Problem-Solving Exercises in Green and Sustainable Chemistry
Contents

Foreword ...................................................................................................................... xi
Preface ....................................................................................................................... xiii
Introduction ............................................................................................................... xv
Author ....................................................................................................................... xvii
Editor ....................................................................................................................... xix

Chapter 1  Toxicity, Accidents, and Chemical Waste ............................................. 1
  1.1 General Background ....................................................................................... 1
  1.2 Toxicity of Chemicals in the Environment .................................................... 2
  1.3 Accidents with Chemicals ............................................................................. 7
  1.4 Waste and Its Minimization ......................................................................... 10
  1.5 Conclusions .................................................................................................. 12

Problems .................................................................................................................. 15
  1.1 Pollution Prevention at an Isocyanates Plant .................................................. 15
  1.2 Curious Polar Bears ..................................................................................... 15
  1.3 After an Industrial Accident ......................................................................... 15
  1.4 A Mighty Safety Dilemma ........................................................................... 15
  1.5 To Burn or Not to Burn? .............................................................................. 18
  1.6 “Delacid”: A Versatile Catalyst .................................................................. 18
  1.7 The Flask Broke ........................................................................................... 18
  1.8 The Tremendous Problem of Climate Change .............................................. 18
  1.9 The Chemist Talks to the Chemical Engineer ............................................. 19
  1.10 Inherently Safer Chemistry ........................................................................ 19
  1.11 A Strange Malady ....................................................................................... 19
  1.12 The Mysterious Case of the Disappearing Filter Paper .......................... 19

References ............................................................................................................... 20

Chapter 2  The Chemistry of Longer Wear ........................................................... 25
  2.1 Why Things Wear Out .................................................................................. 25
  2.2 Stabilizers for Polymers .............................................................................. 27
  2.3 Lubrication, Wear, and Related Subjects .................................................... 31
  2.4 Inhibition of Corrosion ............................................................................... 33
  2.5 Mending ....................................................................................................... 35
  2.6 The Future .................................................................................................... 36

Problems .................................................................................................................. 37
  2.1 I Lost My Pants ............................................................................................ 37
  2.2 My Pantyhose Ran Faster than the Runners in the Boston Marathon ....... 37
  2.3 The Clothes Horse ....................................................................................... 37
2.4 Tires on and in Rubber .................................................. 38
2.5 An Opinion Poll on Clothing and Other Items ........................................ 38
References .......................................................... 38

Chapter 3 The Chemistry of Waste Management and Recycling ............. 43
3.1 Waste .............................................................................. 43
3.2 Recycling .......................................................................... 44
   3.2.1 Introduction .......................................................... 44
   3.2.2 Paper .......................................................................... 45
      3.2.2.1 Recycling versus Incineration ................................. 45
      3.2.2.2 Deinking .......................................................... 46
      3.2.2.3 Enzymatic Repulping .......................................... 46
      3.2.2.4 Extent of Recycling of Paper ................................. 47
   3.2.3 Plastics ......................................................................... 47
      3.2.3.1 Recycling Methods .............................................. 48
      3.2.3.2 Use of Compatibilizers and Handling of Mixtures .......... 49
      3.2.3.3 Use of Chemical Reactions in Recycling ......... 49
      3.2.3.4 Biodegradable Polymers ..................................... 50
   3.2.4 Metals .......................................................................... 51
      3.2.4.1 Methods of Recycling ........................................ 51
      3.2.4.2 Recovery of Metals from Petroleum Residues .......... 52
   3.2.5 Glass ............................................................................ 52
   3.2.6 Miscellaneous Recycling ............................................... 52
      3.2.6.1 Composting ....................................................... 52
      3.2.6.2 Uses for Food-Processing Wastes ......................... 53
      3.2.6.3 Toner Cartridges ................................................ 53
      3.2.6.4 Use of Baths of Molten Metal and Plasma Arcs .......... 53
      3.2.6.5 Uses for Inorganic Wastes (Other than Glass and Metals) ............................................. 53
   3.3 Methods and Incentives for Source Reduction ........................................ 54
   3.3.1 Range of Approaches ................................................. 54
   3.3.2 Throwaway Items and the Consumer ...................................... 55
   3.3.3 Containers and Packaging ............................................ 56
   3.3.4 Using Less Paper ...................................................... 58
   3.3.5 Life-Cycle Analyses .................................................. 59
   3.3.6 Role of Government in Reducing Consumption ...................... 59
   3.4 Overall Picture ............................................................. 60
Problems ............................................................... 61
   3.1 Cost-Effective Handling of Sewage Waste ..................................... 61
3.2 The Computer Age .................................................... 61
3.3 A Printing Challenge .................................................. 61
3.4 It Is Turkey Time ....................................................... 62
3.5 Toys and Games from Trash ........................................ 62
3.6 A Problem of Waste from University ........................... 63
3.7 The Three R’s of the Environment ............................... 63
3.8 A Plastic Bottle Opportunity ....................................... 63

References ........................................................................ 64

Chapter 4 Energy and the Environment ........................................ 73
4.1 Energy-Related Problems ............................................. 73
  4.1.1 Generation of Electric Power .................................... 73
  4.1.2 Transportation ....................................................... 75
  4.1.3 Global Warming .................................................... 76
4.2 Heating, Cooling, and Lighting Buildings ......................... 77
  4.2.1 Use of Trees and Light Surfaces ............................... 78
  4.2.2 Solar Heating and Cooling ...................................... 78
  4.2.3 Heat Storage ........................................................ 79
  4.2.4 Lighting ............................................................... 80
4.3 Renewable Energy for Electricity and Transport .................. 80
  4.3.1 Alternative Fuels .................................................... 80
  4.3.2 A Hydrogen Economy ............................................ 82
  4.3.3 Fuel Cells ............................................................ 83
  4.3.4 Solar Thermal Systems .......................................... 84
  4.3.5 Photovoltaic Cells ............................................... 84
  4.3.6 Other Sources of Renewable Energy ....................... 86
  4.3.7 Energy Storage ...................................................... 87
4.4 Use of Less Common Forms of Energy for Chemical Reactions ..................................................... 89
  4.4.1 Electricity ............................................................. 89
  4.4.2 Light ................................................................. 90
  4.4.3 Ultrasound .......................................................... 91
  4.4.4 Microwaves ......................................................... 92

References ........................................................................ 95

Chapter 5 Environmental Economics ........................................... 109
5.1 Introduction .................................................................. 109
5.2 Nature’s Services ....................................................... 109
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.3</td>
<td>Environmental Accounting</td>
<td>111</td>
</tr>
<tr>
<td>5.3.1</td>
<td>The Ecological Footprint</td>
<td>111</td>
</tr>
<tr>
<td>5.3.2</td>
<td>Life-Cycle Analyses</td>
<td>112</td>
</tr>
<tr>
<td>5.3.3</td>
<td>Cost–Benefit Analyses</td>
<td>114</td>
</tr>
<tr>
<td>5.3.4</td>
<td>Green Accounting</td>
<td>115</td>
</tr>
<tr>
<td>5.4</td>
<td>Corporations</td>
<td>116</td>
</tr>
<tr>
<td>5.4.1</td>
<td>Additional Reasons Why Pollution Prevention May Not Be Adopted</td>
<td>116</td>
</tr>
<tr>
<td>5.4.2</td>
<td>Other Aspects of Corporate Finance</td>
<td>118</td>
</tr>
<tr>
<td>5.5</td>
<td>Environmental Economics of Individuals</td>
<td>119</td>
</tr>
<tr>
<td>5.5.1</td>
<td>Making Choices</td>
<td>119</td>
</tr>
<tr>
<td>5.5.2</td>
<td>Ecotourism</td>
<td>120</td>
</tr>
<tr>
<td>5.6</td>
<td>Government Actions Affecting Environmental Economics</td>
<td>121</td>
</tr>
<tr>
<td>5.6.1</td>
<td>Role of Government</td>
<td>121</td>
</tr>
<tr>
<td>5.6.2</td>
<td>Regulations</td>
<td>122</td>
</tr>
<tr>
<td>5.6.3</td>
<td>Jobs and Regulations</td>
<td>123</td>
</tr>
<tr>
<td>5.6.4</td>
<td>Subsidies</td>
<td>123</td>
</tr>
<tr>
<td>5.6.5</td>
<td>Taxes</td>
<td>124</td>
</tr>
<tr>
<td>Problems</td>
<td></td>
<td>125</td>
</tr>
<tr>
<td>5.1</td>
<td>To Veto or Not</td>
<td>125</td>
</tr>
<tr>
<td>5.2</td>
<td>An Issue at Sea</td>
<td>125</td>
</tr>
<tr>
<td>5.3</td>
<td>The Precious Plant</td>
<td>125</td>
</tr>
<tr>
<td>5.4</td>
<td>Compound X</td>
<td>126</td>
</tr>
<tr>
<td>5.5</td>
<td>A Valuable Community Asset</td>
<td>126</td>
</tr>
<tr>
<td>5.6</td>
<td>Fast Food Litter</td>
<td>126</td>
</tr>
<tr>
<td>5.7</td>
<td>Too Many Cars</td>
<td>126</td>
</tr>
<tr>
<td>5.8</td>
<td>A Problem with Paper</td>
<td>127</td>
</tr>
<tr>
<td>5.9</td>
<td>Should TOSCA Be Replaced or Revised?</td>
<td>128</td>
</tr>
<tr>
<td>5.10</td>
<td>A Downward Spiral</td>
<td>128</td>
</tr>
<tr>
<td>References</td>
<td></td>
<td>128</td>
</tr>
</tbody>
</table>

