P1.12 Homemade Ant Killer

A folk recipe for a homemade ant killer is to mix equal amounts of baking soda (sodium bicarbonate NaHCO_3) and powdered sugar, then spread the mixture in areas infested with ants. The theory is that the ants will be attracted to the sugar, eat some of the mixture, and carry more back to their nest to feed others. The ingested sodium bicarbonate will then react with formic acid present in the ants digestive tract to form a lethal amount of carbon dioxide gas (CO_2).

Assuming the other reaction products are water and sodium formate (HCOONa), write a balanced reaction for what happens inside the ant's digestive tract.

(Note: This is a folk recipe and explanation, there is little evidence regarding whether or not it actually works!)

P1.13 Cleaning Rust with Coca-Cola

As you may know from personal experience, if you cook breakfast in an unseasoned cast iron skillet then leave it the sink for the day without washing, the skillet will likely have spots of rust when you return. Here's a tip. Before scrubbing pour some Coca-Cola into the skillet and let that sit for a few minutes.

Coca-Cola contains phosphoric acid (H_3PO_4) to add a tangy and sour punch to the flavor. Phosphoric acid is used commercially as a rust (iron oxide, Fe_2O_3) remover. Phosphoric acid reacts with rust to form ferric phosphate (FePO_4), a black compound that is easily scrubbed away.

Assuming water is a by-product, use the molecular matrix method to find a balanced chemical reaction to explain this cleaning process.

P1.14 Aluminum and Toilet Bowl Cleaner

A common classroom demonstration is the reaction of aluminum foil (Al) with a household cleanser containing hydrogen chloride (HCl) to produce aluminum chloride (AlCl_3) and hydrogen (H_2).

- Solve for the stoichiometric coefficients for this reaction.



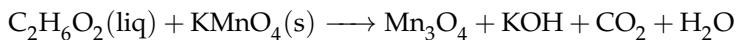
Figure 1.10: Cast iron skillets, the right hand side showing rust in an unseasoned skillet.
Source: Wikimedia Commons
Link to a video on the use of Coca-Cola to clean rust stains from iron skillets.

- b. Demonstrate that the stoichiometric coefficients are in the null space of the corresponding atomic matrix.
- c. Typical household toilet bowl cleaners are 10-12 wt% HCl.² Assuming a cleaner at the high end of this range, and that thickness of a typical aluminum foil is 0.0008 inches, how many square feet of aluminum foil and how many ounces of toilet bowel cleaner would be needed to produce 2 liters of hydrogen gas at standard temperature and pressure?

² A database listing the mass fraction of hydrogen chloride in name brand household cleaners is available at <http://hpdb.nlm.nih.gov/cgi-bin/household/search?tbl=TblChemicals&queryx=7647-01-0>.

P1.15 Hypergolic Reaction – Ethylene Glycol and Potassium Permanganate

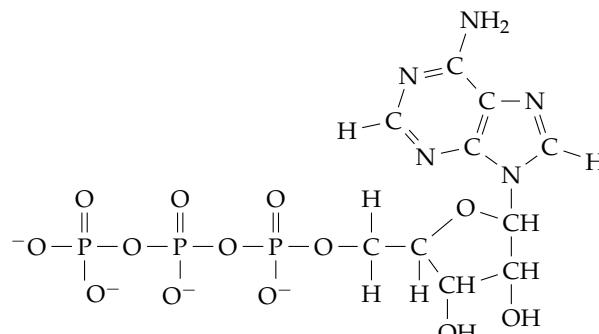
Hypergolic reactions are energetic reactions that occur spontaneously upon mixing of the reactants. One example of a hypergolic reaction is ethylene glycol and potassium permanganate in the unbalanced reaction



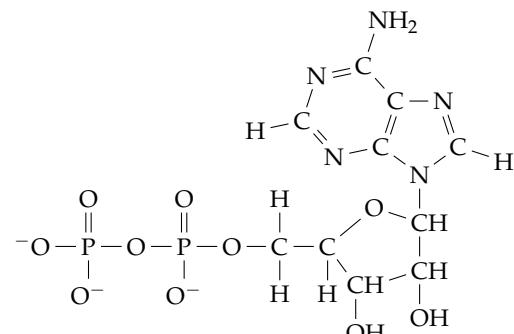
Set up and solve the equations for the stoichiometric coefficients that balance this reaction.

P1.16 Conversion of ATP to ADP

The conversion of adenosine triphosphate (ATP) to adenosine diphosphate (ADP) is one of the most important sources of energy for biological processes in plants and animals.



Adenosine triphosphate (ATP^{4-})



Adenosine diphosphate (ADP^{3-})

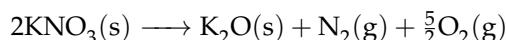
ATP^{4-} and ADP^{3-} carry charges of -4 and -3 , respectively, under normal physiological conditions. The conversion of ATP^{4-} to ADP^{3-} releases hydrogen phosphite (HPO_4^{2-}), and also involves a hydrogen ion (H^+) and water (H_2O).

- a. Construct the molecular matrix including all chemical species that participate in the conversion of ATP^{4-} and ADP^{3-} .

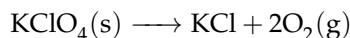
- b. What are the conditions for a balanced reaction?
- c. Solve for the stoichiometric coefficients of the balanced reaction, and write out the reaction using ATP⁴⁻ and ADP³⁻ as shorthand notation for the larger molecules.

P1.17 Chemistry of Fireworks

Fireworks use a range of chemical reactions to achieve a myriad range of display effects. The key ingredients are an oxidizer, typically potassium nitrate (KNO_3) or potassium perchlorate (KClO_4). Potassium nitrate decomposes by the reaction

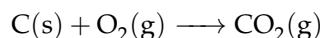


Potassium perchlorate decomposes by the reaction

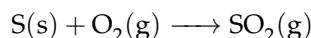


The oxidizer reacts with a fuel chosen to achieve a specific effect.

- a. Explosive effects generally use a black powder mixture consisting of 75 wt% potassium nitrate oxidizer mixed with 15 wt% charcoal (C) and 10 wt% sulfur (S) fuels. The fuels react with oxygen via



and

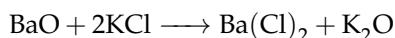


Perform a generation/consumption analysis for this reaction mixture. Would you propose changing the amount of potassium nitrate in the black powder mixture? How many moles of gas are produced per kilogram of black powder?

- b. Design a black powder mixture utilizing potassium perchlorate as the oxidizer, but keeping the ratio of charcoal to sulfur the same. How many moles of gas are produced per kilogram?
- c. Barium chloride (BaCl_2) produces a pleasing green color effect in fireworks. Barium nitrate decomposes by the reaction



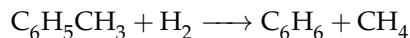
Barium oxide then reacts with a chlorine compound, such as potassium chloride (KCl), to produce barium chloride



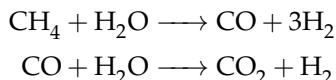
Propose a mixture of barium nitrate, potassium chloride, and charcoal that uses all of the available oxygen and maximizes the production of barium chloride.

P1.18 Simple HDA: Generation-Consumption Analysis

The production of benzene (C_6H_6) by the hydrodealkylation of toluene ($C_6H_5CH_3$) proceeds by the reaction



(possible side-reaction have been neglected). Hydrogen can be produced from methane (CH_4) and water (H_2O) by the steam reforming and water-gas shift reactions

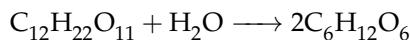


- Perform a generation-consumption analysis to determine the overall process stoichiometry. Sketch the input-output diagram for the overall process indicating molar flow rates necessary to produce 10 metric tons per hour of benzene.
- In January, 2012, the market price for toluene was \$1,294 per metric ton, and for benzene it was \$1,431 per metric ton. Ignoring the value of all other process inputs and outputs, can this process be profitable?

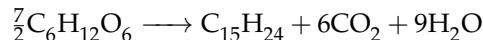
P1.19 Biodiesel Production from Sugarcane

Amyris was founded in 2005 to commercialize a genetically modified strains of yeast for industrial applications. One of Amyris's technologies was the fermentation of sucrose from sugarcane to produce farnesene ($C_{15}H_{24}$) – the same chemical responsible for the distinctive odor in Granny Smith apples). Farnesene can be hydrogenated over a Pd catalyst to produce farnesane ($C_{15}H_{32}$) which is an excellent fuel for diesel engines.

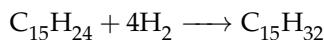
The fermentation is a two step process where sucrose ($C_{12}H_{22}O_{11}$) hydrolyzes to form glucose ($C_6H_{12}O_6$)



and subsequently fermented by yeast to farnesene



Following separation, the farnesene is hydrogenated over a catalyst



Hydrogen can be produced by the steam reforming of methane followed by the water gas shift reaction

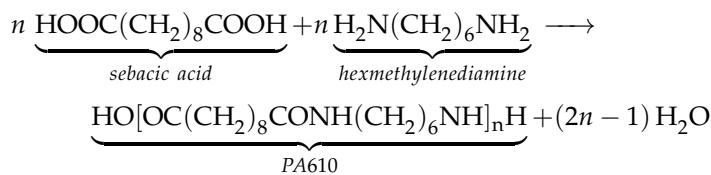




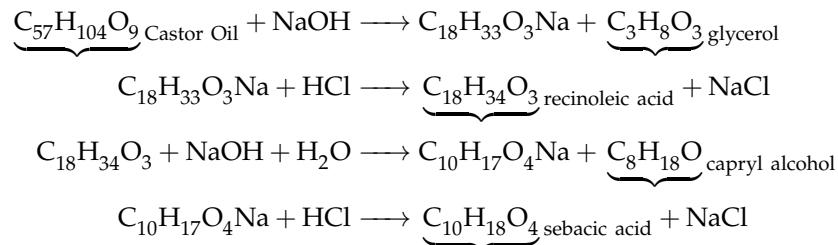
Propose an overall stoichiometry for the production of diesel fuel using sucrose and methane as raw materials (and, if necessary, water).

P1.20 Production of Nylon from Renewable Resources

PA610 is an industrial grade nylon from DuPont sold under the brand name ZYTEL RS³ that uses a renewable raw material, Castor oil, in its production. The final product is produced by the condensation polymerization of sebacic acid ($\text{HOOC(CH}_2)_8\text{COOH}$) with hexamethylenediamine ($\text{H}_2\text{N(CH}_2)_6\text{NH}_2$) via the balanced reaction



Sebacic acid is produced from castor oil in four steps.



Each of these reactions must be carried out under different conditions and in separate devices.

- Balance any unbalanced reactions.
- Assuming Castor oil, hexamethylenediamine, NaOH, and HCl are the available raw materials, perform a generation consumption analysis to determine the overall process stoichiometry. (Assume $n = 100$).

³ Link to ZYTEL RS web page.



Figure 1.11: *Ricinus communis* Castor beans. Source: Wikimedia Commons

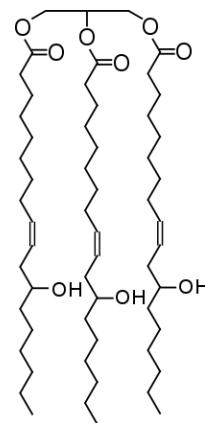


Figure 1.12: The triglyceride that is of the major component of Castor oil. Source: Wikimedia Commons

2

Chemical Processes and Flowsheets

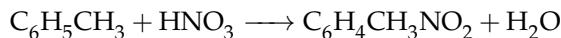
2.1 Summary

Concepts	Skills	Practice Problems
Process Variables	<ul style="list-style-type: none">- Extensive versus intensive process variables- difference between gauge and absolute pressure- variables needed to specify stream 'state'	
Process Diagrams <ul style="list-style-type: none">- Input/Output- Block Flow Diagrams	<ul style="list-style-type: none">- Draw and label a block flow diagram from a process description- Convert block flow diagram to input/output form	P2.23, P2.31
Process elements <ul style="list-style-type: none">- Mixers- Reactors- Separators- Splitters	<ul style="list-style-type: none">- Given a set of reactions and chemistry, sketch a block flow diagram- Write typical performance specifications	P2.27
Operating Modes	<ul style="list-style-type: none">Classify systems as- Continuous- Batch- Semi-batch	P2.31, P2.35
Material Balances	<ul style="list-style-type: none">- Prepare material balances for block flow diagrams	Review chapter examples
Degree of Freedom	<ul style="list-style-type: none">- Diagram and label stream and system variables- Performance Specifications	

2.2 Solved Problems

P2.21 TNT Production

The first step in TNT production is the nitration of toluene with an anhydrous mixture of sulfuric and nitric acid to produce mono-nitrotoluene (MNT). The reaction is

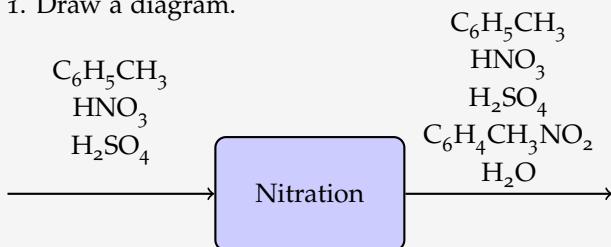


Assume the feed to the reactor consists of 40 mol% HNO_3 , 20 mol% $\text{C}_6\text{H}_5\text{CH}_3$, with the remainder as sulfuric acid. An analysis of the exit stream shows a composition of 8 mol% water. The reactor must be designed to produce 1370 kg/day of MNT.

- Perform a material balance to find all relevant molar flow rates for the required reactor.
- What fraction of the toluene is converted to MNT in a single pass through the reactor?

Solution

Step 1. Draw a diagram.



Step 2. Define the system of interest.

The system consists of the mixer with boundaries slicing through the two inlet and single exit streams.

Step 3. Choose components and stream variables.

The components are $\text{C}_6\text{H}_5\text{CH}_3$ (T), HNO_3 (N), H_2SO_4 (S), $\text{C}_6\text{H}_4\text{CH}_3\text{NO}_2$ (M), and H_2O (W). The stream variables are the component molar flow rates at the inlet and exit of the reactor as labeled in the following diagram.

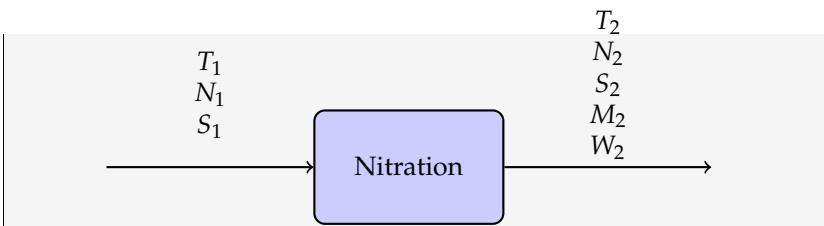


Figure 2.1: TNT Explosive

Species	MW
$\text{C}_6\text{H}_5\text{CH}_3$	92
HNO_3	63
H_2SO_4	98
$\text{C}_6\text{H}_4\text{CH}_3\text{NO}_2$	137
H_2O	18

- Draw a diagram
- Define the system of interest
- Choose components and define stream variables
- Convert all units to consistent units of mass or moles
- Define a basis
- Define system variables
- List specifications
- Write material balance equations
- Solve material balance equations
- Check material balances for closure

Table 2.1: 10 Steps for Material Balances



There are eight stream variables.

Step 4. Cast in consistent units.

The reactor capacity is stated as 1370 kg/day, but the problem asks for molar flowrates and the compositions are given in mol%. So we will convert the performance to molar units

$$1370 \text{ kg MNT/day} \times \text{kgmol}/137 \text{ kg MNT} = 10 \text{ kgmol/day}$$

Step 5. Define a basis.

The basis is the production of 10 kg-mol/day of MNT.

Step 6. Define system variables.

There is one reaction, and we assume the mixer is operated at steady state. System variables are needed to describe the extent of reaction. The new variables are T_{cons} , N_{cons} , M_{gen} , W_{gen} . The relationship among these variables is determined by the reaction stoichiometry. Since we are given the amount of water in the exit stream, we will cast the other system variables in terms of water generated

$$T_{cons} = W_{gen}$$

$$N_{cons} = W_{gen}$$

$$M_{gen} = W_{gen}$$

The steam and system variables are summarized in the following table:

Component	<1> kgmol/day	<2> kgmol/day	Gen. kgmol/day	Cons. kgmol/day
C ₆ H ₅ CH ₃	T_1	T_2		T_{cons}
HNO ₃	N_1	N_2		N_{cons}
H ₂ SO ₄	S_1	S_2		
C ₆ H ₄ CH ₃ NO ₂		M_2	M_{gen}	
H ₂ O		W_2	W_{gen}	

Step 7. List specifications.

The composition specification for the inlet stream provides two equations

$$\begin{aligned} T_1 &= 0.2(T_1 + N_1 + S_1) \\ N_1 &= 0.4(T_1 + N_1 + S_1) \end{aligned}$$

The composition specification for the outlet stream provides one equation

$$W_2 = 0.08(T_2 + N_2 + S_2 + M_2 + W_2)$$

The performance specification provides an equation for the molar flowrate M_2

$$M_2 = 10$$

Step 8. Write material balance equations.

There are five component material balances

$$\begin{aligned} T_1 - T_2 - T_{cons} &= 0 \\ N_1 - N_2 - N_{cons} &= 0 \\ S_1 - S_2 &= 0 \\ -M_2 + M_{gen} &= 0 \\ -W_2 + W_{gen} &= 0 \end{aligned}$$

Step 9. Solve.

At this point the problem is set up and ready to solve. This accounts for almost all of the points. The remaining points are given for actual solution of the equations. Here are two ways to reason to a solution –

- First Approach –
 - There are a total of 12 variables. There are 3 equations from the stoichiometry, 4 performance specifications, and 5 material balances for a total of 12 equations.
 - To solve these, first note $M_{gen} = M_2 = 10$. From the stoichiometric equations we have $W_{gen} = 10$ which tells us $N_{cons} = T_{cons} = 10$ and $W_2 = 10$. This gives us values for six of the 12 variables.

- We know $W_2 = 10$ and that W_2 makes up 8 mol% of the exit stream. That tells us the exit stream has a total flow of 125 kg-mol/day.
- 20 kgmol are generated, and 20 kgmol are consumed. This means the inlet flow is also 125 kg-mol/day. From this and the problem specs, we can fill out the rest of the stream table.

Component	<1> kgmol/d	<2> kgmol/d	Gen. kgmol/d	Cons. kgmol/d
C ₆ H ₅ CH ₃	25	15		10
HNO ₃	50	40		10
H ₂ SO ₄	50	50		
C ₆ H ₄ CH ₃ NO ₂		10	10	
H ₂ O		10	10	
TOTAL	125	125		

- Second Approach

- Alternatively, the solution can be found by manipulating the specification and material balance equations. Using the generation/consumption values in the remaining equations,

$$\begin{aligned} T_1 &= 0.2(T_1 + N_1 + S_1) \\ N_1 &= 0.4(T_1 + N_1 + S_1) \\ 10 &= 0.08(T_2 + N_2 + S_2 + 20) \\ T_1 - T_2 &= 10 \\ N_1 - N_2 &= 10 \\ S_1 - S_2 &= 0 \end{aligned}$$

- The task now is to solve this system of six equations. Solving the last three

$$\begin{aligned} T_2 &= T_1 - 10 \\ N_2 &= N_1 - 10 \\ S_2 &= S_1 \end{aligned}$$

- Plugging these into the last of three specifications,

$$10 = 0.08(T_1 + N_1 + S_1)$$

which tells us the total molar flowrate

-

$$T_1 + N_1 + S_1 = \frac{10}{0.08} = 125$$

- Plugging this into the specification equations allows us to compute all of the necessary flow rates.

Step 10. Check the solution.

We can validate the solution by tabulating the inflow and outflow of each component, and the total inflows and outflows.

Component	<1> kgmol/d	<2> kgmol/d	Gen. kgmol/d	Cons. kgmol/d	Net	Check
C ₆ H ₅ CH ₃	25	15		10	0	✓
HNO ₃	50	40		10	0	✓
H ₂ SO ₄	50	50			0	✓
C ₆ H ₄ CH ₃ NO ₂		10	10		0	✓
H ₂ O		10	10		0	✓
TOTAL	125	125				

P2.22 Gasoline Blending

Oxygenates, such as ethanol, are mixed with gasoline to reduce the emission of carbon monoxide from automobiles. Assume we have two blending components: 'RBOB' which has 0 wt% ethanol, and denatured ethanol 'E85' which is 85 wt% ethanol and the remainder RBOB. Use our 10 step procedure for material balances to compute the amount of each component required to produce 100,000 kg/day of gasoline with 5.9 wt% ethanol. Your answer should explicitly show each step of the 10 step procedure.

Solution

STEP 1. DRAW A DIAGRAM.



STEP 2. DEFINE THE SYSTEM OF INTEREST. The system consists of the mixer with boundaries slicing through the two inlet and single exit streams.

Table 2.2: 10 Steps for Material Balances

1. Draw a diagram
2. Define the system of interest
3. Choose components and define stream variables
4. Convert all units to consistent units of mass or moles
5. Define a basis
6. Define system variables
7. List specifications
8. Write material balance equations
9. Solve material balance equations
10. Check material balances for closure

STEP 3. CHOOSE COMPONENTS AND STEAM VARIABLES.

There is no reaction. The components are the RBOB and Ethanol. The stream variables are the mass flowrates of the inlet and exit stream, F_1 , F_2 , and F_3 , and the weight fractions of RBOB (R) and ethanol (E) in the streams 2 and 3, that is w_{R2} , w_{E2} , w_{R3} , and w_{E3} . Because the RBOB has no ethanol, there is no need to introduce a stream variable for weight fractions in stream 1.



There is no need to introduce a stream variable for weight fractions in stream 1 because the RBOB is a pure component. There are seven stream variables.

STEP 4. CAST IN CONSISTENT UNITS. Units are mass flowrate kg/day and weight fractions. Thus the units are already consistent and no further conversions are necessary.

STEP 5. DEFINE A BASIS. The basis for the material balance is the production of 100,000 kg/day of gasoline,

$$F_3 = 100,000 \text{ kg/day}$$

STEP 6. DEFINE SYSTEM VARIABLES. There are no reactions, and we assume the mixer is operated at steady state. No system variables are necessary.

STEP 7. LIST SPECIFICATIONS. In addition to the production basis, the additional specifications are the composition of the E85 stream

$$w_{E2} = 0.85$$

$$w_{R2} = 1 - w_{E2} = 0.15$$

and the product stream

$$w_{E3} = 0.059$$

$$w_{R3} = 1 - w_{E3} = 0.941$$

The basis and additional specifications produce values for five of the seven stream variables.

STEP 8. WRITE MATERIAL BALANCE EQUATIONS. In the absence of accumulation and reaction, the input must equal the output of each component.

$$\begin{aligned} F_1 + w_{R2}F_2 &= w_{R3}F_3 \quad (\text{RBOB}) \\ w_{E2}F_2 &= w_{E3}F_3 \quad (\text{ethanol}) \end{aligned}$$

STEP 9. SOLVE. Substituting values for the known stream variables,

$$\begin{aligned} F_1 + 0.15F_2 &= 94,100 \text{ kg/day} \\ 0.85F_2 &= 5,900 \text{ kg/day} \end{aligned}$$

Solving for F_2

$$F_2 = \frac{5,900}{0.85} = 6,941 \text{ kg E85/day}$$

Solving for F_1

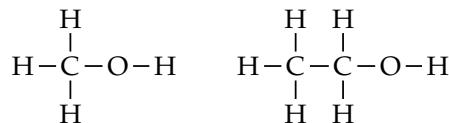
$$F_1 = 94,100 - 0.15F_2 = 93,059 \text{ kg RBOB/day}$$

STEP 10. CHECK THE SOLUTION. We can validate the solution by tabulating the inflow and outflow of each component, and the total inflows and outflows.

	Input	Output	Check
RBOB	$F_1 + w_{R2}F_2 = 94,100.15$	$w_{R3}F_3 = 94,100$	✓
E85	$w_{E2}F_2 = 5899.95$	$w_{E3}F_3 = 5,900$	✓
Total	100,000	100,000	✓

P2.23 Separating a Methanol/Ethanol Mixture

A 1000 kg/hr mixture that is 60 mol% methanol and 40 mol% ethanol needs to be separated into a methanol product stream and a second effluent stream.



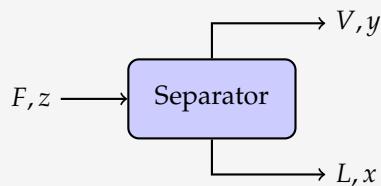
Methanol

Ethanol

The methanol product stream must be 95 mol% methanol, and 90% of the methanol must be recovered in the methanol product. Prepare a diagram of the separator and label the streams with flow rate and methanol compositions.

Solution

We start with a diagram labeled by stream flow rate and composition. The composition variables refer to the mole fraction of methanol.



There are two components so there are two independent material balances. In this case we write a total material balance and a material balance for methanol.

$$F = V + L \quad (\text{total balance})$$

$$Fz = Vy + Lx \quad (\text{methanol balance})$$

At this point we have six process variables and two equations. From the problem statement we seek four additional specifications to fully specify a solution to the problem.

$$F = 1000 \text{ kg-mol/hr}$$

$$z = 0.6$$

$$y = 0.95$$

$$Vy = 0.90Fz$$

Solving the material balances provides process targets

$$V = \frac{0.90Fz}{y} = \frac{0.90 \times 1000 \times 0.6}{0.95} = \boxed{568.4 \text{ kgmol/hr}}$$

$$L = F - V = 1000 - 568.4 = \boxed{431.6 \text{ kg-mol/hr}}$$

$$x = \frac{Fz - Vy}{L} = \frac{Fz - 0.9Fz}{L} = \frac{0.1Fz}{L} = \frac{60}{431.6} = \boxed{0.139}$$

P2.24 Blending Pigments for White Paint

Your task is to make a pigment powder that meets customer specifications for a commercial white paint product. Titanium dioxide (TiO_2) is the most widely-used white paint pigment. It is normally blended with other pigments to reduce cost and to meet other specifications. In this case, the customer has specified that the white pigment powder must contain 60% TiO_2 , 5% ZnO , 25% $CaCO_3/SiO_2$, and 10% $NaCl$ (all units are weight %).

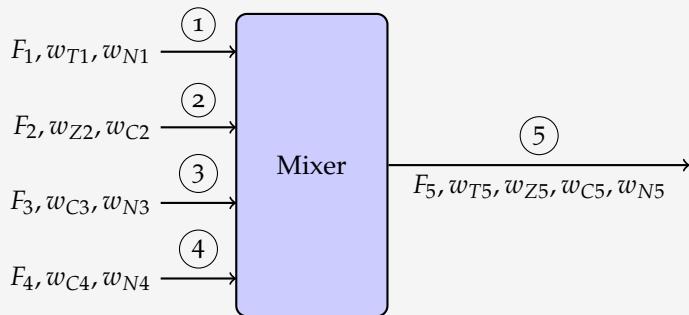
The following powders are available from suppliers.

Component	Powder 1	Powder 2	Powder 3	Powder 4
TiO_2	90	0	0	0
ZnO	0	50	0	0
$CaCO_3/SiO_2$	0	50	75	90
$NaCl$	10	0	25	10

You need to mix these raw materials to produce 1000 kg of white pigment powder that meets the customer specifications. How much of each powder should you order?

Solution

The process can be modeled as mixer combining four feed powders to form a product stream. The streams are specified by mass flows and the weight fractions of the components in each stream.



An alternative set of stream variables would be the mass flows of each component in each stream.



Figure 2.2: White paint. Source:



Figure 2.3: Zinc oxide packaged for shipment as paint pigment. Source:

Material balances

$$\begin{aligned}0 &= w_{T,1}F_1 - w_{T,5}F_5 \\0 &= w_{Z,2}F_2 - w_{Z,5}F_5 \\0 &= w_{C,2}F_2 + w_{C,3}F_3 + w_{C,4}F_4 - w_{C,5}F_5 \\0 &= w_{N,1}F_1 + w_{N,3}F_3 + w_{N,4}F_4 - w_{N,5}F_5\end{aligned}$$

and stream specification

$$F_5 = 1000 \text{ kg}$$

Plugging in the known weight fractions and product flow yields four equations in four unknowns

$$\begin{aligned}600 &= 0.90F_1 \\50 &= 0.50F_2 \\250 &= 0.50F_2 + 0.75F_3 + 0.90F_4 \\100 &= 0.10F_1 + 0.25F_3 + 0.10F_4\end{aligned}$$

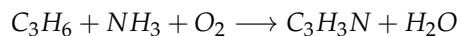
Finding a solution requires solving a pair of linear equations in two unknowns. Solving we get

$$\begin{aligned}F_1 &= 667 \text{ kg} \\F_2 &= 100 \text{ kg} \\F_3 &= 67 \text{ kg} \\F_4 &= 167 \text{ kg}\end{aligned}$$

which can be checked by substituting these values back into the balance equations.

P2.25 Acrylonitrile Production

Acrylonitrile, an important precursor for many plastic materials, is produced by the reaction of propylene, ammonia, and oxygen according to the unbalanced reaction

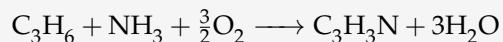


For a particular reactor operating at steady-state, the material entering is 0.1 mole fraction propylene, 0.12 mole fraction ammonia, and the remainder air. Assume a basis of 100 mol/hour of feed. Assume air is 21 mol% O_2 and 79 mol% N_2 .

- What is the maximum amount of acrylonitrile that can be produced?

Solution

The balanced reaction is



We'll assume a basis of 100 kgmol. From the problem data we can fill out the first column of a stream table

	Species	Inlet: <1> kgmol/hr
P	C ₃ H ₆	10
A	NH ₃	12
O	O ₂	78 × 0.21 = 16.4
AN	C ₃ H ₃ N	0
W	H ₂ O	0
N	N ₂	78 × 0.79 = 61.6
	TOTAL	100

The maximum amount of AN that can be produced is equal to the molar amount of propane fed to the reactor, i.e., 10 kg-mol. Enough A and O are present to allow for the complete conversion of P.

- b. What is the limiting reactant?

Solution

Propane is the limiting reactant.

- c. Assume only 30% of the limiting reactant is consumed, so that the reactor effluent contains both reactants and products. What are the molar flowrates of all compounds exiting the reactor?

Solution

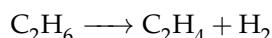
Expand the stream table to include generation and consumption variables. Using the reaction stoichiometry, we can fill out the table using the component material balances.

Species	Inlet <1> kgmol/hr	Exit <2> kgmol/hr	Gen. kgmol/hr	Cons. kgmol/hr
P C ₃ H ₆	10	7		3
A NH ₃	12	9		3
O O ₂	78 × 0.21 = 16.4	11.9		4.5
AN C ₃ H ₃ N		3	3	
W H ₂ O		9	9	
N N ₂	78 × 0.79 = 61.6	61.6		
Total	100	101.5		

Note that total moles are not conserved.

P2.26 Ethylene Production

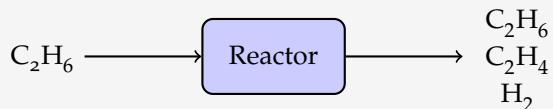
A reactor is operating at steady-state to dehydrogenate ethane to form ethylene by the reaction



The flow rate into the reactor is 300 kg ethane per minute, and the flow rate of hydrogen out of the reactor is 4 kg-mole/min. What are the molar flow rates of ethane and ethylene from this same reactor?

Solution

Step 1. *Diagram.*



Step 2. *Define system of interest.* The system consists of the reactor with boundaries defined at the reactor inlet and exit.

Step 3. *Choose components and stream variables.* Components are ethane (C2), ethylene (E), and hydrogen (H). The corresponding stream table is given below where we have listed the non-trivial stream variables:

Species	Inlet <1> kg-mol/min	Outlet <2> kg-mol/min
C2	C2<1>	C2<2>
E		E<2>
H		H<2>

Step 4. *Cast in consistent units.* We have a reaction, so molar flow rates are appropriate. The inlet ethane flow is 300 kg/min which is equal to $300 \text{ kg/min} \div 30 \text{ kg/kg-mol} = 10 \text{ kg-mol/min}$.

Step 5. *Define a basis.* The basis is the inlet flowrate

$$C2_{<1>} = 10 \text{ kg-mol/min}$$

Step 6. *Define system variables.* The system is at steady-state, so there are no accumulation variables. Components are generated and consumed due to the presence of a reaction. These variables are appended to the stream table below:

Species	Inlet <1> kg-mol/min	Outlet <2> kg-mol/min	Gen. kg-mol/min	Cons. kg-mol/min
C2	C2<1>	C2<2>		C2 _{cons}
E		E<2>	E _{gen}	
H		H<2>	H _{gen}	

Reaction stoichiometry provides two relationships among these three system variables:

$$C2_{cons} = H_{gen}$$

$$E_{gen} = H_{gen}$$

Step 7. *List specifications.* There are two stream specifications

$$C2_{<1>} = 10 \text{ kg-mol/min}$$

$$H_{<2>} = 4 \text{ kg-mol/min}$$

Step 8. Write material balances. There are three component balances.

$$0 = C2_{<1>} - C2_{<2>} - C2_{cons}$$

$$0 = -E_{<2>} + E_{gen}$$

$$0 = -H_{<2>} + H_{gen}$$

Step 9. Solve. We have seven variables and seven equations (two stoichiometric relationships, two stream specifications, and three component balances). From the last component balance we have

$$H_{gen} = H_{<2>} = 4 \text{ kg-mol/min}$$

The stoichiometric relationships give us

$$C2_{cons} = H_{gen} = 4 \text{ kg-mol/min}$$

$$E_{gen} = H_{gen} = 4 \text{ kg-mol/min}$$

Then solving the first two component balances

$$E_{<2>} = E_{gen} = 4 \text{ kg-mol/min}$$

$$C2_{<2>} = C2_{<1>} - C2_{cons} = 6 \text{ kg-mol/min}$$

Step 10. Check.

Species	Inlet <1> kg-mol/min	Outlet <2> kg-mol/min	Gen. kg-mol/min	Cons. kg-mol/min	Net	Check
C2	10	6		4	0	✓
E		4	4		0	✓
H		4	4		0	✓

P2.27 Drying Ethanol

The accompanying figure shows a process flowsheet for the dehydration (i.e., drying) of ethanol using an adsorbant. The feed is 100 kg/hr of an azeotropic mixture comprised of 95 wt% ethanol (E) and 5% wt% water (W). The feed is mixed with a solid adsorbant (A) that preferentially adsorbs water. The adsorbant can adsorb 20% of its weight in water, and 15% of its weight in ethanol. The liquid phase is separated and exits via stream 3.

The wet adsorbant passes to a dryer where all of the ethanol and water are stripped off. In addition, 5% of the adsorbant is lost. Fresh adsorbant is added through stream 8 to makeup for the lost adsor-

bant.

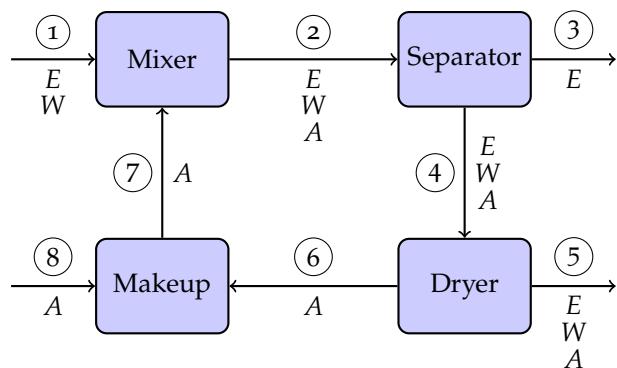


Figure 2.4: Flowsheet for ethanol dehydration using an adsorbant.

- Perform a degree of freedom analysis. How many stream variables are present? How many component balances? From the specifications listed in the problem statement, list the all of the equations necessary to solve for all material flows.
- Solve for all material flows. Present your results in the form of a stream table.
- What is the fractional recovery of ethanol in stream 3 relative to feed stream 1?

Solution

Part a.

There are 15 stream variables indicated, and no system variables due to reaction or accumulation.

Species	Streams							
	1	2	3	4	5	6	7	8
E	E_1	E_2	E_3	E_4	E_5			
W	W_1	W_2		W_4	W_5			
A		A_2		A_4	A_5	A_6	A_7	A_8

The mixer, separator, and dryer units provide 3 component balances each, the makeup mixed provides 1 additional component balance, for a total of 10 component balances.

