


product engineering

MOLECULAR STRUCTURE
and PROPERTIES

James Wei

CD ROM INCLUDED



Product Engineering: Molecular Structure and Properties

James Wei

Princeton University

OXFORD
UNIVERSITY PRESS

2007

OXFORD
UNIVERSITY PRESS

Oxford University Press, Inc., publishes works that further
Oxford University's objective of excellence in research, scholarship,
and education.

Oxford New York
Auckland Cape Town Dar es Salaam Delhi Hong Kong Karachi
Kuala Lumpur Madrid Melbourne Mexico City Nairobi
New Delhi Shanghai Taipei Toronto

With offices in
Argentina Austria Brazil Chile Czech Republic France Greece
Guatemala Hungary Italy Japan Poland Portugal Singapore
South Korea Switzerland Thailand Turkey Ukraine Vietnam

Copyright © 2007 by Oxford University Press, Inc.

Published by Oxford University Press, Inc.
198 Madison Avenue, New York, New York 10016

www.oup.com

Oxford is a registered trademark of Oxford University Press

All rights reserved. No part of this publication may be reproduced,
stored in a retrieval system, or transmitted, in any form or by any means,
electronic, mechanical, photocopying, recording, or otherwise,
without the prior permission of Oxford University Press.

Library of Congress Cataloging-in-Publication Data

Wei, James, 1930–

Product engineering : molecular structure and properties / James Wei.

p. cm. — (Topics in chemical engineering)

ISBN-13 978-0-19-515917-2

ISBN 0-19-515917-9

1. Chemical engineering. 2. Production engineering. I. Title. II. Topics in
chemical engineering (Oxford University Press)

TP155.W378 2005

660—dc22 2005017098

9 8 7 6 5 4 3 2 1

Printed in the United States of America
on acid-free paper

This book is dedicated to my beautiful grandchildren:

Kevin, Cheryl, Cecily, Stacey,

Ryan, Aislyn, Natalie, Vivien

Preface

Engineers make useful things for people, and chemical engineers do it with chemistry. The two main tasks are what we should make, or product engineering, and how we should make it, or process engineering. Both topics are important if we are to make with skill what people want. The current chemical engineering curriculum concentrates on the manufacturing process, which leads to efficient production, reduced cost, and improved safety. However, new and improved products are needed periodically to rejuvenate the industry, and to help customers lead better lives. There was a time that consumers waited eagerly for the introduction of miraculous new chemical products that transformed their lives, such as celluloid, nylon, penicillin, synthetic rubber, Teflon, and Kevlar. But, for the past decade, information technology has held center stage and captured the attention of the public, with new products such as the personal computer, cellular telephone, word processors, spreadsheets, and the Internet. Ambitious new engineering graduates always seek opportunities to demonstrate their prowess, to innovate products with high growth and profit and to avoid stagnant commodities such as sulfuric acid and common salt. The business landscape is littered with the wreckage of once-successful companies that focused exclusively on cost cutting and neglected the development of new products.

It is sometimes said that chemical engineers wait for the chemists to invent new products, and then are summoned to manufacture them in quantity with economy and safety. Indeed, in many companies, the most ambitious new chemical engineering graduates often gravitate toward the process departments, as their education and curriculum seem more relevant to solving process problems. But neither is there anything in the curriculum of chemists that teaches them how to design products. Thomas Midgley, Jr. invented both tetraethyl lead and Freon, two of the most celebrated products in the 20th century, but he only had a bachelor's degree in mechanical engineering, and he had to learn on his own the chemistry of structure-property relations. This exclusive concentration on processes also cuts off the chemical engineers from exposure to the

desires and fears of society, and hinders their development into fully fledged policy makers and organizational leaders.