**Chapter 6**

The Greening of Society .......................................................... 135

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.1</td>
<td>Introduction</td>
<td>135</td>
</tr>
<tr>
<td>6.2</td>
<td>Individuals</td>
<td>135</td>
</tr>
<tr>
<td>6.3</td>
<td>Government</td>
<td>137</td>
</tr>
<tr>
<td>6.4</td>
<td>Businesses</td>
<td>138</td>
</tr>
<tr>
<td>Problems</td>
<td></td>
<td>145</td>
</tr>
<tr>
<td>6.1</td>
<td>Manufacturing Products for a Sustainable Future</td>
<td>145</td>
</tr>
<tr>
<td>6.2</td>
<td>Remediying a Herbal Problem</td>
<td>146</td>
</tr>
<tr>
<td>6.3</td>
<td>Strong Paper Additives?</td>
<td>146</td>
</tr>
<tr>
<td>6.4</td>
<td>A Strange New Disease</td>
<td>146</td>
</tr>
<tr>
<td>6.5</td>
<td>“Adhere” versus “SuperGloop”</td>
<td>147</td>
</tr>
<tr>
<td>6.6</td>
<td>A Water Catastrophe</td>
<td>147</td>
</tr>
</tbody>
</table>
6.7 Avoiding an Expensive Recoat ........................................ 147
6.8 Battling the Business Center ........................................ 148
6.9 Your Viewpoint on Some Green Chemistry and
Sustainability Issues ....................................................... 148

References ........................................................................ 149

Chapter 7 Solutions to In-Chapter Problems ......................... 155

Solutions to Chapter 1: Toxicity, Accidents, and Chemical Waste ........................................................................ 155
Solutions to Chapter 2: The Chemistry of Longer Wear .......... 159
Solutions to Chapter 3: The Chemistry of Waste Management and Recycling ............................................. 161
Solutions to Chapter 4: Energy and the Environment .......... 163
Solutions to Chapter 5: Environmental Economics .......... 165
Solutions to Chapter 6: The Greening of Society ................. 168

References ........................................................................ 170
Foreword

As communication technology has advanced over the last few decades, people have been able to converse at lightning speed. Direct computer to computer e-mailing, phone to phone texting, and collective postings on various aggregate systems has provided an instantaneousness that helps to rapidly disseminate concepts and ideas across huge numbers of people. There are many reasons to celebrate these advances in communication. A more knowledgeable population of individuals should be better equipped to make decisions facing them. Unfortunately, for the obvious reasons of simplicity and efficiency, requirements governing the size and complexity of the information being transmitted have imposed a more abbreviated and simplified content. One could go on and on lamenting the sociological implications of this trend.

Abbreviated communication is relatively new to the human scene. Deep within our being, humans have been accustomed to and require the extended narrative. Even before the written word, storytelling around the campfire by the elders allowed the propagation and dissemination of critical information. Homer’s epic poems *The Iliad* and *The Odyssey*, passed down through countless generations of oral history, are bursting with subtlety and nuance that provide philosophical introspection nearly three millennia later.

The field of green chemistry is not easily reduced into short, simple statements. There are levels of complexity that require the superimposition of several different and often opposing viewpoints relating impacts on human health and the environment. There is a somewhat fractal structure that is often revealed when delving into green chemistry implications. As more questions are answered, new questions arise whose answers give rise to new questions. Limiting communication to 140 characters not only omits the complexity of any topic but also gives the mistaken impression that it is easier or simpler than it really is. This creation of false expectations leads to obvious difficulties when people react to the partial information, often leading to unfortunate consequences.

This book offers a continuation of the human narrative that is green chemistry. Al Matlack has been part of the woven tapestry since the earliest days of the field. His industrial knowledge, insight, and genuine curiosity were uncontainable. Anyone attending any green chemistry symposium or conference grew to anticipate the inevitable question of every speaker who began with the phrase “Al Matlack, University of Delaware….” To some in the audience, Al’s questions might have seemed to come from left field. Some, I suspect, grew impatient, not recognizing the significance of the questions he would ask. But his questions always connected seemingly disconnected concepts that were not only interesting but also significantly important to recognize. He would raise issues that could not be easily addressed at the end of a 45-minute presentation. Perhaps they were not suitable for abbreviated communication. But they were important.

The scientific society and the human society have lost the physical embodiment of Al Matlack. Andrew Dicks has combined his own insight and experience to help shape a book that provides a source of useful and well-developed information.
A quick scan of this book will not do it justice. This is not a collection of “sound bites.” It is also not a complete comprehensive treatise of the field of green chemistry or sustainability. No individual or group of individuals could possibly be capable of representing an entire field. But what this book does offer is an excellent glimpse into how Al Matlack and Andrew Dicks view this complicated and nuanced area. For anyone trying to develop their own understanding of and relationship to green chemistry and sustainability, this book offers an opportunity to see through the viewpoint of deep experience and insight. With or without this book, Al Matlack will forever remain in our collective narrative.

John C. Warner

Warner Babcock Institute, LLC
Preface

This book is written with the intent of highlighting a method that makes our students want to come to class. A course covering aspects of green chemistry, industrial chemistry, and introductory polymer science was taught at the University of Delaware from 1995 to 2013. A semester of organic chemistry was a requirement for the course. A full-year prerequisite would certainly have been better, but students in chemical engineering generally do not take that much. Those enrolled were primarily seniors and first-year graduate students. Some of them worked an 8-hour day before arriving at class as they were often progressing toward a master’s degree. Classes were three hours long and ran from 6:30 to 9:30 p.m. with a 10-minute break in the middle. They were conducted as interactive discussions rather than as formal lectures, as the latter can make it challenging for students to concentrate. The discussion format works only when the students have read the appropriate chapter in the course text (Introduction to Green Chemistry, 2nd Edition, Taylor & Francis) and other required outside reading before coming to class. The only straight lecture was when literature was covered since the text was written in 2010.

Just like anyone else, students can get tired after a day of studying or performing benchwork. However, they became excited to learn when the problem-based learning exercises described in this book were introduced for the last 30–45 minutes of class. The hope is that while less material can be covered this way, the student will remember more of it several years later. It also teaches them how to analyze real-world situations and how to be creative in solving problems. Many of these exercises are based on events that have actually taken place. In terms of organization, the class was split into small groups by letting them draw straws each week. Each group received a name, such as Paleocene, Pentacene, and Anthropocene, and the “problem of the week” to be discussed was presented. After they were no longer working on the problem, the solutions that the students devised were covered, with each group getting a turn. For each turn, a different spokesperson for the group spoke up, and this continued until the students exhausted their answers. The proposals were commented on and the spokesperson asked for further interpretation where necessary. It was emphasized to the class that every answer is of merit and is worthy of further consideration. A 10-minute quiz at the beginning of the next class might include a question regarding the problem-based learning exercise from the previous week.

The book blends some fundamental principles of green chemistry and sustainability from Introduction to Green Chemistry with a total of 50 problems discussed at the University of Delaware. Wherever possible, the problems are organized around appropriate content. As examples, Chapter 1 deals with issues surrounding substance toxicity, chemical accidents, and waste generation/disposal. In the associated end-of-chapter problems, students are placed in the real-world roles of a manufacturing plant chief executive officer, a chemistry department chair, and a chemical engineer. Chapter 4 concerns energy and the environment and the dilemma of a university architect who is designing new buildings expected to be more energy-efficient. Chapter 5 explores the development of new policies, with one problem focusing on
the concern of too many cars on a university campus. Proposed solutions, examples, and comments are collected together in Chapter 7, along with relevant literature references. It is perhaps unsurprising to learn that students are often uncomfortable that there are several “correct” answers to many of the problems. It should be regularly emphasized to them that green chemistry is about decision-making and the weighing of many factors that are often conflicting.

Whether you are teaching green chemistry for the first time or are a seasoned instructor, we hope you find the problems described here both relevant and stimulating. Many thanks go to John Warner and Hal White for writing the foreword and introduction, respectively, and to Hilary LaFoe for her efforts in making this book come to fruition.

Albert S. Matlack  
*Department of Chemistry and Biochemistry*  
*University of Delaware*

Andrew P. Dicks  
*Department of Chemistry*  
*University of Toronto*
Introduction

Problem-based learning in principle is how we learn most of the time outside of school. We are confronted with a problem we have to solve. The way to proceed is not obvious. The problem may seem intractable or there may be many possible solutions, some better than others. One needs to explore possibilities and obtain sufficient information from different realms to make a decision on how to proceed given constraints and expectations. Traditional education is not structured this way. Typically information is first provided in lectures and texts, studied by students, and then applied to discipline-specific problems that often have a single correct answer.