Variables

Steam	15
Reactions	0
Accumulation	0
TOTAL	15

Equations

Component Balances	10
Inlet Stream	2
Adsorbant Capacity Specifications	2
Adsorbant Loss Specification	1
TOTAL	15

$$\text{DOF} = \text{Variables} - \text{Equations} = 0$$

Lists of Equations (mass flow units)

Mixer

$$\begin{aligned} 0 &= E_1 - E_2 \\ 0 &= W_1 - W_2 \\ 0 &= A_7 - A_2 \end{aligned}$$

Separator

$$\begin{aligned} 0 &= E_2 - E_3 \\ 0 &= W_2 - W_4 \\ 0 &= A_2 - A_4 \end{aligned}$$

Dryer

$$\begin{aligned} 0 &= E_4 - E_5 \\ 0 &= W_4 - W_5 \\ 0 &= A_4 - A_5 - A_6 \end{aligned}$$

Makeup

$$0 = A_6 + A_8 - A_7$$

Inlet Specifications

$$\begin{aligned} E_1 &= 0.95 \times 100 = 95 \text{ kg/hr} \\ W_1 &= 0.05 \times 100 = 5 \text{ kg/hr} \end{aligned}$$

Adsorbant Capacity Specifications

$$W_4 = 0.20 \times A_4$$

$$E_4 = 0.15 \times A_4$$

Adsorbant Loss Specification

$$A_5 = 0.05 \times A_4$$

Part b.

The solution of these equations can be found by starting with the specified inlet flows

- $E_1 = 95$. From the mixer mass balance $E_2 = 95$
- $W_1 = 5$ which gives $W_2 = 5$, $W_4 = 5$ and $W_5 = 5$
- From the adsorbant specifications $W_4 = 0.2A_4$ so $A_4 = 5 \times W_4 = 25$
- From the adsorbant specifications $E_4 = 0.15A_4$ so $E_4 = 0.15 \times 25 = 3.75$
- Using the separator balance $E_3 = E_2 - E_4 = 95 - 3.75 = 91.25$
- From the adsorbant loss specification $A_5 = 0.05 \times A_4 = 1.25$
- From the Dryer balances $E_5 = 3.75$ and $A_6 = 25 - 1.25 = 23.75$
- From the makeup and mixer balances $A_8 = 25$ and $A_8 = 1.25$

Species	Streams							
	1	2	3	4	5	6	7	8
E	95	95	91.25	3.75	3.75			
W	5	5		5	5			
A		25		25	1.25	23.75	25	23.75

Part c.

The fractional recovery is that fraction of the ethanol feed, E_1 , that ends up in the product flow E_3 .

$$f_{EtOH,3} = \frac{91.25}{95} = 0.96 = \boxed{96\%}$$

2.3 Exercises

P2.28 Watershed Modeling

Rainy Lake is a 360 square mile lake located on the border between Minnesota and Ontario, and partially within Voyageurs National Park. In June, 2014, a combination of heavy snow fall from the prior winter, an unusually late snow melt and heavy Spring rains led to flooding of surrounding areas.

The single outflow of Rainy Lake is Rainy River. Flow on Rainy River is regulated by adjusting gates on a dam located between International Falls, Minnesota, and Fort Frances, Ontario. On June 19th, 2014, the measured outflow at the dam was $1,060 \text{ m}^3/\text{sec}$. The estimated sum of all inflows to the lake was $1,600 \text{ m}^3/\text{sec}$. The water level in the lake was 30 inches above the target level for that date. The dam had 24 inches of remaining headroom. Local officials were concerned that water levels would rise and flow over the top of the dam resulting in flooding and significant property damage for downstream communities.

- Draw a flow diagram for Rainy Lake. Label the relevant stream and system variables.
- Create a material balance, estimate how many days it would take under current conditions for water to reach a level where it would overflow the dam.
- In a typical year, the summer inflow and outflow of water to Rainy Lake are approximately equal at a measured value of $450 \text{ m}^3/\text{sec}$. The lake has an average depth of 60 feet. What is the average 'residence time' for lake water?

P2.29 Environmental Cleanup

Trichloroethylene (TCE) is a volatile industrial solvent often found as a contaminant in waste water. An estimated 15 grams of TCE was spilled into a tank filled with 20,000 liters of water. To remove the TCE, the tank is being sparged with air at a rate of 10,000 liters of per hour. The mole fraction of TCE in the exiting air is measured to be steady at 0.05 mole %.

- Draw a flowsheet for the process, label stream variables. Assuming the tank is well-mixed, what is the initial concentration of TCE? in units of mg/liter? (note this is the same units as ppm by mass).
- The maximum contaminant level (mcl) specified by the EPA is 0.005 mg/liter . How long will it take to treat the tank?



Figure 2.5: Rainy Lake, Minnesota. Note the flooding of shoreline vegetation. Also note the lower limbs of conifers are well below the grazing height of deer, which is another indication of flooding. Source: jckphotos.

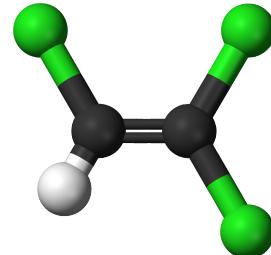


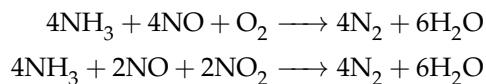
Figure 2.6: Trichloroethylene molecule. Source: Wikimedia Commons

Species	MW
TCE	131.4
Air	28.97
Water	18

Assume the molar volume of air is 24.8 liters/mole.

P2.30 Selective Reduction Catalysis of Diesel Engine Exhaust

Diesel engines emit soot that must be oxidized before release to the atmosphere, and a mixture of nitric oxides (NO , NO_2) that must be selectively reduced before release. Following the oxidation step, urea is injected into the exhaust gas stream which then passes over a selective reduction catalyst. The catalyst promotes reaction between ammonia and the NO_x



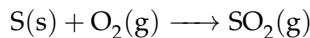
Excess oxygen is present in the exhaust stream under normal operating conditions. The diesel exhaust initially contains 200 ppm by weight NO and 50 ppm by weight NO_2 .

Field measurements show that 95% of each is converted to N_2 . What are the extents of reaction for each reaction?

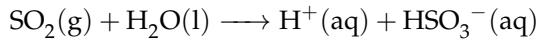
P2.31 Sulfur Burner

Sulfur dioxide (SO_2) is used primarily as precursor to the production of sulfuric acid. It is also used as a food preservative for dried fruits, a sanitation agent in winemaking, a de-colorizer or mild bleach for paper and textiles, and to acidify water for steeping in corn wet-milling operations.

A ‘sulfur burner’ is commonly used for the local production of sulfur dioxide. Solid sulfur is melted and then sprayed into a combustion chamber where it mixes with air and burns by the reaction



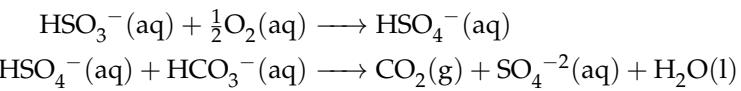
About 2% excess oxygen is required for complete combustion. The product sulfur dioxide is then absorbed into water to produce sulfurous acid by the reaction



- For a large-scale corn wet milling operation you need 1 million kg per day of steep acid which is water with 2000 ppm of SO_2 .¹ Calculate the sulfur, water, and air flow requirements. The air flow should be expressed in units of m^3/day , and also in units of m^3/liter of steep acid.
- Agriculture in the Southwestern United States has to treat and use alkaline sources of irrigation water. HCO_3^- is a major source of the alkalinity in the groundwater available for irrigation. The groundwater HCO_3^- reacts with sulfurous acid and dissolved

¹ Helene Hembrooke and Geri Gay. The laptop and the lecture: The effects of multitasking in learning environments. *Journal of Computing in Higher Education*, 15(1):46–64, 2003

oxygen



Suppose you need to treat 1 million kg per day of groundwater containing 200 ppm HCO_3^- . What flow rates of sulfur and air are required?

3

Material Balances

3.1 Summary

Concepts	Skills	Practice Problems
Material Balances	<ul style="list-style-type: none">- Write formal equations for mass/mole balances- Solve equations for mass or mole flowrates- Write unsteady-state material balances for batch and semi-batch processes	P3.23, P3.41
Systems with Recycle	<ul style="list-style-type: none">- Write material balances- Solve for internal and product flowrates- perform parametric studies of performance- set up solution and parametric studies in Matlab- identify and add purge streams when necessary- Include composition, separation, and reactor performance specifications	P3.47
Degree of Freedom Analysis	Perform DOF analysis on systems with complex interconnections and specifications	Review Nylon-6,6 Example

3.2 Component Balances

3.2.1 Molar Component Balances

$$\frac{dn_i}{dt} = \sum_{j \in \text{Inputs}} \dot{n}_{ij} - \sum_{j \in \text{Outputs}} \dot{n}_{ij} + \sum_k \underbrace{\nu_{ik} \dot{\xi}_k}_{\dot{r}_{ik}}$$
$$\frac{dn^{sys}}{dt} = \sum_{j \in \text{Inputs}} \dot{n}_j - \sum_{j \in \text{Outputs}} \dot{n}_j + \sum_k \left(\sum_i \nu_{ik} \right) \dot{\xi}_k$$

Total moles n^{sys} are not conserved. The last term $\sum_k (\sum_i \nu_{ik}) \dot{\xi}_k$ is the net change in moles.

3.2.2 Mass Component Balances

$$\frac{dm_i}{dt} = \sum_{j \in \text{Inputs}} \dot{m}_{ij} - \sum_{j \in \text{Outputs}} \dot{m}_{ij} + \sum_k \underbrace{M_i v_{ik} \dot{\xi}_k}_{\dot{R}_{ik}}$$

$$\frac{dm^{sys}}{dt} = \sum_{j \in \text{Inputs}} \dot{m}_j - \sum_{j \in \text{Outputs}} \dot{m}_j$$

Total mass m^{sys} is conserved, so there is no net generation or consumption of total mass.

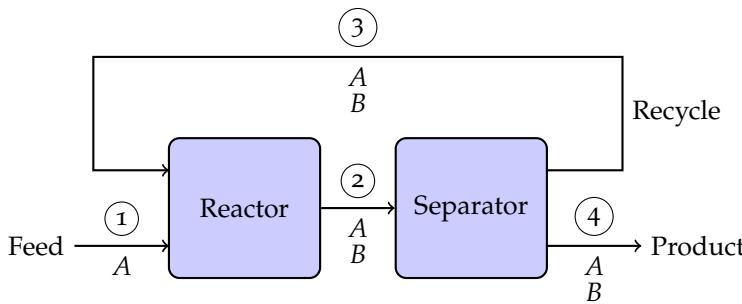
3.3 Solved Problems

P3.32 Reactor with Recycle

Assume the reaction



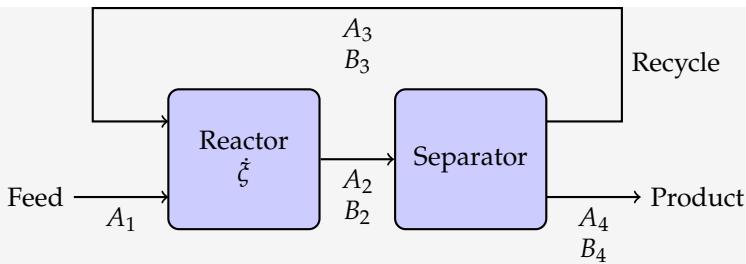
is limited to 20% conversion by thermodynamic constraints. The following flowsheet has been proposed to increase the production of B .



The separator efficiency is 95% for A (that is, 95% of A goes to the recycle stream) and 99% efficient for B (that is, 99% of B goes to the product stream). Calculate the overall conversion of A to B .

Solution

Let's label all of the stream variables and the extent of reaction. There are 7 stream variables and 1 extent of reaction for a total of 8 variables.



There are a total of four material balance equations. In molar units, these may be written

$$\begin{aligned} 0 &= A_1 + A_3 - A_2 - \dot{\xi} \\ 0 &= B_3 - B_2 + \dot{\xi} \\ 0 &= A_2 - A_3 - A_4 \\ 0 &= B_2 - B_3 - B_4 \end{aligned}$$

Performance specifications include the

- 20% conversion of A in the reactor

$$A_2 = 0.80(A_1 + A_3)$$

- 95% separation efficiency for A

$$A_3 = 0.95 A_2$$

- 99% separation efficiency for B

$$B_4 = 0.99 B_2$$

This is a system of 7 linear equations. This is not enough to solve the material balances. However, we are not asked to solve the material balances. All we need to compute is the net process conversion of A to B . For that purpose we can assume a basis

$$A_1 = 100 \text{ kgmol/hr}$$

to provide an eighth equation. Substituting $A_3 = 0.95 A_2$ into the specification for reactor conversion

$$A_2 = 0.80(100 + 0.95 A_2)$$

which can be solved to give

$$A_2 = \frac{80}{1 - 0.80 \times 0.95} = 333.33$$

$$A_3 = 0.95 \times A_2 = 316.67$$

Plugging these numbers into the first material balance

$$\xi = A_1 + A_3 - A_2 = 100 + 316.67 - 333.33 = 83.33$$

From the third material balance we have

$$A_4 = A_2 - A_3 = 333.33 - 316.67 = 16.67$$

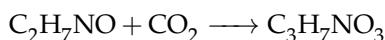
$$f_{conv} = \frac{A_1 - A_4}{A_1} = \frac{100 - 16.67}{100} = \frac{83.33}{100} = 83.3\%$$

This can be verified by the CVX model

```
cvx_begin
    variables A1 A2 A3 A4 B2 B3 B4 X
    0 == A1 + A3 - A2 - X;
    0 == B3 - B2 + X;
    0 == A2 - A3 - A4;
    0 == B2 - B3 - B4;
    (A1 + A3) - A2 == 0.20*(A1 + A3);
    A3 == 0.95*A2;
    B4 == 0.99*B2;
    A1 == 100;
cvx_end
fconv = (A1-A4)/A1
```

P3.33 Carbon Dioxide Scrubber

Scrubbers are used to remove carbon dioxide (CO_2 , MW=44) from the air inside spacecraft, submarines and other closed environments. Monoethanolamine (MEA, $\text{C}_2\text{H}_7\text{NO}$, MW = 61) combines with CO_2 in a reaction producing MEA carbamate (MW = 105)



Consider a continuous scrubber treating 10 kg/min of foul air containing 0.06 mol% CO_2 . The scrubber must remove 80% of the CO_2 to meet air quality standards. MEA is fed at a molar ratio 2:1 of MEA: CO_2 .

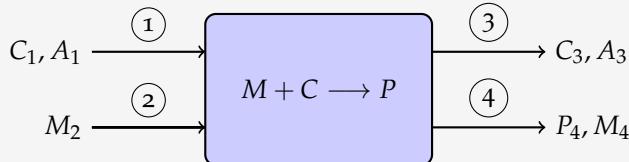
For the purposes of this problem, the portion of air flow that is not CO_2 can be treated as pure component with a molecular weight of 29.

- Sketch the process, label the streams. Identify the stream and system variables.

- b. Perform a degree of freedom analysis for this problem. Write down equations for the material balances and all specifications.
- c. Solve for the mass flows of MEA and MEA carbamate.

Solution

(a) Using abbreviations $C \Rightarrow CO_2$, $A \Rightarrow Air$, $M \Rightarrow MEA$, $P \Rightarrow MEA Carbamate$, a suitable process diagram is



There are 7 stream variables shown in the diagram plus an extent of reaction ξ . All stream variables have units of mass flow.

(b) There are four material balances associated with the four components. Since the stream variables are in mass flow units, and the extent of reaction is in molar units, the molecular weights of the components must be used to relate extent of reaction to the mass flows:

$$0 = C_1 - C_3 - 44\xi$$

$$0 = A_1 - A_3$$

$$0 = M_2 - M_4 - 61\xi$$

$$0 = -P_4 + 105\xi$$

The inlet mass flow of foul air is specified as 10 kg/min

$$C_1 + A_1 = 10 \text{ kg/min}$$

The scrubber performance specification is that 80% of the CO_2 must be removed.

$$C_3 = (1 - 0.8) \times C_1$$

The molar feed rate of MEA is twice that of CO_2 . Again using molecular weight to relate a molar specification to mass flows

$$61M_2 = 2 \times 44C_1$$

The composition specification for the foul air yields

$$C_1 = 0.0006 \times (C_1 + A_1)$$

There are 8 independent equations in 8 unknowns, so the problem has zero DOF and can be solved.

(c) Solving first for C_1

$$\begin{aligned} C_1 &= 0.0006 \times (C_1 + A_1) \\ &= 0.0006 \times 10 = \boxed{0.006 \text{ kg/min}} \end{aligned}$$

then A_1 and A_3

$$\begin{aligned} A_1 &= 10 - C_1 = \boxed{9.994 \text{ kg/min}} \\ A_3 &= A_1 = \boxed{9.994 \text{ kg/min}} \end{aligned}$$

then M_2 and C_3

$$\begin{aligned} M_2 &= \frac{2 \times 44}{61} C_1 = \boxed{0.0087 \text{ kg/min}} \\ C_3 &= 0.2 \times C_2 = \boxed{0.0012 \text{ kg/min}} \end{aligned}$$

The material balance for CO_2 is solved for $\dot{\xi}$

$$\dot{\xi} = \frac{C_3 - C_1}{44} = \frac{0.0048}{44} = \boxed{0.00011 \text{ kg/min}}$$

The remaining material balances

$$\begin{aligned} M_4 &= M_2 - 61\dot{\xi} = 0.0087 - 61 \times 0.00011 = \boxed{0.0021 \text{ kg/min}} \\ P_4 &= 105\dot{\xi} = 105 \times 0.00011 = \boxed{0.011 \text{ kg/min}} \end{aligned}$$

P3.34 Production of Formaldehyde from Methanol (needs formatting)

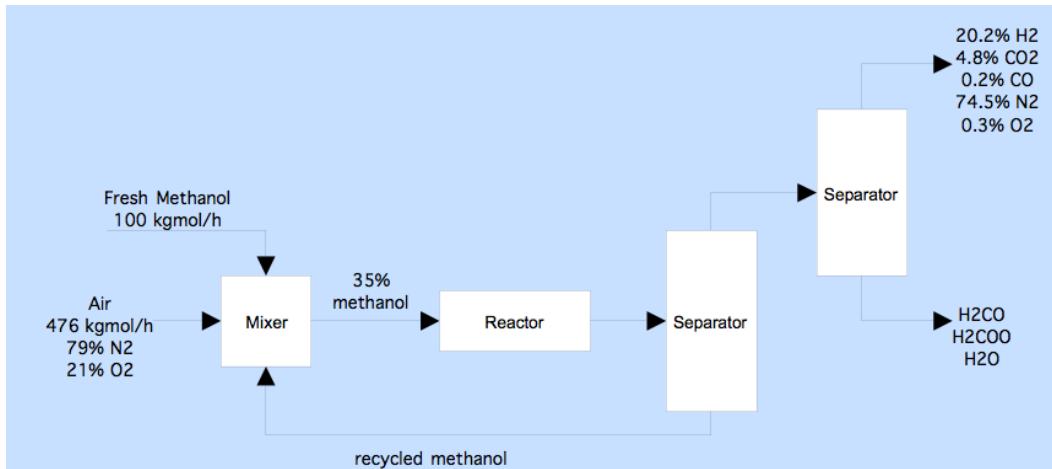
Formaldehyde is produced by the partial oxidation of methanol.



Side reactions occur which produce formic acid (H_2COO), CO, CO_2 , H_2 , and H_2O . You are a process engineer at a formaldehyde plant operating at steady state. 476 kg-mol/hr of air (21 mol% O_2 and 79 mol% N_2) is mixed with 100 kg-mol/hr of fresh methanol some recycled methanol and fed to a reactor. The composition of the streams are

- The reactor inlet stream is 35 mol% methanol.
- The recycled methanol is pure.

- Other compositions are shown in the accompanying figure.



- How many independent reactions are possible?
- List the stream and system variables.
- List all component balances.
- Do you have sufficient information to solve all of the material balances?

Solution

Part (a). There are five independent reactions. The simplest way to see this is note there are eight chemical species involving three atomic species. The chemical species include CH₃OH, O₂, and H₂ which are sufficient to show that the atomic matrix is full rank. Because it is full rank, there are a total of 8-3=5 independent reactions.

Part (b). There are a total of nine species in eight process streams as listed in the accompanying stream table. In addition, there are five extents of reaction as listed in the accompanying table of reactions. Note that any set of five independent reactions will do for the purposes of computing material balances.

Species	S ₁	S ₂	S ₃	S ₄	S ₅	S ₆	S ₇	S ₈	Σ
H ₂				H ₄		H ₆	H ₇		3
N ₂	N ₁		N ₃	N ₄		N ₆	N ₇		5
O ₂	O ₁		O ₃	O ₄		O ₆	O ₇		5
CO				CM ₄		CM ₆	CM ₇		3
CO ₂				CD ₄		CD ₆	CD ₇		3
H ₂ CO				F ₄		F ₆		F ₈	3
H ₂ COO				FA ₄		FA ₆		FA ₈	3
H ₂ O				W ₄		W ₆		W ₈	3
CH ₃ OH		M ₂	M ₃	M ₄	M ₅				4
TOTAL	2	1	3	9	1	8	5	3	32

Reaction	Extent
CH ₃ OH + $\frac{1}{2}$ O ₂ \longrightarrow H ₂ CO + H ₂ O	$\dot{\xi}_1$
CH ₃ OH + O ₂ \longrightarrow H ₂ COO + H ₂ O	$\dot{\xi}_2$
CH ₃ OH + O ₂ \longrightarrow CO + 2H ₂ O	$\dot{\xi}_3$
CH ₃ OH + $\frac{3}{2}$ O ₂ \longrightarrow CO ₂ + 2H ₂ O	$\dot{\xi}_4$
CO + H ₂ O \longrightarrow CO ₂ + H ₂	$\dot{\xi}_5$

Part (c). We write a set of component balances for each unit.
There are a total of 29 balance equations.

Mixer (3 eqns)

$$\begin{aligned} 0 &= N_1 - N_3 \\ 0 &= O_1 - O_3 \\ 0 &= M_2 - M_3 \end{aligned}$$

Reactor (9 eqns)

$$\begin{aligned} 0 &= -H_4 + \dot{\xi}_5 \\ 0 &= N_3 - N_4 \\ 0 &= O_3 - O_4 - \frac{1}{2}\dot{\xi}_1 - \dot{\xi}_2 - \dot{\xi}_3 - \frac{3}{2}\dot{\xi}_4 \\ 0 &= -CM_4 + \dot{\xi}_3 - \dot{\xi}_5 \\ 0 &= -CD_4 + \dot{\xi}_4 + \dot{\xi}_5 \\ 0 &= -F_4 + \dot{\xi}_1 \\ 0 &= -FA_4 + \dot{\xi}_2 \\ 0 &= -W_4 + \dot{\xi}_1 + \dot{\xi}_2 + 2\dot{\xi}_3 + 2\dot{\xi}_4 - \dot{\xi}_5 \\ 0 &= M_3 - M_4 - \dot{\xi}_1 - \dot{\xi}_2 - \dot{\xi}_3 - \dot{\xi}_4 \end{aligned}$$

Separator 1 (9 eqns)

$$\begin{aligned} 0 &= H_4 - H_6 \\ 0 &= N_4 - N_6 \\ 0 &= O_4 - O_6 \\ 0 &= CM_4 - CM_6 \\ 0 &= CD_4 - CD_6 \\ 0 &= F_4 - F_6 \\ 0 &= FA_4 - FA_6 \\ 0 &= W_4 - W_6 \\ 0 &= M_4 - M_5 \end{aligned}$$

Separator 2 (8 eqns)

$$\begin{aligned} 0 &= H_6 - H_7 \\ 0 &= N_6 - N_7 \\ 0 &= O_6 - O_7 \\ 0 &= CM_6 - CM_7 \\ 0 &= CD_6 - CD_7 \\ 0 &= F_6 - F_8 \\ 0 &= FA_6 - FA_8 \\ 0 &= W_6 - W_8 \end{aligned}$$

Part (d). At this point we've identified 37 process variables and 29 balance equations. We next identify process specifications. All units are in kgmol/hour. Note that there are only four independent composition specifications for stream 7.

Specification	Equation
Air Flow	$N_1 + O_1 = 476$
Air Feed Comp.	$O_1 = 0.21(N_1 + O_1)$
Methanol Feed	$M_2 = 100$
Reactor Feed	$M_3 = 0.35(N_3 + O_2 + M_3)$
Stream 7 Comp.	$H_7 = 0.202(H_7 + N_7 + O_7 + CM_7 + CD_7)$
Stream 7 Comp.	$CD_7 = 0.048(H_7 + N_7 + O_7 + CM_7 + CD_7)$
Stream 7 Comp.	$CM_7 = 0.002(H_7 + N_7 + O_7 + CM_7 + CD_7)$
Stream 7 Comp.	$O_7 = 0.003(H_7 + N_7 + O_7 + CM_7 + CD_7)$

All told, there are 8 process specifications. So there $29 + 8 =$

37 equations, 37 variables leaving zero degrees of freedom. There is sufficient information to solve the material balances.

Perform a degree of freedom analysis.

- Adding N₂ to the list of species yields a matrix with 9 columns and 4 rows. The matrix is full rank, so you would reach the same conclusion, that there are 9-4 = 5 independent reactions.
- It is sufficient to say the molecular matrix is full rank by noting the presence of the O₂ and H₂ (and N₂ if that was included). Row reduction would prove linear independence.
- The problem only asked for the number of independent reactions. It is not necessary to actually find them through row reduction.

How many independent reactions are possible?

There are a total of 9 chemical species, but only 8 participate in the reactions. The species participating in the reactions are composed of C, H, and O atoms. The molecular matrix is

	CH ₃ OH	O ₂	H ₂	CO ₂	CO	H ₂ CO	H ₂ COO	H ₂ O
C	1	0	0	1	1	1	1	0
H	4	0	2	0	0	2	2	2
O	1	2	0	2	1	1	2	1

It's easy to see this matrix is full rank – just consider the first three columns. Row reduction would confirm this result. For a full rank matrix, given 8 columns and 3 rows the number of independent reactions will be equal to the difference 8-3=5.

- How many stream and system variables?

Grading Notes.

- The approach taken here provides for the maximum number of stream variables. It's not necessary to introduce all of them, many are known in advance to be zero. So what we're looking for is consistency between how you've introduced the stream variables in part b and how you introduce stream specifications in part d.
- The number of system variables in part b should be equal to the number of independent reactions determined in part a, and consistent with the answer in part c.

There are a total of 8 streams and 9 chemical components. There are a total of $8 \times 9 = 72$ possible stream variables. The system is at steady-state, therefore there are no rates of accumulation. There are five independent reactions, so there are 5 additional extents of reaction associated with the reactor. Altogether there are $72 + 5 = 77$ stream and system variables.

- c. [10 pts] List the system variables.

The system variables are the extents of reactions

$$\dot{\xi}_1, \dot{\xi}_2, \dot{\xi}_3, \dot{\xi}_4, \dot{\xi}_5$$

- d. [10 pts] List any performance and stream specifications.

- Air Inlet Stream: The molar flows of N_2 and O_2 can be computed from the total molar flow multiplied by the mole fraction. The components not present in the stream have zero molar flow. Since we're counting all components in all streams, there are a total of 9 molar flows specified in the Air Inlet Stream.
- Fresh Methanol: Total of 9 molar flows are specified, 100 kg-mol/h for methanol and 0 kg-mol/h for the other 8 components.
- Reactor Inlet: The composition of methanol is specified. Nothing else is specified. So 1 specification.
- Recycle: The recycle stream is known to be pure methanol. This provides 8 independent composition specifications. (Total molar flow is unknown, so there can't be 9 specifications.)
- Off-Gas: The 5 moles fractions add up to 1, therefore the other moles fractions are 0. This is a total of 8 independent specifications.
- Liquid Product: Since the 6 vapor phase components are not present, this means there are 6 independent composition specifications.

All together we have $9+9+1+8+8+6 = 41$ stream specification. These account for all of the reactor and separator specifications.

- e. [10 pts] How many component balances?

Grading Notes.

- While there are different ways to set up the steam specifications and component balances, in the end we should arrive at the same conclusion – that there is sufficient information to solve the material balances.
- The hard part in solving these sorts of problems is to recognize whether you have enough information in the first place. So the hard work is actually done. Actual solution of the material balances is a good exercise, just a little lengthy to complete in a single exam.

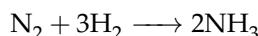
There are a total of 4 units for which we can write 9 component balances each. So there are a total of $4 \times 9 = 36$ component balances (including the reactor).

- f. Has enough data been specified to solve the material balances?
(No need to actually solve the balances).

In parts b&c we showed there were a total of 72 stream variables and 5 extents of reaction. In parts d&e we demonstrated 41 performance specifications and 36 component balances. So there are a total of 77 variables and 77 independent equations. Enough information has been given to solve for all of the component flows and extents of reactions.

P3.35 DOF Analysis for an Ammonia Recycle Reactor

In the final stage in ammonia synthesis of the Haber-Bosch process, the reaction



takes place at steady state over an iron catalyst at high pressure and temperature. A simple process flow-sheet is shown the accompanying figure.

The feed to this unit consists of a stoichiometric ratio of N_2 and H_2 . Argon (Ar) is present in the feedstream at 4 mol%. The reactor converts 15% of the H_2 at the reactor inlet to ammonia. Unreacted N_2 and H_2 is separated with 100% efficiency, but the recovering of NH_3 is incomplete resulting in the recycling of some ammonia. To remove Ar , 5% of the recycle stream is purged from the system. We want to produce 100 kg-mol/hr of ammonia.

Given the data in the statement above, how many degrees of freedom exist? In doing your analysis, show the count of stream and system variables, and a count of stream specifications, performance

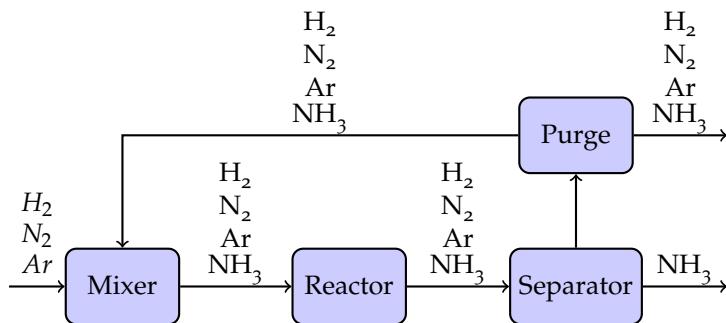
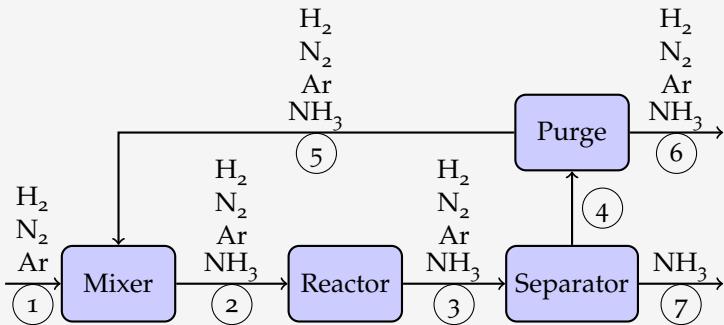


Figure 3.1: Ammonia Synthesis Flow-sheet

specifications and component balances.

Solution



Variables

Begin by numbering all of the streams. The stream variables may be organized in a table

	S1	S2	S3	S4	S5	S6	S7
H_2	$\dot{n}_{H_2,1}$	$\dot{n}_{H_2,2}$	$\dot{n}_{H_2,3}$	$\dot{n}_{H_2,4}$	$\dot{n}_{H_2,5}$	$\dot{n}_{H_2,6}$	—
N_2	$\dot{n}_{N_2,1}$	$\dot{n}_{N_2,2}$	$\dot{n}_{N_2,3}$	$\dot{n}_{N_2,4}$	$\dot{n}_{N_2,5}$	$\dot{n}_{N_2,6}$	—
Ar	$\dot{n}_{Ar,1}$	$\dot{n}_{Ar,2}$	$\dot{n}_{Ar,3}$	$\dot{n}_{Ar,4}$	$\dot{n}_{Ar,5}$	$\dot{n}_{Ar,6}$	—
NH_3	—	$\dot{n}_{NH_3,2}$	$\dot{n}_{NH_3,3}$	$\dot{n}_{NH_3,4}$	$\dot{n}_{NH_3,5}$	$\dot{n}_{NH_3,6}$	$\dot{n}_{NH_3,7}$

consisting of 24 stream variables. In addition, there is one extent of reaction ξ for a total of 25 variables.

Equations

- 4 material balances can be written for the Mixer
- 4 material balances can be written for the Reactor
- 4 material balances can be written for the Separator
- 4 material balances can be written for the Purge
- Feed Stream: 2 composition specifications

$$\dot{n}_{H_2,1} = 3\dot{n}_{N_2,1}$$

$$\dot{n}_{Ar,1} = 0.04 (\dot{n}_{H_2,1} + \dot{n}_{N_2,1} + \dot{n}_{Ar,1})$$

- Reactor Conversion: 1 equation

$$\dot{n}_{H_2,3} = (1 - 0.15)\dot{n}_{H_2,2}$$

- Separator Performance: 0 equations. The 100% separation efficiency for H_2 and N_2 is already implied by the absence of H_2 and N_2 in the product stream. So there are no new equations resulting from this specification.

- Purge: 4 equations

$$\dot{n}_{H_2,6} = 0.05\dot{n}_{H_2,4}$$

$$\dot{n}_{N_2,6} = 0.05\dot{n}_{N_2,4}$$

$$\dot{n}_{Ar,6} = 0.05\dot{n}_{Ar,4}$$

$$\dot{n}_{NH_3,6} = 0.05\dot{n}_{NH_3,4}$$

- Product Stream specification: 1 equation

$$\dot{n}_{NH_3,7} = 100$$

There are 24 equations.

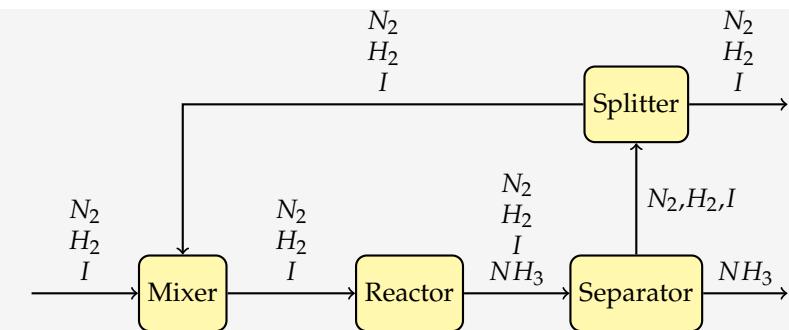
Degrees of Freedom

- 25 Variables - 24 equations = 1 DOF
- The remaining DOF is associated with the lack of a specification for the fraction of NH_3 that is recovered by the separator for the product stream.

Solution

Part a.

Ammonia synthesis flow-sheet with perfect separation. A splitter is needed to purge inerts from the recycle loop.

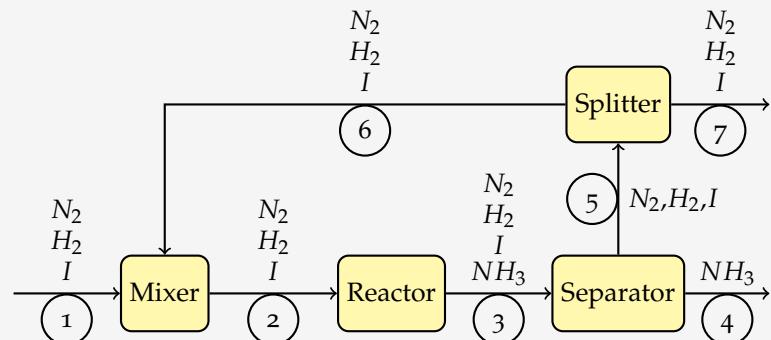


The inert enters in the feed stream, and is recycled by way of complete recovery in the separator. A purge stream must be added to provide a path for the inert to exit the process. The modified flowsheet is shown in the accompanying figure.

Part b.

Start by numbering the streams of the modified flowsheet, and prepare a stream table.

Ammonia synthesis flow-sheet with perfect separation. A splitter is needed to purge inerts from the recycle loop.



Stream Table

	Streams							
	1	2	3	4	5	6	7	
Species	N_2	N_1	N_2	N_3		N_5	N_6	N_7
	H_2	H_1	H_2	H_3		H_5	H_6	H_7
	I	I_1	I_2	I_3		I_5	I_6	I_7
	NH_3	-		A_3	A_4			

Counting variables, there are 18 process variables (20 stream, 1 reaction)

<i>Variables</i>	
Steam	20
Reaction	1
Accumulation	0
TOTAL	21

We can write the following component material balances and process specifications

Equations

Component Balances

Mixer	3
Reactor	4
Separator	4
Splitter	3

Specifications

Product Stream Flow	1
H_2 to N_2 feed ratio	1
Reactor Conversion	1
TOTAL	17

As given, this problem has

$$\boxed{\text{DOF} = 21 - 17 = 4}$$

degrees of freedom. To fully specify the all of the flowsheet variables, we would need to specify the fraction of stream 5 that is purged from the recycle stream (this provides three additional equations for the component flows of stream 7 in terms of stream 6), and specify either the composition or flow of the inert in the feed.