Many chemical engineers currently work in industry and academia on solving product engineering problems, and their work would be much more productive if they were given appropriate toolboxes of theories that are generally applicable, powerful new computer hardware and software, and triumphant cases of historical developments to inspire and show the winning ways. In the last few years, a number of universities in the United States and Europe have started courses and degree programs in product engineering. There are many different approaches to the course contents, depending on the resources of these pioneering teachers. An effective method is to introduce the subject by the historic case method. This shows the patterns of past successes, which methods were fruitful, and which paths were barren. A second method is to provide useful tools in the search for materials that possess the desired properties, as well as ways to modify materials to improve their properties. A third method of teaching is by doing a product design project, perhaps in parallel with the traditional process design project, which must take into consideration market needs and safety and environmental impacts.

This book takes the approach that these three methods all teach valuable lessons, and is thus divided into three parts. Part I describes inspiring historic cases of product innovations, with a focus on the creative product engineering work involved. It is largely descriptive, and provides justifications for the analytical tools and synthesis efforts to follow. Part II covers molecular structure–property relations, which provides the analytical tools to search for materials with desired properties, as well as ways to modify materials to improve their properties. The subject of molecular structure–property relations has been tremendously enhanced by powerful new computer methods. Part III challenges the future product engineers to understand the design goals, and to satisfy both market demand and public acceptance. The culmination is a design project for the students to exercise creativity, and to make trade-offs in synthesizing numerous elements together to make a successful product: What is the market demand for a product and what properties should it have? What may be the product composition and manufacturing technology? What are the safety and environmental problems from extraction to final disposal? What may be the financial reward for launching this product?

New products are urgently needed by the public and the chemical processing industries; and perhaps the understanding and skills of molecular structure and properties, combined with modern computer software and the Internet, would help to give a boost to creativity. In the terminology of Thomas Kuhn, a paradigm is a galaxy of concepts and tools that can solve important problems, becomes widely taught in universities, and generates meaningful research challenges. Perhaps product engineering and molecular structure–property relations can follow the advances of unit operations and transport phenomena, and become the Third Paradigm of Chemical Engineering.

Shortly after the publication of the Amundson Report on the future of chemical engineering in 1989, Edward Cussler and I discussed the need for a book on products. Subsequently, he became the pioneer and coauthored the first modern book in product design. Neither of us has ever designed a product that became a winner in the marketplace. It is customary in our profession that those who write design books have never designed a chemical plant or an oil refinery, but those who have done so do not write. I am indebted to many friends who have participated in the design of successful

products and who are willing to share their experiences: Harold Chung told me about the exciting story of guided-missile fuel, Mauricio Futran and San Kiang told me about the history and development of taxol, and Bob Langer told me about controlled drug delivery.

I acknowledge the gracious permissions by the Nobel Foundation, the Chemical Heritage Foundation, the University of Pennsylvania Library, Cambridge University Press, and John Wiley to reproduce the photographs and figures.

Contents

Part I

Product Innovations

- 1 Product Exploration and Discovery, 3
 - 1.1 Freon CFC, 1928, 5
 - 1.2 Market-Pull, Search for Technology, 12
 - 1.3 Technology-Push, Search for Market, 24
- 2 Product Development to Business, 34
 - 2.1 Nylon: Centralized Development, 35
 - 2.2 Penicillin: Distributed Development, 38
 - 2.3 Taxol: Distributed Development, 41
 - 2.4 Tasks and Skills in Product Innovation, 45

Part II

Molecular Structure–Property Relations

- 3 Search Challenges and Methods, 53
 - 3.1 Forward Search from Material to Property, 55
 - 3.2 Reverse Search from Properties to Material, 59