In the early 1990s, a group of faculty in the sciences at the University of Delaware decided to adopt and adapt problem-based learning to their introductory undergraduate biology, chemistry, biochemistry, and physics courses. Instead of lecturing to students most of the time, we developed real-world problems that required the understanding of the basic science concepts that would have been presented in lecture. This was one of the first concerted efforts to teach using problem-based learning (PBL) at the undergraduate level. It was a few years after the arrival of PBL at the University of Delaware when Al Matlack, a retired chemist from Hercules, began teaching environmental chemistry and industrial chemistry as an adjunct professor at the university.

Sometime later, Al came to my office expressing his frustration with the poor performance of the students in his classes and wanting to learn about my experience with PBL in my biochemistry courses. As with many problems he encountered at work or in life, Al was looking for solutions. He had heard about PBL and wondered if it might be an alternative to his lecturing approach that did not seem to achieve his desired outcome of student learning and understanding. I suspect that was when Al began to think in terms of actively involving students in problem-solving situations in class. Because of Al’s exceptionally broad interests and his long career as an industrial chemist, he had a wealth of experiences that could be transformed into real-world problems for students to work on.

Al’s knowledge and experience was not limited to teaching in the classroom. He had broad interests in the environment that extended well beyond chemistry. As president of the Society of Natural History of Delaware, for many years he organized monthly field trips carefully selected to provide participants with first-hand exploration of environmental issues affecting society. In that context, I became a student of Al Matlack. He took our group to visit paper recycling operations where we saw what happened to paper products spared from the landfill. Our group visited neighborhoods built at different times to see how architecture changed with the advent of air conditioning and the effects that had on landscape plantings and neighborly interactions. With Al, I and others visited various storm water retention basins having different designs and learned about impervious surfaces, ground water restoration, and flood control. There were many other field trips relating to forest management and reforestation, invasive plant species and their impact, recovery of sturgeon populations in the Delaware Bay, the quaternary geology of the Delmarva
Peninsula showing evidence of permafrost, or removal of dams to permit spawning of anadromous fish. All could be considered problems requiring societal solutions, and many had chemical dimensions.

Some of those themes are echoed in the problems in this book. It is a gold mine of relevant problems pertaining to green chemistry and sustainability. The motivated student will find much to ponder here.

Harold B. White
Department of Chemistry and Biochemistry
University of Delaware
To say that my father, Albert S. Matlack, was a chemist doesn’t do him justice. Perhaps Chemist, capitalized in recognition of his passion for the subject, would be better. We have an essay he wrote at around the age of 13 stating his intention of becoming one. No alternatives were mentioned. His chemical career started with the Manhattan project during World War II. Following that, he was an organic chemist for 43 years at Hercules Incorporated in Wilmington, Delaware, retiring at the age of 70 only when forced to do so. Despite his age at the time, he had not yet had enough chemistry and promptly volunteered to teach at the University of Delaware, which he did until only months before his death at the age of 90 in 2013. That also wasn’t enough to satisfy his appetite for chemistry, so at the same time, over the course of more than 10 years, he wrote a (big, long) book, Introduction to Green Chemistry. Then he wrote this one, finishing it—by my calculation—only days before his death. In the months before he died, he and I were approaching chemical journals, successfully, to find him a place where he could write a regular column commenting critically on recent chemical developments. Now, when I am reading the chemical literature and come across something particularly cool, among my thoughts is “It’s sad that Dad will never get to know this.”

You might find such prolonged focus on a technical topic a bit frightening and fear that he was narrow and boring in person. He was not. He was warm, outgoing, and friendly and a relentlessly and passionately constructive man (and a great husband and father). For me, his attitude can be summarized in something he once said while we were discussing the study of history as an occupation: “Some people are interested in the past. I’m interested in the future.”

My father did not join an ongoing, established green chemistry field. Rather, he pre-dated it by decades. He was an environmentalist before the term was coined. Green chemistry combined his two passions: chemistry and the environment. He could clearly see the damage humans are doing to the planet, and he focused his almost unbelievable energy and patience on the problem. He would encourage you to do the same because the problem is acute, getting worse, and of a magnitude that dwarfs anything we have ever dealt with before. Politics aside, much of it comes down to chemistry. We need new energy sources, less pollution, better batteries, renewable starting materials…the list is long. We also need well-informed, passionate people who understand chemistry and can use it creatively to solve these problems. If you contribute to their solution, you will really have accomplished something. As the bumper stickers say: “There is no Planet B.”

Go for it, and good luck.

Kent E.S. Matlack, PhD
Editor

Andrew P. Dicks, PhD, joined the University of Toronto Chemistry Department in 1997. After undergraduate and graduate study in the United Kingdom, he became an organic chemistry sessional lecturer in 1999, and he was hired as part of the university teaching-stream faculty two years later. He has research interests in undergraduate laboratory instruction that involve designing novel and stimulating experiments, particularly those that showcase green chemistry principles. This work has lead to over 45 peer-reviewed publications in the chemical education literature. Following promotion in 2006, he became Associate Chair of Undergraduate Studies for two years and developed an ongoing interest in improving the student experience in his department.

Dr. Dicks has won several pedagogical awards, including the University of Toronto President’s Teaching Award, the Chemical Institute of Canada Award for Chemical Education, a 2011 American Chemical Society-Committee on Environmental Improvement Award for Incorporating Sustainability into Chemistry Education and a 2015 Canadian Green Chemistry and Engineering Award. He has additionally edited a book as a resource for teaching green chemistry (Green Organic Chemistry in Lecture and Laboratory, CRC Press). In 2014 he was co-chair of the 23rd IUPAC International Conference on Chemistry Education, which was held in Canada for the first time since 1989.

Following the passing of Albert Matlack in 2013, Dr. Dicks assumed editorship of Problem-Solving Exercises in Green and Sustainable Chemistry in order to ensure the issues discussed in this book became available to the broader chemistry community.
Toxicity, Accidents, and Chemical Waste

1.1 GENERAL BACKGROUND

This chapter considers what is toxic, what is waste, why accidents occur, and how to reduce all of these. In the glorious days of the 1950s and 1960s, chemists envisioned chemistry as the solution to a host of society’s needs. Indeed, they created many of the things we use today and take for granted. The discovery of Ziegler–Natta catalysis of stereospecific polymerization alone resulted in major new polymers. The chemical industry grew by leaps and bounds until it employed about 1,027,000 workers in the United States in 1998. By 2007, this number had dropped to 872,200. Some may remember the DuPont slogan, “Better things for better living through chemistry.”

In the Sputnik era, the scientist was a hero. At the same time, doctors aided by new chemistry and antibiotics felt that infectious diseases had been conquered. Unfortunately, amid the numerous success stories were some adverse outcomes that chemists had not foreseen.

Thalidomide (Schematic 1.1) was used to treat nausea in pregnant women from the late 1950s to 1962. It was withdrawn from the market after 8000 children in 46 countries were born with birth defects. The compound has other uses as a drug as long as it is not given to pregnant women. In Brazil, it is used to treat leprosy. Unfortunately, some doctors there have not taken the warning seriously enough and several dozen deformed births have occurred. The U.S. Food and Drug Administration (FDA) has approved its use for treating painful inflammation of leprosy. It also inhibits human immunodeficiency virus (HIV) and can prevent the weight loss that often accompanies the acquired immunodeficiency syndrome (AIDS). Celgene is using it as a lead compound for an anti-inflammatory drug and is looking for analogs with reduced side effects. The analog overleaf (Schematic 1.2) is 400–500 times as active as thalidomide. Revlimid (Schematic 1.3) is approved for treating multiple myeloma.

Today, there is often public suspicion toward scientists. Some picture a mad chemist with his stinks and smells. There is a notion among some people “that science is boring, conservative, close-minded, devoid of mystery, and a negative force in society.” Chemophobia has increased. Many people think that chemicals are bad and “all natural” is better, even though a number of them do not know what a chemical is. There is a feeling that scientists should be more responsible for the influence of their work on society. Liability suits have proliferated in the United States. This has caused at least three companies to declare bankruptcy: Johns Manville for asbestos in 1982, A. H. Robins for its “Dalkon Shield” contraceptive device in 1985, and Dow Corning for silicone breast implants in 1995. Doctors used to be the respected pillars of their communities. Today they are subjects of malpractice suits, some of which only serve to increase the cost of health care. Medical implant research is threatened by the unwillingness of companies...
such as DuPont and Dow Corning to sell plastics for the devices to implant companies. The chemical companies fear liability suits. Not long ago drug companies became so concerned about lawsuits on childhood vaccines that many were no longer willing to make them. Now that the U.S. Congress has passed legislation limiting the liability, vaccine research is again moving forward. The lawsuits had not stimulated research into vaccines with fewer side effects, but instead had caused companies to leave the market.

### 1.2 TOXICITY OF CHEMICALS IN THE ENVIRONMENT

The public’s perception of toxicity and risk often differs from that found by scientific testing. The idea that “natural” is better than “chemical” is overly simplistic. Many chemicals that are found in nature are extremely potent biologically. Mycotoxins are among these. Aflatoxins (Schematic 1.4) were discovered when
turkeys fed moldy groundnut (peanut) meal became ill and died. They are among the most potent carcinogens known. Vikings went berserk after eating derivatives of lysergic acid (Schematic 1.5) made by the ergot fungus growing on rye.