P3.36 Process Flowsheeting

Two reactions take place in a stirred-tank reactor



where P is the desired product, and D is an undesired by-product. The process feed consists of 100 kg-mol/hr of pure A. 30% of A is converted in the reactor. In the reactor effluent you measure 10 kg-mol/hr of D. You have three different separators that can separate A, P, and D from the reactor effluent.

- Sketch a process flowsheet for the production of pure P from A.

b. What is the production rate of P from the process?

c. What is the flow of A to the reactor?

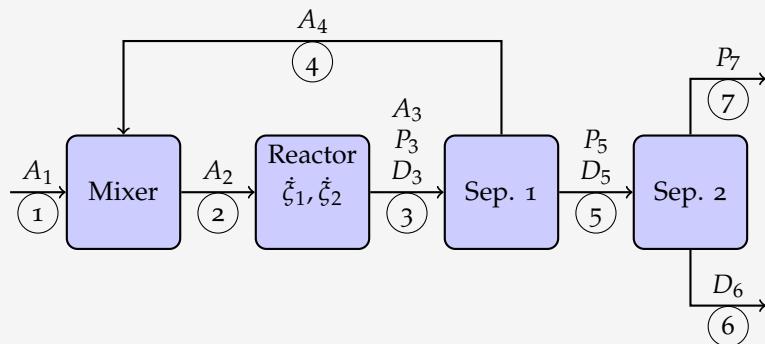
Solution

Part a.

There is not a unique solution to this flowsheet question. There are, however, certain process objectives that any satisfactory answer should achieve:

- Production of pure product P
- Recycle to make maximum use of the raw material
- separation of the undesired by-product before recycle.

Here's one example.



Part b.

This flowsheet includes 10 stream variables, and 2 extents of reaction, for a total of 12 variables.

There are 9 material balances

$$\text{Mixer } \begin{cases} 0 = A_1 + A_4 - A_2 \\ 0 = A_2 - A_3 - \dot{\xi}_1 - 2\dot{\xi}_2 \end{cases}$$

$$\text{Reactor } \begin{cases} 0 = A_2 - A_3 - \dot{\xi}_1 - 2\dot{\xi}_2 \\ 0 = -P_3 + \dot{\xi}_1 \\ 0 = -D_3 + \dot{\xi}_2 \end{cases}$$

$$\text{Separator 1 } \begin{cases} 0 = A_3 - A_4 \\ 0 = P_3 - P_5 \\ 0 = D_3 - D_5 \end{cases}$$

$$\text{Separator 2} \begin{cases} 0 = P_5 - P_7 \\ 0 = D_5 - D_6 \end{cases}$$

2 stream specifications

$$A_1 = 100 \text{ kgmol/hr}$$

$$D_3 = 10 \text{ kgmol/hr}$$

and 1 reactor performance specification

$$A_3 = 0.7 A_2$$

12 Variables - 12 Equations = 0 Degrees of Freedom.

The first round of substitutions plug in values for $A_1 = 100$, $D_3 = 10$, and $A_3 = 0.7A_2$ to reduce to a set of 9 equations in 9 variables.

$$\begin{aligned} 0 &= 100 + A_4 - A_2 \\ 0 &= A_2 - 0.7A_2 - \dot{\xi}_1 - 2\dot{\xi}_2 \\ 0 &= -P_3 + \dot{\xi}_1 \\ 0 &= -10 + \dot{\xi}_2 \\ 0 &= 0.7A_2 - A_4 \\ 0 &= P_3 - P_5 \\ 0 &= 10 - D_5 \\ 0 &= P_5 - P_7 \\ 0 &= D_5 - D_6 \end{aligned}$$

From these we have $D_5 = D_6 = 10$ and $A_4 = 0.7A_2$. From the first material balance

$$0 = 100 + 0.7A_2 - A_2$$

so that

$$A_2 = \frac{100}{0.3} = 333.33 \text{ kgmol/hr}$$

Then from the second material balance and $\dot{\xi}_2 = 10$

$$0 = 0.3A_2 - \dot{\xi}_1 - 2 \times 10$$

so that

$$\dot{\xi}_1 = 0.3 \times 333.33 - 20 = 80 \text{ kgmol/hr}$$

The product flow

$$P_7 = P_5 = P_3 = \dot{\xi}_1 = 80 \text{ kgmol/hr}$$

Part c.

The flowrate to the reactor is A_2 which we previously found

$$A_2 = \frac{100}{0.3} = 333.33 \text{ kgmol/hr}$$

The calculations can be verified with the following Matlab/CVX model

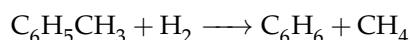
```
cvx_begin
    variables A1 A2 A3 A4
    variables P3 P5 P7
    variables D3 D5 D6
    variables X1 X2
    A1 == 100;
    D3 == 10;
    A3 == 0.7*A2;
    0 == A1 + A4 - A2;
    0 == A2 - A3 - X1 - 2*X2;
    0 == -P3 + X1;
    0 == -D3 + X2;
    0 == A3 - A4;
    0 == P3 - P5;
    0 == D3 - D5;
    0 == P5 - P7;
    0 == D5 - D6;
cvx_end
```

3.4 Exercises

P3.37 Hydrodealkylation of Toluene

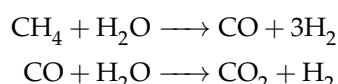
Benzene (C_6H_6) is a precursor to vast array of chemical products.

Benzene can be produced by the hydrodealkylation of toluene ($C_6H_5CH_3$) through the reaction



where certain side-reactions have been neglected.

Hydrogen required for this process can be produced from methane (CH_4) and water (H_2O) by the steam reforming and water-gas shift reactions



Species	Formula	MW
Benzene	C_6H_6	78
Hydrogen	H_2	2
Methane	CH_4	16
Toluene	$C_6H_5CH_3$	92
Water	H_2O	18

- a. Perform a generation-consumption analysis for the production of benzene.
- b. Calculate the mass flow rates necessary to produce 10 metric tons per hour of benzene.
- c. Each of these reactions must be carried out in a separate reactor. Only the reactants for that reaction should be present in the corresponding inlet stream. Sketch a process flowsheet consisting of mixers, reactors, and separators.

4

Reactors

4.1 Summary

Concepts	Skills	Practice Problems
Chemical Reactors	<ul style="list-style-type: none">- describe batch, semi-batch, continuous stirred-tank- describe exothermic versus endothermic- describe kinetic vs. equilibrium models - identify reactor design variables such as volume, residence time, and mode of operation	
Extent of Reaction	<ul style="list-style-type: none">- assign extents of reactions to a system of chemical reactions- derive mass and mole balances for reactors with multiple reactions with known stoichiometry	Example 4.3, 4.4
Performance Specifications	<ul style="list-style-type: none">- calculate yield, selectivity, fractional conversion	
Equilibrium	<ul style="list-style-type: none">- describe chemical equilibrium- write equilibrium quotients for reactions with gas, liquid, or solid phase reactants- compute standard enthalpy $\Delta\hat{H}_{rxn}^\circ$, Gibb's free energy $\Delta\hat{G}_{rxn}^\circ$, and entropy of reaction $\Delta\hat{S}_{rxn}^\circ$- describe exothermic and endothermic reactions with examples and criterion- compute the equilibrium constant at STP- estimate equilibrium constant at other temperatures using Van't Hoff equation- write the equilibrium constant in terms of extent of reaction- solve for the equilibrium extent of reaction	

4.2 Chemical Equilibrium

Some chemical reactions proceed spontaneously, others don't. What are the 'driving forces' for chemical reaction?

4.2.1 Gibb's Free Energy

"Any method involving the notion of *entropy*, the very existence of which depends on the second law of thermodynamics, will doubtless seem to many far-fetched, and may repel beginners as obscure and difficult of comprehension."

– Josiah Willard Gibbs

Gibb's free energy of a system is the energy available to do work at constant temperature and pressure. For a system that starts in state '1' and ends in a state '2', the change in Gibb's free energy is

$$\Delta G(P, T) = \underbrace{G_2(P, T)}_{\text{End State}} - \underbrace{G_1(P, T)}_{\text{Start State}}$$

A negative change, $\Delta G < 0$, means that the end state has less available energy for work implying the system either did actual mechanical work on the surroundings, or else wasted the potential for work by releasing energy as heat to the surroundings.

There are a large number of chemical and physical phenomena that can potentially contribute to the change in Gibb's free energy. In most situations we have to include at least three factors:

Internal Energy The internal energy is the kinetic and potential energy of the atoms, of the chemical bonds that form them into molecules, and of the interaction among molecules. Internal energy, denoted by the symbol U , is a function of the thermodynamic state. The change in internal energy is measured by

$$U_2 - U_1 = \Delta U$$

Interaction with the Environment A chemical system may interact with the surrounding environment. For example, if there is a change in volume $V_2 - V_1$ at constant temperature T and pressure P , then the work performed by the chemical system on the environment is given by

$$P(V_2 - V_1) = P\Delta V$$

Tendency to Disorder Entropy measures the degree of disorder in a system. All other things being equal, chemical systems will spontaneously change from more ordered to less ordered states. A change in entropy $S_2 - S_1$ will be positive for a system becoming

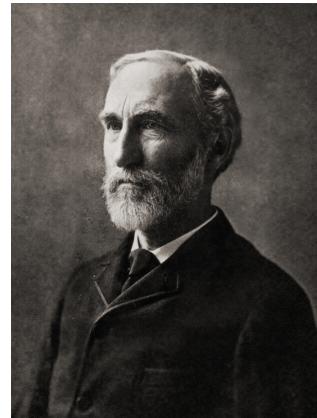


Figure 4.1: Josiah Willard Gibbs

First American doctorate in Engineering (Yale, 1863). Albert Einstein called him "the greatest mind in American history."

more disordered. At constant temperature T , the energy released by a positive change in entropy $S_2 - S_1$ is given by

$$-T(S_2 - S_1) = -T\Delta S$$

The change in the Gibb's free energy is the net effect of the contribution these three terms to the potential of a chemical system to produce mechanical work. Summing these terms gives us

$$\Delta G(P, T) = \underbrace{\Delta U + P\Delta V}_{\Delta H(P, T)} - T\Delta S$$

This can be simplified by combining terms

The term $\Delta H(P, t)$, the change in enthalpy, is a useful means of encapsulating the terms associated with an energy balance at constant temperature and pressure.

This expression clearly shows tradeoff between changes in internal energy, work on the surroundings, and the transition from order to disorder. Additional terms may be important in some situations, such as when a chemical system interacts with an external electrical or magnetic field.

4.2.2 Spontaneous Change

A core principle of chemical equilibria is that spontaneous change can occur if a system has the capacity to perform work on its surroundings. Examples of systems that have the capacity to perform work on their surroundings are

- A ball at the top of a hill.
- A gas at high pressure connected to a chamber at lower pressure.
- A hot object in contact with a cold object.
- A stoichiometric mixture of methane and oxygen.

Note the conditional words in the statement about spontaneous change. First, the fact that a spontaneous change 'can' occur doesn't mean it 'will' occur. The ball at the top of the hill, for example, could remain balanced forever, or the methane/oxygen mixture may never receive the spark needed for ignition.

Second, the capacity to perform work implies the existence of a device capable of transforming the released energy into mechanical work. Such a device may not exist for every situation, and then there are inevitable inefficiencies of practical devices. In any case, the portion of available energy that does not get converted to work is released to the surroundings as heat.

Chemical systems may be *reversible*, that is, the chemical transformation under consideration can proceed in either the forward or

reverse direction. Examples include phase changes such as vaporization and condensation, melting and freezing, and many biological and electrochemical reactions.

Taking these considerations into account, for a given change in the state of a chemical system, we can say that

- $\Delta G < 0$ implies the possibility of spontaneous change in the forward direction,
- $\Delta G > 0$ implies the possibility of spontaneous change in the reverse direction.
- $\Delta G = 0$ implies the system is at *equilibrium*.

The last condition occurs when there is no potential for spontaneous change, that is if $\Delta G = 0$. If there is no potential for spontaneous change then the system is at *equilibrium*.

4.2.3 Gibbs Free Energy of Reaction

The work required to conduct a 'mole of reaction' at constant temperature and pressure.

$$\Delta \hat{G}_{rxn} = \underbrace{\Delta \hat{U}_{rxn} + P\Delta \hat{V}_{rxn}}_{\Delta \hat{H}_{rxn}} - T\Delta \hat{S}_{rxn}$$

- A transition from order (low S) to disorder (high) produces positive $\Delta \hat{S}$, therefore negative $\Delta \hat{G}$, and therefore can produce work.
- $\Delta \hat{G}_{rxn} < 0$ can produce work
- $\Delta \hat{G}_{rxn} > 0$ requires work to proceed

4.2.4 Enthalpy of Reaction

The amount of energy absorbed by a reaction conducted at constant temperature and pressure.

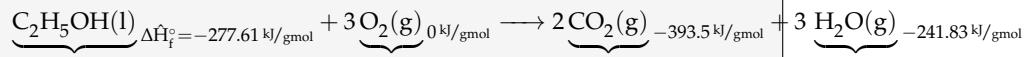
$$\underbrace{\Delta \hat{H}_{rxn}}_{\Delta \hat{U}_{rxn} + P\Delta \hat{V}_{rxn}} = \Delta \hat{G}_{rxn} + T\Delta \hat{S}_{rxn}$$

- $\Delta \hat{H}_{rxn}$ – enthalpy of reaction.
- $\Delta \hat{H}_{rxn}$ – molar enthalpy of reaction.
 - $\Delta \hat{H}_{rxn} > 0$ is an endothermic reaction.
 - $\Delta \hat{H}_{rxn} < 0$ is an exothermic reaction.

Example: Standard Enthalpy of Reaction for the Combustion of Ethanol

How much energy is produced by burning a gram mole of ethanol at STP (1 atm, 298K)?

Solution

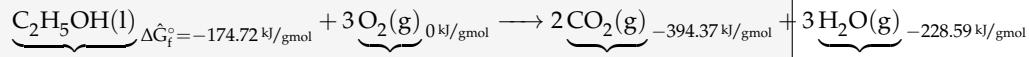


$$\begin{aligned}\Delta \hat{H}_r^\circ &= \sum_i \nu_i \Delta \hat{H}_{i,f}^\circ \\ &= -1 \times (-277.61) - 3 \times (0) + 2 \times (-393.5) + 3 \times (-241.83) \\ &= -1,235 \text{ kJ/gmol} \\ &= -1,235 \text{ kJ/gmol} \times \frac{1 \text{ gmol}}{46.07 \text{ g}} \times \frac{1000 \text{ g}}{1 \text{ kg}} = -26,810 \text{ kJ/kg}\end{aligned}$$

Example: Standard Gibb's Free Energy of Reaction for the Combustion of Ethanol

How much work can be produced by burning a gram mole of ethanol at STP (1 atm, 298K)?

Solution



$$\begin{aligned}\Delta \hat{G}_r^\circ &= \sum_i \nu_i \Delta \hat{G}_{i,f}^\circ \\ &= -1 \times (-174.72) - 3 \times (0) + 2 \times (-394.37) + 3 \times (-228.59) \\ &= -1,299.8 \text{ kJ/gmol} \\ &= -1,299.8 \text{ kJ/gmol} \times \frac{1 \text{ gmol}}{46.07 \text{ g}} \times \frac{1000 \text{ g}}{1 \text{ kg}} = -28,213 \text{ kJ/kg}\end{aligned}$$

4.2.5 Calculating the Equilibrium Constants

Given a reaction with stoichiometric coefficients ν_i —

$$0 = \sum_i \nu_i \mathcal{A}_i$$

Gibbs Free Energy $\Delta \hat{G}_{rxn}$

$$K_a = \exp \left(\frac{-\Delta \hat{G}_{rxn}}{RT} \right)$$

Units

$$[RT] = \frac{\text{Joules}}{\text{K gmol}} \times \text{K} = \frac{\text{Joules}}{\text{gmol}}$$

Note that this holds for all temperatures.

For all temperatures

$$K_a = \exp\left(\frac{-\Delta\hat{G}_{rxn}}{RT}\right) \implies \ln K_a = -\frac{\Delta\hat{G}_{rxn}}{RT}$$

Using

$$\Delta\hat{G}_{rxn} = \Delta\hat{H}_{rxn} - T\Delta\hat{S}_{rxn}$$

We get

$$\ln K_a = -\frac{1}{R} \left[-\Delta\hat{S}_{rxn} + \frac{\Delta\hat{H}_{rxn}}{T} \right]$$

If $\Delta\hat{S}_{rxn}$ and $\Delta\hat{H}_{rxn}$ don't change much with temperature then we can estimate them from standard conditions

$$\Delta\hat{S}_{rxn} \approx \Delta\hat{S}_{rxn}^\circ = \frac{\Delta\hat{H}_{rxn}^\circ - \Delta\hat{G}_{rxn}^\circ}{T^\circ}$$

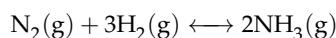
$$\Delta\hat{H}_{rxn} \approx \Delta\hat{H}_{rxn}^\circ$$

van't Hoff Equation

$$\ln K_{a,T} = -\frac{1}{R} \left[\frac{\Delta\hat{G}_r^\circ - \Delta\hat{H}_r^\circ}{298} + \frac{\Delta\hat{H}_r^\circ}{T} \right]$$

Example: Equilibrium Constant for the Production of Ammonia at 750K

What is the equilibrium constant for



at 750K?

Solution

Gibb's Free Energy and Enthalpy of Formation at STP (1 atm, 25 °C) come from the textbook appendix.

Compound	$\Delta\hat{G}_{i,f}^\circ$	$\Delta\hat{H}_{i,f}^\circ$
$\text{N}_2(\text{g})$	0	0
$\text{H}_2(\text{g})$	0	0
$\text{NH}_3(\text{g})$	-16,600 J/gmol	-46,150 J/gmol

Standard Enthalpy of Reaction

$$\begin{aligned} \Delta\hat{H}_{rxn}^\circ &= \sum_i v_i \Delta\hat{H}_{i,f}^\circ \\ &= -1 \times 0 - 3 \times 0 + 2 \times (-46,150) \\ &= -92,300 \text{ J/gmol} \end{aligned}$$

How do you interpret this result?



Figure 4.2: Jacobus van't Hoff

First winner of the Nobel Prize in Chemistry (1901).

Standard Gibb's Free Energy of Reaction

$$\begin{aligned}\Delta\hat{G}_{rxn}^{\circ} &= \sum_i v_i \Delta\hat{G}_{i,f}^{\circ} \\ &= -1 \times 0 - 3 \times 0 + 2 \times (-16,600) \\ &= -33,200 \text{ J/gmol}\end{aligned}$$

How do you interpret this result?

Standard Entropy of Reaction

From the definition of Gibb's Free Energy

$$\Delta\hat{G}_{rxn} = \Delta\hat{H}_{rxn} - T\Delta\hat{S}_{rxn}$$

Solving for Entropy of Reaction at STP

$$\begin{aligned}\Delta\hat{S}_{rxn}^{\circ} &= \frac{\Delta\hat{H}_{rxn}^{\circ} - \Delta\hat{G}_{rxn}^{\circ}}{298} \\ &= \frac{(-92,300) - (-33,200)}{298} \\ &= -198.32 \text{ J/Kg mol}\end{aligned}$$

How do you interpret this result? Does it make sense?

van't Hoff Equation

$$\begin{aligned}\ln K_{a,T} &= -\frac{1}{R} \left[\frac{\Delta\hat{G}_{rxn}^{\circ} - \Delta\hat{H}_{rxn}^{\circ}}{298} + \frac{\Delta\hat{H}_{rxn}^{\circ}}{T} \right] \\ &= -\frac{1}{8.3144} \left[\frac{(-33,200) - (-92,300)}{298} + \frac{-92,300}{T} \right] \\ &= -23.85 + \frac{11,100}{T}\end{aligned}$$

- How do you interpret this expression? Do you expect to see the equilibrium constant decrease with temperature?
- $K_{a,750K} = 0.001172$.

4.3 Measures of Reactor Performance

4.3.1 Limiting and Excess Reactants

Limiting Reactant For a single reaction, the *limiting reactant* is the species that establishes an upper limit on the extent of reaction'.

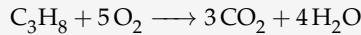
Excess Reactant The amount of a reactant left after the limiting reactant has been completely consumed.

Example: Propane Burner

Suppose 100 gmol/hr of propane (C_3H_8) and 600 gmol/hr of oxygen are fed to a burner. What is the limiting reactant? What is the degree to which the other reactant is in excess?

Solution

The balanced combustion reaction is



At steady-state the molar balances are given by the equations

$$0 = \underbrace{\dot{n}_{C_3H_8,in}}_{100 \text{ gmol/hr}} - \dot{n}_{C_3H_8,out} - \dot{\xi}$$

$$0 = \underbrace{\dot{n}_{O_2,in}}_{600 \text{ gmol/hr}} - \dot{n}_{O_2,out} - 5\dot{\xi}$$

$$0 = \underbrace{\dot{n}_{CO_2,in}}_{0 \text{ gmol/hr}} - \dot{n}_{CO_2,out} + 3\dot{\xi}$$

$$0 = \underbrace{\dot{n}_{H_2O,in}}_{0 \text{ gmol/hr}} - \dot{n}_{H_2O,out} + 4\dot{\xi}$$

Solving for the outlet flowrates

$$\dot{n}_{C_3H_8,out} = 100 \text{ gmol/hr} - \dot{\xi}$$

$$\dot{n}_{O_2,out} = 600 \text{ gmol/hr} - 5\dot{\xi}$$

$$\dot{n}_{CO_2,out} = 3\dot{\xi}$$

$$\dot{n}_{H_2O,out} = 4\dot{\xi}$$

All of these outlet molar flowrates must be non-negative for a chemically meaningful solution.

$$100 \text{ gmol/hr} - \dot{\xi} \geq 0 \implies \dot{\xi} \leq 100 \text{ gmol/hr}$$

$$600 \text{ gmol/hr} - 5\dot{\xi} \geq 0 \implies \dot{\xi} \leq 120 \text{ gmol/hr}$$

$$3\dot{\xi} \geq 0 \implies \dot{\xi} \geq 0$$

$$4\dot{\xi} \geq 0 \implies \dot{\xi} \geq 0$$

Examining the expressions, we find the mole balance for propane determines the maximum feasible extent of reaction

$$0 \leq \dot{\xi} \leq 100 \text{ gmol/hr}$$

The propane fed to the reactor limits the extent of reaction to $\dot{\xi}^{\max} = 100 \text{ gmol/hr}$. The limiting reactant is propane. Had oxygen been the limiting reactant, then the extent of reaction could have been 120 gmol/hr. Therefore oxygen is in excess by $\frac{120-100}{100} = 20\%$.

4.3.2 Fractional Conversion

Fractional conversion is the fraction of a reactant that is converted to any product or by-product. This is a simple measure of how much of a given reactant is consumed in a reactor.

For component i fed to a continuous reactor, the fractional conversion is given by the ratios

$$f_{C,i} = \frac{\dot{n}_{i,in} - \dot{n}_{i,out}}{\dot{n}_{i,in}} \quad \text{or} \quad f_{C,i} = \frac{\dot{m}_{i,in} - \dot{m}_{i,out}}{\dot{m}_{i,in}}$$

which will be a value between 0 and 1. The value is the same whether the calculations are done in mass or molar units.

For a batch reactor, fractional conversion is computed using starting and ending amounts of a reactant rather than the inlet and outlet reactant flow rates.

An alternative expression can be constructed from the steady state material balances.

$$f_{C,i} = -\frac{\sum_k v_{i,k} \dot{\xi}_k}{\dot{n}_{i,in}} \quad \text{or} \quad f_{C,i} = -\frac{\sum_k v_{i,k} M_i \dot{\xi}_k}{\dot{m}_{i,in}}$$

4.3.3 Conversion, Yield, and Selectivity

Conversion measures the fraction of a feed that is converted, whether or not the conversion results in a desired product or undesired by-products. Referring the reactor flow diagram,

$$C = \frac{A_{in} - A_{out}}{A_{in}}$$

which will be a fraction between 0 and 1, and will be the same value whether computed for molar or mass flows.

Yield measures how much of a product is produced compared to the quantity of raw material fed to a reactor.

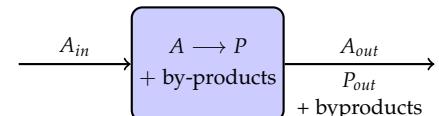
$$Y = \frac{P_{out}}{A_{in}}$$

In this case the units of flow do matter and should be chosen to best reflect the context of the problem.

Selectivity measures how much of the feed that is converted ends up in the desired product.

$$S = \frac{P_{out}}{A_{in} - A_{out}}$$

In systems with recycle, unreacted feed separated from the product stream can be sent back for another pass through the reactor. In these cases, selectivity is a particularly important measure of performance.



$$\begin{aligned} \text{Yield } Y &= \frac{P_{out}}{A_{in}} \\ \text{Selectivity } S &= \frac{P_{out}}{A_{in} - A_{out}} = \frac{Y}{C} \\ \text{Conversion } C &= \frac{A_{in} - A_{out}}{A_{in}} = \frac{Y}{S} \end{aligned}$$

Figure 4.3: Relationship among primary measures of reactor performance. Each of the measures (Conversion, Yield, Selectivity) can be expressed as a product or ratio of the other two.

Note that each of these primary performance measures can be expressed as a product or ratio of the other two. The relationships are diagrammed in the accompanying figure.

4.4 Solved Problems

P4.38 Soyuz Spacecraft Soft-Landing Rockets

The descent module of the Soyuz spacecraft is designed to land on hard ground. To soften the impact, a gamma ray altimeter senses when the spacecraft is one meter above the surface, then fires a soft-landing thruster to slow the descent rate to 2 m/sec.

The Soyuz soft-landing thruster uses unsymmetrical dimethyl hydrazine ($C_2H_8N_2$, UMDH) as fuel and hydrogen peroxide (H_2O_2) as the oxidizer. The products of the reaction are carbon dioxide (CO_2), water (H_2O), and nitrogen (N_2).

The total mass of propellant (i.e., the combined weight of fuel and oxidizer) in the descent module is 45 kg. Assuming the fuel and oxidizer are loaded in a stoichiometric ratio, set up and solve the material balances for the masses of all species involved in the operation of the soft-landing thrusters.

Solution

The first step is to construct a balanced reaction. Setting up the atomic matrix

	$C_2H_8N_2$	H_2O_2	CO_2	H_2O	N_2
C	2	0	1	0	0
H	8	2	0	2	0
O	0	2	2	1	0
N	2	0	0	0	2

Using UMDH as the basis and setting the corresponding stoichiometric coefficient to -1 results in a set of equations for the remaining stoichiometric coefficients

$$0 = -2 + \nu_{CO_2}$$

$$0 = -8 + 2\nu_{H_2O_2} + 2\nu_{H_2O}$$

$$0 = 2\nu_{H_2O_2} + 2\nu_{CO_2} + \nu_{H_2O}$$

$$0 = -2 + 2\nu_{N_2}$$

Solving the first equation for $\nu_{CO_2} = 2$ and the fourth for $\nu_{N_2} =$



Figure 4.4: Soyuz spacecraft.
Source: Wikimedia Commons

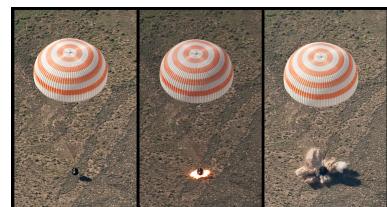


Figure 4.5: Landing sequence for the Soyuz descent module.
Source: Wikimedia Commons



Figure 4.6: The 17 by 20 cm Soyuz soft landing thruster.
Source: Steve Jurvetson

Species	Formula	MW
UMDH	$C_2H_8N_2$	60
Hydrogen Peroxide	H_2O_2	34
Water	H_2O	18
Nitrogen	N_2	28
Carbon Dioxide	CO_2	44

1, and substituting those results into the second and third equation gives a pair of equations in two unknowns

$$\begin{aligned} 8 &= 2v_{\text{H}_2\text{O}_2} + 2v_{\text{H}_2\text{O}} \\ -4 &= 2v_{\text{H}_2\text{O}_2} + v_{\text{H}_2\text{O}} \end{aligned}$$

Solving these gives $v_{\text{H}_2\text{O}} = 12$ and $v_{\text{H}_2\text{O}_2} = -8$. So the balanced reaction is



The next step in the solution is to set up mass balance equations for operation of the soft-landing rockets. Sketching a diagram



Mass balances give

$$\begin{aligned} 0 &= U_1 - 60\dot{\xi} \\ 0 &= P_1 - 8 \times 34\dot{\xi} \\ 0 &= -C_2 + 2 \times 44\dot{\xi} \\ 0 &= -W_2 + 12 \times 18\dot{\xi} \\ 0 &= -N_2 + 28 \times \dot{\xi} \end{aligned}$$

From the problem data we know $U_1 + P_1 = 45 \text{ kg}$. Adding the first two equations together we get

$$U_1 + P_1 = (60 + 8 \times 34)\dot{\xi} = 45$$

Solving for $\dot{\xi}$

$$\dot{\xi} = \frac{45}{60 + 8 \times 34} = \frac{45 \text{ kg}}{332 \text{ kg/kg-mol}} = 0.136 \text{ kg-mol}$$

Substituting this value into the remaining equations gives the masses of the thruster reactants

$$45 \text{ kg} \begin{cases} U_1 = 60\dot{\xi} = 8.1 \text{ kg} \\ P_1 = 8 \times 34\dot{\xi} = 36.9 \text{ kg} \end{cases}$$

and of the thruster exhaust gases

$$45 \text{ kg} \begin{cases} C_2 = 2 \times 44\dot{\zeta} = 11.9 \text{ kg} \\ W_2 = 12 \times 18\dot{\zeta} = 29.3 \text{ kg} \\ N_2 = 28\dot{\zeta} = 3.8 \text{ kg} \end{cases}$$

P4.39 Biodiesel Production (to be modified)

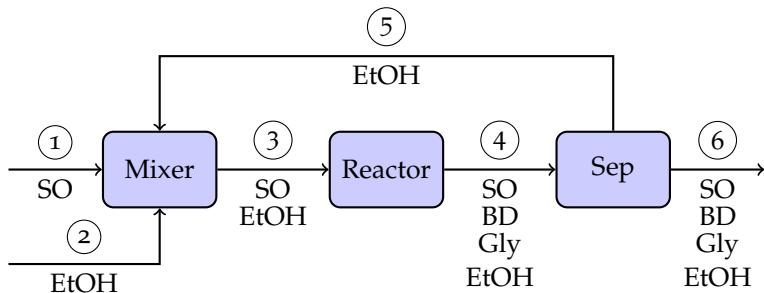
Soybean oil, like many animal and vegetable fats, is a triglyceride that can be converted to a usable diesel fuel through a transesterification reaction.

The following reaction takes place in the transesterification reactor shown in the accompanying flowsheet



Species	Abbrev.	Formula	MW	Density [kg/l]
Ethanol	EtOH	C ₂ H ₅ OH	46.07	0.789
Glycerol	Gly	C ₃ H ₈ O ₃	92.09	1.261
Sodium Hydroxide	NaOH	NaOH	40.00	n/a
Soybean Oil	SO	C ₅₇ H ₉₅ O ₆	876.4	0.926
S.O. Ethyl Esters	BD	C ₂₀ H ₃₄ O ₂	306.5	0.88

Figure 4.7: Soybeans ready for harvesting. Source: Acuweather



The following data has been measured –

- $SO_1 = 1000 \text{ kg/hour}$
- $EtOH_2 = 200 \text{ kg/hour}$
- $EtOH_5 = 75 \text{ kg/hour}$
- The fractional conversion of SO is 80%

From this data, compute the following quantities:

- (i) Molar extent of reaction.
- (ii) Mass flow of *EtOH* in stream 6.
- (iii) The fractional recovery of *EtOH* from stream 4 to stream 5.

Solution

Part a.

Let's start with a degree of freedom analysis. After plugging in for the known feed rates, we have 13 stream variables plus one reaction extent for a total of 14 variables. There are 2 material balances for the mixer, 4 for the reactor, and 4 for the separator, for a total of 10 material balance equations. We'll need 4 additional specifications to complete the calculation, and those are given as the inlet flow rates, and the fractional conversion of SO, and the fractional recovery of the separator.

Species	Streams					
	1	2	3	4	5	6
SO	S_1		S_3	S_4		S_6
EtOH		E_2	E_3	E_4	E_5	E_6
BD				B_4		B_6
Gly				G_4		G_6

The 10 material balance equations involving 14 variables are given by

$$\begin{aligned}
 0 &= S_1 - S_3 \\
 0 &= E_2 + E_5 - E_3 \\
 0 &= S_3 - S_4 - M_{SO} \dot{\xi} \\
 0 &= E_3 - E_4 - 3 M_{EtOH} \dot{\xi} \\
 0 &= -B_4 + 3 M_{BD} \dot{\xi} \\
 0 &= -G_4 + M_{Gly} \dot{\xi} \\
 0 &= S_4 - S_6 \\
 0 &= E_4 - E_5 - E_6 \\
 0 &= B_4 - B_6 \\
 0 &= G_4 - G_6
 \end{aligned}$$

As a first step, plug in the 4 specifications $S_1 = 1000$, $E_2 = 200$, $S_4 = (1 - 0.8)S_3$, and $E_5 = 0.5E_4$. This leaves us with 10 equations in 10 unknowns. We trying to solve for $\dot{\xi}$. We can see there's a simple way to compute $\dot{\xi}$

Use this one $\rightarrow 0 = 1000 - S_3$

$$0 = 200 + 0.5E_4 - E_3$$

and this one $\rightarrow 0 = S_3 - 0.2S_3 - M_{SO}\dot{\xi}$

$$0 = E_3 - E_4 - 3M_{EtOH}\dot{\xi}$$

$$0 = -B_4 + 3M_{BD}\dot{\xi}$$

$$0 = -G_4 + M_{Gly}\dot{\xi}$$

$$0 = 0.2S_3 - S_6$$

$$0 = E_4 - 0.5E_4 - E_6$$

$$0 = B_4 - B_6$$

$$0 = G_4 - G_6$$

From the first equation we have $S_3=1000 \text{ kg/hr.}$ Plugging into the third equation and solving for the molar extent of reaction

$$\dot{\xi} = \frac{0.8S_3}{M_{SO}} = \frac{0.8 \times 1000}{876.4} = 0.913 \text{ kg-mol/hr}$$

Part b.

The equations that are left

$$0 = 200 + 0.5E_4 - E_3$$

$$0 = E_3 - E_4 - 3M_{EtOH}\dot{\xi}$$

Solve this one $\rightarrow 0 = -B_4 + 3M_{BD}\dot{\xi}$

Solve this one $\rightarrow 0 = -G_4 + M_{Gly}\dot{\xi}$

Solve this one $\rightarrow 0 = 0.2S_3 - S_6$

$$0 = E_4 - 0.5E_4 - E_6$$

Solve this one $\rightarrow 0 = B_4 - B_6$

Solve this one $\rightarrow 0 = G_4 - G_6$

We have $\dot{\xi}$ which we can substitute into the material balance

equations to obtain values for many of the other mass flowrates

$$B_4 = 3 M_{BD} \dot{\xi} = 3 \times 306.5 \times 0.913 = 839.5 \text{ kg/hr}$$

$$G_4 = M_{Gly} \dot{\xi} = 92.09 \times 0.913 = 84.1 \text{ kg/hr}$$

$$S_6 = 0.2 S_3 = 0.2 \times 1000 = 200 \text{ kg/hr}$$

$$B_6 = B_4 = 839.5 \text{ kg/hr}$$

$$G_6 = G_4 = 84.1 \text{ kg/hr}$$

The equations that are left are

$$\text{Solve this one} \rightarrow 0 = 200 + 0.5E_4 - E_3$$

$$\text{Solve this one} \rightarrow 0 = E_3 - E_4 - 3 M_{EtOH} \dot{\xi}$$

$$0 = E_4 - 0.5E_4 - E_6$$

The first two of these equations are pair of equations in two unknowns.

$$0.5E_4 - E_3 = -200$$

$$E_3 - E_4 = 3 M_{EtOH} \dot{\xi} = 3 \times 46.07 \times 0.913 = 126.2$$

Adding these two equations together cancels E_3 . The remaining equation is

$$-0.5E_4 = -73.8$$

or

$$E_4 = 147.6 \text{ kg/hr}$$

The very last equation to solve

$$E_6 = 0.5E_4 = 73.8 \text{ kg/hr}$$

Part c.

At this point we have solved for almost all of the stream variables. We need to go back and solve for the recycle flowrate E_5

$$E_5 = 0.5E_4 = 73.8 \text{ kg/hr}$$

For completeness, we can find E_3

$$E_3 = E_4 + 126.2 = 147.6 + 126.2 = 273.8 \text{ kg/hr}$$

to complete the stream table

Species	Streams					
	1	2	3	4	5	6
SO	1000	-	1000	200	-	200
EtOH	-	200	273.8	147.8	73.8	73.8
BD	-	-	-	839.5	-	839.5
Gly	-	-	-	84.1	-	84.1

P4.40 Production of Methanol

Methanol (CH_3OH) can be produced from synthesis gas (36 mol% CO, 60 mol% H_2 , and 4 mol% inert N_2) as shown in the accompanying figure.