- 3.3 Searches from Technology to Markets, 61
- 3.4 Literature and Databases, 62
- 4 Theory and Quantitative Predictions, 72
 - 4.1 Single Molecules, 72
 - 4.2 Statistical Thermodynamics, 105
 - 4.3 Gases, Solids, and Liquids, 124
- 5 Predictions by Correlations, 153
 - 5.1 Populations, Predictors, and Functions, 153
 - 5.2 Regression with a Single Predictor, 161
 - 5.3 Regression with Several Predictors, 174
 - 5.4 Group Contribution Methods, 182
 - 5.5 Mixtures and Composite Materials, 188
- 6 Estimation by Associations and Trends, 199
 - 6.1 Empirical Structure–Property Relations, 200
 - 6.2 Structure Effects and Ambient Influences on Properties, 203
 - 6.3 Risk Assessment, 211
- 7 Random Searches, 229
 - 7.1 Strategies of Random Searches, 229
 - 7.2 Combinatorial Chemistry, 234
- 8 Research Frontiers, 237
 - 8.1 Synthesis and Discovery, 237
 - 8.2 Measurement and Discovery, 238
 - 8.3 Understanding of Molecular Structure–Property Relationships, 239
 - 8.4 Prediction of Molecular Structure–Property Relationships, 240

Part III

Product Engineering

- 9 Product Marketing, 245
 - 9.1 The Sellers: The Chemical Processing Industries, 246
 - 9.2 The Buyers, 254
 - 9.3 Marketing Gasoline: A Mature Product, 268
 - 9.4 Marketing Ink for Inkjet Printers, 277

10 Safety, Health, and Environment, 284

- 10.1 The Responsibilities of the Chemical Processing Industries, 285
- 10.2 Health and Safety Problems, 290
- 10.3 Environmental Problems, 296
- 10.4 Green Engineering, 299

11 Product Design, 308

- 11.1 Bottled Drinking Water: Fluid Compound, 310
- 11.2 Missile Fuel: Homogeneous Fluid Solution, 316
- 11.3 Adsorbents for Separation: Solid Material, 320
- 11.4 Controlled Drug Release: Composite Solid, 325
- 11.5 Evaluation, Selection, and Business Plan, 329

12 Product Innovation Opportunities, 340

- 12.1 Market-Pull Opportunities, 341
- 12.2 Technology-Push Opportunities, 345

Appendix, 351

Index, 357

Part I

Product Innovations

Great product innovations change the world, improve the way we live, and prepare the foundations to further innovations. How does one distinguish between a good innovation and a great innovation? The commonly accepted criteria of a great innovation include one or more of the following aspects:

1. It addresses and solves an important need of the world and improves lives.
2. It is widely used by many people over a long time.
3. It advances the state of science and technology, leading to other great inventions.

The evolution of an innovative product can be divided into four phases: the initial exploration–discovery–invention phase, creating a product concept; the development–design phase, making plans and blueprints to specific products and manufacturing processes; the commercialization phase, implementing the blueprints to make and to sell the products for the market; and the business and maintenance phase, monitoring outside responses to the new products and making continuous product improvements. The work of innovation is carried out by a relay team, staffed by people with different expertise in different phases of the race. The inventor who started the race may leave the relay team soon, but the race cannot be won without the other team members and their creative contributions and problem solving in all four phases. The press and historians often concentrate on the excitements of the exploration–discovery phase, and neglect the critical roles of the follow up. Out of the thousands of inventions each year, only a handful manage to find resourceful and effective champions to arrange the finance and oversee the transformation of an idea into reality; that is, a widely used product innovation.

In Part I we examine a number of great historical product innovations. Students of product engineering should study the successful paths taken in the past, learn the problems encountered and solved, and examine the effective methods used, as well as the failures that should be avoided in the future. Chapter 1 is concerned principally with the exploration–discovery phase of the innovation. Chapter 2 is concerned with the tasks involved in the development, planning, commercialization, and business phases of the innovation.

