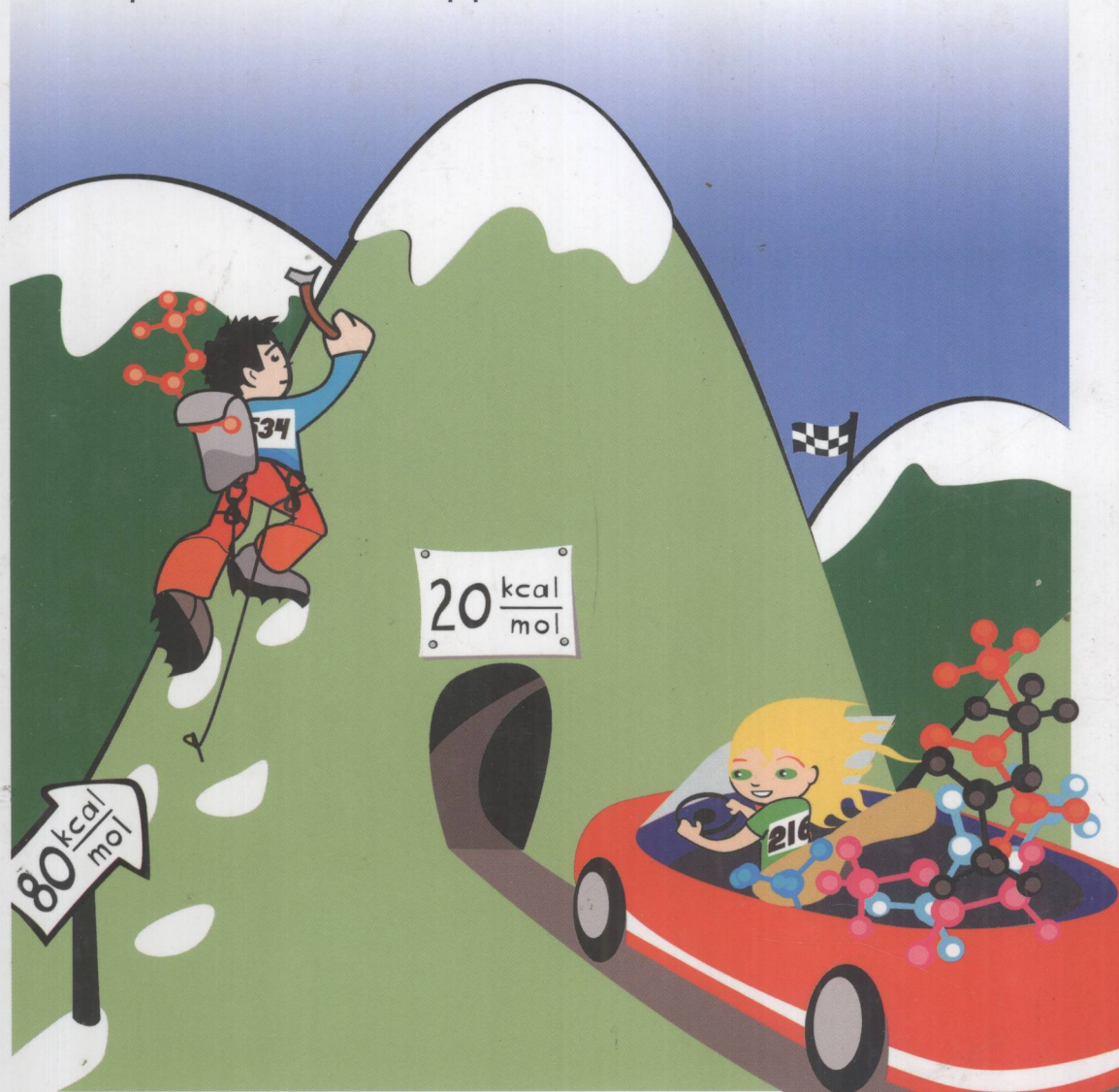


Gadi Rothenberg

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Catalysis

Concepts and Green Applications



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Gadi Rothenberg

Catalysis

I never write *metropolis* for seven cents, because I can get the same price for *city*.