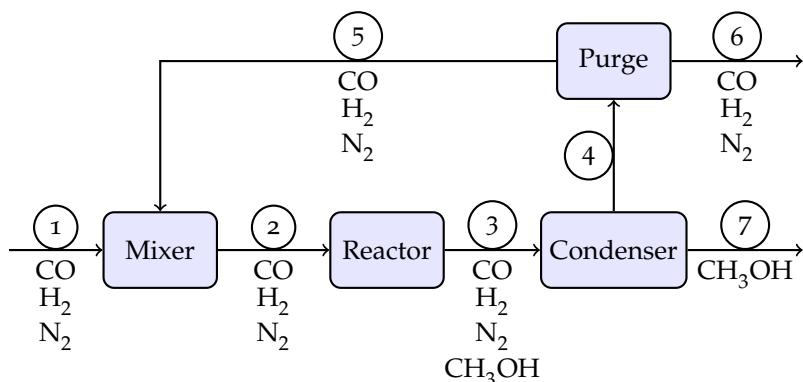


Figure 4.8: Flowsheet for the production of methanol from synthesis gas.

The reaction is



In steady-state operation the reactor has a fractional conversion of 20% of the limiting reactant. 5% of the recycled gas is purged.

- Perform a degree of freedom analysis.
- What fraction of the incoming CO is converted to CH_3OH ? What fraction of the incoming H_2 is converted to methanol?
- What fraction of the reactor inlet consists of inert?

Solution

Part a. Constructing a stream table

	1	2	3	4	5	6	7
CO	$C_{<1>}$	$C_{<2>}$	$C_{<3>}$	$C_{<4>}$	$C_{<5>}$	$C_{<6>}$	-
H ₂	$H_{<1>}$	$H_{<2>}$	$H_{<3>}$	$H_{<4>}$	$H_{<5>}$	$H_{<6>}$	-
N ₂	$N_{<1>}$	$N_{<2>}$	$N_{<3>}$	$N_{<4>}$	$N_{<5>}$	$N_{<6>}$	-
CH ₃ OH	-	-	$M_{<3>}$	-	-	-	$M_{<7>}$

shows there are 20 stream variables. There is one extent of reaction variable for a total of 21 process variables.

Mixer Material Balances (3)

$$0 = C_{<1>} + C_{<5>} - C_{<2>} \quad (4.1)$$

$$0 = H_{<1>} + H_{<5>} - H_{<2>} \quad (4.2)$$

$$0 = N_{<1>} + N_{<5>} - N_{<2>} \quad (4.3)$$

Reactor Material Balances (4)

$$0 = C_{<2>} - C_{<3>} - \dot{\xi} \quad (4.4)$$

$$0 = H_{<2>} - H_{<3>} - 2\dot{\xi} \quad (4.5)$$

$$0 = N_{<2>} - N_{<3>} \quad (4.6)$$

$$0 = -M_{<3>} + \dot{\xi} \quad (4.7)$$

Condenser Material Balances (4)

$$0 = C_{<3>} - C_{<4>} \quad (4.8)$$

$$0 = H_{<3>} - H_{<4>} \quad (4.9)$$

$$0 = N_{<3>} - N_{<4>} \quad (4.10)$$

$$0 = M_{<3>} - M_{<7>} \quad (4.11)$$

Purge Material Balances (3)

$$0 = C_{<4>} - C_{<5>} - C_{<6>} \quad (4.12)$$

$$0 = H_{<4>} - H_{<5>} - H_{<6>} \quad (4.13)$$

$$0 = N_{<4>} - N_{<5>} - N_{<6>} \quad (4.14)$$

Feed Specifications (only 2 of 3 are independent) (2)

$$C_{<1>} = 0.36(C_{<1>} + H_{<1>} + N_{<1>}) \quad (4.15)$$

$$H_{<1>} = 0.60(C_{<1>} + H_{<1>} + N_{<1>}) \quad (4.16)$$

Fractional Conversion Specification for the limiting reactant
(1)

$$H_{<3>} = 0.80H_{<2>} \quad (4.17)$$

Purge Specifications (3)

$$C_{<5>} = 0.95C_{<4>} \quad (4.18)$$

$$H_{<5>} = 0.95H_{<4>} \quad (4.19)$$

$$N_{<5>} = 0.95N_{<4>} \quad (4.20)$$

There are a total of 14 material balances and 6 independent specifications forming a total of 20 equations.

21 process variables - 20 equations = 1 DOF

The extra degree of freedom exists because there is no specification that determines the magnitude of the material flows.

Part b. To start this calculation, assume the total feed is 100 kgmol/hr. This resolves the extra degree of freedom and will allow us to solve for the requested yield and compositions. With this basis, the feed specifications become

Feed Specifications (3)

$$C_{<1>} = 36 \text{ kgmol/hr}$$

$$H_{<1>} = 60 \text{ kgmol/hr}$$

$$N_{<1>} = 4 \text{ kgmol/hr}$$

Starting with the equations involving the inert, we have

$$N_{<2>} = 4 \text{ kgmol/hr} + N_{<5>}$$

Because $N_{<5>} = 0.95N_{<4>}$ and $N_{<4>} = N_{<3>}$ and $N_{<3>} = N_{<2>}$, we can substitute $N_{<5>} = 0.95N_{<2>}$ to get

$$N_{<2>} = 4 \text{ kgmol/hr} + 0.95N_{<2>}$$

Solving for $N_{<2>}$

$$N_{<2>} = \frac{4 \text{ kgmol/hr}}{1 - 0.95} = 80 \text{ kgmol/hr}$$

At this stage we can fill out a portion of the stream table

	1	2	3	4	5	6	7
CO	36	$C_{<2>}$	$C_{<3>}$	$C_{<4>}$	$C_{<5>}$	$C_{<6>}$	-
H ₂	60	$H_{<2>}$	$H_{<3>}$	$H_{<4>}$	$H_{<5>}$	$H_{<6>}$	-
N ₂	4	80	80	80	76	4	-
CH ₃ OH	-	-	$M_{<3>}$	-	-	-	$M_{<7>}$

Hydrogen is the limiting reactant

$$H_{<2>} = 60 \text{ kgmol/hr} + H_{<5>}$$

We have $H_{<5>} = 0.95H_{<4>}$, $H_{<4>} = H_{<3>}$, and $H_{<3>} = 0.80H_{<2>}$ which gives

$$H_{<2>} = 60 \text{ kgmol/hr} + 0.95 \times 0.80H_{<2>}$$

Solving

$$H_{<2>} = \frac{60 \text{ kgmol/hr}}{1 - 0.95 \times 0.80} = 250 \text{ kgmol/hr}$$

We can now fill out another line of the stream table

	1	2	3	4	5	6	7
CO	36	$C_{<2>}$	$C_{<3>}$	$C_{<4>}$	$C_{<5>}$	$C_{<6>}$	-
H ₂	60	250	200	200	190	10	-
N ₂	4	80	80	80	76	4	-
CH ₃ OH	-	-	$M_{<3>}$	-	-	-	$M_{<7>}$

Solving for the extent of reaction

$$\xi = \frac{H_{<2>} - H_{<3>}}{2} = 25 \text{ kgmol/hr}$$

This allows us to solve for $M_{<3>}$ and $M_{<7>}$

	1	2	3	4	5	6	7
CO	36	$C_{<2>}$	$C_{<3>}$	$C_{<4>}$	$C_{<5>}$	$C_{<6>}$	-
H ₂	60	250	200	200	190	10	-
N ₂	4	80	80	80	76	4	-
CH ₃ OH	-	-	25	-	-	-	25

We now have all the information needed to compute yield.

$$\text{Yield with respect to CO} = \frac{25 \text{ kgmol/hr}}{36 \text{ kgmol/hr}} = \boxed{0.694} = \boxed{69.4\%}$$

$$\text{Yield with respect to H}_2 = \frac{25 \text{ kgmol/hr}}{\frac{60 \text{ kgmol/hr}}{2}} = \boxed{0.833} = \boxed{83.3\%}$$

The factor of 2 is needed because two moles of H₂ are required to produce each mole of CH₃OH. Another way to see this is that 10 kgmol/hr of H₂ is removed from the process through the purge stream, so the other 50 kgmol/hr is converted to the methanol product. Thus

$$\text{Yield with respect to H}_2 = \frac{50 \text{ kgmol/hr}}{60 \text{ kgmol/hr}} = \boxed{0.833} = \boxed{83.3\%}$$

Part c. We need to finish solving the material balances to find the reactor inlet composition. For the CO flow rates

$$C_{<2>} = 36 \text{ kgmol/hr} + C_{<5>}$$

where $C_{<5>} = 0.95C_{<4>}$, $C_{<4>} = C_{<3>}$, and $C_{<3>} = C_{<2>} - 25 \text{ kgmol/hr}$, so

$$C_{<2>} = 36 \text{ kgmol/hr} + 0.95(C_{<2>} - 25 \text{ kgmol/hr})$$

Solving

$$C_{<2>} = \frac{36 \text{ kgmol/hr} - 0.95 \times 25 \text{ kgmol/hr}}{1 - 0.95} = 245 \text{ kgmol/hr}$$

	1	2	3	4	5	6	7
CO	36	245	220	220	209	11	-
H ₂	60	250	200	200	190	10	-
N ₂	4	80	80	80	76	4	-
CH ₃ OH	-	-	25	-	-	-	25
TOTAL	100	575	525	500	475	25	25

The reactor inlet is stream < 2 >. The fraction of inert in that stream is

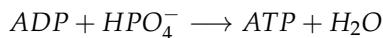
$$y_{N_2,<2>} = \frac{80 \text{ kgmol/hr}}{575 \text{ kgmol/hr}} = \boxed{0.139} = \boxed{13.9\%}$$

compared to 4% in the process inlet stream.

P4.41 ATP/ADP Equilibrium at Standard Conditions (NEEDS WORK)

<http://sandwalk.blogspot.com/2011/11/better-biochemistry-free-energy-of-atp.html>

Chemical energy for cellular metabolism is stored by the reaction of ADP to form ATP



for which $\Delta\hat{H}_r^\circ = +20.5 \text{ kJ/gmol}$ and $\Delta\hat{G}_{rxn}^\circ = -3.4 \text{ kJ/gmol}$ under standard conditions. (Note the signs are different).

- (15pts) What is the equilibrium constant for this reaction under physiological conditions (i.e., $T = 37^\circ\text{C}$)?
- (10pts) Assume the mole fraction of water is 1, and of HPO_4^- is 0.0001. What would be the ratio of ATP to ADP at equilibrium? (The body maintains this ratio far from equilibrium, which is a good thing.)

Solution

Part a.

The equilibrium constant at 37°C is determined with the Van't Hoff equation

$$\begin{aligned} \ln K_r &= -\frac{1}{R} \left[\frac{\Delta\hat{G}_r^\circ - \Delta\hat{H}_r^\circ}{298} + \frac{\Delta\hat{H}_r^\circ}{T} \right] \\ &= \frac{1}{8.314 \text{ J/gmol-K}} \left[\frac{(-3,400) - (20,500)}{298} + \frac{20,500}{273 + 37} \right] \\ &= 1.693 \end{aligned}$$

so that

$$K_r = \boxed{5.44}$$

Part b. At equilibrium the equilibrium constant is equal to the

equilibrium quotient

$$\begin{aligned} K_r &= \frac{a_{ATP}a_{H_2O}}{a_{ADP}a_{HPO_4^-}} \\ &= \frac{x_{ATP}x_{H_2O}}{x_{ADP}x_{HPO_4^-}} \\ &= \frac{x_{ATP} \times 1}{x_{ADP} \times 0.0001} \end{aligned}$$

where we have used the ideal liquid assumption for activity $a_k = x_k$. Solving for the ratio ATP to ADP

$$\begin{aligned} \frac{x_{ATP}}{x_{ADP}} &= \frac{0.0001}{1} \times K_r \\ &= \boxed{0.000544} \end{aligned}$$

STP is 25 °C and 1 atm.

	$\Delta\hat{G}_f^\circ$ kJ/gmol	$\Delta\hat{H}_f^\circ$ kJ/gmol
O ₂ (g)	0	0
SO ₂ (g)	-299.9	-296.81
SO ₃ (g)	-370.66	-394.93

$$\ln K_q = \frac{-\Delta G_{rxn}}{RT}$$

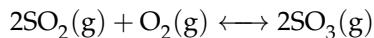
$$\ln K_{q,T} = -\frac{1}{R} \left[\frac{\Delta\hat{G}_{rxn}^\circ - \Delta\hat{H}_{rxn}^\circ}{298} + \frac{\Delta\hat{H}_{rxn}^\circ}{T} \right]$$

$$\Delta G = \Delta H - T\Delta S$$

$$R = 8.314 \text{ J/gmol}\cdot\text{K}$$

P4.42 Contact Process for Sulfuric Acid

One step in the Contact Process for the production of sulfuric acid is the homogeneous gas phase conversion of sulfur dioxide (SO₂) to sulfur trioxide (SO₃) via the reaction



The reaction is conducted in a steady-state continuous reactor with a vanadium oxide (V₂O₅) catalyst operating at 450 °C and 2 atm.

The feed is a 100 kgmol/hr equimolar mixture of sulphur dioxide and oxygen.

- Calculate the standard enthalpy, Gibb's free energy, and entropy of reaction.
- Compute the equilibrium constant at the reactor operating conditions.
- Set up and solve for the composition of the reactor exit stream.

Solution

Part a. The standard enthalpy of reaction is given by

$$\begin{aligned}\Delta\hat{H}_{rxn}^\circ &= \sum_{s=1} v_s \Delta\hat{H}_{f,s}^\circ \\ &= -2\Delta\hat{H}_{f,\text{SO}_2}^\circ - \Delta\hat{H}_{f,\text{O}_2}^\circ + 2\Delta\hat{H}_{f,\text{SO}_3}^\circ \\ &= -2(-296.81 \text{ kJ/gmol}) - 1(0) + 2(-394.93 \text{ kJ/gmol}) \\ &= \boxed{-196.24 \text{ kJ/gmol}}\end{aligned}$$

For the standard Gibb's free energy

$$\begin{aligned}\Delta\hat{G}_{rxn}^\circ &= \sum_{s=1} v_s \Delta\hat{G}_{f,s}^\circ \\ &= -2\Delta\hat{G}_{f,\text{SO}_2}^\circ - \Delta\hat{G}_{f,\text{O}_2}^\circ + 2\Delta\hat{G}_{f,\text{SO}_3}^\circ \\ &= -2(-299.9 \text{ kJ/gmol}) - 1(0) + 2(-370.66 \text{ kJ/gmol}) \\ &= \boxed{-141.52 \text{ kJ/gmol}}\end{aligned}$$

The standard entropy of reaction is given by

$$\begin{aligned}\Delta\hat{S}_{rxn}^\circ &= \frac{\Delta\hat{H}_{rxn}^\circ - \Delta\hat{G}_{rxn}^\circ}{T^\circ} \\ &= \frac{(-196.24 \text{ kJ/gmol}) - (-141.52 \text{ kJ/gmol})}{298.15 \text{ K}} \\ &= \boxed{-0.1835 \text{ kJ/gmol}\cdot\text{K}} \\ &= \boxed{-183.5 \text{ J/gmol}\cdot\text{K}}\end{aligned}$$

Part b. The equilibrium constant at another temperature is computed using the van't Hoff equation

$$\begin{aligned}\ln K_{a,T} &= -\frac{1}{R} \left[\frac{\Delta\hat{G}_{rxn}^\circ - \Delta\hat{H}_{rxn}^\circ}{298} + \frac{\Delta\hat{H}_{rxn}^\circ}{T} \right] \\ &= -\frac{1}{8.314 \text{ J/gmol}\cdot\text{K}} \left[\frac{(-141,520 \text{ J/gmol}) - (-196,240 \text{ J/gmol})}{298 \text{ K}} + \frac{(-196,240 \text{ J/gmol})}{(450 + 273.15) \text{ K}} \right] \\ &= 10.554\end{aligned}$$

Taking the exponential

$$K_a = e^{10.554} = \boxed{38,322}$$

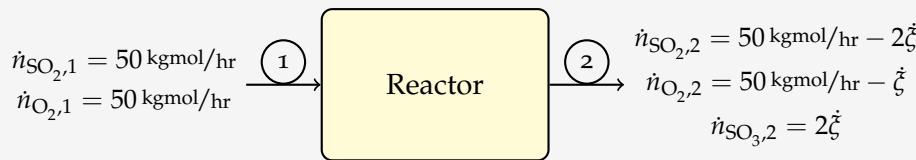
Which tells us that the forward reaction is strongly favored at the operating conditions of the reactor.

Part c. The equilibrium quotient for this gas phase reaction is

given by

$$\begin{aligned} K_a &= \frac{a_{\text{SO}_3}^2}{a_{\text{SO}_2}^2 a_{\text{O}_2}} \\ &= \frac{(y_{\text{SO}_3} P)^2}{(y_{\text{SO}_2} P)^2 y_{\text{O}_2} P} \\ &= \frac{y_{\text{SO}_3}^2}{y_{\text{SO}_2}^2 y_{\text{O}_2} P} \end{aligned}$$

Drawing a diagram of the process



where we have included the material balances. The total molar flow of the reactor effluent is

$$\dot{n}_{\text{Total}} = 100 \text{ kgmol/hr} - \dot{\xi}$$

The mole fractions in the reactor effluent are then

$$\begin{aligned} y_{\text{SO}_2} &= \frac{50 \text{ kgmol/hr} - 2\dot{\xi}}{100 \text{ kgmol/hr} - \dot{\xi}} \\ y_{\text{O}_2} &= \frac{50 \text{ kgmol/hr} - \dot{\xi}}{100 \text{ kgmol/hr} - \dot{\xi}} \\ y_{\text{SO}_3} &= \frac{2\dot{\xi}}{100 \text{ kgmol/hr} - \dot{\xi}} \end{aligned}$$

Substituting these values into the equilibrium expression

$$\begin{aligned} K_a &= \frac{\left(\frac{2\dot{\xi}}{100 \text{ kgmol/hr} - \dot{\xi}}\right)^2}{\left(\frac{50 \text{ kgmol/hr} - 2\dot{\xi}}{100 \text{ kgmol/hr} - \dot{\xi}}\right)^2 \left(\frac{50 \text{ kgmol/hr} - \dot{\xi}}{100 \text{ kgmol/hr} - \dot{\xi}}\right) P} \\ &= \frac{(2\dot{\xi})^2 (100 \text{ kgmol/hr} - \dot{\xi})}{(50 \text{ kgmol/hr} - 2\dot{\xi})^2 (50 \text{ kgmol/hr} - \dot{\xi}) P} \\ K_a P &= \frac{(2\dot{\xi})^2 (100 \text{ kgmol/hr} - \dot{\xi})}{(50 \text{ kgmol/hr} - 2\dot{\xi})^2 (50 \text{ kgmol/hr} - \dot{\xi})} \end{aligned}$$

Plugging in values, we need to find a value of ξ which satisfies

$$76,664 = f(\xi) = \frac{(2\xi)^2 (100 - \xi)}{(50 - 2\xi)^2 (50 - \xi)}$$

The maximum meaningful value for ξ is 25 for which the right hand side would have a value of infinity. Let's try a number slightly smaller, say $\xi = 24.5$ we get

$$f(24.5) = 7,109$$

Try a larger number, $\xi = 24.9$ we get

$$f(24.9) = 185,509$$

So we have a decent bound on the answer. To solve this in Matlab, we use the following two lines of code

```
f = @(x) ((2*x)^2 * (100-x))/((50-2*x)^2*(50-x)) - 76664
fzero(f,[24.5,24.9])
```

which returns the answer $\xi = 24.8449$. Evaluating the expressions for the mole fractions of the reactor effluent gives us our final answer.

$$y_{SO_2} = \boxed{0.004}$$

$$y_{O_2} = \boxed{0.334}$$

$$y_{SO_3} = \boxed{0.661}$$

4.5 Exercises

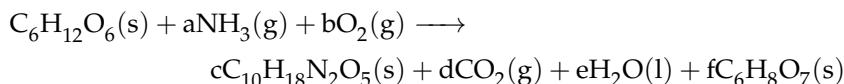
P4.43 Short Answer Questions

The inlet flow to a reactor consists of 1 kg/hour of A, the outlet flow is 0.25 kg/hour of A, 0.3 kg/hour of the desired product P, and the remainder is a waste by product.

- a. What is the conversion?
- b. What is the yield?
- c. What is the selectivity?

P4.44 Citric Acid Production

Citric acid ($\text{C}_6\text{H}_8\text{O}_7$) is manufactured by the fermentation of glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) at 25°C



The material $\text{C}_{10}\text{H}_{18}\text{N}_2\text{O}_5(\text{s})$ refers to the biomass produced as a byproduct of the fermentation.

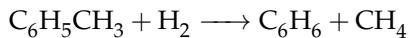
Two product streams exit from the fermentor. One is a liquid stream consisting of water, all dissolved solids, and ammonia. The other is a vapor stream that contains all gases and one tenth of the water produced in the reaction. All streams are at atmospheric pressure and 25°C .

The inlet flowrate of glucose is 20 kg/hour, and the inlet flowrate of ammonia is 0.4 kg/hour. Oxygen is feed at a rate of 7.5 kg/hour. The fractional conversion of glucose is 0.91.

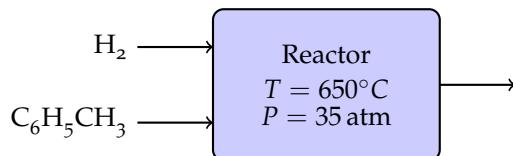
- How many independent reactions can be constructed from these components?
- From the process data given, estimate the values of a, b, c, d, e, and f in the above reaction).

P4.45 HDA Reactor

The reaction



takes place in a well-mixed, homogeneous, vapor phase reactor at 650°C and 35 atm. To avoid coking, hydrogen must be fed to the reactor in a 5:1 molar ratio of hydrogen:toluene. In a laboratory setting, the reactor effluent is measured to contain 5 mol% toluene.



- What is the fractional conversion of toluene?
- What is the composition of the reactor effluent?
- Is the reactor operating at or near the reaction equilibrium? (Hint: This question does not require you to solve for the equilibrium composition).

Species	MW
$\text{C}_6\text{H}_{12}\text{O}_6$	180.16
NH_3	17.03
O_2	32.00
$\text{C}_{10}\text{H}_{18}\text{N}_2\text{O}_5$	246.26
CO_2	44.01
H_2O	18.01
$\text{C}_6\text{H}_8\text{O}_7$	192.13

$$\ln K_a = \frac{-\Delta G_{rxn}}{RT}$$

P4.46 Equilibrium Reaction Problem

Glucose can be isomerized to fructose over an enzyme catalyst. At 25 °C the reaction



$$R = 8.314 \text{ J/gmol}\cdot\text{K}$$

is fast, but the conversion at equilibrium is only 40%. Estimate the Gibb's free energy of reaction at 25 °C.

$$\ln K_{a,T} = -\frac{1}{R} \left[\frac{\Delta \hat{G}_{rxn}^\circ - \Delta \hat{H}_{rxn}^\circ}{298} + \frac{\Delta \hat{H}_{rxn}^\circ}{T} \right]$$

$$\Delta G = \Delta H - T\Delta S$$

P4.47 Reaction Equilibrium

A common laboratory demonstration is the equilibrium reaction



NO_2 has a brown color often seen in polluted urban air, while N_2O_4 is colorless. Changing of the equilibrium mixture changes its color. Consider a gas mixture at 1 atm with an initial mole fraction for NO_2 of 0.5, the remainder inerts. Compute the equilibrium constant, the equilibrium extent of reaction, and the fractional conversion for this mixture at 0 °C and 40 °C.

5

Separations

5.1 Summary

Concepts	Skills	Practice Problems
Phase Diagrams	<ul style="list-style-type: none">- label regions on a pure component phase diagram- identify and describe triple point- identify and describe critical point- obtain pure component data from textbook tables and standard reference sources- Calculate pure component vapor pressure with Antoine's equation- plot vapor/liquid equilibrium line using Antoine's equation - Use Gibbs phase rule to determine how much information is necessary to specify the thermodynamic state of a system	
Vapor-Liquid Equilibria	<ul style="list-style-type: none">- use Pxy and Txy diagrams for ideal and nonideal systems- identify azeotropes- Calculate mixture vapor pressure and composition for a multicomponent mixture using Raoult's law- locate bubble and dew point curves on a Txy- translate a Txy diagram to an xy diagram- Solve for the dew point temperature/composition of a binary mixture- Solve for the bubble point temperature/composition of a binary mixture- estimate flash flow rates using the lever rule	

Isothermal Flash

- Calculate K-factors from pure component data
- Solve isothermal flash at known P and T using the Rachford-Rice Equation
- Solve material balances using vapor fraction.

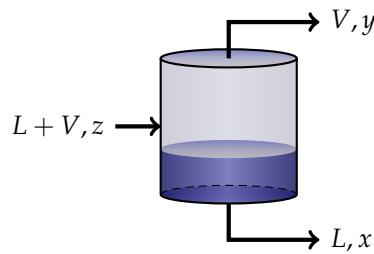
Binary Distillation

- draw and label major components, internal and external flows
- explain difference between distillation and flash
- draw operating lines on a xy diagram
- estimate minimum reflux
- estimate the number of trays required
- estimate boilup and reflux ratios
- estimate location for the feed tray

5.2 Txy Diagrams

5.2.1 Lever Rule

The lever rule provides significant insight into the use and interpretation of the Txy diagram. We begin by considering a component balance on a simple flash separator.



Given liquid and vapor flowrates L and V , the mass balance for any species is

$$0 = (L + V)z - Lx - Vy$$

or

$$L(z - x) = V(y - z)$$

where x and y are the fractions of the component in the liquid and vapor streams, and z is the fraction in the feed stream. Note that is true whether we are working in mass or molar units.

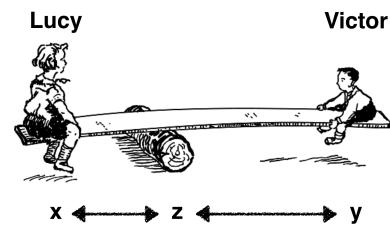
Solving for the ratio of vapor to liquid gives us the *lever rule*

$$\frac{V}{L} = \frac{z - x}{y - z}$$

The differences $y - z$ and $y - z$ are the change in composition from the feed to the vapor and liquid streams. The lever rule shows us the ratio of the vapor to liquid flow rates is equal to the inverse of the ratio of the change in compositions.

WHY IS IT CALLED THE LEVER RULE?

Lucy (mass L) and Victor (mass V) have positioned themselves on a teeter-totter so that they exactly balance.



The teeter-totter is balanced when the ratio of masses is equal to the inverse of the ratio of lever arms. That is, when

$$\frac{V}{L} = \frac{z - x}{y - z}$$

That is why this formula is called the *Lever Rule*.

5.3 Binary Distillation

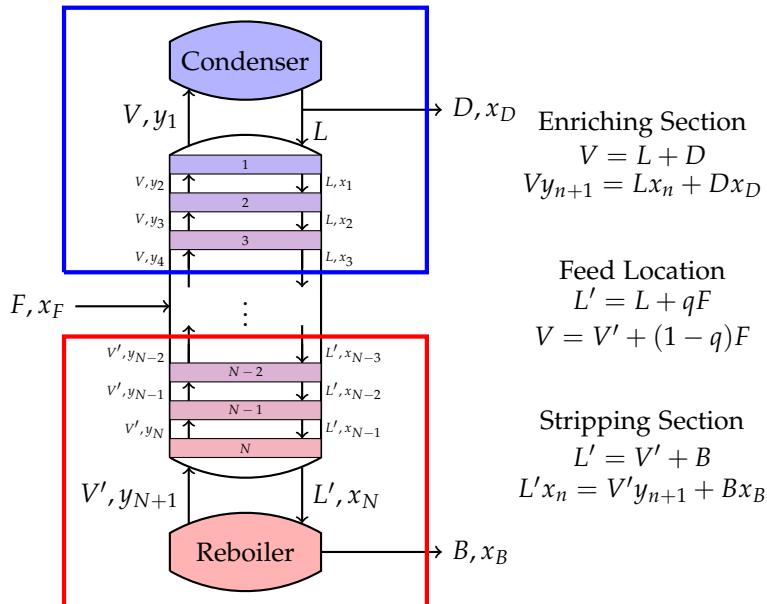


Figure 5.1: Binary Distillation

Enriching Section

$$V = L + D$$

$$V y_{n+1} = L x_n + D x_D$$

Feed Location

$$L' = L + qF$$

$$V = V' + (1 - q)F$$

Stripping Section

$$L' = V' + B$$

$$L' x_n = V' y_{n+1} + B x_B$$

5.3.1 Enriching (Rectifying) Section

Mole Balance for trays 1 through n

$$V = L + D$$

$$V y_{n+1} = L x_n + D x_D$$

Operating Line

$$\begin{aligned} y_{n+1} &= \frac{L}{V} x_n + \frac{D}{V} x_D \\ &= \frac{L}{L+D} x_n + \frac{D}{L+D} x_D \end{aligned}$$

Enriching Operating Line

$$y_{n+1} = \frac{R}{R+1} x_n + \frac{1}{R+1} x_D \quad \text{for Reflux Ratio } R = \frac{L}{D}$$

5.4 Solved Problems

P5.48 Quick Answer Questions

The following questions should be answered in one sentence, a quick sketch, or a single formula or calculation.

- What is vapor pressure?
- What is an equilibrium stage?
- What is Raoult's law?

Solution

Raoult's law says that the vapor pressure of each component of an ideal solution is equal to the product of the saturation pressure times the mole fraction. That is,

$$P_i = P_i^{sat}(T)x_i$$

Assuming the vapor phase is also an ideal mixture

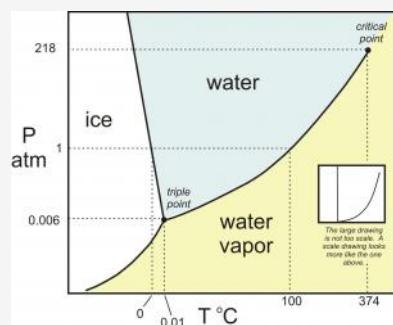
$$Py_i = P_i^{sat}(T)x_i \quad \text{or} \quad y_i = \frac{P_i^{sat}(T)x_i}{P}$$

P5.49 Quick Answer Question

Sketch a phase diagram for a pure substance, such as water. Identify the triple point, the critical point, the vapor-liquid equilibrium line. Label the regions of the diagram as either liquid, solid, or vapor.

Solution

A typical phase diagram is shown in this figure.



P5.50 Quick Answer Question

Henry's law constant $H_i = \frac{y_i P}{x_i}$ for oxygen in water is 40,100 atmospheres. The gas phase mole fraction of oxygen is 0.21. How many grams of oxygen (MW = 32) are in one liter (i.e., 55.5 moles) of water?

Solution

Rearranging Henry's law

$$x_i = \frac{y_i P}{H_i} = \frac{0.21 \times 1 \text{ atm}}{40,100 \text{ atm}} = 0.000052$$

so the mass of oxygen is given by

$$m_i = 55.5 \text{ gmol/liter} \times 32 \text{ g/gmol} \times 0.000052 = \boxed{0.0093 \text{ g/liter}}$$

Out of curiosity, what is the corresponding gas volume?

$$V_{O_2} = \frac{nRT}{P} = \frac{55.5 \times 0.000052 \times 0.082 \times 298.15}{1 \text{ atm}} = 0.007 \text{ liters} = 7 \text{ ml}$$

The equivalent air volume would be approximately 35 ml which is how fish survive. The Henry's law constant for O_2 decreases sharply with temperature, which is why many species of fish prefer cold water.

P5.51 Flash Separation of n-Hexane and n-Octane

A liquid mixture of 40 mol% n-hexane and 60 mol% n-octane is fed to a flash drum maintained at steady state operating temperature of 130 deg C and pressure of 1520 mmHg. The feed rate is 100 kg-mol/min. The vapor and liquid are removed continuously.

- What are the flowrates of the exiting vapor and liquid streams?
- What are the compositions of the liquid and vapor streams?
- What is the fractional recovery of n-hexane in the vapor stream, and the fractional recovery of n-octane in the liquid stream?

Solution

What we have here is an isothermal flash modeled by the Rachford-Rice equation

$$0 = \frac{z_H (K_H - 1)}{1 + \phi (K_H - 1)} + \frac{z_O (K_O - 1)}{1 + \phi (K_O - 1)}$$

where ϕ is the vapor fraction and $z_H = 0.4$ and $z_O = 0.6$. As shown in class, the case of two components can be simplified to

$$0 = z_H (K_H - 1) (1 + \phi (K_O - 1)) + z_O (K_O - 1) (1 + \phi (K_H - 1))$$

Antoine's equation

$$\log_{10} P^{sat}[\text{mmHg}] = A - \frac{B}{C + T[\text{K}]}$$

	Coefficients		
	A	B	C
n-Hexane	6.87601	1171.17	224.41
n-Octane	6.91868	1351.99	209.15

Solving for ϕ ,

$$\phi = -\frac{z_H (K_H - 1) + z_O (K_O - 1)}{z_H (K_O - 1) + z_O (K_H - 1)}$$

Computing the K-values

$$K_H = \frac{P_H^{sat}(T)}{P} = \frac{10^{A_H - B_H / (C_H + T)}}{1520} = \frac{3727}{1520} = 2.4525$$

$$K_O = \frac{P_O^{sat}(T)}{P} = \frac{10^{A_O - B_O / (C_O + T)}}{1520} = \frac{855.6}{1520} = 0.5629$$

Plugging into the given formula

$$\phi = -\frac{0.4 \times 1.4525 + 0.6 \times (-0.4371)}{0.4 \times (-0.4371) + 0.6 \times 1.4525} = 0.502$$

Antoine Coefficients

	A	B	C
CH ₃ CHO	6.81089	992	230
C ₂ H ₅ OH	8.04494	1554.3	222.65
CH ₃ COOC ₂ H ₅	7.09808	1238.7	217

P5.52 Vapor-Liquid Equilibrium Problem

The reactor effluent in the above example is all gas and composed of 41.7 mol% ethanol, 30.65 mol% hydrogen, 24.6 mol% acetaldehyde, and 3.0 mol% ethyl acetate. The effluent stream is passed through a membrane separator recovering 100% of the hydrogen. The remaining vapor is sent to a condenser operating at a steady temperature of 65 °C. Using Raoult's law,

- How high would the operating pressure be to completely condense the vapor?

Solution

Consider a basis consisting of 1 gmol of effluent gas. Once the hydrogen has been removed, the composition of the remaining vapor is given by

$$z_{EtOH} = \frac{0.417}{0.417 + 0.246 + 0.03} = 0.6017$$

$$z_{Acet} = \frac{0.246}{0.417 + 0.246 + 0.03} = 0.355$$

$$z_{EtAc} = \frac{0.03}{0.417 + 0.246 + 0.03} = 0.04329$$

To completely condense the vapor, the operating pressure needs to be greater than the sum of partial pressures. Assuming all of the feed is in the liquid phase at that point (i.e., $x_i = z_i$),

we use Raoult's law

$$\begin{aligned} P &\geq P_{EtOH} + P_{Acet} + P_{EtAc} \\ &\geq z_{EtOH} P_{EtOH}^{sat}(65) + z_{Acet} P_{Acet}^{sat}(65) + z_{EtAc} P_{EtAc}^{sat}(65) \end{aligned}$$

Using the Antoine parameters provided in the problem statement

$$P_{EtOH}^{sat}(65) = 10^{8.04494 - \frac{1554.3}{222.65+65}} = 438.0 \text{ mmHg}$$

$$P_{Acet}^{sat}(65) = 10^{6.81089 - \frac{992}{230+65}} = 2806.6 \text{ mmHg}$$

$$P_{EtAc}^{sat}(65) = 10^{7.09808 - \frac{1238.7}{217+65}} = 507.6 \text{ mmHg}$$

Plugging these numbers into the

$$P \geq 1044.2 \text{ mmHg}$$

- b. At what pressure would the first drop of condensate appear?

Solution

The first drop of condensate occurs when almost all of the feed is in the vapor phase (i.e., $y_i = z_i$) and $z_i P = x_i P_i^{sat}(T)$. The equation we need to solve is

$$\sum_i x_i = \sum_i z_i \frac{P}{P_i^{sat}(T)} = P \sum_i \frac{z_i}{P_i^{sat}(T)} = 1$$

which has the solution

$$P = \frac{1}{\sum_i \frac{z_i}{P_i^{sat}(T)}}$$

plugging in the numbers from above

$$P = 630 \text{ mmHg}$$

So what we've determined is that the mixture begins to condense at a pressure of 630 mmHg, and is completely condensed when the pressure reaches 1044 mmHg.