Some *Amanita* mushrooms are notorious for the poisons that they contain. A Japanese fish delicacy of globefish or other fishes may contain potent poisons (such as tetrodotoxin; Schematic 1.6) if improperly prepared. Tainted fish cause death in 6–24 hours in 60% of those who consume it. They die from paralysis of the lungs. Oysters may also contain poisons acquired from their diet. The extract of the roots of the sassafras tree (*Sassafras albidum*) (Schematic 1.7) is used to flavor the soft drink “root beer” but contains the carcinogen safrole, which must be removed before use.

**SCHEMATIC 1.4** Aflatoxin B₁

**SCHEMATIC 1.5** Lysergic acid

**SCHEMATIC 1.6** Tetrodotoxin
The U.S. Congress added the Delaney clause to the Food, Drug, and Cosmetic Act in 1958.\textsuperscript{17} The clause reads: “No additive shall be deemed to be safe if it is found to induce cancer when ingested by man or animal, or if it is found, after tests which are appropriate for the evaluation of the safety of food additives, to induce cancer in man or animal.” It does not cover natural carcinogens in foods or environmental carcinogens, such as chlorinated dioxins and PCBs. Some Americans feel that food additives are an important source of cancer, and that the Delaney clause should have been retained. Bruce Ames,\textsuperscript{18} the father of the Ames test for mutagens, disagrees. The Delaney clause was repealed on August 3, 1996.\textsuperscript{19}

Ames feels that, instead of worrying so much about the last traces of contaminants in foods, we should focus our attention on the real killers.

### Annual Preventable Deaths in the United States\textsuperscript{20}

<table>
<thead>
<tr>
<th>Cause</th>
<th>Deaths</th>
</tr>
</thead>
<tbody>
<tr>
<td>Active smoking</td>
<td>430,700</td>
</tr>
<tr>
<td>Overweight and sedentary</td>
<td>400,000</td>
</tr>
<tr>
<td>Alcoholic beverages</td>
<td>100,000</td>
</tr>
<tr>
<td>Passive smoking</td>
<td>53,000</td>
</tr>
<tr>
<td>Auto accidents</td>
<td>43,300</td>
</tr>
<tr>
<td>AIDS</td>
<td>37,500</td>
</tr>
<tr>
<td>Homicides</td>
<td>34,000</td>
</tr>
<tr>
<td>Suicides</td>
<td>30,575</td>
</tr>
<tr>
<td>Falls</td>
<td>14,900</td>
</tr>
<tr>
<td>Drowning</td>
<td>4400</td>
</tr>
<tr>
<td>Fires</td>
<td>3200</td>
</tr>
<tr>
<td>Cocaine</td>
<td>4202</td>
</tr>
<tr>
<td>Heroin and morphine</td>
<td>4175</td>
</tr>
<tr>
<td>Bee stings</td>
<td>3300</td>
</tr>
<tr>
<td>Radon, to nonsmokers</td>
<td>2,500</td>
</tr>
<tr>
<td>Lightning</td>
<td>82</td>
</tr>
<tr>
<td>Recalcitrant farm animals</td>
<td>20</td>
</tr>
<tr>
<td>Dog mauling</td>
<td>17</td>
</tr>
<tr>
<td>Snakebite</td>
<td>12</td>
</tr>
</tbody>
</table>

The World Health Organization (WHO) estimates that the number of smoking deaths worldwide is about 3 million/year.\textsuperscript{21} Cigarette use is increasing among American college students, despite these statistics.\textsuperscript{22} Indoor radon contributes to about 12% of the lung cancer deaths in the United States each year.\textsuperscript{23} Infectious diseases cause 37% of all deaths worldwide.\textsuperscript{24} Many of these could be prevented by
improved sanitation. There are 3 million pesticide poisonings, including 220,000 fatalities and 750,000 chronic illnesses, in the world each year. Smoke from cooking with wood fires kills 4 million children in the world each year.

It is estimated that perhaps 80% of cancers are environmental in origin and related to lifestyle. There is “convincing” evidence of a connection between excess weight and cancers of the colon, rectum, esophagus, pancreas, kidney, and breast in postmenopausal women.\(^{25}\) (There are genetic factors, now being studied by the techniques of molecular biology, that predispose some groups to heightened risk, e.g., breast cancer in women.\(^{26}\) In addition to cancers caused by tobacco and ethanol, there are those caused by being overweight,\(^{27}\) too much sun, smoked foods, foods preserved with a lot of salt, and viruses (for cancers of the liver and cervix). Consumption of the blue-green alga, \textit{Microcystis}, has increased liver cancer in China.\(^{28}\) Many species of cyanobacteria produce the neurotoxin (Schematic 1.8).\(^{29}\)

Perhaps the biggest killer is sodium chloride, a compound necessary for life, which plays a role in the regulation of body fluids and blood pressure.\(^{30}\) It raises the blood pressure of many of the 65 million Americans with hypertension, increasing the risk of osteoporosis, heart attack, and stroke.\(^{31}\) The U.S. National Academy of Sciences suggests limiting the consumption of sodium chloride to 4 g/day (1.5 g of sodium).\(^{32}\) This means cutting back on processed foods (source of 80% of the total), such as soups, frozen dinners, salted snacks, ham, soy sauce (18% salt), ready-to-eat breakfast cereals, and others. The Dietary Approaches to Stop Hypertension (DASH) diet, which reduces salt, has lots of fruits and vegetables, and minimizes saturated fat from meat and full-fat milk, is as effective as drugs in lowering blood pressure in many cases. However, this may not be the whole story. If there is an adequate intake of calcium, magnesium, and potassium, together with fruits and vegetables in a low-fat diet, the sodium may not need to be reduced, as shown in a 1997 study.\(^{33}\) The DASH diet also reduces the risk of heart disease by 24% and of stroke by 18%.\(^{34}\) People who do not smoke, are active physically, drink alcohol in moderation, and eat at least five servings of fruits and vegetables a day live 14 years longer on average than those who do none of these.\(^{35}\) In the United States, snacks and soft drinks have tended to supplant nutrient-rich foods, such as fruits, vegetables, and milk. Not eating fruits and vegetables poses a greater cancer risk than traces of pesticides in foods.\(^{36}\) Fruits and vegetables often contain natural antioxidants,\(^{37}\) such as the resveratrol (Schematic 1.9) found in grapes. Resveratrol inhibits tumor initiation, promotion, and progression.\(^{38}\) Sirtus Pharmaceuticals was founded in 2004 to develop derivatives of resveratrol for age-related diseases.\(^{39}\)

![Schematic 1.8](image)

\textbf{Schematic 1.8}  Neurotoxin from cyanobacteria
Antioxidants have also reduced atherosclerotic heart disease.\textsuperscript{40} Thus, foods contain many protective substances, as well as some antinutrients, such as enzyme inhibitors and natural toxins.\textsuperscript{41}

A U.S. National Research Council report concludes that natural and synthetic carcinogens are present in human foods at such low levels that they pose little threat.\textsuperscript{42} It points out that consuming too many calories as fat, protein, carbohydrates, or ethanol is far more likely to cause cancer than consuming the synthetic or natural chemicals in the diet. However, it also mentions several natural substances linked to increased cancer risk: heterocyclic amines, such as nitrosamines, aflatoxins, and other mycotoxins, formed in the overcooking of meat.\textsuperscript{43} Typical of the heterocyclic amine mutagens are compounds Schematic 1.10 and Schematic 1.11, the first from fried beef and the second from broiled fish.\textsuperscript{44}

Deep frying with soybean, sunflower, and corn oil allows air oxidation of linoleates to highly toxic (2E)-4-hydroxy-2-nonenal (Schematic 1.12), which has been linked to Parkinson’s and Alzheimer’s diseases.\textsuperscript{45}
Two reviews cover the incidence of cancer and its prevention by diet and other means.\textsuperscript{46} Cancer treatments have had little effect on the death rates, so prevention is the key.\textsuperscript{47}

Being sedentary is a risk factor for diseases such as heart attack and late-onset diabetes. One-third of adult Americans are obese, perhaps as much the result of cheap gasoline as the plentiful supply of food.\textsuperscript{48} Obesity-related complications result in 400,000 premature deaths in the United States each year. This is less of a problem in most other countries. For example, the incidence of obesity in the United Kingdom is 20%.