Mark Twain

Preface

This textbook covers the basics of catalysis from a “green chemistry” perspective. Its main message is that heterogeneous catalysis, homogeneous catalysis, and biocatalysis are all one discipline, so you need to understand only once how catalysis works. The book is divided in three sections. Chapters 1 and 2 introduce and explain the fundamentals of sustainable chemistry, catalysis, and reaction kinetics. Chapters 3, 4 and 5 show how these principles are applied in homogeneous, heterogeneous, and biocatalysis, respectively. Finally, Chapter 6 gives an overview of the exciting and fast-growing field of computer applications in catalysis research, with a special section on predictive modeling.

I have written this book for senior undergraduate students, as well as graduate researchers. Thus, each chapter includes detailed literature references, as well as exercises that embed the knowledge in a practical context. I assume that you have some background in chemistry/chemical engineering, life sciences, or earth/environmental sciences. To help you master the catalysis jargon, key terms in catalysis are printed in **bold** and defined the first time they appear in the text. They are also included in the index.

The website accompanying this book, www.catalysisbook.org, features additional teaching material (exercises, answers, and lecture slides). It also contains a searchable list of all the references, each with its corresponding digital object identifier (DOI) hyperlink. Access to this website is free of charge.

The bulk of the references are original papers and review articles in peer-reviewed journals. I cite reviews and books when introducing a subject, and articles when discussing specific examples. Chapter 1 also contains a “Further Reading” list of recommended books on related specialized subjects.

I thank my wife Live for her constant support throughout the writing of this book, and my colleagues Jurriaan Beckers, Hans Boelens, Kees Elsevier, Anil Gaikwad, Jos Hageman, Klaas Hellingwerf, Huub Hoefsloot, Christopher Lowe, Marjo Mittelmeijer-Hazeleger, Dorette Tromp, Ron Wever, and Gooitzen Zwanenburg for their constructive and insightful comments. Thanks also to my sister Ada, who drew the cover picture, and to the Wiley-VCH editors Axel Eberhard, Joe Richmond, Gudrun Walter, and Waltraud Wüst for their encouraging and professional attitude.

As you will see, catalysis is one of the most exciting and fun subjects in chemistry. Hopefully you will share some of my enthusiasm and fascination after reading this book.

Amsterdam, December 2007

Gadi Rothenberg

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1

Introduction

This chapter outlines the principles of green chemistry, and explains the connection between catalysis and sustainable development. It covers the concepts of environmental impact, atom economy, and life-cycle analysis, with hands-on examples. Then it introduces the reader to heterogeneous catalysis, homogeneous catalysis, and biocatalysis, explaining what catalysis is and why it is important. The last two sections give an overview of the tools used in catalysis research, and a list of recommended books on specialized subjects in catalysis.

1.1

Green Chemistry and Sustainable Development

In the 20th century, chemistry changed our lives. It has shaped our modern technological society by supplying us with energy, medicines, crop protection, foodstuffs, and new materials worldwide. Unfortunately, even though chemistry is the science with the highest impact on our everyday lives, chemicals and the chemical industry have a poor public image. This is partly due to misconceptions and media scares, but there is also a valid reason: the traditional chemical industry, certainly until the 1980s, was a hazardous and polluting one. It generated stoichiometric amounts of waste, causing much pollution of both air and water. A number of major chemical accidents have reinforced this image in recent decades [1,2]. The most infamous are the Bhopal catastrophe in 1984, where 3000 people were killed and more than 40 000 injured [1], and the grounding of the *Exxon Valdez* [3] in the Prince William Sound in Alaska in 1989, that still affects the marine ecosystem nearly 20 years later [4].