- c. If the operating pressure was 760 mmHg, what fraction of the feed would remain in the vapor phase?

Solution

The Rachford-Rice equation solves this problem.

$$\sum_i \frac{z_i(K_i - 1)}{1 + \phi(K_i - 1)} = 0$$

where $K_i = \frac{P_i^{sat}(T)}{P}$ and where ϕ is the vapor fraction. At an operating pressure of 1 atm

$$K_{EtOH} = \frac{2806.6}{760} = 3.69$$

$$K_{Acet} = \frac{438.0}{760} = 0.576$$

$$K_{EtAc} = \frac{507.6}{760} = 0.668$$

The equation to solve is then

$$0 = \frac{0.355(3.69 - 1)}{1 + \phi(3.69 - 1)} + \frac{0.6017(0.576 - 1)}{1 + \phi(0.576 - 1)} + \frac{0.04329(0.668 - 1)}{1 + \phi(0.668 - 1)}$$

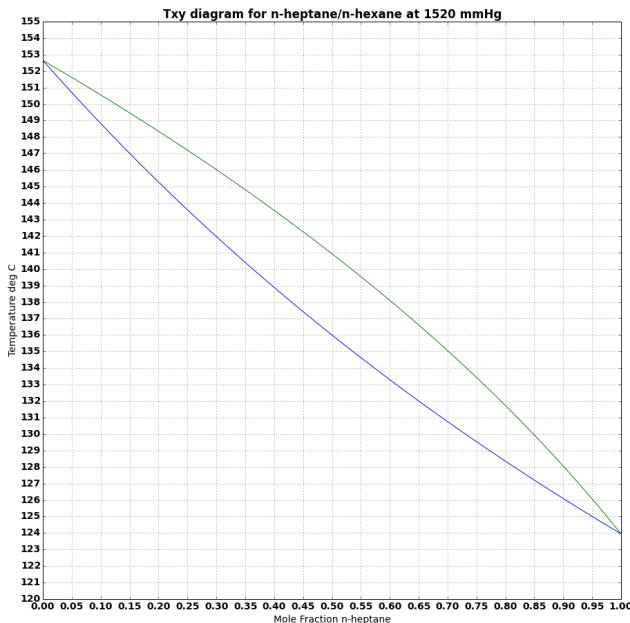
$$0 = \frac{0.355(2.69)}{1 + \phi(2.69)} + \frac{0.6017(-0.424)}{1 + \phi(-0.424)} + \frac{0.04329(-0.332)}{1 + \phi(-0.332)}$$

The solution to this equation is $\phi = 0.609$.

P5.53 Binary Distillation of an n-heptane/n-octane Mixture

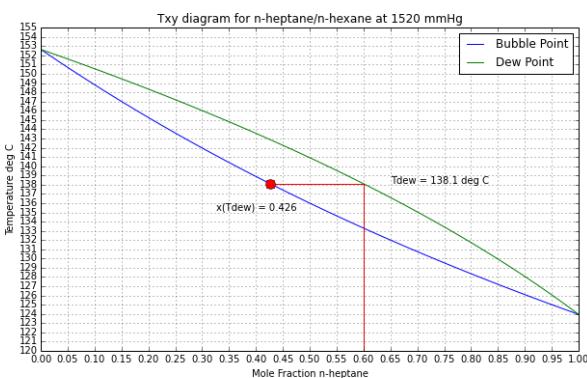
A chemicals plant receives from a nearby refinery a 500 kg-mol/hour stream containing 60 mol% n-heptane, 40 mol% n-octane. The operator needs to separate the mixture so that one product stream is 95 mol% pure n-octane. The operator would like to recover at least 95% of the n-octane.

- a. Can the desired product purity be accomplished in a single flash drum? Show why or why not on the accompanying Txy diagram.



Solution

The problem asked if the purity specification for the n-octane stream can be met in a single stage flash drum. The feed concentration of n-heptane is 60 mol%. The desired n-octane product would have an n-heptane concentration of 5 mol%. For the given feed, we see the minimum possible concentration of n-heptane would be at the dew point of approximate 138 deg C, yielding a liquid phase composition of about 43 mol% n-heptane, and 57 mol% n-octane. This is far short of the stream specification, so the answer is NO.



- Determine the feed and product stream flows and compositions

for a binary distillation column meeting the specifications.

Solution

The mass balances are

$$F = D + B$$

$$Fx_F = Dx_D + Bx_B$$

where we know

$$F = \boxed{500 \text{ kgmol/hour}}$$

$$x_F = \boxed{0.6 \text{ mol fraction}}$$

$$x_B = \boxed{0.05 \text{ mol fraction}}$$

From the recovery specification, 95% of the feed n-octane goes the bottoms stream, so $0.95F(1 - x_F) = B(1 - x_B)$ and

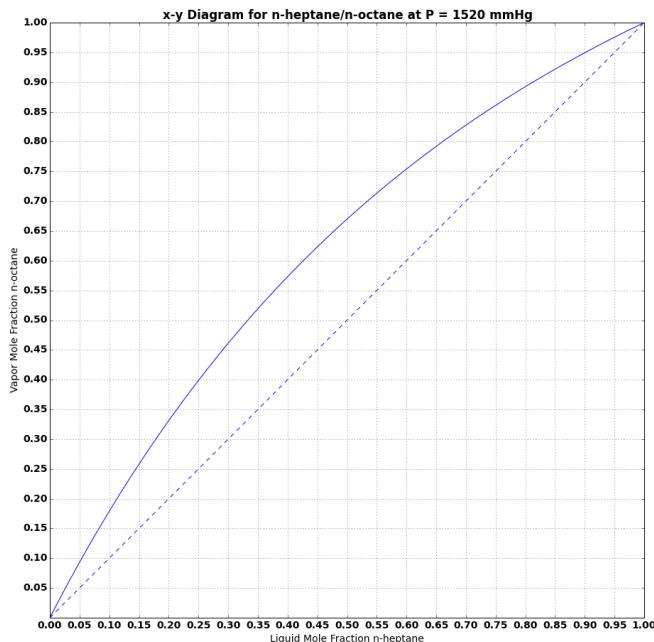
$$B = \frac{0.95F(1 - x_F)}{1 - x_B} = \frac{0.95 \times 500 \times (1 - 0.6)}{1 - 0.05} = \boxed{200 \text{ kgmol/hour}}$$

Substituting

$$D = F - B = 500 - 200 = \boxed{300 \text{ kgmol/hour}}$$

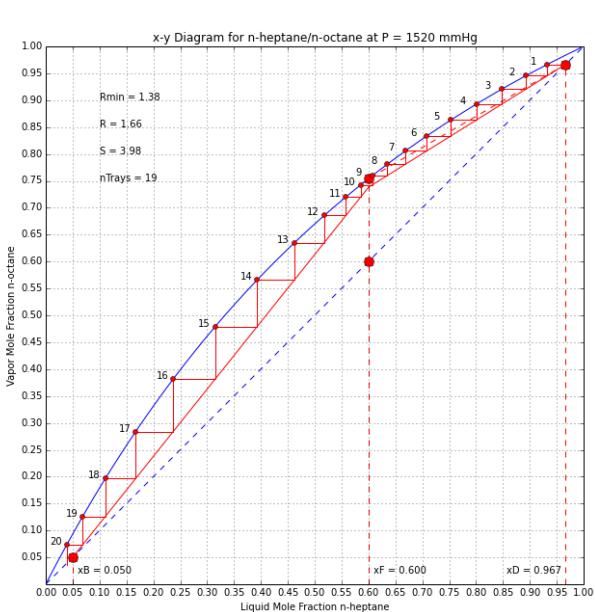
$$x_D = \frac{Fx_F - Bx_B}{D} = \frac{500 \times 0.6 - 200 \times 0.05}{300} = \boxed{0.967 \text{ mol fraction}}$$

- c. Solve for the reflux ratio, boilup ratio, and number of equilibrium trays needed to meet the specifications.



Solution

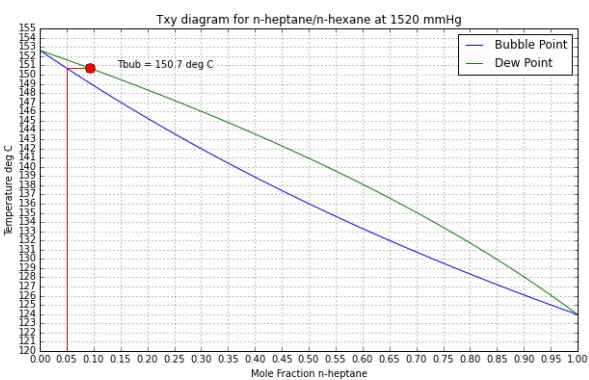
The solution is found using the McCabe-Thiele method assuming a reflux ratio equal to 1.2 times the minimum reflux ratio.



- d. What is the operating temperature of the reboiler?

Solution

The liquid phase composition of the reboiler is the same as the bottoms stream, that is x_B . The operating temperature is the bubble point of an n-heptane/n-octane stream where $x_B = 0.05$ mol%. The bubble point curve on the Txy diagram gives an approximate temperature of 151 deg C. A more bubble point calculation gives a more precise answer of 150.7 C.



5.5 Exercises

P5.54 Txy Diagram for 1,4 Dioxane/Water

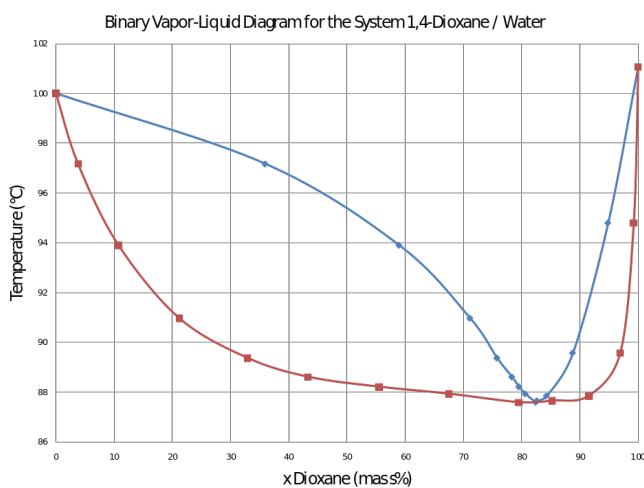


Figure 5.2: Txy diagram for binary 1,4 dioxane/water system at 1 atm. Source: Wikimedia Commons

A Txy diagram for a binary mixture of 1,4 dioxane and water is displayed in the accompanying figure. Note that the composition variables are expressed in mass fraction.

A feed stream composed of 30 wt% dioxane at 50 kg/hr is processed in a flash drum operating at 1 atm and 92 °C.

- What are the liquid and vapor phase compositions?
- What are the flow rates of the liquid and vapor streams leaving the flash drum?

P5.55 Solving Separation Problems

A gas stream contains 40 mol% isopropanol in air and flows at 240 gmol/min, 70°C, and 1 atm. You are using a condenser operating at a lower temperature to liquefy and recover the isopropanol for reuse in the process. The present condenser uses a chilled water coil to cool the gas stream to 25°C and produces a liquid condensate stream in equilibrium with the existing gas stream.

- Sketch a process flowsheet.
- What physical property data will you need to solve this problem? Be explicit.
- Assume you have a matlab function K(T,P) to compute the K-value of isopropanol. Write out the material balance equations to solve for the process flows. Try to make your solution as close to workable Matlab/CVX file as you can.
- We wish to change the condenser operating temperature to recover 98% of the isopropanol. Outline the matlab calculations necessary to solve this problem. If you're unable to write out the Matlab code, at least show what additional equation(s) you need to solve, a flowchart showing how the calculation would work, what Matlab function(s) you'd need to use.

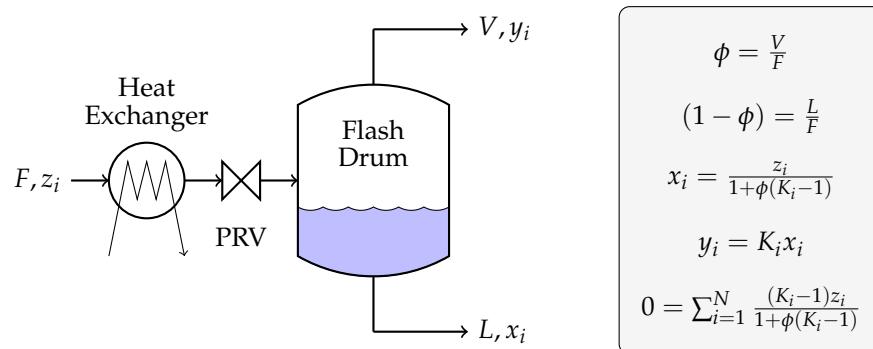
P5.56 Isothermal Flash for a Four Component System

After cooling, the reactor exit gases are initially separated in a flash drum operating at 147 °C and 3.5 atm.

- Based on the wide differences in volatility, the vapor fraction ϕ is sure to be close to a value of 0.85. Verify if this is true using the Rachford-Rice equation.
- Assuming a value $\phi = 0.85$, determine the compositions of the vapor and liquid phases exiting the isothermal flash.

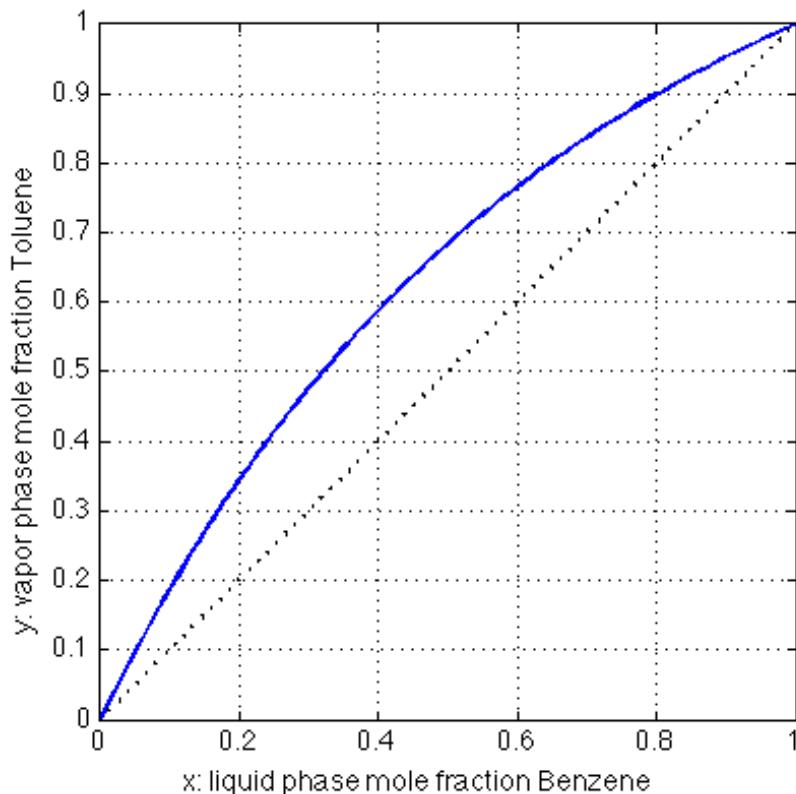
Species	z_i	T_b [°C]	K_i
Hydrogen	0.70	-253	99
Methane	0.15	-161	20
Benzene	0.10	80	0.01
Toluene	0.05	111	0.004

c. What is the fractional recovery of benzene?



P5.57 Binary Distillation Design

A saturated liquid of benzene and toluene, with the benzene mole fraction of $2/3$ has to be separated. The column operates at 3.5 atm. The benzene product must have a composition no less than 98 mol% and recover 95% of the benzene. Phase equilibrium data is shown below.



- a. If the inlet flowrate is 10 moles per hour, what are the the flowrates and compositions of the distillate and bottoms streams exiting the distillation tower?

- b. Estimate the number of trays required for the separation, and the location of the feed tray.

P5.58 Txy Diagram from Experimental Data

Dioxane ($C_4H_8O_2$) is used as a solvent, as a stabilizer for the transport of 1,1,1-trichloroethane in aluminum containers, and as an NMR reference standard in chemistry laboratories. It is also a common by-product and contaminant in the production of cosmetics. Dioxane is a possible carcinogen that has affected groundwater supplies in some geographic areas.

The accompanying table displays experimental data ¹ for a binary 1,4 dioxane/water system at 1 atm. Composition variables x and y refer to the dioxane mole fraction in the liquid and vapor phases, respectively.

- Prepare a Txy diagram for the 1,4 dioxane/water binary system. How would you describe this system?
- Suppose you are in charge of designing a process to clean up groundwater contaminated with 1,4 dioxane. What are the implications of this data for the design?

Chemical structure of 1,4 dioxane.
Source: Wikimedia Commons

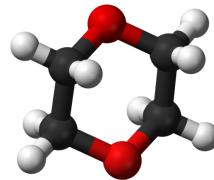


Table 5.2: Experimental Txy data for binary 1,4 dioxane/water system at 1 atm.

T [°C]	x [mol%]	y [mol%]
100.00	0.000	0.000
97.17	0.008	0.103
93.90	0.024	0.227
90.97	0.052	0.335
89.27	0.091	0.390
88.61	0.135	0.425
88.21	0.203	0.443
87.93	0.298	0.460
87.59	0.442	0.490
87.65	0.540	0.493
87.85	0.688	0.523
89.57	0.865	0.618
94.80	0.963	0.790
101.07	1.000	1.000

¹ Charles H. Schneider and Cecil C. Lynch. The ternary system: Dioxane—ethanol—water. *Journal of the American Chemical Society*, 65(6):1063–1066, 2014/06/05 1943

6

Energy Balances

6.1 Summary

Concepts	Skills	Practice Problems
Forms of Energy	<ul style="list-style-type: none">- describe kinetic, potential, and internal energy- provide definitions for internal, enthalpy, and Gibb's free energy	
State Variables	<ul style="list-style-type: none">- describe a 'state' variable- give examples of state variables- identify reference states for energy balance problems- generate "fictitious paths" from your reference state to your desired state- use heat capacities and phase data to calculate H and U from fictitious paths- describe and identify isothermal, adiabatic, isentropic process	
Steam Tables	<ul style="list-style-type: none">- compute liquid and vapor properties of sat. steam- determine thermodynamic and physical properties of superheated steam- solve energy balance problems - solve available work problems using Ts diagram	
Mechanical Work	<ul style="list-style-type: none">- Explain the difference between shaft work and flow work	
Adiabatic Flame Temperature	Calculate the adiabatic flame temperature for a specified combustion reaction	

6.2 Force, Work, and Power

6.2.1 Force

What is force? From Newton's law, force is equal to mass times acceleration

$$F = m \times A$$

Some typical units of force:

- Newton: The force required to accelerate 1 kg at 1 m/sec²
- dyne: The force required to accelerate 1 gram at 1 cm/sec²
- lb_f : The force to accelerate a mass weighing 1 lb at rate of 32.174 ft/sec².
(Think carefully about this one! Is a pound a measure of mass or of force?)



Force is direction and additive.

Force = the rate of change of momentum

$$F = m \frac{d^2x}{dt^2} = m \frac{dv}{dt} = \frac{dp}{dt}$$

Explain what is going on here. Force is being exerted on the door, but why are there no momentum changes?



6.2.2 Mechanical Work

Work is force acting through a distance

$$W = \int_C \vec{F} \cdot d\vec{s} = \int_{t_1}^{t_2} \vec{F} \cdot \frac{d\vec{s}}{dt} dt = \int_{t_1}^{t_2} \vec{F} \cdot \vec{v} dt$$



What to see a kJ? Other units are $ft - lb_f$, ergs.

6.2.3 Power

Power is the rate at which work is done.

- 1 horsepower = 33,000 ft-lb/minute
- 1 Watt = 1 Joule/second
- 1 horsepower = 745.6 Watts



6.3 Types of Energy

Given a process stream j , the energy associated with the stream entering Each energy stream carries energy into the system.

$$E_j = E_{j,kinetic} + E_{j,potential} + \underbrace{U_j + P_j V_j}_{H_j}$$

- $E_{j,kinetic}$ is the kinetic energy associated with stream j . For example, for a stream at velocity v the kinetic energy (i.e., kinetic energy per unit mass) would be $\frac{1}{2}v^2$. For chemical processes this quantity is typically very small compared to other terms in the energy balance.
- $\hat{E}_{j,potential}$ is the specific potential energy associated with a stream. For example for a stream at height h relative to a common reference, the specific potential energy is gh where g is denotes gravitational acceleration.
- \hat{U}_j is the specific internal energy of a stream relative to the pure components at standard temperature and pressure. The internal energy consists of the energy stored in chemical bonds and molecular motion. For pure components \hat{U} is a function of T and P alone.
- $P_j \hat{V}_j$ is the flow work associated with a stream with specific volume \hat{V}_j entering a system at pressure P_j .
- $\hat{H}_j = \hat{U}_j + P_j \hat{V}_j$ is the specific enthalpy of a stream. It is useful in modeling energy balances in open systems because it accounts for both transport of internal energy into the system and the flow work necessary to transport the stream across the system boundaries. For pure components, \hat{H} is a function of T and P alone.

6.4 Specific Energy

A custom in process analysis is to represent the energy associated with a process flow in terms of specific energy. That is, for a stream with mass flowrate \dot{m}_j , the *mass specific energy* is given by

$$\hat{E}_j = \frac{\dot{E}_j}{\dot{m}_j}$$

6.5 Types of Energy

Each energy stream carries energy into the system.

$$\hat{E}_j = \hat{E}_{j,kinetic} + \hat{E}_{j,potential} + \underbrace{\hat{U}_j + P_j \hat{V}_j}_{\hat{H}_j}$$

- $\hat{E}_{j,kinetic}$ is the specific kinetic energy associated with a stream. For example, for a stream at velocity v the specific kinetic energy (i.e., kinetic energy per unit mass) would be $\frac{1}{2}v^2$. For chemical processes this quantity is typically very small compared to other terms in the energy balance.
- $\hat{E}_{j,potential}$ is the specific potential energy associated with a stream. For example for a stream at height h relative to a common reference, the specific potential energy is gh where g is denotes gravitational acceleration.
- \hat{U}_j is the specific internal energy of a stream relative to the pure components at standard temperature and pressure. The internal energy consists of the energy stored in chemical bonds and molecular motion. For pure components \hat{U} is a function of T and P alone.
- $P_j \hat{V}_j$ is the flow work associated with a stream with specific volume \hat{V}_j entering a system at pressure P_j .
- $\hat{H}_j = \hat{U}_j + P_j \hat{V}_j$ is the specific enthalpy of a stream. It is useful in modeling energy balances in open systems because it accounts for both transport of internal energy into the system and the flow work necessary to tranport the stream across the system boundaries. For pure components, \hat{H} is a function of T and P alone.

If this is done for every stream, then

$$\frac{dE_{sys}}{dt} = \sum_{j \in in} \dot{m}_j \hat{E}_j - \sum_{j \in out} \dot{m}_j \hat{E}_j + \sum_{j \in heat} \dot{Q}_j + \sum_{j \in shaft work} \dot{W}_j$$

Specific energy may also be expressed on a molar basis. For a stream with molar flow \dot{n}_j , the *molar specific energy* is given by

$$\hat{E}_j = \frac{\dot{E}_j}{\dot{n}_j}$$

If this is done for every stream, then

$$\frac{dE_{sys}}{dt} = \sum_{j \in in} \dot{n}_j \hat{E}_j - \sum_{j \in out} \dot{n}_j \hat{E}_j + \sum_{j \in heat} \dot{Q}_j + \sum_{j \in shaft work} \dot{W}_j$$

Note that we use the \sim notation to represent specific energy on either a mass or molar basis. This is consistent with common engineering notation. To avoid confusion, the key is, in a particular problem, to adopt the most convenient basis for your calculations, then be careful to always label quantities with the associated units.

6.6 Energy Balances

The basic energy balance for process systems is given by

$$\frac{dE_{sys}}{dt} = \sum_{j \in in} \dot{E}_j - \sum_{j \in out} \dot{E}_j + \sum_{j \in heat} \dot{Q}_j + \sum_{j \in work} \dot{W}_j$$

This is based on the basic concept that energy is conserved, i.e., energy is neither created or destroyed in process operations.

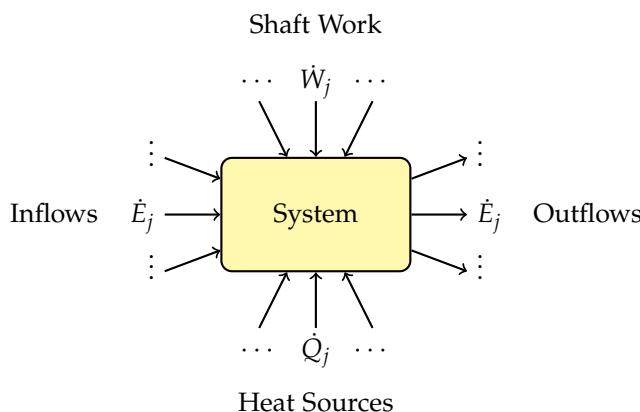


Figure 6.1: General configuration for energy balances.

Heat inputs and work inputs can be positive or negative. If either \dot{Q}_j (or \dot{W}_j) is positive, then it corresponds to an energy input. If negative, then it corresponds to an energy output.

6.7 Process Energy Balance

In typical chemical engineering applications involving the reaction and separation of chemical species, the dominant terms in \dot{E}_j are \dot{U}_j

and $P_j \hat{V}_j$. The kinetic and potential energy terms are generally very small compared to energy that is consumed and released by chemical change.

$$\hat{E}_j = \underbrace{\hat{E}_{j,kinetic}}_{\approx 0} + \underbrace{\hat{E}_{j,potential}}_{\approx 0} + \underbrace{\hat{U}_j + P_j \hat{V}_j}_{\hat{H}_j}$$

In the cases, to a good approximation the energy balance can be written as

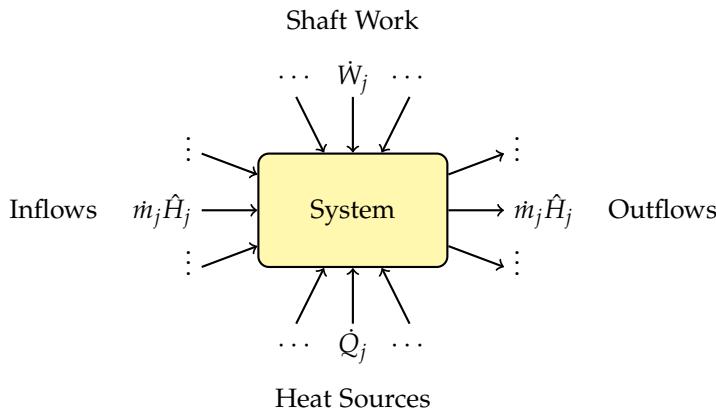


Figure 6.2: For most chemical processes the kinetic and potential energy of the input and output flows will be negligible. Accounting for flow work, and neglecting kinetic and potential energy, results in

For mass flows

$$\frac{dE_{sys}}{dt} = \sum_{j \in in} \dot{m}_j \hat{H}_j - \sum_{j \in out} \dot{m}_j \hat{H}_j + \sum_{j \in heat} \dot{Q}_j + \sum_{j \in shaft work} \dot{W}_j$$

For molar flows

$$\frac{dE_{sys}}{dt} = \sum_{j \in in} \dot{n}_j \hat{H}_j - \sum_{j \in out} \dot{n}_j \hat{H}_j + \sum_{j \in heat} \dot{Q}_j + \sum_{j \in shaft work} \dot{W}_j$$

Figure 6.3: Generic Energy Balance Equations.

Example: Isothermal Compression of an Ideal Gas

A scuba tank is filled by compressing 80 cubic feet of air at 25°C and atmospheric pressure to fill the scuba tank to 3000 psig at 25°C. Assume the compressor is designed so that the engine can apply a constant 5.5 horsepower of mechanical work, and that the compressor converts 70% of the mechanical work to thermodynamic shaft work. If air behaves as an ideal gas, how long will it take to fill the scuba tank?

Solution

In molar units, the energy balance for the compressor is given by

$$0 = \dot{n}_{air} \hat{H}_{air,in} - \dot{n}_{air} \hat{H}_{air,out} + \dot{Q} + \dot{W}_{shaft}$$

Figure 6.4: Scuba tank and compressor.



The enthalpy of an ideal gas depends on temperature alone. Since the inlet and outlet temperatures are the same, $\hat{H}_{air,in} = \hat{H}_{air,out}$. The energy balance becomes

$$0 = \dot{Q} + \dot{W}_{shaft}$$

From the data given,

$$\dot{W}_{shaft} = 0.7 \times 5.5 \text{ hp} \times \frac{745.7 \text{ watts}}{1 \text{ hp}} = 2,871 \text{ watts} = 2.87 \frac{\text{kJ}}{\text{sec}}$$

The work necessary to compress an ideal gas under isothermal conditions is given by integrating

$$\dot{W}_{shaft} = -P \frac{dV}{dt}$$

Substituting the known value for \dot{W}_{shaft} gives a differential equation. The pressure increases as the volume decreases, so it is necessary to provide an equation for P as a function of V . For this we can use the ideal gas law

$$P = \frac{n_{air}RT}{V}$$

where the number of moles of air. Substituting

$$-\frac{n_{air}RT}{V} \frac{dV}{dt} = \dot{W}_{shaft}$$

This is a simple differential equation that can be solved by integration

$$-n_{air}RT \int_{V_1}^{V_2} \frac{1}{V} dV = \dot{W}_{shaft} \int_{t_1}^{t_2} dt$$

where V_1 is the initial volume, and V_2 is the final volume. which leads to the formula

$$n_{air}RT \ln \frac{V_1}{V_2} = \dot{W}_{shaft}(t_2 - t_1)$$

This equation simplifies some more by noting

$$n_{air}RT = P_1V_1 = P_2V_2$$

which gives us

$$P_1V_1 \ln \frac{P_2}{P_1} = \dot{W}_{shaft}(t_2 - t_1)$$

Solving for the time required to fill the scuba tank

$$\begin{aligned} t_2 - t_1 &= \frac{P_1 V_1}{\dot{W}_{shaft}} \ln \frac{P_2}{P_1} \\ &= \frac{101,325 \frac{\text{N}}{\text{m}^2} \times 80 \text{ ft}^3 \times 0.0283 \frac{\text{m}^3}{\text{ft}^3}}{2,871 \frac{\text{N}\cdot\text{m}}{\text{sec}}} \ln \frac{(3000 + 14.7) \text{ psia}}{14.7 \text{ psia}} \\ &= 347 \text{ sec} = \boxed{5.8 \text{ min}} \end{aligned}$$

This calculation has assumed the compressor engine operates at a constant 5.5 hp. If that's not true then this is a lower bound on the time required to fill the scuba tank.

6.8 Steam Tables

Water is commonly used to transport energy and to provide mechanical power. For these reasons, the thermodynamic properties of pure water have been carefully measured and the data is made available in the form of 'Steam Tables', graphical charts, and engineering software.

6.8.1 Sources of Data

The International Association for the Properties of Water and Steam (IAPWS) maintains authoritative data on the properties of water and steam. Data tabulated by IAPWS is available from the National Institute of Science and Technology as report NISTIR 5078.

XSteam is a very thorough Matlab implementation of the IAPWS 1997 Industrial Formulation for steam data available under and open source license from Matlab Central..

Appendix B.16 of the textbook provides an abbreviated version of a typical steam table. The data provided in Appendix B.16 of the Murphy textbook provides a table of values for $\hat{H}(T, P)$, $\hat{U}(T, P)$, and $\hat{V}(T, P)$ as functions of temperature T and pressure P .

NISTIR 5078 is available at
<http://www.nist.gov/srd/upload/NISTIR5078.htm>

Example: Computing Enthalpy from Internal Energy and Specific Volume

Specific enthalpy \hat{H} is related to specific internal energy \hat{U} by the identity

$$\hat{H} = \hat{U} + PV$$

Use the steam table to verify this relationship for 'steam' at 1 bar and 50 °C, and at 20 bar and 300 °C.

Solution

From the steam table for water at 1 bar and 50 °C

$$\hat{H} = 209.46 \text{ kJ/kg}$$

$$\hat{U} = 209.36 \text{ kJ/kg}$$

$$\hat{V} = 0.00101 \text{ m}^3/\text{kg}$$

Under these conditions water is a liquid which can be seen from the small specific volume and low values for enthalpy and internal energy. Noting that 1 bar = 100,000 N/m²

$$\begin{aligned}\hat{U} + P\hat{V} &= 209.36 \text{ kJ/kg} + 100,000 \text{ N/m}^2 \times 0.00101 \text{ m}^3/\text{kg} \times 1 \text{ kJ/1000 J} \\ &= 209.36 \text{ kJ/kg} + 0.101 \text{ kJ/kg} \\ &= 209.46 \text{ kJ/kg}\end{aligned}$$

which is consistent with the reported value for \hat{H} .

From the steam table for water at 1 bar and 50 °C

$$\hat{H} = 3024.2 \text{ kJ/kg}$$

$$\hat{U} = 2773.2 \text{ kJ/kg}$$

$$\hat{V} = 0.1255 \text{ m}^3/\text{kg}$$

Under these conditions water is a vapor. Noting that 1 bar = 100,000 N/m²

$$\begin{aligned}\hat{U} + P\hat{V} &= 2773.2 \text{ kJ/kg} + 20 \text{ bar} \times 100,000 \text{ N/m}^2 \times 0.1255 \text{ m}^3/\text{kg} \times 1 \text{ kJ/1000 J} \\ &= 2773.2 \text{ kJ/kg} + 251 \text{ kJ/kg} \\ &= 3024.2 \text{ kJ/kg}\end{aligned}$$

which is consistent with the reported value for \hat{H} . Compared to water in the liquid state, in the vapor state there is a significant difference between specific enthalpy and specific internal energy.

Example: Steam Catapult for an Aircraft Carrier

A steam catapult on an aircraft carrier is capable of launching a fully loaded F-18 (23,500 kg) at a speed of 175 mph (approx. 80 m/s). Assume steam enters the catapult at $T = 450^\circ\text{C}$ and $P = 60$ bar and is released as saturated vapor at $P = 1$ bar. What mass of steam is required, and what are the beginning and ending volumes?

Solution

We start by writing mass and energy balances for the steam

$$0 = m_{in} - m_{out}$$

$$0 = m_{in}\hat{H}_{in} - m_{out}\hat{H}_{out} - W$$

From the mass balance we have $m_{in} = m_{out}$ which we call m_{steam} ,



so the energy balance becomes

$$W = m_{steam}(\hat{H}_{out} - \hat{H}_{in})$$

where W corresponds to the work done by the catapult to bring the aircraft up to launch speed.

$$\begin{aligned} W &= \frac{1}{2}m_{plane}v^2 \\ &= \frac{1}{2} \times 23,500 \text{ kg} \times (80 \text{ m/s})^2 \\ &= 75,200,000 \text{ J} \\ &= 75,200 \text{ kJ} \end{aligned}$$

\hat{H}_{out} is the specific enthalpy of steam at $T = 450^\circ\text{C}$ and $P = 60 \text{ bar}$. The steam tables from Appendix B.16 of the Murphy textbook give a table of values for $\hat{H}_{steam}(T, P)$ as a function of temperature and pressure. The closed to values for \hat{H}_{out} are

$$\begin{aligned} \hat{H}_{steam}(400, 60) &= 3,178.2 \text{ kJ/kg} \\ \hat{H}_{steam}(500, 60) &= 3,423.1 \text{ kJ/kg} \end{aligned}$$

Interpolating

$$\begin{aligned} \hat{H}_{in} &= \hat{H}_{steam}(450, 60) \\ &= \hat{H}_{steam}(400, 60) + \frac{450 - 400}{500 - 400} \times (\hat{H}_{steam}(500, 60) - \hat{H}_{steam}(400, 60)) \\ &= 3,178.2 + \frac{50}{100} \times (3,423.1 - 3,178.2) \\ &= 3,300.65 \text{ kJ/kg} \end{aligned}$$

The specific enthalpy of the outlet steam corresponds to saturated vapor at 1 bar.

$$\begin{aligned} \hat{H}_{out} &= \hat{H}_{steam}^{sat. vap}(1 \text{ bar}) \\ &= 2,674.9 \text{ kJ/kg} \end{aligned}$$

Solve the energy balance for the required amount of steam

$$\begin{aligned} m_{steam} &= \frac{W}{\hat{H}_{in} - \hat{H}_{out}} \\ &= \frac{75,200 \text{ kJ}}{3,300.65 \text{ kJ/kg} - 2,674.9 \text{ kJ/kg}} \\ &= \boxed{120 \text{ kg}} \end{aligned}$$

The specific volume of steam at the inlet conditions can be found

by interpolation of values tabulated in the steam tables.

$$\begin{aligned}\hat{V}_{in} &= \hat{V}_{steam}(450, 60) \\ &= \hat{V}_{steam}(400, 60) + \frac{450 - 400}{500 - 400} \times (\hat{V}_{steam}(500, 60) - \hat{V}_{steam}(400, 60)) \\ &= 0.0474 + \frac{50}{100} (0.0567 - 0.0474) \\ &= 0.05205 \text{ m}^3/\text{kg}\end{aligned}$$

So

$$V_{in} = 120 \text{ kg} \times 0.05205 \text{ m}^3/\text{kg} = 6.25 \text{ m}^3$$

For the outflow volume

$$V_{out} = 120 \text{ kg} \times \hat{V}_{steam}^{sat. vap.}(1 \text{ bar}) = 120 \text{ kg} \times 1.6939 \text{ m}^3/\text{kg} = 203.3 \text{ m}^3$$

6.9 Heat Capacity

The specific enthalpy of a material changes with changes in temperature. The rate of change of specific enthalpy with respect to temperature is the heat capacity.

$$\frac{\partial \hat{H}}{\partial T} = C_p$$

If $C_p(T)$ is a function of temperature, then

$$\hat{H}_2 - \hat{H}_1 = \int_{T_1}^{T_2} C_p(T) dT$$

In many cases, C_p is approximately a constant over moderate ranges of temperature. In those situations we have

$$\hat{H}_2 - \hat{H}_1 = C_p(T_2 - T_1)$$

Example: Hair Dryer

A hair dryer has a rating of 1875 watts. If the inlet air temperature is 25 °C, calculate the required volumetric air flow to maintain the outlet temperature below a safe temperature of 60 °C. Assume the heat capacity of dry air is 1 J/g-C and that the density of air is 1.2 g/liter.