Prevention of disease is underused.\textsuperscript{49} Needle exchange programs could prevent 17,000 AIDS infections in the United States each year. Vaccines are not used enough. For example, only 61\% of the people in Massachusetts are fully vaccinated. Only 15\%–30\% of elderly, immunocompromised persons, and those with pulmonary or cardiac conditions have been vaccinated against pneumonia. A 1998 study, in New Jersey and Quebec, of patients older than 65 who had been prescribed cholesterol-lowering drugs found that, on average, the prescription went unfilled 40\% of the year. Good drug compliance lowered the cholesterol level by 39\%, whereas poor compliance lowered it by only 11\%.\textsuperscript{50}

### 1.3 ACCIDENTS WITH CHEMICALS

Chemists take pride in their ability to tame dangerous chemicals in an effort to make the things that society needs. In fact, some companies seek business by advertising their ability to do custom syntheses with such chemicals.\textsuperscript{51} Aerojet Fine Chemicals offers syntheses with azides and vigorous oxidations.\textsuperscript{52} Carbolabs offers custom syntheses with phosgene, fluorinating agents, and nitration. Custom syntheses with phosgene are also offered by PPG Industries, Hatco, Rhone-Poulenc, and SPNE. Pressure Chemical, Dynamit Nobel, and Rutgers suggest that they can do the hazardous reactions for others.\textsuperscript{53} A hazardous reagent may be attractive for fine chemical syntheses if it gives a cleaner product with less waste or saves two or three steps. It may also be used because it is the traditional way of doing the job. Methods for screening unknown reactions for hazards have been summarized.\textsuperscript{54}

Chemistry is a relatively safe occupation. (Underground coal mining is one of the most dangerous in the United States. A total of 47 coal miners lost their lives in 1995 from surface and underground mining.\textsuperscript{55}) In the United States in 1996, the nonfatal injury and illness rate for chemical manufacturing was 4.8:100 full-time workers, compared with 10.6 for all of manufacturing. There were 34 deaths in the chemical industry, about 5\% of those for all manufacturing.\textsuperscript{56} The injury rate of the chemical industry in the United Kingdom fell to an all-time low in 1997,
0.37 accidents per 100,000 hours. This was in the middle of those for manufacturing industries, worse than the textile industry, but better than the food, beverage, and tobacco industries. However, despite countless safety meetings and inspections and safety prizes, accidents still happen. In chemistry, just as in airline safety, some of the accidents can be quite dramatic. There were 23,000 accidents with toxic chemicals in the United States in 1993–1995 (i.e., 7670/year compared with 6900/year in 1988–1992). The accidents in 1993–1995 included 60 deaths and the evacuation of 41,000 people. Statistics for the United States compiled by the Chemical Safety and Hazard Investigation Board reveal an average of 1380 chemical accidents resulting in death, injury, or evacuation each year for the 10 years before 1999. Each year, these accidents caused an average of 226 deaths and 2000 injuries. About 60,000 chemical accidents are reported annually in the United States. The American Chemistry Council in the United States reported 793 fires, explosions, and chemical releases in 1995. American Chemistry Council members reported about 2000 accidents in 2003, about the same as a decade before. About 50% of global chemical incidents are in the United States and 30% in the EU. The United Kingdom is second only to the United States in recorded incidents.

Knowing the cause should help eliminate accidents in the future. Then engineering steps may be taken to produce a fail-safe system. These may involve additional alarms, interlocks (such as turning off microwaves before the oven door can be opened), automatic shutoffs if any leaks occur, and secondary vessels that would contain a spill. A special sump contained a leak of nerve gas when an O-ring failed at an incinerator at Tooele, Utah. Underground storage tanks (made of noncorroding materials) may be fitted with a catchment basin around the fill pipe, automatic shutoff devices to prevent overfilling, and a double-wall complete with an interstitial monitor. Clearly, such methods can work, but they have not reduced the overall incidence of accidents, as shown in the foregoing data. The best solution will be to satisfy society’s needs with a minimum of hazardous chemicals. A few of the many accidents will be discussed in the following to show how and why they occurred, together with some green approaches that could eliminate them.

The explosion of the nuclear reactor at Chernobyl (spelling changed recently to Chornobyl) in the Ukraine on April 26, 1986 sent radioactive material as far away as Sweden. The current death toll is 65. There has been a huge increase in childhood thyroid cancer, with cases as far as 500 km away. (U.S. bomb tests have also increased the incidence of thyroid cancers in the western United States.) There is a 30-km exclusion zone around the plant where no one is allowed to live. This was created by the evacuation of 135,000 people. The accident is said to have happened “because of combination of the physical characteristics of the reactor, the design of the control rods, human error and management shortcomings in the design, and implementation of the safety experiment.”

The realization of the seriousness of global warming has led to many proposals for more nuclear plants. Electricity need not be generated by nuclear power. Generating it from fossil fuels contributes to global warming. Producing it from renewable sources, such as wind, wave power, hydropower, geothermal, and solar energy, does not. Sweden has voted to phase out nuclear energy. The German government has agreed to phase out the country’s 19 nuclear reactors. It has been
Toxicity, Accidents, and Chemical Waste

estimated that offshore wind power sources could produce electricity 40% more cheaply than the nuclear power stations planned for Japan.\textsuperscript{72} Energy conservation can help a great deal in reducing the amount of energy needed.

The flammable gases used by the petrochemical industry have been involved in many accidents.\textsuperscript{73} A fire and explosion following a leak of ethylene and isobutane from a pipeline at a Phillips plant in Pasadena, Texas, in 1989, killed 23 people and injured 130.\textsuperscript{74} The Occupational Health and Safety Administration (OSHA) fined the company US$4 million. Accidents of this type can happen anywhere in the world where petrochemical industries are located. There have been explosions at an ethylene plant in Beijing, China,\textsuperscript{75} at a Shell air separation plant in Malaysia,\textsuperscript{76} at a Shell ethylene and propylene plant in Deer Park, Texas,\textsuperscript{77} at a Shell propylene plant in Norco, Louisiana,\textsuperscript{78} at a BASF plant in Ludwigshafen, Germany, that used pentane to blow polystyrene,\textsuperscript{79} and at a Texaco refinery at Milford Haven, England.\textsuperscript{80} The problems at the BASF plant could have been avoided by blowing the polystyrene with nitrogen or carbon dioxide instead of pentane. Two weeks before this incident at the BASF plant, four people were injured by a fire from a benzene leak.\textsuperscript{81} BASF had two other accidents in October 1995, a polypropylene fire in Wilton, England, and spraying of a heat transfer fluid over the plant and adjacent town in Ludwigshafen, Germany.\textsuperscript{82} There was an explosion in the hydrogenation area of the company’s 1,4-butanediol plant in Geismar, Louisiana, on April 15, 1997,\textsuperscript{83} which resulted from internal corrosion of a hydrogen line. This corrosion might have been detected by periodic nondestructive testing with ultrasound. The explosion and fires at the Texaco refinery have been attributed to making modifications in the plant but not training people on how to use the modified equipment, having too many alarms (2040 in the plant), insufficient inspection of the corrosion of the equipment, not learning from experience, and reduced operator staffing.\textsuperscript{84} Investigation of an explosion and fire at Shell Chemical’s Belpre, Ohio, thermoplastic elastomer plant revealed that at the time of the accident, roughly seven times the normal amount of butadiene had inadvertently been added to the reactor. Alarms indicated that the reactor had been overcharged, but interlocks were manually overridden to initiate the transfer of raw materials into the reactor vessel, contrary to established procedures.\textsuperscript{85} The federal government fined the company US$3 million for the various citations in relation to the accident.\textsuperscript{86}

These examples show that even though companies have a great deal of experience in handling hazardous materials, accidents can still occur. This includes toxic gases as well. A leak in the hydrogen cyanide unit at a Rohm & Haas, Deer Park, Texas plant sent 32 workers to the hospital.\textsuperscript{87} Presumably, the hydrogen cyanide was being used to react with acetone in the synthesis of methyl methacrylate. An alternative route that does not use hydrogen cyanide is available.\textsuperscript{88} Isobutylene is oxidized catalytically to methacrolein and then to methacrylic acid, which is esterified with methanol to give methyl methacrylate. The methacrolein can also be made by the hydroformylation of propyne, although this does involve the use of toxic carbon monoxide and flammable hydrogen.\textsuperscript{89} These processes also eliminate the ammonium bisulfate waste from the process using hydrogen cyanide. A leak of hydrogen fluoride at a Marathon Petroleum plant in Texas City, Texas, sent 140 people to the hospital for observation and treatment of inflamed eyes and lungs and caused the evacuation of 3000 more.\textsuperscript{90} Replacement of the hydrogen fluoride with a nonvolatile
solid acid would eliminate such a problem. Many companies in the United Kingdom do not store hazardous materials correctly, which has resulted in some fires and explosions.\textsuperscript{91} More than 44 million Americans live or work near places that pose risks from the storage or use of dangerous industrial chemicals.\textsuperscript{92} The cost of accidents may be more than just a monetary one to the company. A fire and explosion occurred on July 4, 1993, at a Sumitomo Chemical plant in Niihama, Japan, that made over half of all the epoxy-encapsulation resin for semiconductor chips used in the entire world. Cutting off the supply would have been a serious inconvenience to the customers. The company took the unusual step of letting other companies use its technology until it could rebuild its own plant, so that a supply crisis never developed. The company still supplied 50\% of the world’s requirements for that resin in 1999.\textsuperscript{93}

Why do these accidents continue to happen? One critic says, “Hourly workers struggle to maintain production in the face of disabled or ignored alarms, undocumented and often uncontrollable bypasses of established components, operating levels that exceed design limits, postponed and severely reduced turnaround maintenance and increasing maintenance on ‘hot’ units by untrained, temporary non-union contract workers.”\textsuperscript{94} Another source mentions “institutional realities that undercut corporate safety goals, such as incentives that promote safety violations in the interest of short-term profitability, shielding upper management from ‘bad news’ and turnover of management staff.”\textsuperscript{95} A third says that “Many chemical plant disasters have been precipitated by an unplanned change in process, a change in equipment or a change in personnel.”\textsuperscript{96}

### 1.4 WASTE AND ITS MINIMIZATION

Nearly everything made in the laboratory ends up as waste. After the materials are made, characterized, and tested, they may be stored for a while, but eventually they are discarded. In schools, the trend is to run experiments on a much smaller scale, which means that less material has to be purchased and less waste results.\textsuperscript{97} (Even less material will be used if chemistry-on-a-chip becomes commonplace.\textsuperscript{98}) Two things limit how small a scale industrial chemists can use. One is the relatively large amount of a polymer needed for the fabrication of molded pieces for testing physical properties. There is a need to develop smaller scale tests that will give data that are just as good. The second factor is the tendency of salesmen to be generous in offering samples for testing by potential customers. A lot of the samples received by the potential customer may never be used.