Product Exploration and Discovery

1.1 Freon CFC, 1928

1.2 Market-Pull, Search for Technology

- Modifying current products
- Search for materials not currently used
- Creation of new synthetic material

1.3 Technology-Push, Search for Market

- Adapt “platform” technology to new markets
- Invention of new technologies

References

Further Reading

Websites

Discussion Topics

Exercises

It is sometimes said that “necessity is the mother of invention.” Many product innovations have begun with the observation and recognition that many people are in need of a new or improved product, and investigators then looked for a technology that would produce such a product to satisfy this market need. Investigators may examine current products to find what properties need improvement and whether these properties can be modified; for example, raw rubber is brittle when cold and is sticky when hot, whereas vulcanized rubber, which is used to make tires and gaskets, remains flexible whether hot or cold. Investigators may take the more ambitious approach of looking for materials that are not currently used for a particular product to see whether they have better properties to offer: for example, the use of ether as an anesthetic relieved the pain from surgery and childbirth that people were subjected to previously. The more ambitious investigator would attempt to create new synthetic materials to suit a particular market: Freon, a chlorofluorocarbon (CFC), was invented to make a safe refrigerant for home refrigerators. These are called the Market-Pull products, or market looking for a technology.

Another frequent innovation path begins with a technology that is dormant or under-utilized, followed by the search for new markets. When Freon was established as a safe

refrigerant, it became the platform for new markets, such as air conditioning, aerosol propellants, and computer cleaning. Some technologies began as accidental discoveries when investigators were looking for something else, or were driven by curiosity. Penicillin is one of the best known examples of serendipity, of making unexpected discoveries. The most ambitious paths start from planned explorations to create a new technology, followed by the quest for a place in the market. Carothers created the field of synthetic condensation polymerization, and DuPont decided that this method could be used to make nylon fibers to replace silk stockings. These are called the Technology-Push products, or technology looking for a market. Figure 1.1 shows some historic innovations that began from a high market need with low technical identification, with examples from vulcanized rubber to Kevlar, as well as innovations that began from a high technology capability with low market identification, including synthetic dyes to Post-It notes.

We often give the greatest admiration to pioneering innovations; that is, the bold introduction of a totally new technology or the creation of a new market, one with great potential combined with great risk. This type of innovation can be likened to the spring season. When a new market has already been created by a new product, the task of the fast-follower is to come up with a better, or me-too, product that usually has less potential and less risk; this can be compared to summer. A mature product in an established market can be compared to autumn, where there may be limited opportunities to improve the existing products by a new formulation or a new process to lower costs. A declining product can be compared to winter, where caretakers take rearguard maintenance efforts to prevent obsolescence. Figure 1.2 shows a product life cycle, with tissue engineering as an example of spring, ink for inkjet printers as an example of summer, gasoline as an example of autumn, and sulfuric acid as an example of winter.

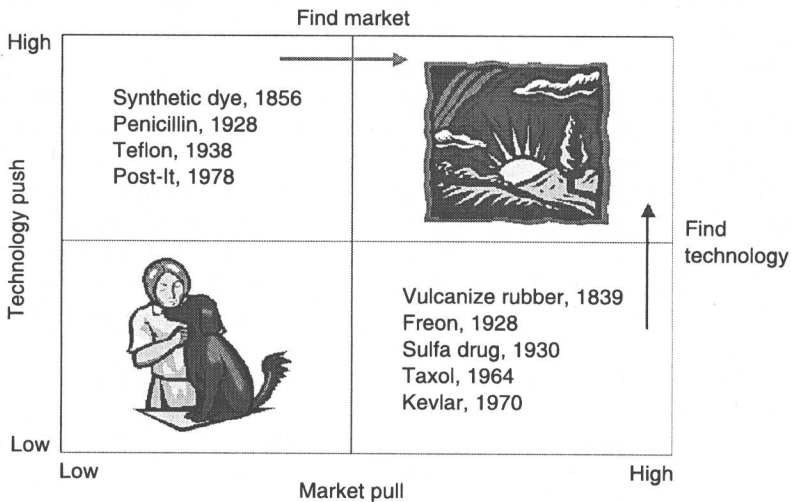


Figure 1.1 Historic innovations that began as Market-Pull and Technology-Push identifications