Solution

The mass and energy balances for the air flow through the hair

Figure 6.5: The Conair Model 259NP hair dryer is rated at 1875 watts.



dryer are given by

$$\begin{aligned} 0 &= \dot{m}_{in} - \dot{m}_{out} \\ 0 &= \dot{m}_{in}\hat{H}_{in} - \dot{m}_{out}\hat{H}_{out} + \dot{Q} \end{aligned}$$

We'll use $\dot{m} = \dot{m}_{in} = \dot{m}_{out}$ to denote the mass flow of air. Then from the second equation we have

$$\dot{Q} = \dot{m}(\hat{H}_{out} - \hat{H}_{in})$$

Assuming air has a constant heat capacity,

$$\dot{Q} = \dot{m}C_p(T_{out} - T_{in})$$

which can be solved for \dot{m}

$$\begin{aligned} \dot{m} &= \frac{\dot{Q}}{C_p(T_{out} - T_{in})} \\ &= \frac{1875 \frac{\text{J}}{\text{sec}}}{1.0 \frac{\text{J}}{\text{g-C}}(60^\circ\text{C} - 25^\circ\text{C})} \\ &= 53.6 \frac{\text{g}}{\text{sec}} \end{aligned}$$

The volumetric flow is then

$$\dot{V} = \frac{1}{\rho} \dot{m} = \frac{53.6 \frac{\text{g}}{\text{sec}}}{1.2 \frac{\text{g}}{\text{liter}}} = \boxed{44.6 \frac{\text{liter}}{\text{sec}}}$$

Coming through the narrow neck of a hair dryer, that corresponds to a very high air velocity, probably too high for comfort. Most users would probably prefer a much lower heat setting than indicated by advertised power for this hair dryer.

Example: LNG Vaporization

Liquified Natural Gas (LNG) provides a means for transporting natural gas from production fields to distant markets. Upon reaching the destination, it is necessary to vaporize the liquified gas to conditions suitable for pipeline distribution.

Assume LNG has the physical properties of methane, and is available as a saturated liquid at its normal boiling point of -161.6°C and a latent heat of vaporization of $\Delta H_{vap} = 510 \text{ kJ/kg}$. Compute the heat required to deliver natural gas to a pipeline at 1 atmosphere pressure at 15.6°C .

*Solution
To Be Completed.*

Figure 6.6: LNG Tanker.



Example: Partial Condensation

A 60 kg/hr stream of superheated steam at 1 bar and 200°C enters the 'hot' side of a partial condenser where a portion of the steam condenses. The condensate exits as saturated water at 1 bar, and the

uncondensed steam exits as saturated vapor at 1 bar. 1200 kg/hr of water at 15°C enters the 'cold' side of the condenser and exits at 75°C. What is the mass flow of the liquid condensate?

Solution

Start by finding the amount of heat transported from the cold to hot side of the condenser. Designating the cooling water flow as $\dot{m}_{cw} = 400 \text{ kg/hr}$, the energy balance becomes

$$0 = \dot{m}_{cw}(\hat{H}_{cw,in} - \hat{H}_{cw,out}) + \dot{Q}$$

Using a heat capacity model, and solving for \dot{Q}

$$\begin{aligned}\dot{Q} &= \dot{m}_{cw}(\hat{H}_{cw,out} - \hat{H}_{cw,in}) \\ &= \dot{m}_{cw}C_p(T_{cw,out} - T_{cw,in}) \\ &= 400 \text{ kg/hr} \times 4.19 \text{ kJ/kg°C} \times (75 - 15)^\circ\text{C} \\ &= 100,560 \text{ kJ/hr}\end{aligned}$$

We start by writing mass and energy balances for the 'hot' side of the condenser

$$0 = \dot{m}_{steam,in} - \dot{m}_{steam,out} - \dot{m}_{cond,out}$$

$$0 = \dot{m}_{steam,in}\hat{H}_{steam,in} - \dot{m}_{steam,out}\hat{H}_{steam,out} - \dot{m}_{cond,out}\hat{H}_{cond,out} - \dot{Q}$$

where the unknowns are $\dot{m}_{steam,out}$ and $\dot{m}_{cond,out}$. Setting this up as a pair of equations for the two unknowns

$$\begin{aligned}\dot{m}_{steam,out} + \dot{m}_{cond,out} &= \dot{m}_{steam,in} \\ \dot{m}_{steam,out}\hat{H}_{steam,out} + \dot{m}_{cond,out}\hat{H}_{cond,out} &= \dot{m}_{steam,in}\hat{H}_{steam,in} - \dot{Q}\end{aligned}$$

From the steam tables

$$\hat{H}_{steam,in} = 2875.5 \text{ kJ/kg}$$

$$\hat{H}_{steam,out} = 2674.9 \text{ kJ/kg}$$

$$\hat{H}_{cond,out} = 417.5 \text{ kJ/kg}$$

Substituting all of the known parameters values

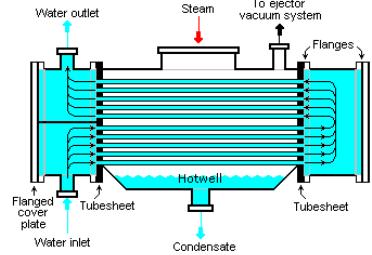
$$\dot{m}_{steam,out} + \dot{m}_{cond,out} = 60$$

$$2674.9 \dot{m}_{steam,out} + 417.5 \dot{m}_{cond,out} = 60 \times 2875.5 - 100,560$$

Setting these equations up in a matrix/vector format as $Ax = b$ where

$$\underbrace{\begin{bmatrix} 1 & 1 \\ 2674.9 & 417.5 \end{bmatrix}}_A \underbrace{\begin{bmatrix} \dot{m}_{steam,out} \\ \dot{m}_{cond,out} \end{bmatrix}}_x = \underbrace{\begin{bmatrix} 60 \\ 71,970 \end{bmatrix}}_b$$

Figure 6.7: Surface Condenser.



the solution is found in Matlab with the command $x = A \setminus b$ to give

$$\dot{m}_{steam,out} = 20.8 \text{ kg/hr}$$

$$\dot{m}_{cond,out} = 39.2 \text{ kg/hr}$$

Example: Fire Piston

A fire piston is a simple device used for starting fires. A common story is that Professor Carl von Linde saw this device while on a lecture tour in Malaysia in the mid-1870's. He subsequently demonstrated the device by lighting a cigarette during a lecture at the Munich Technical University attended by one of his students, Rudolf Diesel. Whether or not that story is accurate, the device has a long history among indigenous cultures in the Pacific and Asia.

A fire piston is operated by quickly plunging a piston into a narrow, sealed, air-filled tube. The tip of the piston holds a flammable piece of cloth. Compression of the air raises the temperature of the cloth above its auto-ignition temperature. Assuming a 10-to-1 compression ratio and that no heat is exchanged with the surroundings, what will be the resulting gas temperature?

Solution

Energy balance

$$\frac{dE}{dt} = \dot{Q} + \dot{W}$$

We'll assume the process is so fast there is no time for appreciable heat transfer, so that $\dot{Q} = 0$. Because this is a closed system, $E = n_{air}\hat{U}$. Assuming air behaves as an ideal gas, then \hat{U} is a function of temperature alone, so that

$$\begin{aligned} \frac{dE}{dt} &= \frac{d(n_{air}\hat{U})}{dt} \\ &= n_{air} \frac{d\hat{U}}{dt} \\ &= n_{air} \frac{\partial \hat{U}}{\partial T} \frac{dT}{dt} \\ &= n_{air} C_v \frac{dT}{dt} \end{aligned}$$

On the other side of the equation, the rate of work done on the system is proportional to the pressure times the decrease in volume

$$\begin{aligned} \dot{W} &= -P \frac{dV}{dt} \\ &= -P \frac{d(n_{air}\hat{V})}{dt} \\ &= -n_{air} \frac{RT}{\hat{V}} \frac{d\hat{V}}{dt} \end{aligned}$$

Figure 6.8: Demonstration of a fire piston.



Setting the two sides equal, the factor n_{air} cancels leaving

$$C_v \frac{dT}{dt} = -\frac{RT}{\hat{V}} \frac{d\hat{V}}{dt}$$

Rearranging, we get the equality

$$C_v \int_1^2 \frac{1}{T} dT = -R \int_1^2 \frac{1}{\hat{V}} d\hat{V}$$

which, after performing the integrations, gives

$$C_v \ln \frac{T_2}{T_1} = -R \ln \frac{\hat{V}_1}{\hat{V}_2}$$

or

$$\frac{T_2}{T_1} = \left(\frac{\hat{V}_1}{\hat{V}_2} \right)^{\frac{R}{C_v}}$$

The gas constant is $R = 8.314 \frac{\text{J}}{\text{gmol}\cdot\text{K}}$. The molar heat capacity of air is approximately $C_V = 20.8 \frac{\text{J}}{\text{gmol}\cdot\text{K}}$. The resulting temperature

$$T_2 = T_1 \left(\frac{\hat{V}_1}{\hat{V}_2} \right)^{\frac{R}{C_V}} = (25 + 273.15) \left(\frac{10}{1} \right)^{\frac{8.314}{20.8}} = 748 \text{ K} = 475^\circ\text{C}$$

which is above the ignition temperature of common flammable materials.

6.10 Reference States

Process and physical property variables can be defined on either absolute or relative scales. Specific volume, for example, is commonly measured in

Variables such as absolute pressure P and specific volume \hat{V} are measured on absolute scales. When we say the pressure is 101.325 kPa, or the specific volume is 1.12 liters/kg, those values can be used directly to compute quantities of engineering interest, such as forces exerted on a surface, or the volume necessary to hold a certain mass of liquid.

Other process variables, such as temperature or gauge pressure, are measured on scales relative to a reference condition. In the case of temperature measured in degrees Centigrade, the reference conditions is the melting point water at atmospheric pressure. For the Fahrenheit scale, the reference condition of

The careful reader will notice that enthalpy appears in the energy balances as \hat{H}_j whereas in most calculations we're concerned with changes in enthalpy that can be expressed as $\Delta\hat{H}_j = \hat{H}_{j,out} - \hat{H}_{j,in}$.

Example: Tankless Water Heater

The heat capacity of liquid water is approximately 1.0 BTU/lbm-F. Assuming the inlet water temperature is 60 °F, a flowrate of 2.65 gallons/minute, and a heat transfer of 78,000 BTU per hour, what is the outlet water temperature?

Solution

Considering just the water heater portion of the device, the mass and energy balances are

$$\begin{aligned} 0 &= \dot{m}_{in} - \dot{m}_{out} \\ 0 &= \dot{m}_{in}\hat{H}_{in} - \dot{m}_{out}\hat{H}_{out} + \dot{Q} \end{aligned}$$

Since in the inflow and outflows are the same, and assuming the specific enthalpy of water is given by

$$\hat{H}_{water}(T) = C_p(T - T_{ref})$$

the model becomes

$$\begin{aligned} \dot{Q} &= \dot{m}(\hat{H}_{out} - \hat{H}_{in}) \\ &= \dot{m}(C_p(T_{out} - T_{ref}) - C_p(T_{in} - T_{ref})) \\ &= \dot{m}C_p(T_{out} - T_{in}) \end{aligned}$$

On hourly basis, the mass flow of water is

$$\dot{m} = 2.65 \text{ gal/min} \times 60 \text{ min/hour} \times 8.35 \text{ lbm/gal} = 1,328 \text{ lbm/hour}$$

Solving for T_{out}

$$\begin{aligned} T_{out} &= T_{in} + \frac{\dot{Q}}{\dot{m}C_p} \\ &= 60^\circ\text{F} + \frac{78,000 \text{ BTU/hr}}{1,328 \text{ lbm/hr} \times 1.0 \text{ BTU/lbm-F}} \\ &= 60^\circ\text{F} + 58.7^\circ\text{F} \\ &= \boxed{118.7^\circ\text{F}} \end{aligned}$$

Example: Cooling coffee using ice.

You're looking for a quick cup of coffee between classes. A 16 ounce cup of coffee is served to you at a temperature of 185°F. This is too hot for drinking quickly, so you add one ounce of ice served at a temperature of -5°F. Assuming no heat losses, and that coffee can be treated as pure water, what is the temperature after the ice melts?

Solution

To keep calculations simple, we'll do this problem in English units using the information in the accompanying table.

Figure 6.9: Eccotemp Model L-10 tankless propane water heater. The water heater has a output of 78,000 BTU delivering 2.65 gallons per minute of hot water.

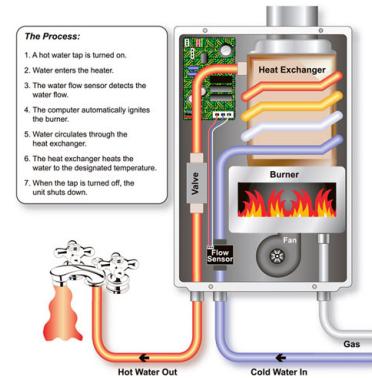


Table 6.1: Properties of Water

C_p^{ice}	0.48	BTU/lbm-F
C_p^{liq}	1.0	BTU/lbm-F
$\Delta \hat{H}_m$	144	BTU/lbm-F

Assuming no other heat losses, the mass and energy balances are

$$\begin{aligned} 0 &= m_{hot} + m_{ice} - m_{coffee} \\ 0 &= m_{hot}\hat{H}_{hot} + m_{ice}\hat{H}_{ice} - m_{coffee}\hat{H}_{coffee} \end{aligned}$$

The reference state will be liquid water at 32°F and 1 atm. Under these conditions specific enthalpies are

$$\begin{aligned} \hat{H}_{hot} &= C_p^{liq}(T_{hot} - T_{ref}) \\ \hat{H}_{ice} &= C_p^{ice}(T_{ice} - T_{ref}) - \Delta\hat{H}_m \\ \hat{H}_{coffee} &= C_p^{liq}(T_{coffee} - T_{ref}) \end{aligned}$$

Plugging back in obtains

$$m_{coffee}C_p^{liq}(T_{coffee} - T_{ref}) = m_{hot}C_p^{liq}(T_{hot} - T_{ref}) + m_{ice}C_p^{ice}(T_{ice} - T_{ref}) - m_{ice}\Delta\hat{H}_m$$

or

$$T_{coffee} = T_{ref} + \frac{m_{hot}C_p^{liq}(T_{hot} - T_{ref}) + m_{ice}C_p^{ice}(T_{ice} - T_{ref}) - m_{ice}\Delta\hat{H}_m}{(m_{hot} + m_{ice})C_p^{liq}}$$

Plugging in numerical values

$$\begin{aligned} T_{coffee} &= 32 + \frac{\frac{16}{16} \times 1.0 \times (185 - 32) + \frac{1}{16} \times 0.48 \times (-5 - 32) - \frac{1}{16} \times 144}{(\frac{16}{16} + \frac{1}{16}) \times 1.0} \\ &= 166.5^{\circ}\text{F} \end{aligned}$$

Suppose this is still too hot. How much ice would be required to cool the coffee to 150°F ?

6.11 Heat of Vaporization

Example: Vaporization of Propane

Propane is typically delivered for use as a liquid in a pressurized cylinder. What is the heat of vaporization of propane at 25°C ?

Solution

6.12 Energy Balances with Reactions

Example: Adiabatic Flame Temperature

Liquid propane at is burned with air in a perfectly insulated

Solution

6.13 Enthalpy of Combustion $\Delta\hat{H}_c^\circ$

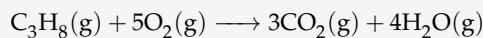
The enthalpy of combustion, $\Delta\hat{H}_c^\circ$, is the enthalpy of reaction corresponding to the complete reaction of a compound in the presence of oxygen under standard conditions, with any water product in the vapor phase.

Example

What is the enthalpy of combustion for propane?

Solution

Propane combustion is given by the reaction



Gathering the following data from Appendix B of the textbook

	$\Delta\hat{H}_f^\circ$ kJ/gmol	$\Delta\hat{H}_c^\circ$ kJ/gmol
$\text{C}_3\text{H}_8(\text{g})$	-104.68	-2043.1
$\text{O}_2(\text{g})$	0	0
$\text{CO}_2(\text{g})$	-393.5	0
$\text{H}_2\text{O}(\text{g})$	-241.83	0

Computing, we find the molar enthalpy of combustion

$$\begin{aligned}\Delta\hat{H}_c^\circ &= 3 \times (-393.5) + 4 \times (-241.83) - 1 \times (-104.68) - 5 \times (0) \\ &= \boxed{-2043.1 \text{ kJ/gmol}}\end{aligned}$$

Note that the computed value of -2043.1 kJ/gmol matches the quantity given Appendix B for the molar enthalpy of combustion for propane. $\Delta\hat{H}_c^\circ$ is often reported as the specific enthalpy of combustion. The molecular weight of propane is 44.1, therefore we have

$$\begin{aligned}\Delta\hat{H}_c^\circ &= -2043.1 \text{ kJ/gmol} \times 1 \text{ gmol}/44.1 \text{ g} \\ &= \boxed{-46.33 \text{ kJ/g}} \\ &= \boxed{-46.33 \text{ MJ/kg}}\end{aligned}$$

6.14 Higher and Lower Heating Values

The heating value of a fuel is frequently used in engineering calculations to determine the amount of fuel required in particular applications. The *Higher Heating Value* (HHV) is the heat released upon combustion with oxygen at standard conditions with any wa-

ter product in the liquid phase. The higher heating value provides an upper limit on the amount of heat that can be extracted from a fixed amount of fuel.

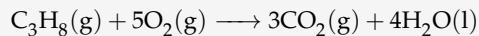
In typical applications, the combustion products leave at an elevated temperature and with water in the vapor phase. This leads to the definition of the Lower Heating Value (LHV) as the heat released upon combustion with oxygen with the reactants at standard conditions, combustion products at 150°C, and water in the vapor phase.

Example: The higher and lower heating values of propane

What is the higher heating value (HHV) for propane? What is the lower heating value (LHV)? What is the efficiency of a device that extracts the LHV of propane when compared the HHV that could be potentially extracted?

Solution

The higher heating value of propane is the enthalpy of reaction at standard conditions for



Gathering the following data from Appendix B of the textbook

	$\Delta\hat{H}_f^\circ$ kJ/gmol	$\Delta\hat{H}_c^\circ$ kJ/gmol	C_p J/gmol-K
C_3H_8 (g)	-104.68	-2043.1	73.6
N_2 (g)	0	0	29.1
O_2 (g)	0	0	29.3
CO_2 (g)	-393.5	0	37.0
H_2O (g)	-241.83	0	33.6
H_2O (l)	-285.84	44.01	75.4

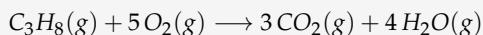
Computing, we find the molar enthalpy of reaction is

$$\begin{aligned}\Delta\hat{H}_{rxn}^\circ &= 3 \times (-393.5) + 4 \times (-285.84) - 1 \times (-104.68) - 5 \times (0) \\ &= -2219.2 \text{ kJ/gmol}\end{aligned}$$

By convention, HHV is normally reported on a mass basis.

$$\begin{aligned}\text{HHV} &= 2219.2 \text{ kJ/gmol} \times \text{gmol}/44.1 \text{ g} \times \frac{1000 \text{ g/kg}}{1000 \text{ kg/MJ}} \\ &= \boxed{50.32 \text{ MJ/kg}}\end{aligned}$$

For the lower heating value (LHV), we start with the heat of combustion corresponding to the reaction



which is given by $\Delta\hat{H}_c^\circ = -2,043.1 \text{ kJ/gmol}$. From this we subtract the enthalpy required to raise the combustion products to a temperature of

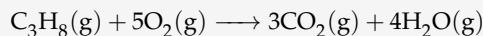
TO BE COMPLETED

Example: Propane fuel requirement for heating water

How much propane is required to provide the heat necessary to heat 100 liter/day of water from 10 °C to 50 °C? Assume that propane is burned in a stoichiometric ratio with air, and that the combustion products leave the water heater at 200 °C.

Solution

We previously computed the heat requirement to be 16,720 kJ/day. Propane combustion is given by the reaction



Keep in mind that for when burning propane in air there would be an additional $5 \times \frac{0.79}{0.21} = 18.8$ moles of N₂ present in the reaction products. We gather the following information from Appendix B of the textbook.

	T _b °C	ΔH _{vap} kJ/gmol	ΔH _f kJ/gmol	ΔH _c kJ/gmol	C _p J/gmol · K
C ₃ H ₈ (g)	-42	15.7	-104.68	-2043.1	73.6
N ₂ (g)			0	0	29.1
O ₂ (g)			0	0	29.3
CO ₂ (g)			-393.5	0	37.0
H ₂ O (g)			-241.83	0	33.6
H ₂ O (l)	100	40.79	-285.84	-44.0	75.4

Computing the enthalpy of reaction at STP

$$\begin{aligned}\Delta\hat{H}_{rxn}^\circ &= 3 \times (-393.5) + 4 \times (-241.83) - 1 \times (-104.68) - 5 \times (0) \\ &= -2043.1 \text{ kJ/gmol}\end{aligned}$$

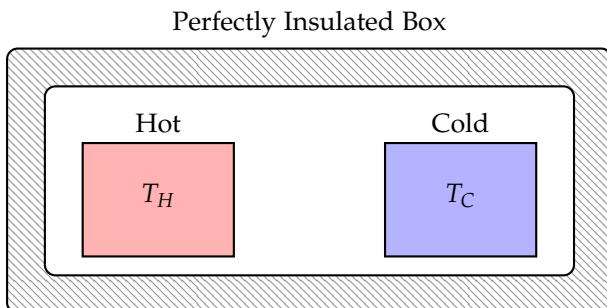
which, as you can see from the table, corresponds to the standard enthalpy of combustion ΔH_c[°].

The enthalpy change (to be completed)

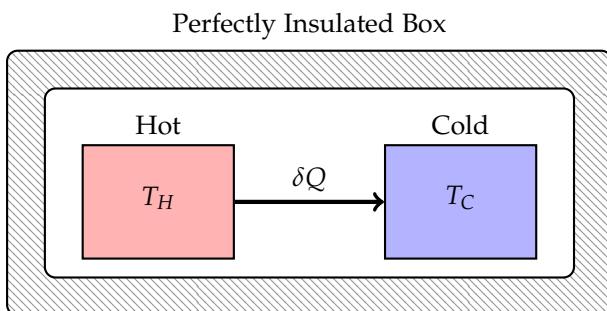
6.15 Second Law

6.15.1 Thought Experiment

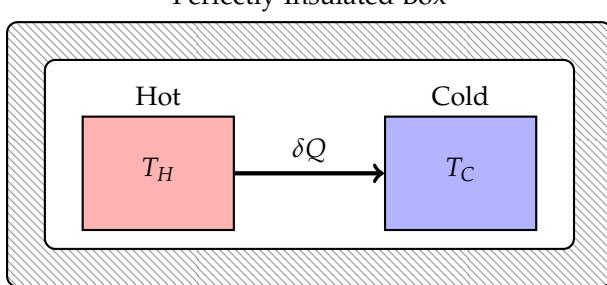
What do you expect to happen?



Transfer of heat from hot to cold.



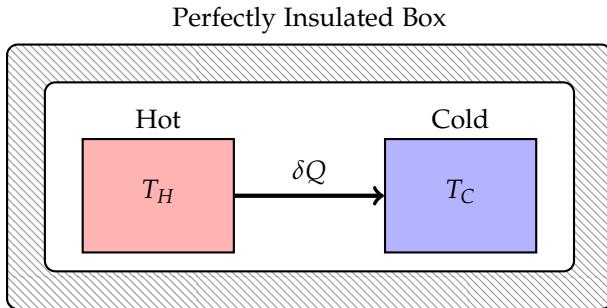
6.15.2 Introducing Entropy



$$\delta S_{Hot} = -\frac{\delta Q}{T_H} \quad \delta S_{Cold} = +\frac{\delta Q}{T_C}$$

6.15.3 The Second Law and Time's Arrow

The law that entropy always increases, the second law of thermodynamics, holds, I think, the supreme position among the laws of Nature.
– Eddington, 1935



Irreversible transfer of heat from a hot to cold object.

$$\delta S_{Total} \geq 0 \Leftrightarrow \delta S_{Hot} + \delta S_{Cold} > 0 \Leftrightarrow -\frac{\delta Q}{T_H} + \frac{\delta Q}{T_C} > 0$$

6.15.4 Carnot Efficiency

Extracting Energy as Useful Work

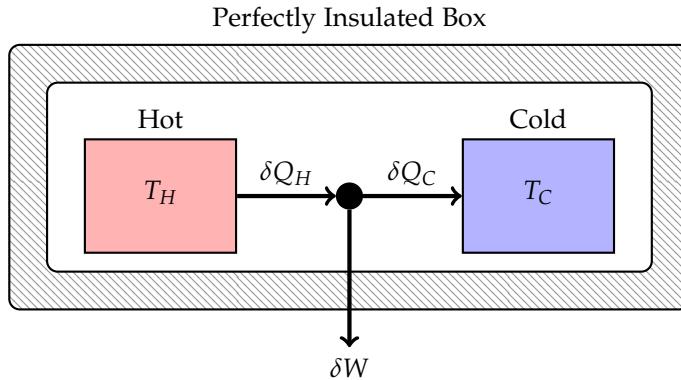


Figure 6.10: Sadi Carnot

First Law

$$\delta W = \delta Q_H - \delta Q_C$$

Second Law

$$\delta S_{Total} = -\frac{\delta Q_H}{T_H} + \frac{\delta Q_C}{T_C} > 0$$

Reversibility Establishes a Limit on Available Work

Substituting $\delta Q_C^{Rev} = \delta W^{Rev} - \delta Q_H^{Rev}$, and treating the second law as a constraint

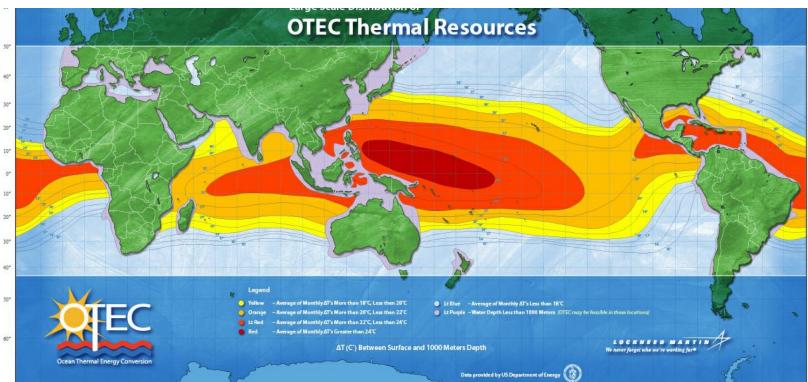
$$-\frac{\delta Q_H^{Rev}}{T_H} + \frac{\delta Q_H^{Rev} - \delta W^{Rev}}{T_C} \geq 0$$

Carnot Efficiency η_C

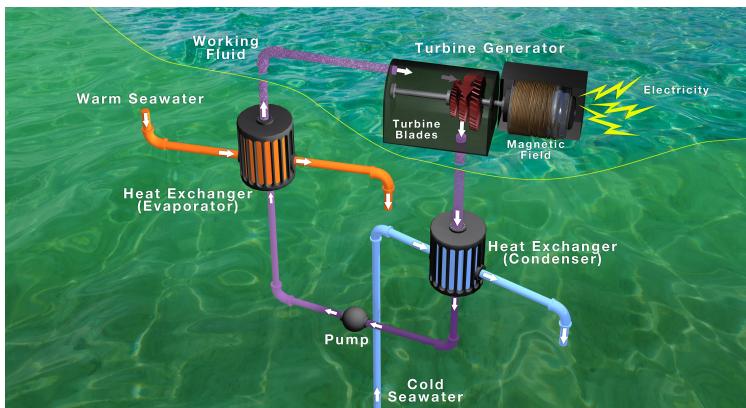
$$\frac{\delta W^{Rev}}{\delta Q_H^{Rev}} \leq \underbrace{1 - \frac{T_C}{T_H}}_{\eta_C}$$

No heat engine can have higher efficiency.

6.15.5 Ocean Thermal Energy Conversion (OTEC)



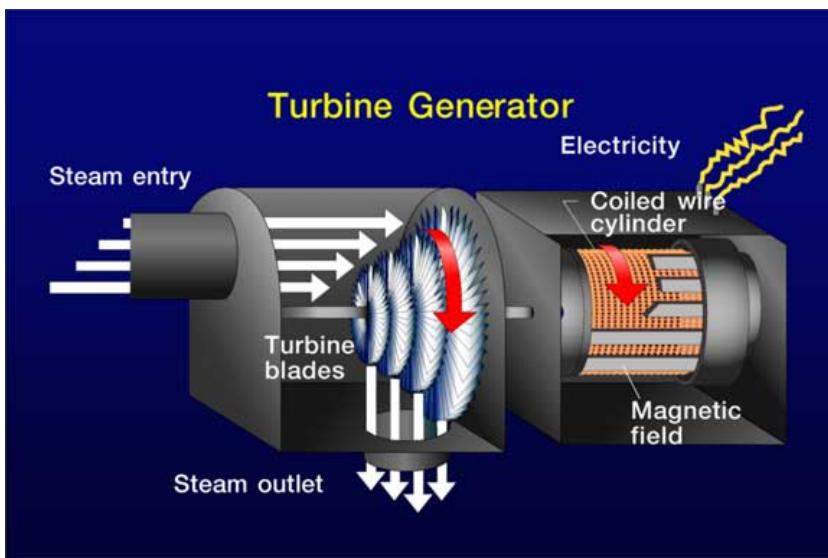
What is the Maximum Achievable Efficiency?

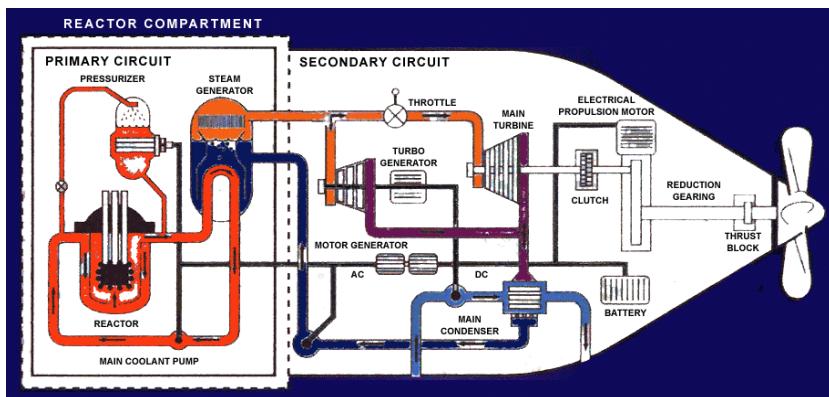


$$\eta_C = 1 - \frac{T_C}{T_H} = 1 - \frac{1 + 273.15}{25 + 273.15} = 0.081 = 8.1\%$$

No more than 8.1% of the extracted heat can be converted to electricity.

6.15.6 Steam Turbines



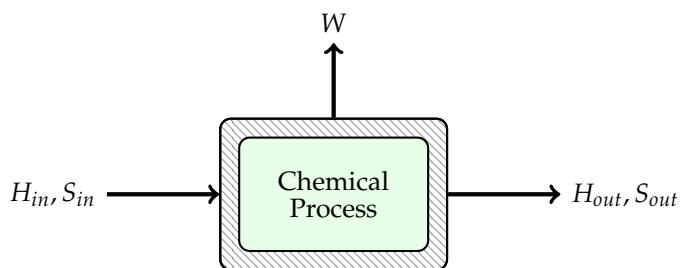


Type	Steam parameters (up to)	Output (MW)											
		1	2	3	4	5	6	7	8	9	10	11	12
SST-010	70 bar, 5 °C (Gas)												
SST-040	40 bar, 400 °C												
SST-050	101 bar, 500 °C												
SST-060	131 bar, 530 °C												
SST-110	131 bar, 530 °C												
SST-111	131 bar, 530 °C												

$$\eta_C = 1 - \frac{T_C}{T_H} = ?$$

6.15.7 Adiabatic Processes

Entropy is a State Function



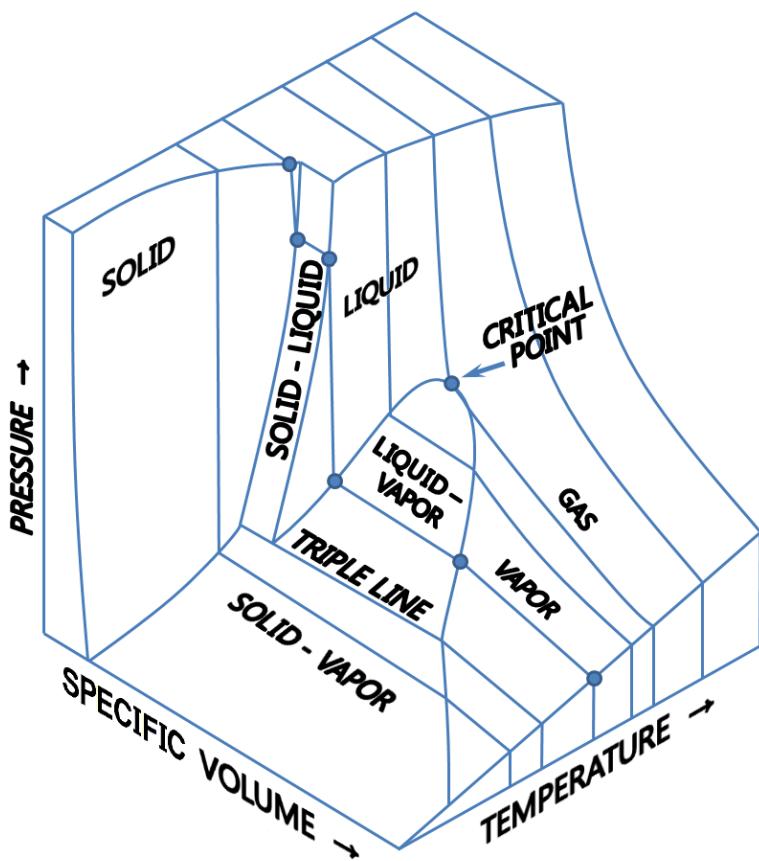
First Law:

$$0 = H_{in} - H_{out} - W$$

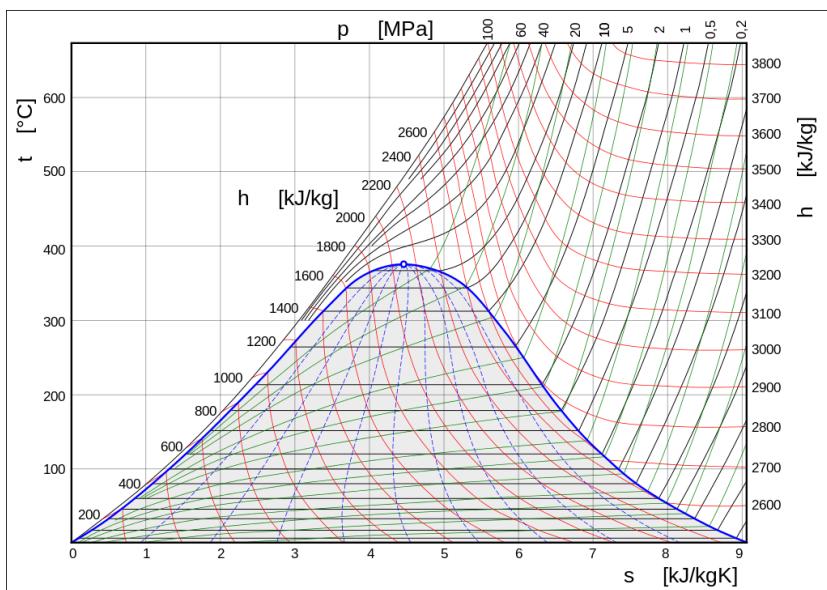
Second Law:

$$S_{out} - S_{in} \geq 0 \quad \Rightarrow \quad S_{out} \geq S_{in}$$

6.15.8 PVT Diagrams

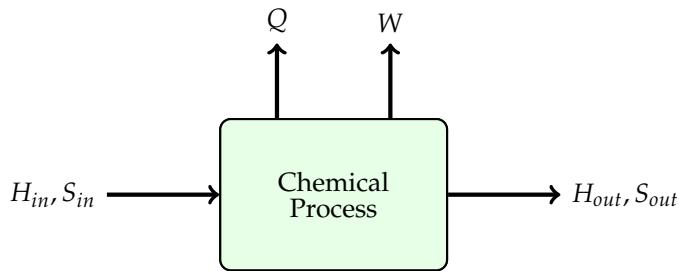


6.15.9 T-S Diagrams



6.15.10 Because Entropy is a State Function

Entropy is a State Function



First Law:

$$0 = H_{in} - H_{out} - Q - W$$

Second Law:

$$S_{out} + \frac{Q}{T} - S_{in} \geq 0 \quad \Rightarrow \quad Q \geq T(S_{out} - S_{in})$$

6.15.11 Available Work

From the First and Second Law

$$W \leq (H_{in} - H_{out}) - T(S_{out} - S_{in})$$

$$W \leq \Delta H - T\Delta S$$

Gibb's Free Energy

$$\Delta G = \underbrace{\Delta U + P\Delta V}_{\Delta H} - T\Delta S$$

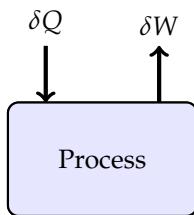
For processes operating in a constant temperature and pressure environment

$$W \leq \Delta G$$

and $T\Delta S$ is the energy unavailable to produce work.