Some industrial wastes result because it is cheaper to buy new material than to reclaim used material. Some catalysts fall into this category. The 1996 American Chemical Society National Chemical Technician Award went to a technician at Eastman Chemical who set up a program for recovering cobalt, copper, and nickel from spent catalysts for use by the steel industry.\textsuperscript{99} This process for avoiding landfill disposal gave Eastman significant savings. Some waste metal salts can be put in fertilizer as trace elements that are essential for plant growth. However, this practice has been abused in some cases by putting in toxic waste (e.g., some that contain...
dioxins and heavy metals).\textsuperscript{100} Even a waste as cheap as sodium chloride can be converted back to the sodium hydroxide and hydrochloric acid that it may have come from, by electrodialysis using bipolar membranes.\textsuperscript{101} Waste acid can be recovered by vacuum distillation in equipment made of fluoropolymers.\textsuperscript{102}

Improved housekeeping can often lead to reduced emissions and waste.\textsuperscript{103} The leaky valves and seals can be fixed or they can be replaced with new designs that minimize emissions.\textsuperscript{104} These include diaphragm valves, double mechanical seals with interstitial liquids, magnetic drives, better valve packings, filled fabric seals for floating roof tanks, and so on. Older plants may have some of the worst problems.\textsuperscript{105} The U.S. Environmental Protection Agency (EPA) fined Eastman Kodak US$8 million for organic solvents leaking from the 31 miles of industrial sewers at its Rochester, New York, plant. This emphasizes the need for regular inspections and preventive maintenance, which in the long run is the cheapest method. Vessels with smooth interiors lined with non- or low-stick poly(tetrafluoroethylene) can be selected for batch tanks that require frequent cleaning. These might be cleaned with high-pressure water jets instead of solvents. Perhaps a vessel can be dedicated to a single product, instead of several, so that it does not have to be cleaned as often. If a product requires several rinses, the last one can be used as the first one for a new lot of product. Volatile organic compounds can be loaded with dip tubes instead of splash loading. Exxon (now Exxon-Mobil) has used such methods to cut emissions of volatile organic compounds by 50\% since 1990.\textsuperscript{106} Install automatic high-level shut-offs on tanks. Use wooden pallets over again, instead of considering them throwaway items. The current ethic should be “reduce,” “reuse,” and “recycle” in that order.

A waste is not a waste if it can be reused. For example, one steel manufacturer drops pickle liquor down a 100-ft-tall tower at 1200°F to recover iron oxide for magnetic oxide and hydrogen chloride for use again in pickle liquor.\textsuperscript{107} The pomace left over from processing pears and kiwis can be dried and used to increase the dietary fiber in other foods.\textsuperscript{108} Food-processing wastes and wastes from biocatalytic processes often become feed for animals. A refinery stream of ethane, methane, butane, and propane, which was formerly flared as waste, will be processed to recover propane for conversion to propylene and then to polypropylene.\textsuperscript{109} Organic chemical wastes may end up as fuel for the site’s power plant or for a cement kiln, but more valuable uses would be preferable. Waste exchanges are being set up. One company’s waste may be another’s raw material. For example, calcium sulfate from flue gas desulfurization in Denmark and Japan ends up in drywall for houses. If the waste exchange merely pairs up an acid and a base so that the two can be neutralized, rather than reclaimed, the result is waste salts. Admittedly, these are probably not as toxic as the starting acid and base, but they still have to be disposed of somewhere. Several general references on waste minimization and pollution prevention are available.\textsuperscript{110} The hydroformylation\textsuperscript{111} of propene to form butyraldehyde invariably produces some isobutyraldehyde at the same time (Schematic 1.13).\textsuperscript{112} One of the best processes uses a water-soluble rhodium phosphine complex to produce 94.5\% of the former and 4.5\% of the latter.\textsuperscript{113} The products form a separate layer that is separated from the water. Rhodium is expensive, so it is important to lose as little as possible.
In 10 years of operation by Rhone-Poulenc-Ruhrchemie, 2 million metric tons of butyraldehyde have been made with the loss of only 2 kg of rhodium. The process is 10% cheaper than the usual one. Higher olefins are not soluble enough in water to work well in the process. The process does work for omega-alkenecarboxylic acids such as 10-undecenoic acid, where a 97:3 normal/iso compound is obtained in 99% conversion. For higher alkenecarboxylic acids, a phase-transfer catalyst, such as dodecyltrimethylammonium bromide, must be used. However, this lowers the normal/iso ratio. Over the years a variety of uses have been found for isobutyraldehyde by Eastman Chemical and others. It is converted to isobutyl alcohol, neopentyl glycol, isobutyraldehyde, isobutyric acid, isobutylidenediurea, methylisoamyl ketone, and various hydrogenation and esterification products (Schematic 1.14).

1.5 CONCLUSIONS

The challenge is to reduce the incidence and severity of accidents, waste, the toxicity of chemicals, and the amount of energy used, while still providing the goods that society needs. Several provocative papers suggest some ways of doing this. The key is in the preparation of more sophisticated catalysts. Thus, solid acids may be able to replace the risky hydrogen fluoride and sulfuric acid used in alkylation reactions in the refining of oil. Zeolites offer the promise of higher yields through size and shape selectivity. With the proper catalysts, oxidations with air and hydrogen peroxide may replace heavy metal-containing oxidants. Enantioselective catalysis may
allow the preparation of the biologically active optical isomer without the unwanted one. It may be possible to run the reaction in water at or near room temperature using biocatalysis instead of in a solvent or at high temperature. Some processes yield more by-product salts than the desired product. Sheldon recommends a salt-free diet by improved catalytic methods.

Bodor has suggested the design of biologically safer chemicals through retrometabolic design. For example, the ethylene glycol used widely as an antifreeze in cars might be replaced with less hazardous propylene glycol. The former is converted by the body to glycolaldehyde, glyoxylic acid, and oxalic acid (Schematic 1.15), whereas the latter gives the normal body metabolites lactic acid and pyruvic acid (Schematic 1.16).

A lethal dose of ethylene glycol for a man is 1.4 mL/kg. The problem is that its sweet taste makes it attractive to children and pets. An alternative approach is to add a bittering agent to it. The estimated lethal dose of propylene glycol for a man is 7 mL/kg.

The U.S. National Science and Technology Council has laid out a research and development strategy for toxic substances and waste. Hirschhorn has suggested ways of achieving prosperity without pollution.

Propylene used to be converted to isotactic polypropylene with titanium tetrachloride and diethylaluminum chloride in a hydrocarbon solvent. The atactic polypropylene obtained by evaporation of the solvent after filtration of the desired isotactic polymer was of little value, some going into adhesives. An acidic deashing step was necessary to remove residual titanium, aluminum, and chloride from the polymer, the metal-containing residues ending up in a landfill. This process was supplanted by high mileage catalysts during which the titanium chloride was supported on magnesium chloride. These were activated by triethylaluminum in the presence of ligands that enhance the stereoselectivity of the catalysts. The result was a product that required no deashing and no removal of atactic polymer. In the next step in the evolution, the solvent was eliminated by polymerization in the gas phase or in liquid propylene. By the proper choice of catalyst, the polymer can be obtained in large enough granules so that the older practice of extruding molten polymer to form a strand that was chopped into “molding powder” is no longer necessary. The field is still evolving. Metallocene single-site catalysts allow greater control of the product and have led to new products. Ethylene-$\alpha$-olefin copolymers can be made from ethylene alone,
the α-olefin being made in situ.\textsuperscript{125} A typical catalyst is shown in Schematic 1.17. It is activated by methyl alumoxane. Methods of preparing syndiotactic polypropylene in a practical way are now available. A new polypropylene made with such catalysts may be able to supply the properties now found only in plasticized polyvinyl chloride. All but the last type of catalyst show little tolerance to air, moisture, and polar groups. The catalyst in Schematic 1.18 is active in the presence of ethers, ketones, esters, and water.\textsuperscript{126} Ethylene can even be polymerized in water by one of the palladium diimine catalysts.\textsuperscript{127} The initial polymerization probably forms a shell of polyethylene that protects the catalyst from the water. To make the products even greener, consumer use must be reduced, the lower level of reuse and recycle must be raised, and a renewable source of the propylene, rather than petroleum, must be used. Propylene could be made by reduction and then dehydration of acetone from fermentation.