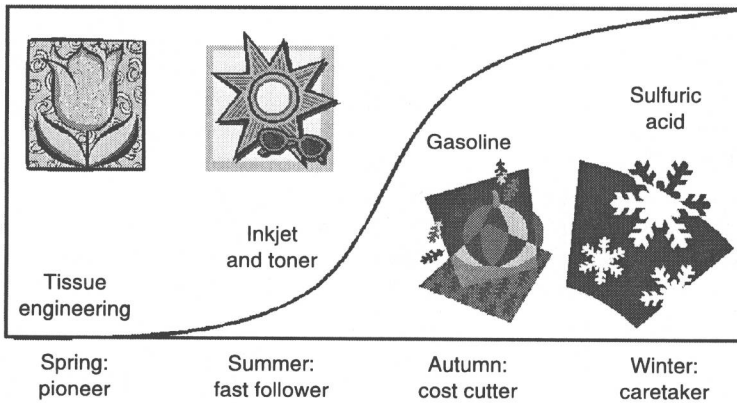


Figure 1.2 Product life cycle divided into spring, summer, autumn and winter

1.1 Freon CFC, 1928

Thomas Midgley, Jr. invented chlorofluorocarbons (CFCs), or Freon, as a safe refrigerant for the home refrigerator, on assignment from his boss Charles Kettering. He set out with a specific purpose in mind, and he bent all his intellectual powers to that quest (McGrayne and Sharon 2001).

The preservation of food was one of mankind's first problems. When our ancestors came down from the trees in East Africa 2 million years ago, they changed their diet from gathered plants and fruits to hunted small animals. When they managed a kill, they could eat the meat for a few days by hiding the kill from scavengers, like hyenas and vultures, but they could not keep it for long from bacteria and maggots which would turn the meat putrid. Joseph helped the Egyptians to survive 7 years of famine by storing 7 years' harvest of dry grains. The American Indians would preserve an abundant salmon catch in the fall by drying, to tide them over until the spring.

The traditional methods of food preservation included drying (such as for fish and grains), which discourages bacteria growth. There are many other ways to decrease the availability of water in foods, such as by the salting of fish, the sugar-curing of hams, and the acid-pickling of vegetables. Another method is to lower the temperature, such as by packing fish in ice, to decrease the speed of bacteria growth.

The evaporation of liquids, such as water or liquid ammonia, removes the faster molecules and cools down the liquid that remains. This would also make the air more saturated with water, so this process cannot operate for long without bringing in fresh, dry air. The vapor compression refrigerator operates on the principle of capturing and condensing the evaporated vapor, by mechanical compression and cooling, so as to regenerate the liquid for the next round of evaporation. In 1748, William Cullen of Glasgow was reputed to be the inventor of the first vapor compression refrigerator, and the evaporating liquid refrigerant was diethyl ether. As we all know, the inhalation of ether will cause unconsciousness, and eventual death, so that it would be prudent to

locate an ice-making machine in a remote industrial area away from homes, and to have the product ice delivered to homes and offices on horse-drawn carts.

In 1859, Ferdinand Carré of France used ammonia as the refrigerant. This was not much better, as ammonia can leak from the refrigerator and has a bad odor and irritating properties. In 1928, there were some 2.5 million home refrigerators in the United States, and the refrigerants used were: nitrous oxide (boiling point -88°C), ammonia (-33°C), sulfur dioxide (-10°C), methyl amine (-6.7°C), butane (-0.5°C), ether (34.6°C), and chloroform (61°C). It is dangerous to have these compounds in the average person's kitchen. A Cleveland hospital had a leaking refrigerator, and more than 100 people died as a consequence. The newspapers were clamoring for a law to stop the "killer refrigerators."

In 1928, Charles Kettering of General Motors asked Thomas Midgley, Jr., to develop a nontoxic and nonflammable refrigerant (Midgley 1937, Wilson 1937). Midgley did a systematic and logical analysis of the property requirements of such a refrigerant, studied the data available in the literature of existing refrigerants, considered molecular structures that had the potential for such properties, synthesized the compound and tested it to determine that it was nonflammable and nontoxic, all in 3 days!