6.15.12 Extracting Useful Work from Internal Energy

The surroundings are at constant pressure P and constant temperature T .



First Law:

$$\delta U_{sys} = \delta Q - \delta W$$

Second Law:

$$\delta S_{sys} + \delta S_{surr} > 0$$

6.15.13 Reversible Processes

For a reversible process

$$\delta S_{sys} = \frac{\delta Q^{Rev}}{T}$$

So that the energy balance becomes

$$\delta U = T\delta S_{sys} - \delta W^{Rev}$$

The reversible work done by the system is a combination of the P-V work done on the surroundings and reversible shaft work.

$$\delta W^{Rev} = \delta W_{shaft}^{Rev} + P\delta V_{sys}$$

$$-\delta W_{shaft}^{Rev} = \underbrace{\delta U_{sys} + P\delta V_{sys}}_{\delta G_{sys}} - T\delta S_{sys}$$

6.15.14 Irreversible Process

For an irreversible processes

$$\delta S_{sys} + \delta S_{surr} = \delta S_{irr} \geq 0$$

where $\delta S_{irr} > 0$ represents the extra entropy generated through friction and other losses, and $\delta S_{surr} = -\frac{\delta Q}{T}$. So

$$\delta Q = T\delta S_{sys} - T\delta S_{irr}$$

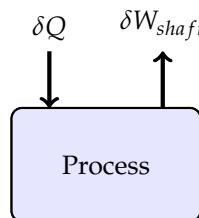
$$\delta U_{sys} = T\delta S_{sys} - T\delta S_{irr} - \delta W$$

Again splitting work into P-V and shaft components,

$$-\delta W_{shaft} = \underbrace{\delta U_{sys} + P\delta V_{sys}}_{\delta G_{sys}} - T\delta S_{sys} + T\delta S_{irr}$$

6.15.15 Available Work

For an isothermal system at constant pressure



Energy Balance

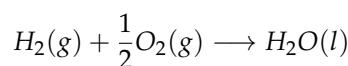
$$\delta H_{sys} = \delta Q - \delta W_{shaft}$$

Available Work

$$\delta W_{shaft} \leq -\delta G_{sys}$$

6.15.16 Hydrogen Economy

Hydrogen and Oxygen at 1 atm, 25 deg C.



Data

$$\Delta \hat{G}_{f,H_2O}^\circ = -237.19 \text{ kJ/gmol}$$

$$\Delta \hat{H}_{f,H_2O}^\circ = -285.84 \text{ kJ/gmol}$$

6.15.17 Hydrogen Economy

Questions:

- How much energy is required to produce $H_2(g)$?

$$-\Delta\hat{H}_{f,H_2O}^\circ = 285.84 \text{ kJ/gmol}$$

- How much mechanical energy can be recovered by $H_2(g)$ in fuel cell?

$$W_{shaft} \leq W_{shaft}^{Rev} = -\Delta\hat{G}_{f,H_2O}^\circ = 237.19 \text{ kJ/gmol}$$

- What is the maximum possible energy efficiency for the use of Hydrogen as a carrier of electrical energy?

$$\text{efficiency} \leq \frac{237.19 \text{ kJ/gmol}}{285.84 \text{ kJ/gmol}} = 83\%$$

6.15.18 Three Big Ideas!

- Energy is conserved.
- Mechanical work can be converted to thermal energy.
- Entropy is the thermal energy per unit temperature unavailable for mechanical work.

These facts have huge implications for chemical engineers. (For that matter, society at large).

6.16 Solved Problems

P6.59 Reclaiming Freshwater from Seawater

Freshwater can be reclaimed from seawater by freezing or by evaporation. Starting with seawater at 20 deg C and operations at 1 atm, and assuming at heat capacity of 4.2 kJ/kg, a heat of melting of 6.008 kJ/gmol, heat of vaporization of 40.65 kJ/gmol, and a MW of 18,

- How much energy must be removed to freeze 1kg of water?

Solution

There are two steps to the final state:

- Cool from 20 to 0

$$\Delta\hat{H}_{cool} = \hat{C}_p(T_2 - T_1) = 4.2 \text{ kJ/kg}(0 - 20) = -84 \text{ kJ/kg}$$

- Freeze

$$\Delta\hat{H}_{freeze} = -\Delta\hat{H}_m = \frac{-6.008 \text{ kJ/gmol} \times 1000 \text{ g/kg}}{18 \text{ g/gmol}} = -334 \text{ kJ/kg}$$

Total enthalpy requirement

$$\Delta\hat{H} = -84 - 334 = \boxed{-418 \text{ kJ/kg}}$$

- b. How much energy must be added to evaporate 1kg of water?

Solution

There are two steps to the final state:

- (i) Cool from 20 to 0

$$\Delta\hat{H}_{heat} = \hat{C}_p(T_2 - T_1) = 4.2 \text{ kJ/kg}(100 - 20) = 336 \text{ kJ/kg}$$

- (ii) Freeze

$$\Delta\hat{H}_{vap} = \Delta\hat{H}_v = \frac{-40.65 \text{ kJ/gmol} \times 1000 \text{ g/kg}}{18 \text{ g/gmol}} = 2258 \text{ kJ/kg}$$

Total enthalpy requirement

$$\Delta\hat{H} = +336 + 2258 = \boxed{+2594 \text{ kJ/kg}}$$

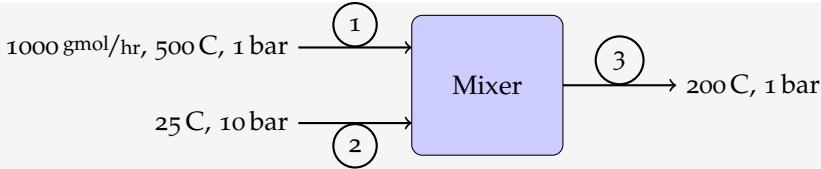
P6.6o Energy Balance for Mixing Benzene Streams

A hot benzene stream (1000 gmol/h) at 500 °C and 1 bar pressure is rapidly cooled to by mixing with a cold liquid benzene stream at 25 °C and 10 bar pressure. The final temperature of the combined benzene streams must be 200 °C at 1 bar. How much liquid benzene must be added?

Species	MW [g/gmol]	ρ at 25 °C [kg/m³]	T_b [°C]	$\Delta\hat{H}_{vap}(T_b)$ [kJ/gmol]	C_p^{liq} [J/gmol-K]	C_p^{vap} [J/gmol-K]
Benzene	78.11	0.8765	80.1	30.7	134.3	81.7

Solution

Begin with a diagram to define the process and streams.



Setting up the mass and energy balances

$$0 = \dot{m}_1 + \dot{m}_2 - \dot{m}_3$$

$$0 = \dot{m}_1 \hat{H}_1 + \hat{H}_2 \dot{m}_2 - \hat{H}_3 \dot{m}_3$$

We'll use liquid benzene at 25 C and 1 bar as the reference state. We need to compute enthalpies for each stream relative to the reference state. The hot stream consists of benzene in the vapor phase.

$$\begin{aligned}\hat{H}_1 &= C_p^{liq}(T_b - 25) + \Delta\hat{H}_{vap} + C_p^{vap}(500 - T_b) \\ &= 134.1(80.1 - 25) + 30,700 + 81.7(500 - 80.1) \\ &= 72,395 \text{ J/gmol}\end{aligned}$$

The cold stream is liquid benzene at 10 bar.

$$\begin{aligned}\hat{H}_2 &= \hat{V}(P_2 - P_{ref}) \\ &= \frac{78.11 \text{ g/gmol}}{0.8765 \text{ kg/liter} \times 1000 \text{ liter/m}^3 \times 1000 \text{ g/kg}} (10^6 \text{ N/m}^2 - 10^5 \text{ N/m}^2) \\ &= 80.2 \text{ J/gmol}\end{aligned}$$

The outlet stream also benzene in the vapor phase.

$$\begin{aligned}\hat{H}_3 &= C_p^{liq}(T_b - 25) + \Delta\hat{H}_{vap} + C_p^{vap}(200 - T_b) \\ &= 134.1(80.1 - 25) + 30,700 + 81.7(200 - 80.1) \\ &= 47,885 \text{ J/gmol}\end{aligned}$$

Substituting into the material and energy balances

$$\begin{aligned}0 &= 1000 + \dot{m}_2 - \dot{m}_3 \\ 0 &= 1000 \times 72,395 + 80.2\dot{m}_2 - 47,885\dot{m}_3\end{aligned}$$

Solving the first equation for the outlet flow

$$\dot{m}_3 = 1000 + \dot{m}_2$$

which leaves the equation

$$72,395,000 = 47,885(1000 + \dot{m}_2) - 80.2\dot{m}_2$$

Solving

$$\begin{aligned}\dot{m}_2 &= \frac{72,395,000 - 47,885,000}{47,885 - 80.2} \\ &= \boxed{512.7 \text{ gmol/hr}}\end{aligned}$$

P6.61 Steam Properties

Steam from a power plant at 350°C and 40 bar is captured in a 200 liter container, and then the container is cooled until the pressure is 1 bar.

- a. What is the temperature after cooling?
- b. What is the volume of liquid left in the container?
- c. How much heat was released?

Solution

- a. Cooling the container will result in partial condensation of steam so the final condition corresponds to saturation conditions. From the steam table, T_{sat} at 1 bar is $\boxed{99.6^{\circ}\text{C}}$.

- b. The initial mass of steam is

$$m_{in} = \frac{200 \text{ liters}}{\hat{V}} = \frac{200 \text{ liters}}{0.0666 \text{ m}^3/\text{kg} \times 1000 \text{ liters/m}^3} = 3.01 \text{ kg}$$

Performing a mass balance, and satisfying the volume constraint requires

$$\begin{aligned}m_{in} &= m_{vap} + m_{liq} \\ V &= \hat{V}_{vap}m_{vap} + \hat{V}_{liq}m_{liq}\end{aligned}$$

From Part a and from the steam tables we have

$$\begin{aligned}3.01 &= m_{vap} + m_{liq} \\ 0.200 &= 1.6939m_{vap} + 0.00104m_{liq}\end{aligned}$$

Solving we have

$$0.200 = 1.6939(3.01 - m_{liq}) + 0.00104m_{liq}$$

or

$$m_{liq} = \frac{1.6939 \times 3.01 - 0.200}{1.6939 - 0.00104} = 2.894 \text{ kg}$$

The volume of liquid is

$$\begin{aligned} V_{liq} &= \hat{V}_{liq} m_{liq} \\ &= 0.00104 \frac{\text{m}^3}{\text{kg}} \times 1000 \frac{\text{liters}}{\text{m}^3} \times 2.894 \text{ kg} \\ V_{liq} &= \boxed{3.01 \text{ liters}} \end{aligned}$$

c. The energy balance is

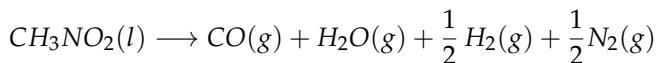
$$0 = \hat{H}_{in} m_{in} - \hat{H}_{vap} m_{vap} - \hat{H}_{liq} m_{liq} - Q$$

where Q is the heat removed. Solving for Q

$$\begin{aligned} Q &= \hat{H}_{in} m_{in} - \hat{H}_{vap} m_{vap} - \hat{H}_{liq} m_{liq} \\ &= 3093.3 \times 3.01 - 2505.6 \times (3.01 - 2.894) - 417.5 \times 2.894 \\ &= \boxed{7809 \text{ kJ}} \end{aligned}$$

P6.62 Energetics of a Monopropellant

Nitromethane (CH_3NO_2) is an important industrial solvent also used as a fuel for race cars and rocket thrusters. An interesting property of nitromethane is that it can function as a *monopropellant* through the reaction



- Compute the standard specific enthalpy $\Delta\hat{H}_{rxn}^\circ$ and specific Gibb's free energy $\Delta\hat{G}_{rxn}^\circ$ of reaction. Report your answer in units of energy released per unit mass of nitromethane.
- Compute the standard specific entropy $\Delta\hat{S}_{rxn}^\circ$ of reaction. Would you expect this to be positive or negative? Why?
- Suppose the temperature of the liquid is 25 °C and the exhaust temperature is 850 °C, what is the net enthalpy available for propulsion?

Solution

Part a. Computing enthalpy of reaction

$$\begin{aligned}\Delta\hat{H}_{rxn}^{\circ} &= -\Delta\hat{H}_{f,CH_3NO_2(l)}^{\circ} + \Delta\hat{H}_{f,CO(g)}^{\circ} + \Delta\hat{H}_{f,H_2O(g)}^{\circ} + \frac{1}{2}\Delta\hat{H}_{f,H_2(g)}^{\circ} + \frac{1}{2}\Delta\hat{H}_{f,N_2(g)}^{\circ} \\ &= -(-81.0) + (-110.53) + (-241.83) + \frac{1}{2}(0) + \frac{1}{2}(0) \\ &= -271.36 \text{ kJ/gmol}\end{aligned}$$

Converting to mass units

$$\begin{aligned}\Delta\hat{H}_{rxn}^{\circ} &= -271.36 \text{ kJ/gmol} \times \frac{1}{61 \text{ g/gmol}} \\ &= \boxed{-4.41 \text{ kJ/g}}\end{aligned}$$

Computing the Gibb's free energy of reaction

$$\begin{aligned}\Delta\hat{G}_{rxn}^{\circ} &= -\Delta\hat{G}_{f,CH_3NO_2(l)}^{\circ} + \Delta\hat{G}_{f,CO(g)}^{\circ} + \Delta\hat{G}_{f,H_2O(g)}^{\circ} + \frac{1}{2}\Delta\hat{G}_{f,H_2(g)}^{\circ} + \frac{1}{2}\Delta\hat{G}_{f,N_2(g)}^{\circ} \\ &= -(-14.3) + (-137.27) + (-228.59) + \frac{1}{2}(0) + \frac{1}{2}(0) \\ &= -351.56 \text{ kJ/gmol}\end{aligned}$$

Converting to mass units

$$\begin{aligned}\Delta\hat{G}_{rxn}^{\circ} &= -351.56 \text{ kJ/gmol} \times \frac{1}{61 \text{ g/gmol}} \\ &= \boxed{-5.76 \text{ kJ/g}}\end{aligned}$$

Part b. The definition of Gibb's free energy is

$$\Delta\hat{G}_{rxn} = \Delta\hat{H}_{rxn} - T\Delta\hat{S}_{rxn}$$

so that

$$\begin{aligned}\Delta\hat{S}_{rxn} &= \frac{\Delta\hat{H}_{rxn} - \Delta\hat{G}_{rxn}}{T} \\ &= \frac{(-271.36) - (-351.56)}{298.15} \\ &= \boxed{269 \text{ J/gmol-K}}\end{aligned}$$

A positive entropy of reaction is consistent with the production of 3 moles of gas for every mole of liquid nitromethane consumed.

Part c. The net enthalpy of reaction if the exhaust gas is 850 °C

is given by

$$\begin{aligned}
 \Delta\hat{H} &= \Delta\hat{H}_{rxn} + C_{p,CO(g)}(850 - 25) + C_{p,H_2O(g)}(850 - 25) + \frac{1}{2}C_{p,H_2(g)}(850 - 25) + \frac{1}{2}C_{p,N_2(g)}(850 - 25) \\
 &= \Delta\hat{H}_{rxn} + \left(C_{p,CO(g)} + C_{p,H_2O(g)} + \frac{1}{2}C_{p,H_2(g)} + \frac{1}{2}C_{p,N_2(g)} \right) (850 - 25) \\
 &= -271.36 + \left(29.1 + 33.6 + \frac{1}{2}29 + \frac{1}{2}29.1 \right) (850 - 25) \times \frac{1 \text{ kJ}}{1000 \text{ J}} \\
 &= \boxed{-195.67 \text{ kJ/gmol}}
 \end{aligned}$$

P6.63 Steam Turbine Performance

A Siemens model SST-300 turbine can accommodate steam at 150 bar and 500 °C to produce electricity. The exiting condition of the steam is a saturated vapor at 10 bar. The turbine produces 10 megawatts of electricity at an efficiency of 93%. (i.e, 93% of enthalpy is converted to electrical energy).

- a. What is the required steam flow in kg/hour?

Solution

From the steam tables we find

$$\hat{H}_1(150 \text{ bar}, 500 \text{ C}) = 3310.8 \text{ kJ/kg}$$

$$\hat{H}_2(10 \text{ bar}, \text{Sat.Vap}) = 2777.1 \text{ kJ/kg}$$

$$\Delta\hat{H}_{steam} = \hat{H}_2 - \hat{H}_1 = -533.7 \text{ kJ/kg}$$

The turbine requires

$$\dot{H}_{turbine} = \frac{10 \text{ MJ/sec} \times 3,600 \text{ sec/hr}}{0.93} = 38,710 \text{ MJ/hr}$$

$$\dot{m}_{steam} = \frac{38,710 \text{ MJ/hr}}{0.5337 \text{ kJ/kg}} = \boxed{70,870 \text{ kg/hr}}$$

That's a lot of steam! Over a ton/minute.

- b. The exiting steam is condensed at 10 bar, then pumped to a pressure of 150 bar before returning to the boiler. How much pump power is required?

Solution

The work necessary to pressurize the water is

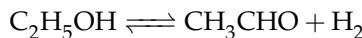
$$\begin{aligned}\dot{W} &= \dot{m}\hat{V}(P_2 - P_1) \\ &= 67,087 \text{ kg/hr} \times 0.00113 \text{ m}^3/\text{kg} \times (150 \text{ bar} - 10 \text{ bar}) \\ &= 1.06 \times 10^9 \text{ J/hour}\end{aligned}$$

recalling that 1 bar = 100,000 Pa = 100,000 N/m²

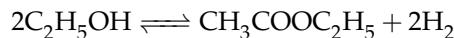
$$\begin{aligned}\dot{W} &= 1.06 \times 10^9 \text{ J/hour} \times \frac{1 \text{ hour}}{3,600 \text{ sec}} \times \frac{1 \text{ kJ}}{1,000 \text{ J}} \\ &= \boxed{295 \text{ kW} = 395 \text{ hp}}\end{aligned}$$

P6.64 Acetaldehyde Production

Acetaldehyde (CH₃CHO) is produced by the dehydrogenation of ethanol (C₂H₅OH) according to the reaction



An undesired side reaction produces ethyl acetate (CH₃COOC₂H₅)



The reactor is continuously fed with 120 gmol ethanol/sec at 200 °C and 760 mmHg. The reactor effluent flow is 166 gmol/sec. The effluent is all gas containing 41.7 mol% ethanol, 30.65 mol% H₂, 24.6 mol% acetaldehyde, and 3.0 mol% ethyl acetate.

Compound		T _b °C	Δ̂H _{vap} (T _b) kJ/gmol	C _p J/gmol·K	Δ̂H _f ^o kJ/gmol
H ₂	gas	-252.76	0.904	29	0
CH ₃ CHO	liq	20.2	25.1	89	-166.2
	gas			55	
C ₂ H ₅ OH	liq	78.5	38.58	112	-277.63
	gas			65	-235.31
CH ₃ COOC ₂ H ₅	liq	77	32.23	170	-463.2
	gas			114	-426.8

- What are the molar extents of reactions? (Be sure to show your work, including the component balances).
- What is the fractional conversion of ethanol?

- c. What is the fractional selectivity for producing acetaldehyde from ethanol?
- d. Assuming the reactor operates at 200 °C, how much heat is produced (or consumed) in the reactor?
- e. If 2500 kJ/sec of heat is being added to the reactor, what is the temperature of the reactor effluent gases?

Solution

Part a.

Writing the component balances

$$\begin{aligned} 0 &= \dot{n}_{EtOH,IN} - \dot{n}_{EtOH,OUT} - \dot{\xi}_1 - 2\dot{\xi}_2 \\ 0 &= -\dot{n}_{H_2,OUT} + \dot{\xi}_1 + 2\dot{\xi}_2 \\ 0 &= -\dot{n}_{Acet,OUT} + \dot{\xi}_1 \\ 0 &= -\dot{n}_{EtAc,OUT} + \dot{\xi}_2 \end{aligned}$$

The component balances for Acet and EtAc are especially easy to solve using the problem data. From these we find

$$\begin{aligned} \dot{\xi}_1 &= \dot{n}_{Acet,OUT} = 0.03 \times 166 = 4.98 \text{ gmol/s} \\ \dot{\xi}_2 &= \dot{n}_{EtAc,OUT} = 0.246 \times 166 = 40.836 \text{ gmol/s} \end{aligned}$$

Part b.

The fractional conversion is the fraction of ethanol in the feed stream that is converted. In this case

$$f_{EtOH}^{Conv} = \frac{\dot{n}_{EtOH,IN} - \dot{n}_{EtOH,OUT}}{\dot{n}_{EtOH,IN}} = \frac{120 - 0.417 \times 166}{120} = 0.423$$

Part c.

The fractional selectivity for acetaldehyde is the fraction of ethanol converted that ends up as acetaldehyde

$$f_{Acet}^{Sel} = \frac{\dot{n}_{Acet,OUT}}{\dot{n}_{EtOH,IN} - \dot{n}_{EtOH,OUT}} = \frac{0.246 \times 166}{120 - 0.417 \times 166} = 0.804$$

Part d.

Since we've already computed the extents of reaction, and there are no other sources of heat other than by reaction, our strategy will be to compute the molar heats of reaction at 200 °C,

then multiple by the extents of reaction. All of the species are in the vapor phase at 200 °C and 1 atm. For reaction 1

$$\begin{aligned}\Delta\hat{H}_{Rxn1}^{200} &= \underbrace{-166.2 - (-235.31)}_{\Delta\hat{H}_{Rxn}^\circ} + \underbrace{(29 + 55 - 65)}_{\Delta C_p} \underbrace{(200 - 25)}_{\Delta T} \frac{1 \text{ kJ}}{1000 \text{ J}} \\ &= 72.43 \text{ kJ/gmol}\end{aligned}$$

For reaction 2

$$\begin{aligned}\Delta\hat{H}_{Rxn2}^{200} &= \underbrace{-426.8 - 2 \times (-235.31)}_{\Delta\hat{H}_{Rxn}^\circ} + \underbrace{(2 \times 29 + 114 - 65)}_{\Delta C_p} \underbrace{(200 - 25)}_{\Delta T} \frac{1 \text{ kJ}}{1000 \text{ J}} \\ &= 62.54 \text{ kJ/gmol}\end{aligned}$$

Computing heat requirements

$$\begin{aligned}\dot{Q} &= 40.836 \times 72.43 + 4.98 \times 62.54 \\ &= 3268 \text{ kJ/sec}\end{aligned}$$

These are endothermic reactions, thus heat is required to maintain the reactor at 200 °C.

Part e.

If only 2500 kJ/sec is added to the reactor, then there is a deficit of $2500 - 3268 = 768$ kJ/sec. The molar heat capacity of the reactor effluent is

$$C_p = 0.417 \times 65 + 0.3065 \times 29 + 0.246 \times 55 + 0.03 \times 114 = 56.4 \text{ J/gmol/C}$$

Solving $\dot{Q} = C_p \Delta T$ for the desired temperature

$$T = 200 - \frac{768 \text{ kJ/sec}}{166 \text{ gmol} \times 56.4 \text{ J/gmol/C} \times \frac{1 \text{ kJ}}{1000 \text{ J}}} = 118 \text{ }^\circ\text{C}$$

6.17 Exercises

P6.65 Short Answer Questions

- Write a one sentence description of shaft work. Give two examples.
- Write a one sentence description of flow work. How is it different from shaft work?

P6.66 Short Answer Questions

- What is Gibb's free energy?
- What is enthalpy?

P6.67 Short Answer Questions

- What is the adiabatic flame temperature?
- What are the upper and lower heating values?

P6.68 Kinetic Energy Comparisons

A typical NCAA regulation softball has a maximum mass of 7 ounces, and is pitched with a velocity up to 80 mph. An NCAA regulation baseball has a maximum mass of 5.25 ounces, and pitched at a speed up to 91 mph. Which situation corresponds to higher energy?

P6.69 Energy Transfer by Gasoline

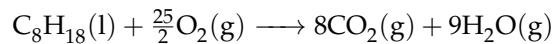
Suppose you can fill the 15 gallon fuel tank of an automobile in 3 minutes. Assume the density of gasoline is 0.72 kg/liter, and that 19% of the lower heating value can be converted to mechanical work. What is the equivalent rate of mechanical energy transfer from the gasoline pump to the car? Report your answer in kilowatts and in horsepower.

P6.70 Diesel Engine Efficiency

A figure of merit for the efficiency of an internal combustion engine is the brake specific fuel consumption. This measures the flowrate of fuel necessary to maintain a specific output of mechanical power at the brake (the point at which the power is available for use). For modern marine diesel engines used in the largest ships, this measure is 0.254 lb/hp-hr. The lower heating value of diesel fuel is approximately 18,500 BTU/lb. What is the energy efficiency of the engine?

P6.71 Automobile Energy Balance

At steady state, on a level stretch of highway traveling 70 mph, an automobile burns gasoline (C_8H_{18} , MW = 114, density = 0.72 kg/liter) at a rate of 35 mpg while producing power at an average of $\dot{W} = 15 \text{ hp}$. The balanced reaction is



with a standard heat of combustion $\Delta\hat{H}_c^\circ = -5400 \text{ kJ/gmol}$. The exhaust gas, consisting of CO₂, H₂O, and N₂, leaves the system at a temperature of 850 °C. Waste heat \dot{Q}_w is removed from the system through a radiator.

- Draw a process diagram showing the flows of gasoline, air, and exhaust. Assume the molar ratio of N₂ to O₂ is 4:1. Compute the mass flow rates for all three streams. (Hint, use units of grams/sec for mass flows).
- What is the engine efficiency measured as the fraction of the heat of combustion that's converted to power?
- Perform a steady state energy balance on the car engine. Compute the waste heat flow \dot{Q}_w .

P6.72 Steam Conditions for an Aircraft Catapult

A 30,000 kg aircraft is to be launched from the deck of an aircraft carrier using a steam catapult. The 100 meter long catapult must accelerate the aircraft to 80 meters/second. To a rough approximation, all of the energy for the launch comes from a steam catapult. The catapult is initially charged with 75 kg of steam at 40 bar (absolute) and 350 °C. Following launch, the steam pressure inside the catapult is measured to be 5 bar (absolute).

Assuming no other energy losses, how much of the steam has condensed? What is the volume of the remaining vapor?

P6.73 Free Energy of Reaction of Nitromethane

Nitromethane (CH₃NO₂) is an important industrial solvent that's also used as a fuel ('nitro') for race cars, rockets, and model airplanes.

- When burned in the presence of oxygen, the stoichiometry is given by the balanced reaction



What is the molar enthalpy of reaction at standard temperature and pressure?

- An interesting feature of nitromethane is that it can be used as a *monopropellant*. In this case the reaction is given by



Assume the temperature of the liquid is 25 °C and the exhaust temperature is 1,300 °C, what is the molar enthalpy of this reaction?



Figure 6.11: An F-14 Tomcat launches from the waist catapult as four F/A-18 Hornets wait to launch from the bow catapults on USS Enterprise (CVN 65) during operations in the Adriatic Sea on Feb. 23, 1999.

- c. A typical racer has a mass of 1000 kg and accelerates to a speed of 336 mph (150 m/s). Compute the kinetic energy of the racer ($\frac{1}{2}mv^2$) at the top speed. For the second reaction, given the molecular weight of CH_3NO_2 is 64, the liquid density of CH_3NO_2 is 1.1371 kg/liter, and that 20% of the enthalpy of reaction can be converted to kinetic energy, what volume of nitromethane is required to accelerate the racer to top speed? (If you do not have an answer from part b, assume a molar enthalpy of reaction equal to -150 kJ/gmol).

P6.74 Sublimation of Ice

It's a beautiful but cold winter day (-20 °C) in South Bend during which we're blessed with a 4 inch snow fall (corresponding to approximately 1 cm depth of water). The sun provides heat at a rate of 600 W/m² of which 10% is absorbed by the snow. The snow can sublime, that is can directly change from the solid phase to the vapor phase.

- Calculate the heat of sublimation at -20 °C.
- How many hours of sun will be required for complete sublimation of the snowfall? (The molar mass of water is 18 g/gmol, and the density is 1 g/mL).

Species	ϕ	T_m °C	$\Delta\hat{H}_m(T_b)$ kJ/gmol	T_b °C	$\Delta\hat{H}_{vap}(T_b)$ kJ/gmol	C_p J/gmol·K	$\Delta\hat{H}_f^\circ$ kJ/gmol	$\Delta\hat{G}_f^\circ$ kJ/gmol	Table 6.2: Data
H ₂	g		-252.76	0.904	29	0	0	0	
O ₂	g				29.3	0	0	0	
N ₂	g				29.1	0	0	0	
CO	g				29.1	-110.53	-137.27		
CO ₂	g				37.0	-393.5	-394.37		
H ₂ O	s	o	6.008		37.9				
		1		100	40.65	75.4	-285.84	-237.19	
		g				33.6	-241.83	-228.59	
CH ₃ NO ₂	l			101	34.0	106	-81.0	-14.3	
		g					-113.0	-14.4	
NO ₂	g					33.3	51.3		
N ₂ O ₄	g					9.33	97.95		

P6.75 Condenser Heat Duty

The gases exiting the reactor are a mixture of highly volatile hydrogen and methane, and the much lower volatility benzene and toluene. The compositions as given in the accompanying table. The condenser cools reactor gases from 650 °C to 150 °C. As a good approximation, at the operating pressure of 35 atm you can assume all of the benzene and toluene condense, but none of the hydrogen or methane condense. How much heat must be removed by the condenser per mole of reactor exit gases?

P6.76 Flash Separation of n-Hexane and n-Octane

A liquid mixture of 40 mol% n-hexane and 60 mol% n-octane is fed to a flash drum maintained at an operating temperature of 130 deg C and a pressure of 1520 mmHg. The feed rate is 100 kg-mol/min. The vapor and liquid are removed continuously.

- Calculate the flowrate and composition of the liquid and vapor streams.
- What are the fractional recoveries of n-hexane in the vapor stream, and n-octane in the liquid stream?
- Assuming the liquid and vapor phases are ideal solutions, and the feed is at 25 °C, how much heat is required to operate the flash unit?

P6.77 Thermite Reaction

A thermite reaction is a strongly exothermic oxidation-reduction reaction that can be used to weld metals. The most commonly used thermite reaction uses red iron oxide (Fe_2O_3) and aluminum (Al) in powdered form to produce liquid iron (Fe) and solid aluminum oxide (Al_2O_3) through the reaction



- How much iron oxide powder and aluminum powder would be required to produce 100 g of thermite?
- The reaction requires a high temperature ignitor, but once started it will burn to completion. Assuming the powder mixture starts at standard conditions, what is the maximum temperature that can be attained? Is the heat produced by the reaction sufficient to melt all of the reaction products?

Necessary thermophysical data can be found from the NIST Chemistry Webbook.

Species	z_i	T_b [°C]	K_i
Hydrogen	0.70	-253	99
Methane	0.15	-161	20
Benzene	0.10	80	0.01
Toluene	0.05	111	0.004

Antoine's equation

$$\log_{10} P^{\text{sat}}[\text{mmHg}] = A - \frac{B}{C + T[\text{°C}]}$$

Coefficients		
	A	B
n-Hexane	6.87601	1171.17
n-Octane	6.91868	1351.99
		224.41
		209.15

Physical Property Data

	$\Delta\hat{H}_{\text{vap}}^\circ$ kJ/gmol	T_b °C	C_p J/gmol C
n-Hexane (g)	-	-	143.1
n-Hexane (l)	28.9	68.74	189.1
n-Octane (g)	-	-	188.7
n-Octane (l)	34.4	125.52	255.0

Heats of Formation

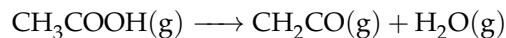
Species	$\Delta\hat{H}_f^\circ$ kJ/gmol
$\text{Al}_2\text{O}_3(\text{s})$	-1,675.7
$\text{Fe}_2\text{O}_3(\text{s})$	-825.5



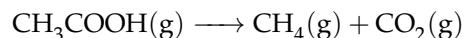
Figure 6.12: Iron thermite welding for joining railroad sections. Source: Wikimedia Commons.

P6.78 Reactor Analysis for the Production of Ketene from Acetic Acid

Acetic acid (CH_3COOH) is passed through a furnace at 100 kg/hour to produce ketene (CH_2CO) via the reaction



and methane (CH_4) via the reaction



The conversion rate of acetic acid is 80%, and the fractional yield of ketene is 0.0722. (That is, of the mass of acetic acid converted, 7.22% ends up as ketene).

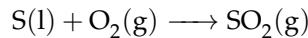
- Sketch a flow diagram, and perform a degree of freedom analysis.
- Write out all of the relevant material balance equations.
- Solve for all of the mass flow rates.
- If the feed is at 300°C, and the reaction is at 700°C, what is the furnace heat requirement?

Molecular Weights

Species	MW
$\text{CH}_3\text{COOH(g)}$	60.05
$\text{CH}_2\text{CO(g)}$	42.04
$\text{H}_2\text{O(g)}$	18.01
$\text{CH}_4\text{(g)}$	16.04
$\text{CO}_2\text{(g)}$	44.01

P6.79 Adiabatic Flame Temperature for a Sulfur Burner

A sulfur burner is used to produce SO_2 for use in various industrial, food, and agricultural operations. Solid sulfur is melted, then sprayed into a combustion chamber with air where the reaction



takes place. Combustion is essentially complete in the presence of 2% excess oxygen. Heat to melt the sulfur is extracted from the hot effluent gases.

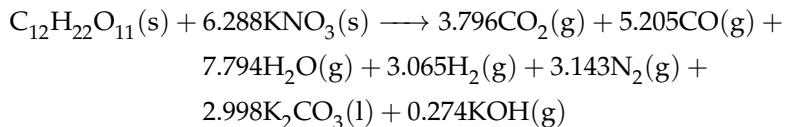
- Assume the air is available at standard conditions (25 °C and 1 bar), and that the sulfur enters the burner in liquid state at 130 °C. What is the adiabatic flame temperature?
- The combustion gases are used to melt and heat the sulfur to conditions necessary for operation of the boiler. Assuming sulfur enters the heater at standard conditions, what is the temperature of the effluent gas?

P6.80 Rocket Motors from Sugar, Stump Remover, and Kitty Litter

An internet recipe for making toy rocket motors specifies a mixture of 65 grams of commercially available 'stump remover' (i.e., potassium nitrate, KNO_3) and 25 grams of sugar (i.e., sucrose, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$).

This particular mixture has been proven to give good results through repeated experiments. The reaction produces a complex set of products as given by the reaction

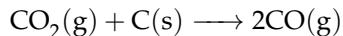
<http://www.nakka-rocketry.net/succhem.html>



- Assuming the pressure inside the combustion chamber is 1000 psia, calculate the adiabatic flame temperature.
- Compute the ratio of heat capacities, $k = \frac{C_p}{C_v}$, for the reaction products.
- Assuming isentropic expansion, how much work can be extracted from the reaction products? What is the temperature of the exhaust gases?