Hirschhorn\textsuperscript{128} feels that “An environmentally driven industrial revolution is beginning.” Brain Rushton, President of the American Chemical Society in 1995, said that “We will gradually eliminate environmentally unsound processes and practices from our industry. We will build a better environment to work and live in. We will keep scientists and engineers both employed and at the cutting edge of technology as they serve the competitive needs of the nation. Last but by no means least, we will create a better image for chemistry and the profession.”\textsuperscript{129}
Lastly, Gro Harlem Brundtland, former head of the WHO and former prime minister of Norway and the Secretary General of the World Commission on Environment and Development, has noted that “The obstacles to sustainability are not mainly technical. They are social, institutional and political.”

PROBLEMS

1.1 Pollution Prevention at an Isocyanates Plant
You are the chief executive officer at an isocyanates manufacturing plant based in North America. Isocyanates are used in the manufacture of pesticides (methyl isocyanate was the compound responsible for the 1984 Bhopal disaster in India, which is a highly toxic lachrymator). With the help of a nongovernmental organization, a study by company engineers has identified several opportunities to prevent pollution at one of your major production plants. The savings would be $1 million per year, with payback periods potentially ranging from 15 months to 5 years. The newly designed processes would eliminate 500,000 lb. of waste per year, and allow the expensive hazardous waste incinerator to be decommissioned. In addition to the savings in dollars, it could drastically help to improve public relations.

Considering the significant up-front capital expenses involved, should you implement the plan? If so, how would you implement it?

1.2 Curious Polar Bears
Some polar bears on Svalbard in the high arctic above Norway were found to have sexual organs of both sexes. This looks like a case of endocrine disruption. How would you find out what compound or compounds were involved? How did they get to this remote place? Pesticides are likely, but there is no gardening on Svalbard. What could be done about it, if anything?

1.3 After an Industrial Accident
You are the on-site manager of a production plant that uses a lot of chlorine gas. Recently, a storage tank ruptured due to an accident, which released about 500 lb. of chlorine. Fortunately, weather conditions prevented the gas from settling over nearby towns. However, if a similar incident happens there may be serious repercussions, such as necessary evacuation of houses. What can you do (both mechanically and chemically) to ensure that there will be no reoccurrence of this incident?

1.4 A Mighty Safety Dilemma
You are the chairman of the Chemistry Department at a state university with 20,000 students. Your department has had an exemplary safety record for many years, even winning awards for it. However, something has gone wrong. There have been three incidents in the last two weeks. Although there have been no injuries, you know that the difference between an incident and an injury, or even a fatality, may depend on where the person is standing at the time. Since these incidents, the parade of administrators through your office and the building has been steady. This
is more attention than your department has received in years. You have also met the emergency team of the state environmental agency, the local fire department, and the OSHA inspectors.

Your primary concern is that no student gets hurt when undertaking experimental work. You remember a woman who lost an eye when the solution that she was boiling in a test tube bumped and hit her in the face. Three other concerns are (1) will the adverse publicity reduce the number of students taking chemistry?; (2) will the alumni stop donating to the department?; and (3) will the US$1 million bill for the cleanup ruin the department’s budget for the year? You want to be viewed as a strong leader who takes action and not as a wishy-washy one who is indecisive. Should you stop all laboratory work for a month of intensive safety training? The first incident involved a student who added ether to toluene, which was heated above the boiling point of the ether. The fire occurred when the vapors ignited on the hot plate. The second incident involved the explosion of a stoppered glass bottle to which concentrated nitric acid and organic waste had been added. Apparently, the student involved did not realize that nitrogen oxides form when organic matter is oxidized by nitric acid. The third incident was a 3:00 a.m. explosion and fire involving a Diels-Alder reaction being carried out in a sealed glass vessel. This last incident set off the fire sprinkler system, which flooded both the third floor of the wing and the floors beneath it. Who was responsible for these incidents? While students were present in each case, their professors should have given them better training. You realize that it is your responsibility to see that the professors do their jobs. It is up to you to devise a carrot-stick approach that will prevent future problems of this type.

Which, if any, of the following should you do?

1. Call the incidents “human errors.” Tell the students that chemistry can be dangerous and that they should be more careful.
2. Chastise the students and the professors for being stupid.
3. Get a psychologist from the university Psychology Department to see if the students and their professors were under undue stress at the time.
4. Have the students fill out detailed safety reports on the incidents, then go over these with their professors, then with the professor in charge of safety, and finally with you.
5. Put the students on probation or suspend them until they complete a rigorous course in safety training.
6. Encourage the students to transfer to another department.
7. Demote the professors or delay their getting tenure.
8. See if the professors are spending all their time writing grant proposals so that they do not devote enough time to their students.
9. Hire an outside safety consultant to assess the department.
10. Solicit help from safety engineers at local companies.
11. Appoint a different professor to be in charge of departmental safety.
12. Adopt the methods used by industry, for example, unannounced safety inspections, safety prizes, safety slogans in prominent places, etc.
13. Post tables of flash points of common solvents at every desk.
14. Prohibit the use of ether and other solvents with low flash points.
15. Require training in the use of alternative reaction media with higher flash points.
16. Prohibit the use of concentrated nitric acid and/or require that all acids be neutralized prior to disposal.
17. Put a copy of the American Chemical Society manual on disposal of wastes on every desk.
18. Require that all waste containers be vented to a fume hood.
19. Provide more training before students are allowed to work on their own.
20. Limit the scale of reactions to no more than one gram. Require that all students and professors take a course in microscale chemistry. Purchase some microscale glassware for the undergraduate and graduate laboratories.
21. Require all students and faculty to take a course in inherently safer chemistry, that is, green chemistry.
22. Require a permit for all unattended overnight reactions to be issued after a review with a safety engineer.
23. Require that all unattended overnight reactions be run first by differential scanning calorimetry to see how exothermic they are and to see what pressures develop.
24. Insist that all reactions in glass vessels that may develop more than 5 lb. of pressure be encased in heavy metal cans (with small vents) that will contain glass if it breaks. A plastic shield should be used in front of this and the reaction should be conducted in a fume hood.
25. Build a new facility for reactions to be done under pressure, where work is done in steel autoclaves remotely behind several inches of concrete wall. Or, farm out the work to a nearby facility that has such equipment.
26. Provide every lab with a “Thermo-Watch” temperature controller.
27. Have all students and faculty take a training course in conducting reactions under pressure. This should include handling of high-pressure gas cylinders.
28. Use combinatorial chemistry to find a suitable catalyst system for a Diels-Alder reaction.
29. Hunt for alternative, less hazardous media for the Diels-Alder reaction.
30. Initiate a big brother or big sister system in the labs where every new student is mentored by a more experienced graduate student for the first two years.
31. Provide for an automatic shutdown of the sprinkler system when sensors indicate that a fire is out.
32. Rebuild the wing with a floor drain in every laboratory.
33. Do not allow carpets on the floors of offices.
34. Do not allow any files, file cabinets, or stacks of papers within one foot of the floor. Anything placed closer than a foot from the floor must be something that will not be damaged by water.
35. Solicit ideas from all faculty members, including those in the Department of Chemical Engineering.
1.5 To Burn or Not to Burn?
You are in charge of a state agency that regulates air and water emissions. A large company has applied for a permit to incinerate about 12,000 t of hazardous waste each year at its research center, which is located in a residential area. About three-quarters of the waste will be brought in from other sites of the company. Although the company has announced a goal of zero waste, substantial amounts of chlorinated solvents will be burned. You wonder why the company is still using these since they cause liver damage and cancer. Why is it not switching to processes that use less solvent and less harmful solvents? Why is it not practicing more recovery and reuse of solvents?

Trial burns have shown emissions of As, Be, Cd, and Cr(VI) to be within EPA limits. No data has been presented for Hg, which is the metal most likely to come out of the stack. The company does have a program to collect batteries and fluorescent lamps separately. However, the compliance rate of employees is unknown to you. Medical incinerators are the largest source of dangerous chlorodioxins, and the new incinerator could produce these. The company has no data on these from trial burns. The amounts of particulates will be low, but there has been no check for harmful particles under 2.5 μm, the size that a person’s breathing system has problems with. Since the 75 ft. stack of the incinerator is located in a narrow valley, it might be possible for the untrapped 3 lb./day to linger in a mass of stagnant air in the valley on a day when there is no wind. Could this be enough to annoy or harm local residents? The company has a good record, and most of what it proposes is credible. How should you proceed?

1.6 “Delacid”: A Versatile Catalyst
A local inventor has approached your university for funding for a revolutionary acid catalyst. It is insoluble under aqueous conditions and in all organic solvents. It can be made available in each of liquid, solid, and film forms. The material can be used whenever Brønsted and Lewis acid catalysts are needed. It is capable of replacing hydrofluoric acid, sulfuric acid, boron trifluoride, aluminum chloride, and so on, and is completely stable to air and water. Recovery for reuse is simple, and catalyst life is measured in years. Spent catalyst can be used as a bulking agent in hamburgers. Catalyst cost in large volumes is estimated to be as little as $1.00/lb.