Thomas Midgley, Jr. (figure 1.3), was born 1889 in Pennsylvania. He received a bachelor's degree in mechanical engineering from Cornell in 1911. He appeared to have received no formal education in chemistry or chemical engineering. In 1921, he invented tetraethyl lead (TEL), which was used to boost the octane number of gasoline—a revolutionary invention that had tremendous impact for half a century. One of the consequences of TEL use is the by-product of lead aerosol from the tailpipe of automobiles, which can be a health hazard to breathing and to skin exposure. Besides the safe refrigerant, he had numerous other inventions. Owing to the prestige his inventions brought him, Thomas Midgley became president of the American Chemical Society in 1946. He died by accident in 1948.



Figure 1.3 Thomas Midgley, Jr.
1889–1944

Let us follow Thomas Midgley's journey of discovery of his revolutionary refrigerant. When he received the 1937 Perkin Medal for his development of both antiknock motor fuels and safe refrigerants, he wrote an article "From the Periodic Table to Production" (Midgley 1937) that described how he did it.

I was in the laboratory one morning and called Kettering in Detroit about something of minor importance. After we had finished this discussion, he said: "Midge, I was talking with Lester Keilholtz last night and we came to the conclusion that the refrigeration industry needs a new refrigerant if they ever expect to get anywhere." What was wanted was obvious—a nontoxic, nonflammable refrigerant. I expressed myself as very doubtful that we would be able to find a single substance suited to the task, but that there might be some hope of greatly reducing the existing hazards by using mixtures where nonflammable but toxic materials would be mixed with nontoxic but flammable compounds, to give a mixture substantially nonflammable and considerably less toxic than the refrigerants then commonly employed.

The desired combination of properties was a boiling point between 0 and -40°C , stability, nontoxicity, and nonflammability. The *International Critical Tables* gave us a partial summary of the volatile organic compounds, and gave the mistaken information that carbon tetrafluoride boiled at -15°C . This struck us in the face and started us thinking about fluorine. No one could doubt at that time that it was terribly toxic, probably too toxic to use even with isobutane. Perhaps we could add some chlorine compound to it with beneficial results. Henne suggested chlorofluorides as a class to be investigated further. Recognizing that the *International Critical Tables* list was very incomplete, I decided to bring into play the periodic table. Perhaps volatility could be related to it in some way. It takes but a fraction of a second to see that this is true. The elements on the right-hand side are the only ones which make compounds sufficiently volatile for the purpose in hand. Volatile compounds of boron, silicon, phosphorous, arsenic, antimony, bismuth, selenium, tellurium, and iodine are all too unstable and toxic to consider. The inert gases are too low in boiling points. Flammability decreases from left to right, and toxicity (in general) decreases from the heavy elements at the bottom to the lighter elements at the top. These two desiderata focus on fluorine. It was an exciting deduction. Seemingly no one previously had considered it possible that fluorine might be nontoxic in some of its compounds. This possibility had certainly been disregarded by the refrigeration engineers. Everything looked right except that old fear of hydrofluoric acid burns. As it turns out, hydrofluoric acid burns are a special case, and gaseous hydrofluoric acid is less toxic than hydrochloric acid, but we did not know it that afternoon.

Carbon tetrafluoride seemed rather hard to make. And then how could dichlorodifluoromethane boil at -20°C , and carbon tetrafluoride at -15°C ? Plotting of boiling points, hunting for data, corrections, slide rules, log paper, eraser dirt, pencil shavings, and all the rest of the paraphernalia that takes the place of tea leaves and crystal spheres in the life of the scientific clairvoyant, were brought into play. We decided that carbon tetrafluoride boiled at about -136°C , or else it was a very special kind of substance. (Not long after this, a publication on the subject appeared. Carbon tetrafluoride boils at -128°C , not -15°C .) Feeling pretty certain at the time that -15°C was wrong and that it was a sizable research problem to make carbon tetrafluoride, we selected dichloromonofluoromethane as the starting point for experimentation.