P6.81 Coke Gasification with CO₂

Coke can be converted to CO, a fuel gas, in the following reaction



Coke containing 84 wt% carbon (the remainder noncombustible ash) is fed to a reactor with a stoichiometric amount of CO₂. The coke is feed at 25 °C, and the CO₂ enters at 200 °C. Heat is transferred to the reactor in the amount of 13,600 kJ/kg of coke. The gaseous products and solid reactor effluent (the ash and unburned carbon) leave the reactor at 1000 °C. The heat capacity of all solids is 1.1 J/g K.

Species	MW	$\Delta\hat{H}_f^\circ$ kJ/gmol	C_p
CO ₂	44.01	-393.5	37.0 J/gmol C
C	12.01	0	1.1 J/g C
CO	28.01	-110.53	29.1 J/gmol C
Ash	-	-	1.1 J/g C

- Draw the flow diagram, label all streams and mass flows.
- Do a degree of freedom analysis. Write down all of the equations required to solve this problem.
- Calculate the fractional conversion of coke.

7

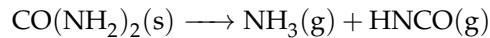
Projects

7.1 The Stoichiometry of NO_x Emissions Control in Diesel Engines using Urea/SCR - Combine with Next Problem

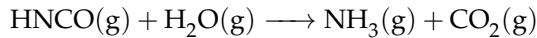
The DEF is injected into a hot, post-combustion exhaust stream where the water evaporates and the urea forms solid or molten droplets



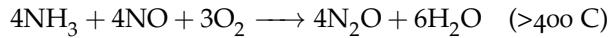
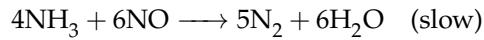
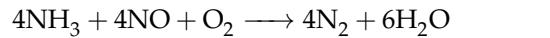
The urea immediately heats up and undergoes thermal decomposition to form ammonia and isocyanic acid



The isocyanic acid is stable in the gas phase. The hot gas stream is passed over a solid oxide catalyst to hydrolyze the isocyanic acid forming additional ammonia.

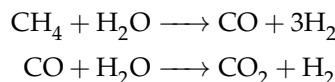


The hot exhaust then passes over the selective reduction catalyst to promote reaction between ammonia and the various forms of NO_x:

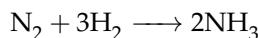


- a. Assume the NO_x in the diesel engine exhaust consists of 90 mol% NO and 10 mol% NO₂. Perform a generation/consumption analysis to determine the overall stoichiometry for the reduction of NO_x to N₂.

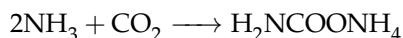
- b. Assume a car produces 3g/mile of NO_x comprised of 90 mol% NO and 10 mol% NO₂. How many gallons of Adblue will be theoretically required per 10,000 miles of travel? Typical driver experience is that about 5 gallons of Adblue is required per 10,000 miles of travel. How does this compare to the theoretical result?
- c. The commercial route to urea is to produce ammonia from natural gas followed by conversion of the ammonia to urea. Ammonia production is a two step process in which hydrogen produced by the steam reforming of natural gas followed by water-gas shift



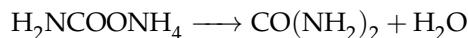
and then the Haber-Bosch process to produce ammonia.



The Bosch-Meiser process for urea production is also a two step process. Ammonia is combined with dry ice to produce ammonium carbamate and water



which then decomposes to form urea and water



- (a) For an integrated urea production facility, what is the overall stoichiometry for the production of urea from natural gas?
- (b) Based on energy content, the equivalent of 1 U.S. gallon of gasoline is 0.88 U.S. gallons of #2 Diesel fuel, or 126.67 cu. ft. of natural gas at STP. What is the diesel fuel equivalent of the natural gas required to treat 3g/mile of NO_x for 100 miles of travel? How does this compare to the diesel fuel required to power the vehicle for 100 miles?
- d. The report quoted below is taken from a story published by Consumer Reports on January 4, 2010, in a review of the Mercedes-Benz GL320. The composition specification for Adblue was established in the DIN70070 standard that can be found on-line at <http://www.din70070.com/>. Current spot prices for bulk urea can be found at <http://www.fertilizerworks.com/html/market/BasketPrice.pdf>. What is the cost of the raw materials needed to produce one gallon of Adblue? How does this compare to the price of Adblue implied by the story in Consumer Reports? How does it compare to 'truck-stop' prices you can find on the internet?

"The total bill just for adding AdBlue? A stunning \$316.99. We were down to 18% full on the additive at 16,566 miles. It took 7.5 gallons to fill the tank, costing an eye-opening \$241.50 for the fluid alone. The labor to add the fluid plus tax accounted for the rest. None of this was covered by the warranty."¹

¹ Consumer Reports, January 4, 2010.

7.2 NO_x Emissions Control in Diesel Engines

This project integrates topics we've been discussing since the start of the course including stoichiometry, generation/consumption analysis, material balances, and extents of reaction.

Diesel engines offer greater energy efficiency than equivalently sized gasoline engines by operating at higher compression and combustion temperatures. The problem, however, is that diesel engines produce more particulates because the fuel is injected late in the compression cycle, and produces greater NO_x emissions because of the higher combustion temperatures.

Here we look into a particular technology for treating NO_x that has found wide spread use in heavy trucks and recently has been introduced in the automobile and light truck marketplace. The Mercedes-Benz "BlueTEC" system, for example, comprises a selective catalytic reduction (SCR) converter and the AdBlue reagent. Adblue, also known by the generic name of exhaust fluid (DEF), is a registered trademark for AUS32 (Aqueous Urea Solution 32.5%) that consists of 32.5 wt% Urea in deionized water with a density of 1.09 g/ml.

Figure 7.1: Adblue is a trademark for Diesel Exhaust Fluid (DEF) consisting of 32.5 wt% urea in deionized water.

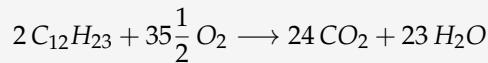


P7.82 Exhaust Flowrate

An average chemical formula for diesel fuel is C₁₂H₂₃ with a density of 0.832 kg/liter. A typical diesel light truck exhibits gets about 21 mpg on the highway. Assuming air (which is a mixture of 21 mol% O₂ and 79 mol% N₂) is mixed with diesel fuel at the stoichiometric ratio. Assume complete combustion of the diesel fuel which produces CO₂, H₂O. What is the exhaust gas flowrate in units of g/mile?

Solution

We need to do a material balance for the combustion process that takes place inside the vehicle engine. The balanced combustion reaction is



Because the answer is requested in mass flow units, we'll do this

Hint: The purpose of this first calculation is obtain an estimate for the exhaust gas flowrate. Because NO_x is a trace component of the exhaust, at this stage it is not necessary to consider any additional reactions other than the combustion of C₁₂H₂₃.)

problem using mass (rather than molar) flowrates. For this system we can prepare the following table of mass flows.

Species	M_i	In	Out	Extent
		g/mile	g/mile	$\dot{\xi}$
$C_{12}H_{23}$	167.31	\dot{m}_{D1}	0	$-2 M_D \dot{\xi}$
O_2	32	\dot{m}_{O1}	0	$-35.5 M_O \dot{\xi}$
N_2	28.01	\dot{m}_{N1}	\dot{m}_{N2}	0
CO_2	44.01	0	\dot{m}_{C2}	$24 M_C \dot{\xi}$
H_2O	18.02	0	\dot{m}_{W2}	$23 M_W \dot{\xi}$
TOTAL				

Because $C_{12}H_{23}$ and O_2 are fed in stoichiometric ratio, complete combustion means both components are completely consumed by the reaction. \dot{m}_{D1} is the mass flow of diesel fuel to the engine. Converting 21 mpg to mass flow units,

$$\dot{m}_{D1} = \frac{1 \text{ gallon}}{21 \text{ miles}} \times \frac{3.785 \text{ liters}}{\text{gallon}} \times \frac{832 \text{ g}}{\text{liter}} = 150 \frac{\text{g}}{\text{mile}}$$

Solving the first material balance

$$\dot{\xi} = \frac{\dot{m}_{D1}}{2 M_D} = \frac{150}{2 \times 167.31} = 0.448$$

Using this value, we can fill out the rest of the mass flow table for the other components participating in the reaction

Species	M_i	In	Out	Extent
		g/mile	g/mile	$\dot{\xi} = 0.448$
$C_{12}H_{23}$	167.31	$\dot{m}_{D1} = 150$	0	$-2 M_D \dot{\xi}$
O_2	32	$\dot{m}_{O1} = 509$	0	$-35.5 M_O \dot{\xi}$
N_2	28.01	\dot{m}_{N1}	\dot{m}_{N2}	0
CO_2	44.01	0	$\dot{m}_{C2} = 473$	$24 M_C \dot{\xi}$
H_2O	18.02	0	$\dot{m}_{W2} = 186$	$23 M_W \dot{\xi}$
TOTAL				

The molar flowrate of N_2 flowrate is proportional to the molar flowrate of O_2 at the inlet, i.e.,

$$\frac{0.79}{0.21} = \frac{\dot{n}_{N1}}{\dot{n}_{O1}} = \frac{\frac{\dot{m}_{N1}}{M_N}}{\frac{\dot{m}_{O1}}{M_O}} = \frac{\dot{m}_{N1}}{\dot{m}_{O1}} \times \frac{M_O}{M_N}$$

Converting to mass flows

$$\dot{m}_{N1} = \frac{0.79}{0.21} \times \frac{M_N}{M_O} \times \dot{m}_{O1} = 1676.5$$

Species	M_i	In	Out	Extent
		g/mile	g/mile	$\xi = \dot{\xi}$
$C_{12}H_{23}$	167.31	$\dot{m}_{D1} = 150$	o	$-2 M_D \dot{\xi}$
O_2	32	$\dot{m}_{O1} = 509$	o	$-35.5 M_O \dot{\xi}$
N_2	28.01	$\dot{m}_{N1} = 1676$	$\dot{m}_{N2} = 1676$	o
CO_2	44.01	o	$\dot{m}_{C2} = 473$	$24 M_C \dot{\xi}$
H_2O	18.02	o	$\dot{m}_{W2} = 186$	$23 M_W \dot{\xi}$
TOTAL		2335	2335	o

The total mass flow of exhaust is 2,335 g/mile.

P7.83 Catalytic Decomposition of Urea

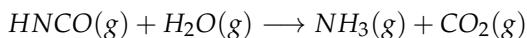
DEF is injected into a hot, post-combustion exhaust stream where the water evaporates and the urea forms solid or molten droplets



The urea immediately heats up and undergoes thermal decomposition to form ammonia and isocyanic acid



The isocyanic acid is stable in the gas phase. The hot gas stream passes over a solid oxide catalyst to hydrolyze the isocyanic acid forming additional ammonia.



Using a generation/consumption analysis, what is the net reaction?

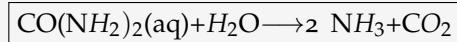
Solution

The generation/consumption table shows that we don't have independent control over stoichiometry of H_2O and CO_2 . Because of reaction 3, the consumption of water is in lockstep with the production of CO_2 .

Choosing the basis as the consumption of one mole of urea fixes the value $\chi_1 = 1$. The remaining coefficients are chosen to minimize the production of intermediates of the two intermediates $CO(NH_2)_2(s)$ and $HNCO$.

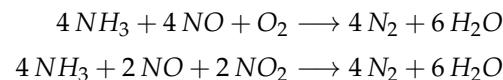
	Rxn 1 $\chi_1 = 1$	Rxn 2 $\chi_2 = 1$	Rxn 3 $\chi_3 = 1$	Net $\sum \chi_i \nu_i$	
$CO(NH_2)_2(aq)$	-1			-1	← Reactant
$CO(NH_2)_2(s)$	1	-1		0	← Intermediate
NH_3		1	1	2	
$HNCO$		1	-1	0	← Intermediate
H_2O			-1	-1	← Reactant
CO_2			1	1	

The desired net stoichiometry is



P7.84 Selective Catalytic Reduction of NO_x

Following hydrolysis of the urea, the hot exhaust then passes over the selective reduction catalyst that promotes reaction between ammonia and the NO_x :



Under normal conditions, excess oxygen is present in the exhaust stream. Assume the diesel exhaust initially contains 200 ppm by weight NO and 50 ppm by weight NO_2 . Field measurements demonstrate that 95% of each is converted to N_2 . What are the extents of reaction for each reaction?

Solution

The following table of detailing the component mass balances.

Species	M_i	In g/mile	Out g/mile	$\dot{\xi}_1$	$\dot{\xi}_2$
NH_3	M_A	\dot{m}_{A1}		$-4 M_A \dot{\xi}_1$	$-4 M_A \dot{\xi}_2$
NO	M_{NO}	$\dot{m}_{NO,1} = 0.467$	$\dot{m}_{NO,2}$	$-4 M_{NO} \dot{\xi}_1$	$-2 M_{NO} \dot{\xi}_2$
NO_2	M_{NO_2}	$\dot{m}_{NO_2,1} = 0.117$	$\dot{m}_{NO_2,2}$	0	$-2 M_{NO_2} \dot{\xi}_2$
O_2	M_O	\dot{m}_O	0	$-M_O \dot{\xi}_1$	0
N_2	M_N	0	\dot{m}_{N2}	$4 M_N \dot{\xi}_1$	$4 M_N \dot{\xi}_1$
H_2O	M_W	0	\dot{m}_{W2}	$6 M_W \dot{\xi}_1$	$6 M_W \dot{\xi}_1$
TOTAL					

The mass flows of NO and NO_2 are determined using the re-

Hint: ppm means 'parts per million'. For example, to compute the mass flow of NO , take $(200 \times 10^{-6}) \times \dot{m}_{exhaust}$ where $\dot{m}_{exhaust}$ is the mass flow computed in part 1 of the homework set.

sults of problem 1.

$$\dot{m}_{NO,1} = 0.000200 \times 2,335 = 0.467 \frac{\text{g}}{\text{mile}}$$

$$\dot{m}_{NO_2,1} = 0.000050 \times 2,335 = 0.117 \frac{\text{g}}{\text{mile}}$$

The problem data tells us that 95% of NO and NO_2 are converted.

$$\dot{m}_{NO,2} = (1 - 0.95) \times 0.467 \frac{\text{g}}{\text{mile}} = 0.0234 \frac{\text{g}}{\text{mile}}$$

$$\dot{m}_{NO_2,2} = (1 - 0.95) \times 0.117 \frac{\text{g}}{\text{mile}} = 0.0059 \frac{\text{g}}{\text{mile}}$$

The mass balance for NO_2 depends on $\dot{\xi}_2$ and not $\dot{\xi}_1$. Solving

$$0 = \dot{m}_{NO_2,1} - \dot{m}_{NO_2,2} - 2 M_{NO_2} \dot{\xi}_2$$

for $\dot{\xi}_2$

$$\dot{\xi}_2 = \frac{\dot{m}_{NO_2,1} - \dot{m}_{NO_2,2}}{2 M_{NO_2}} = \frac{0.117 - 0.059}{2 \times 46} = \boxed{0.00121}$$

The mass balance for NO

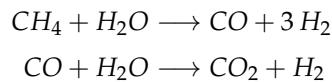
$$0 = \dot{m}_{NO,1} - \dot{m}_{NO,2} - 4 M_{NO} \dot{\xi}_1 - 2 M_{NO} \dot{\xi}_2$$

Solving for $\dot{\xi}_1$

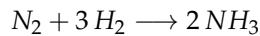
$$\begin{aligned}\dot{\xi}_2 &= \frac{\dot{m}_{NO,1} - \dot{m}_{NO,2} - 2 M_{NO} \dot{\xi}_2}{4 M_{NO}} \\ &= \frac{0.467 - 0.023 - 2 \times 30 \times 0.00121}{4 \times 30} \\ \dot{\xi}_2 &= \boxed{0.0031}\end{aligned}$$

P7.85 Production of Urea from Natural Gas

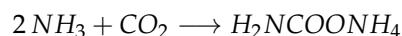
The commercial route to urea is to produce ammonia from natural gas, then convert the ammonia to urea. Ammonia production is a two step process in which hydrogen produced by the steam reforming of natural gas followed by water-gas shift



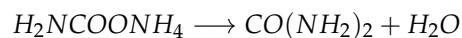
followed by the Haber-Bosch process to produce ammonia.



The Bosch-Meiser process for urea production is also a two step process. Ammonia is combined with dry ice to produce ammonium carbamate and water



which then decomposes to form urea and water



For an integrated urea production facility, what is the overall stoichiometry for the production of urea from natural gas?

<i>Solution</i>							
	Rxn 1 χ_1	Rxn 2 χ_2	Rxn 3 χ_3	Rxn 4 χ_4	Rxn 5 χ_5	Net $\sum \chi_i v_i$	
CH_4	-1					≤ 0	← Raw Material
H_2O	-1	-1			1		
CO	1	-1				0	
H_2	3	1	-3			≥ 0	← H_2 Product
CO_2		1		-1			
N_2			-1			≤ 0	← Raw Material
NH_3			2	-2		≥ 0	← NH_3 Product
$\text{H}_2\text{NCOONH}_4$				1	-1	0	
$\text{CO}(\text{NH}_2)_2$					1	≥ 0	← Urea Product

There are three potentially valuable products from this set of reactions: $\text{CO}(\text{NH}_2)_2$, H_2 , and NH_3 . Let's explore this a bit. There are five unknowns – χ_1 , χ_2 , χ_3 , χ_4 , and χ_5 – that must satisfy a set of constraints imposed by the feasible process stoichiometries.

We can eliminate three of these variables. Choosing the primary raw material CH_4 as the basis sets $\chi_1 = 1$. Requiring no net production for CO and $\text{H}_2\text{NCOONH}_4$ forces $\chi_2 = \chi_1$ and $\chi_4 = \chi_5$. With these three equations we can eliminate 3 of the 5 unknowns. Eliminating χ_1 , χ_2 , and χ_4 , we are left with χ_5 , which is equal to the process stoichiometric coefficient for urea, and χ_3 .

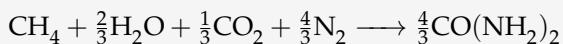
Making the substitutions,

	Rxn 1 $\chi_1 = 1$	Rxn 2 $\chi_2 = 1$	Rxn 3 χ_3	Rxn 4 $\chi_4 = \chi_5$	Rxn 5 χ_5	Net $\sum \chi_i v_i$
CH_4	-1					-1
H_2O	-1	-1			1	$\chi_5 - 2$
CO	1	-1				0
H_2	3	1	-3			$4 - 3\chi_3 \leftarrow \text{Must be } \geq 0$
CO_2		1		-1		$1 - \chi_5$
N_2			-1			$-\chi_3 \leftarrow \text{Must be } \leq 0$
NH_3			2	-2		$2\chi_3 - 2\chi_5 \leftarrow \text{Must be } \geq 0$
$H_2NCOONH_4$				1	-1	0
$CO(NH_2)_2$					1	$\chi_5 \leftarrow \text{Must be } \geq 0$

χ_3 and χ_5 are the 'decision variables' for this problem. From the stoichiometric constraints on N_2 and urea we see $\chi_3 \geq 0$ and $\chi_5 \geq 0$.

The problem asked for the process stoichiometry for the production of urea. Assuming no constraints on purchase of CO_2 , this corresponds to the case $\chi_3 = \chi_4 = \frac{4}{3}$

	Rxn 1 $\chi_1 = 1$	Rxn 2 $\chi_2 = 1$	Rxn 3 χ_3	Rxn 4 $\chi_4 = \chi_5$	Rxn 5 χ_5	Net $\sum \chi_i v_i$
CH_4	-1					-1
H_2O	-1	-1			1	$-\frac{2}{3}$
CO	1	-1				0
H_2	3	1	-3			0
CO_2		1		-1		$-\frac{1}{3}$
N_2			-1			$-\frac{4}{3}$
NH_3			2	-2		0
$H_2NCOONH_4$				1	-1	0
$CO(NH_2)_2$					1	$\frac{4}{3}$



which exhibits a remarkable 100% atom efficiency! That solves the problem.

Though we have solved the problem as posed, let's explore this example a bit further. Ignoring any constraints on the purchase or release of CO_2 , the stoichiometric constraints on H_2 and NH_3 production require $4 - 3\chi_3 \geq 0$ and $\chi_3 - \chi_5 \geq 0$. Putting this together, we are left with a simple system of constraints to describe feasible values for the two decision variables:

$$0 \leq \chi_5 \leq \chi_3 \leq \frac{4}{3}$$

To develop a better insight into the tradeoffs among competing process stoichiometries, we introduce P_{H_2} , P_{NH_3} , and P_{urea} to denote the prices of possible process products. For each mole of methane consumed, the revenue generated by the process is given by

$$\begin{aligned} \text{Revenue} &= P_{H_2} M_{H_2} (4 - 3\chi_3) + P_{NH_3} M_{NH_3} (2\chi_3 - 2\chi_5) + P_{urea} M_{urea} \chi_5 \\ &= 4P_{H_2} M_{H_2} + (2P_{NH_3} M_{NH_3} - 3P_{H_2} M_{H_2})\chi_3 + (P_{urea} M_{urea} - 2P_{NH_3} M_{NH_3})\chi_5 \end{aligned}$$

It turns out that there are three cases, each corresponding to the production of a single product. The key is compute the three quantities $3P_{H_2} M_{H_2}$, $2P_{NH_3} M_{NH_3}$, and $P_{urea} M_{urea}$, then produce the product corresponding to the largest value.

Constraints on CO_2 results in different conclusions. If one cannot purchase CO_2 as a raw material, then $\chi_5 \leq 1$ which eliminates the single product strategy for urea. Instead, depending on the relative prices, the strategies are either H_2 only, NH_3 only, urea with H_2 , or urea with NH_3 .

On the hand, if production of CO_2 is not allowed, then the production strategies are either urea alone, or the co-production of urea and either H_2 or NH_3 .

P7.86 DEF Consumption Rate

In a review published by Consumer Reports on January 4, 2010, regarding the Mercedes-Benz GL320

"The total bill just for adding AdBlue? A stunning \$316.99. We were down to 18% full on the additive at 16,566 miles. It took 7.5 gallons to fill the tank, costing an eye-opening \$241.50 for the fluid alone. The labor to add the fluid plus tax accounted for the rest. None of this was covered by the warranty."²

Using the results you found above, how much Adblue would you estimate is needed to drive 16,566 miles assuming a vehicle gets 21 mpg? How does this compare to the numbers quoted in the review? What assumption would you need to revise in order to match the observed consumption of Adblue?

There was a recent presentation at the 2009 AIChE Annual Meeting on this topic: P. Ghougassian and V. Manousiouthakis, "Hydrogen Production Plant with Urea Co-Production", paper 613c, <http://apps.aiche.org/proceedings/Abstract.aspx?PaperID=613c>

² Consumer Reports, January 4, 2010.

Solution

Referring to the mass balances developed for problem 2, and assuming complete conversion of the ammonia, the mass balance

tells us the consumption of NH_3

$$\begin{aligned}\dot{m}_{NH_3} &= 4 M_A \dot{\zeta}_1 + 4 M_A \dot{\zeta}_2 \\ &= 4 \times 17.03 \times (0.0031 + 0.00121) \\ &= 0.294 \frac{g - NH_3}{mile}\end{aligned}$$

Two moles of NH_3 are derived from each mole of urea.

The required mass of urea is therefore

$$\begin{aligned}\dot{m}_{urea} &= \frac{1}{2} \times \frac{M_{urea}}{M_{NH_3}} \times 0.294 \frac{g - NH_3}{mile} \\ &= \frac{1}{2} \times \frac{60.06}{17.03} \times 0.294 \frac{g - NH_3}{mile} \\ &= 0.518 \frac{g - urea}{mile}\end{aligned}$$

according to thTo createFor 16,566 miles driven we need

$$0.518 \times 16,566 = 1 = 8.58 \text{ kg - urea}$$

Commercial Adblue is 32.5 wt% urea, so 1 gallon holds

$$0.325 \frac{kg - urea}{kg - Adblue} \times 1.09 \frac{kg - Adblue}{liter} \times 3.785 \frac{liter}{gallon} = 1.34 \frac{kg - urea}{gallon}$$

Therefore we predict a need for

$$\frac{8.58 \text{ kg - urea}}{1.34 \frac{kg - urea}{gallon}} = \boxed{6.40 \text{ gallons Adblue}}$$

of Adblue. This is lower than the observed consumption of Adblue assuming an exhaust gas concentration of 250 ppm NO_x .

Using our model, the observed consumption would correspond to

$$250 \text{ ppm} \times \frac{7.5}{6.40} = \boxed{293 \text{ ppm } NO_x}$$

P7.87 Cost of Raw Materials for DEF

Current spot prices for bulk urea can be found on-line. What is the cost of the raw materials needed to produce one gallon of Adblue?

How does this compare to the price of Adblue implied by the story in Consumer Reports?

[http://www.fertilizerworks.com/
html/market/BasketPrice.pdf](http://www.fertilizerworks.com/html/market/BasketPrice.pdf)

Solution

The current spot price of urea is \$535.15/metric ton, corresponding to

$$\$535.15 \frac{1}{1000\text{kg}} \times 1.34 \frac{\text{kg - urea}}{\text{gallon}} = \$0.72/\text{gallon}$$

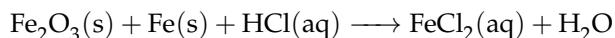
The price paid by the review, not including labor, was

$$\frac{\$241.50}{7.5} = \$32.20/\text{gallon}$$

Clearly the auto dealer is charging a premium for diesel exhaust fluid.

7.3 Regeneration of Spent Pickling Liquor

The production of metal products, such as automobiles, consumer appliances and office furniture, begins with a metal cleaning process to remove rust, scale, and other debris. For steel products, a common chemical process is ‘pickling’ with a solution of hydrochloric acid (HCl). In the process, iron oxide scale (i.e., rust) (Fe_2O_3) is removed by the *unbalanced* reaction



to produce ferrous chloride (FeCl_2).

P7.88 Estimating Iron Loss

In a particular application, sheet steel is continuously rolled through a well-mixed pickling bath. The measured composition of the pickling bath is 10.5 wt% HCl and 17.0 wt% FeCl_2 . An aqueous makeup stream of 18.7 wt% HCl is continuously added to the bath. Waste pickle liquor is removed at a rate of 256 kg/hr. Setup and solve the material balances for all component flowrates. In addition to the scale being removed, how much additional iron is being etched from the steel rolls?

P7.89 Neutralization and Disposal of SPL

Spent pickle liquor (SPL) is classified by the Environmental Protection Agency as a hazardous waste. About 1.5 billion gallons of spent pickle liquor is produced each year in the United States. One method of disposal is to neutralize the acid component of the waste using sodium hydroxide (NaOH), then inject the solution into underground sandstone formations.³

Figure 7.2: A steel pickling line.
Source: <http://xcelsteel.com/>



³ Link to details on a 2013 EPA hearing regarding the renewal of a permit to continue injecting spent pickle liquor into an underground sandstone formation.

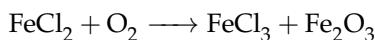
Using the data from part a, calculate the amount of sodium hydroxide required per kg of spent pickle liquor. How much waste solution is produced per kg of Fe_2O_3 scale removed from the incoming steel?

P7.90 PORI Process

The PORI process⁴ is a multi-step hydrometallurgical process for the regeneration of hydrogen chloride from spent pickle liquor.

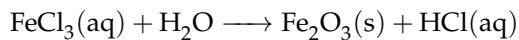
In the first step, the spent pickle liquor is concentrated by evaporating water and hydrogen chloride to produce a stream that is 40 wt% ferrous chloride with only trace amounts of hydrogen chloride.

The aqueous ferrous chloride is then heated to 350 °F at a pressure of 150 [psig]. The hot solution is mixed with air in a reactor where the *unbalanced* oxidation reaction



converts the ferrous chloride to ferric chloride.

After exiting the reactor, the mixture is cooled and the ferric chloride decomposes through the *unbalanced* hydrolysis reaction



Depending on the circumstances, it may be necessary to add water so the concentration of HCl is below the azeotropic concentration of 20.2 wt%.

Sketch the flowsheet for this process. Assume the feeds to the process are the spent pickle liquor described in part a, air, and makeup water (if needed). The products of this process are an aqueous solution of 18.7 wt% hydrochloric acid and any unavoidable by-products.

⁴ G.L. Kovacs. Treatment of waste hci pickle liquor, August 8 1972. US Patent 3,682,592; and N. Takahashi, O. Taki, H. Weissenbaeck, and D. Vogl. Processing method for recovering iron oxide and hydrochloric acid, January 14 2014. US Patent 8,628,740

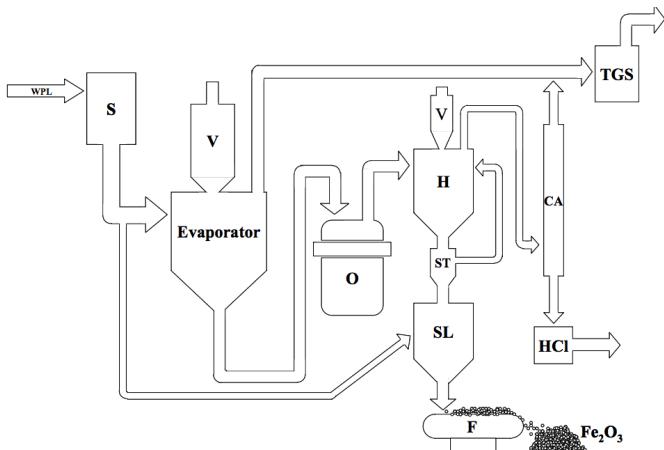


Figure 7: The PORI HCl Regeneration Process. (WPL, Waste Pickle Liquor; S, Storage; O, Oxidizer-Autoclave; H, Hydrolyzer, CA, Adiabatic Absorber; ST, Settling Tank; SL, Slurry Tank; F, Filter; TGS, Tail Gas Scrubber, V, Venturi Nozzle [64]).

P7.91 By-Products of the PORI Process

Assuming the PORI process is used to regenerate hydrogen chloride, how much waste is produced per kg of Fe_2O_3 scale removed from the incoming metal? Is it possible to do further recycling of the waste stream?

P7.92 Optimal Waste Reduction

Perform a generation-consumption analysis for the combined pickling and hydrogen chloride regeneration system. Attempt to find a theoretical limit on the minimum amount of waste product. Compare this result to the direct disposal of neutralized SPL.

7.4 Battery Technologies for the Electricity Grid

The production of electricity from renewable solar and wind resources is plagued by the problem of ‘intermittency’, that is, the highly variable nature of the energy resource. Energy sources need to be steady and ‘dispatchable’ for use on commercial power grids. To solve this problem, a number of novel battery technologies have been proposed that use energy storage to change intermittent power sources into reliable, steady, and dispatchable resources for the electric power grid.

This project explores various chemical technologies that are being developed for grid level storage of electricity.

P7.93 Liquid Metal Batteries

A novel liquid metal battery technology has been developed at MIT and is the process of being commercialized by AMBRI with venture capital support from Vinod Khosla and Bill Gates. A key goal of the technology is to design to a large scale and low cost point by using earth abundant materials, and employing devices that are easy to manufacture on a large scale.⁵

One version of the technology employs a three layer cell operating at 450°C in which molten lithium (Li) floats over a molten salt electrolyte which, in turn, floats over a layer consisting of molten antimony-lead mixture (Sb–Pb). In the discharge phase, the negative electrode releases electrons by the half-reaction

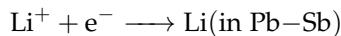


The electrons reach the positive electrode through an external circuit. The lithium ion is transported through the molten electrolyte (a mixture of LiF, LiCl, and LiI in a 20:50:30 ratio by mole fraction) to the

[Click this link to a TED Talk by Donald Sadoway entitle "The missing link to renewable energy."](#)

⁵ Hojong Kim, Dane A. Boysen, Jocelyn M. Newhouse, Brian L. Spatocco, Brice Chung, Paul J. Burke, David J. Bradwell, Kai Jiang, Alina A. Tomaszwoska, Kangli Wang, Weifeng Wei, Luis A. Ortiz, Salvador A. Barriga, Sophie M. Poizeau, and Donald R. Sadoway. Liquid metal batteries: Past, present, and future. *Chemical Reviews*, 113(3):2075–2099, 2014/06/29 2013

positive electrode where the reaction



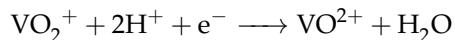
When fully charged the positive electrode is a 30:70 mole fraction Sb-Pb mixture. When fully discharged the positive electrode is a 45:38:17 mole fraction Li-Sb-Pb mixture. The average discharge voltage is 0.66 volt.

- What is the minimum mass of lithium, antimony, and lead would be required to build the electrodes for a 2 MWH storage facility? Using the densities of the pure elements, what would be the minimum electrode volume?
- A critical cost target for the industry is to build electricity storage systems for less than 100 \$/kWh. If Li costs 0.43 \$/mol, Sb costs 1.8 \$/mol, and Pb costs 0.52 \$/mol, is it feasible for this technology to meet this cost target?

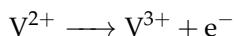
P7.94 Vanadium Flow Batteries

Redox flow batteries are devices that store electrolyte solutions in external tanks. Pumps circulate the solutions through a device where redox half-reactions take place at positive and negative electrodes located in chambers separated by an ion-selective membrane. Electrons move through an external circuit to produce useful work. Charge neutrality is maintained within the device by a corresponding flux of ions moving through the ion-selective membrane. The enormous flexibility in design makes flow batteries attractive for stationary grid storage applications.

Vanadium is a transition metal that can exist in solution in four common oxidation states. This fact is exploited in a vanadium redox flow battery.⁶ In the discharge phase, the reaction at the positive electrode is given by



and reaction at the negative electrode is



To maintain charge neutrality and separation of the electrolyte solutions, the positive and negative electrode chambers are separated by a proton exchange membrane (that is, an ion-selective membrane that allows only hydrogen ions to diffuse). The operating voltage is typically 1.4 volts.

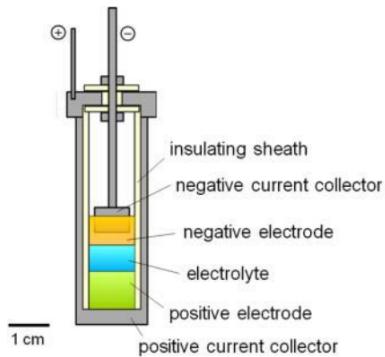


Figure 7.3: Schematic diagram of a liquid metal battery. Source: Figure 15a from Kim, et. al., 2013.

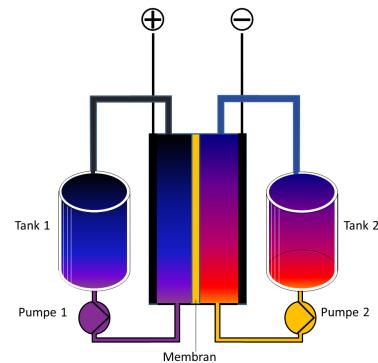


Figure 7.4: Schematic diagram of a redox flow battery. Source: Wikimedia Commons



Figure 7.5: Vanadium can exist in solution in four common oxidation states. From left-to-right, VO_2^+ (yellow), VO^{2+} (blue), V^{3+} (green), and V^{2+} (purple). Source: Wikimedia Commons
⁶ M. Rychcik and M. Skyllas-Kazacos. Characteristics of a new all-vanadium redox flow battery. *Journal of Power Sources*, 22(1):59–67, 1988

- a. Assume the electrolyte solutions are prepared from an aqueous mixture of vanadyl sulfate (VOSO_4) and sulfuric acid (H_2SO_4), each at a concentration of 2 M. What minimum volume of electrolyte solutions required for a 2 MWH storage facility?
- b. The current price of vanadium pentoxide (V_2O_5) is 6.50 \$/lb. Sulfuric acid is sold as 98 wt% aqueous solution at a price of approximately 70 \$/ton. Calculate the costs of the electrolyte solutions for a 2 MWH storage facility. Is it feasible for this technology to meet a cost target of 100 \$/KWH?

P7.95 Evaluating Commercial Technologies for Grid Electricity Storage

A number of battery technologies are entering the market for providing electricity storage for the national energy grid. Examples include products from Aquion, American Vanadium, and others. Survey the technologies, choose one, and prepare a brief report on the underlying technology. Your report should include:

- a. The chemical reactions occurring at the positive and negative electrodes.
- b. A schematic diagram of the device.
- c. An estimate of the lowest possible cost for a 2 MWH facility.
- d. An evaluation of the feasibility of the technology to meet a cost target of 100 \$/KWH of capacity.

7.5 Production of Biodiesel from Waste Coffee Grounds

Coffee is one of

<http://phys.org/news/2014-06-car-coffee.html>

7.6 PHA Biopolymers