You strongly suspect that this appears too good to be true. However, you feel obliged to see what the catalyst actually is before some state legislator inquires about it. How can you characterize the few grams of powder that the inventor has left with you, and how can you decide what it is actually good for?

1.7 The Flask Broke
A 5-L round-bottomed flask broke when a solvent was being dried over a sodium/potassium alloy. The student was burned, but recovered and graduated from the school. How could this accident have been prevented?

1.8 The Tremendous Problem of Climate Change
Climate change is certainly here. It is caused by emission of carbon dioxide, a greenhouse gas that has reached 400 ppm in the atmosphere. Devise ways to synthesize the polymers that modern society relies on that will release no carbon dioxide.
1.9 The Chemist Talks to the Chemical Engineer

Pretend that you are a chemical engineer in charge of scaling up an industrial process. Your chemist colleague is proud of the overall yield of 90% that he has achieved in a multistep methodology. The starting material cost is only $1.00/g when purchased from Sigma-Aldrich. The first step is an oxidation with acidic potassium dichromate to produce a carboxylic acid. This is converted to a methyl ester with diazomethane. The ester is subsequently reduced by lithium aluminum hydride in diethyl ether. The resulting alcohol is then protected by reaction with dihydropyran, with the protecting group being removed after the next step.

A further reaction step produced a 100% yield when a 5% solution in dioxane/2-methoxyethanol was left for 48 hours at room temperature using a mercuric acetate catalyst. The following step gave the best yields when run over a 24-hour period at -78 °C. A final step worked best at a pressure of 7 kbar. The desired product was purified by distillation at 0.01 Torr using a 100-plate column. You point out to the chemist that he should have talked to you sooner. What has he done wrong, and why?

1.10 Inherently Safer Chemistry

Deaths and injuries in the chemical industry have not declined in the past decade. How many of these does it take to make a ton of chemicals? Environmentalists and trade unions have pushed for inherently safer chemistry that follows the principles of green chemistry. Industry objects violently, saying that “We don’t need government officials telling us how to run our business.” What does this really mean? Surely they do not condone deaths in the workplace. What are they afraid of? The Toxics Reduction Act of Massachusetts has worked well for the past 25 years. Why is industry complying with it while objecting to inherently safer chemistry? What is its secret?

1.11 A Strange Malady

There are no longer any young peregrine falcons, eagles, ospreys, and pelicans. As older birds die off, the species will become extinct. The only eagles will be in sports teams and Boy Scout patrols. Florida pelicans attract tourists, so its tourism revenue will eventually decline. Is this analogous to the canary in the coal mine? How can the cause be determined? What can be done about the problem?

1.12 The Mysterious Case of the Disappearing Filter Paper

You are a professor at a large university in North America. One of your students reported the disappearance of the filter paper when he tried to filter a reaction mixture containing an ionic liquid. You felt that something was wrong, so you had him repeat the process. It still gave the same result. You had the student repeat the experiment as you watched. The filter paper disappeared again. You called the manufacturer to be sure that they had not supplied substandard filter paper. They sent a new batch that gave exactly the same result. Should you use inorganic filter paper or another medium for filtration purposes, such as Celite? Should you call Sherlock Holmes for help? Since the effect is definitely real, what can you do to use it to your advantage?
REFERENCES

Toxicity, Accidents, and Chemical Waste


24

Problem-Solving Exercises in Green and Sustainable Chemistry


References

1 Chapter 1: Toxicity, Accidents, and Chemical Waste


89. R.A. Sheldon, Chemtech, 1994, 24(3), 38.
92. (a) Nowhere To Hide, National Environmental Law Center, Boston, 1995; (b) Chem. Ind. (London), 1995, 677.
103. (a) N. Chadha, Chem. Eng. Prog., 1994, 90(11), 32; (b) Office of Technology Assessment, Industry, Technology and the Environment: Competitive Challenges and Business


122. J. Boor, Jr., Ziegler–Natta Catalysts and


29. (a) J.T. Kumpulainen and J.T. Salonen, Natural Antioxidants and Food Quality in Atherosclerosis and Cancer Prevention, Royal Society of Chemistry, Cambridge,


37. (a) Anon., R&D (Cahners), 1998, 40(10), 180; (b) Diamonex Performance Products, Allentown, PA, August 1998.


53. R.D. Kane, Chem. Eng., 2007, 114(6), 34.


74. L.A. Liddell, Clothes and Your Appearance, Good-heart–Willcox, South Holland, IL, 1988, 175, 185.

Chapter 3: The Chemistry of Waste Management and Recycling


5. (a) S. Cassel, Technol. Rev., 1992, 95(6), 20; (b) ID2 Communications, Victoria, British Columbia, Canada gives 100-200 lb per worker per year, 2008.


27. (a) J.K. Borchard, Kirk-Othmer Encyclopedia of Chemical


33. J. Milliken, TAPPI J., 1997, 80(9), 79.


39. (a) J. Woodward, Biotechnology, 1994, 12, 905; (b) R. Dinus and T. Welt, Prog. Pap. Recycl., 1994, 3(4), 63, 64.


62. (a) W. Weizer, Chem. Ind. (Lond.), 1995, 1013; (b) R.A. Denison, EDF Lett. (Environmental Defense Fund), New York,


76. (a) R. Pfaendner, H. Herbst, K. Koffmann, and F. Sitek, Angew. Makromol. Chem., 1995, 232, 193; (b) M.K. Loultchea, M. Proietto, N. Jilov, and F.P. La Mantia,

77. L. Willis, Chemtech., 1994, 24(2), 51.


101. W. Rathje and C. Murphy, Rubbish: The Archaeology of


131. Information from Brookrock Corp. Newark, DE.


163. R. Graff and B. Fishbein, Reducing Office Paper Waste,


179. (a) G. Gardner and P. Sampat, Mind Over Matter: Recasting the Role of Materials in Our Lives. Worldwatch Paper, 144, World Watch Institute, Washington, DC, 1998; (b) J.B. Schor, The Overspent American—Why We Want What We


40. J.H. Kay, Asphalt Nation, Crown, New York, 1997; (b)


67. (a) A.S. Moffat, Science, 1997, 277, 315; (b) D.H.


09. (a) G. Rockendorf, S. Janssen, and H. Felten, Sol. Energy, 1996, 58, 33; (b) H. Gunnewick, E. Brundrett, and


105. (a) P. Brousseau and M. Lacroix, Energy Convers. Manage., 1996, 37, 599; (b) D.W.Hawes and D. Feldman, Sol.


110. G. Weaver, private communication.


112. (a) Anon., Environment, 1994, 36(10), 24; (b) Chem. Ind. (Lond.), 1994, 844.


137. (a) J.M. Ogden and R.H. Williams, Solar Hydrogen—Moving Beyond Fossil Fuels, World Resources Institute, Washington, DC, 1989; (b) J.C. Cannon,


2009.


167. J.J. Romm, The Hype about Hydrogen: Fact and Fiction in the Race to Save the Planet, Island Press, Washington,


189. S. Winderbaum, O. Reinhold, and F. Yun, Sol. Energy


233. R.J. Farris, University of Massachusetts at Amherst, private communication, June, 1997.


262. N.S. Nandurkar, M.D. Bhor, S.D. Samant, and B.M.


274. W.C. Conner and R. Laurence, Department of Chemical
Engineering, University of Massachusetts at Amherst, private communication, June 1997.
5 Chapter 5: Environmental Economics


Heal, Nature and the Marketplace, Capturing the Value of Ecosystem Services, Island Press, Washington, DC, 2000;


27. (a) J.A. Cichowicz, How to Control Costs in Your Pollution Prevention Program, Wiley, New York, 1997; (b) J.H. Clark, Chemistry of Waste Minimisation, Chapman & Hall, London, 1995; (c) S.T. Thomas, Facility Manager's


50. J. Ecotourism and J. Sustainable Tourism, both from Channel View Publications, Bristol, UK.


58. (a) A. Esty, Am. Sci., 2004, 92(6), 513; (b) Anon., Conserv. Mag., 2009, 10(1), 22.


78. New Jersey Discharger (New Jersey Department of Environmental Protection), Trenton, NJ, 1997, 5(1).


103. (a) Taxation and the Environment, Organization for


6 Chapter 6: The Greening of Society


4. J. John, Simple Things You Can Do to Save the Earth. Earthworks Press, Berkeley, CA, 1989 (some typical actions that a consumer can take).


44. (a) Anon., Chem. Ind. (Lond.), 1995, 164, 906; (b) B. Dale, Chem. Ind. (Lond.), 1994, 976.


101. Chevron, Report to shareholders for the second quarter


Chapter 7: Solutions to In-Chapter Problems


2. B.M. Jenssen, Environ. Health Perspect., 2006, 114 (Suppl. 1), 76.


8. R.G. Hicks, Asphalt Rubber Design and Construction Guidelines, which can be located via Google: “asphalt rubber design and construction guidelines.”