Apart from the immediate health and environmental hazards, there is also the problem of resource management. The chemical industry during the past 200 years drew heavily on resources. Today, the escalating costs of petrochemicals, and the increasing energy and raw material demands in Asia's emerging markets, are forcing a change. Two popular terms associated with this change are **sustainability**, or

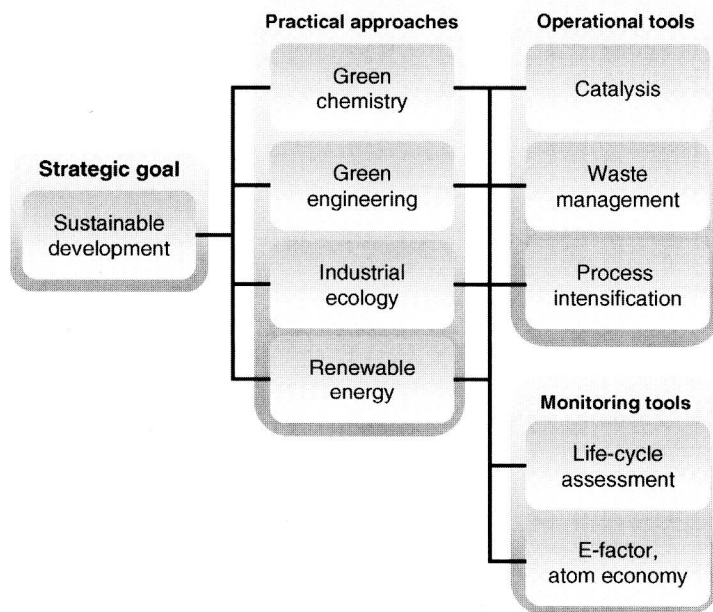


Figure 1.1 The strategic goal of sustainable development relies on practical approaches such as green chemistry, industrial ecology, and green engineering. These approaches use various operational tools (e.g., catalysis), and monitoring tools (e.g., life-cycle assessment).

sustainable development. A sustainable society is one that “meets the needs of the current generation without sacrificing the ability to meet the needs of future generations.” Sustainable development is a strategic goal. It can be reached using various approaches, and this is where green chemistry comes in. Figure 1.1 shows the relationship between the strategic goals, the practical approaches, and the operational and monitoring tools. Thus, green chemistry is just one step (albeit an important one) along the road to sustainability.

1.1.1

What is “Green Chemistry”?

In the 1990s, the concept of “green chemistry” was initiated in both the US and Europe, and has since been adopted widely by the chemical industry [5]. Green chemistry deals with designing chemical products and processes that generate and use fewer (or preferably no) hazardous substances. By applying the **principles of green chemistry**, companies embrace cleaner and more efficient technologies, with an *a priori* commitment to a cleaner and healthier environment. The green chemistry message is simple: “Seek prevention, not cure.” In 1998, Anastas and Warner formulated the following 12 principles of green chemistry [6,7] (I have rephrased these in the active voice, in keeping with the spirit of this book):

- Prevent waste instead of treating it.
- Design atom-efficient synthetic methods.
- Choose synthetic routes using nontoxic compounds where possible.
- Design new products that preserve functionality while reducing toxicity.
- Minimize the use of auxiliary reagents and solvents.
- Design processes with minimal energy requirements.
- Preferably use renewable raw materials.
- Avoid unnecessary derivatization.
- Replace stoichiometric reagents with catalytic cycles.
- Design new products with biodegradable capabilities.
- Develop real-time and on-line process analysis and monitoring methods.
- Choose feedstocks and design processes that minimize the chance of accidents.

Green chemistry offers an alternative to the traditional environmental protection agenda, mainly because it deals with avoiding hazards, rather than treating and solving exposure problems. Three forces drive the green chemistry initiative [8]: Government legislation, societal pressure, and economic benefit (Figure 1.2). The new 800-page EU Directive on the registration, evaluation, and assessment of chemicals (**REACH**) [9] is changing the chemical industry across Europe. Similar regulations are expected worldwide in the coming decade. But legislation is just one of the drivers. Societal pressure is also important: the public favors industrial green chemistry initiatives, as they lead to safer and eco-friendly products and processes.

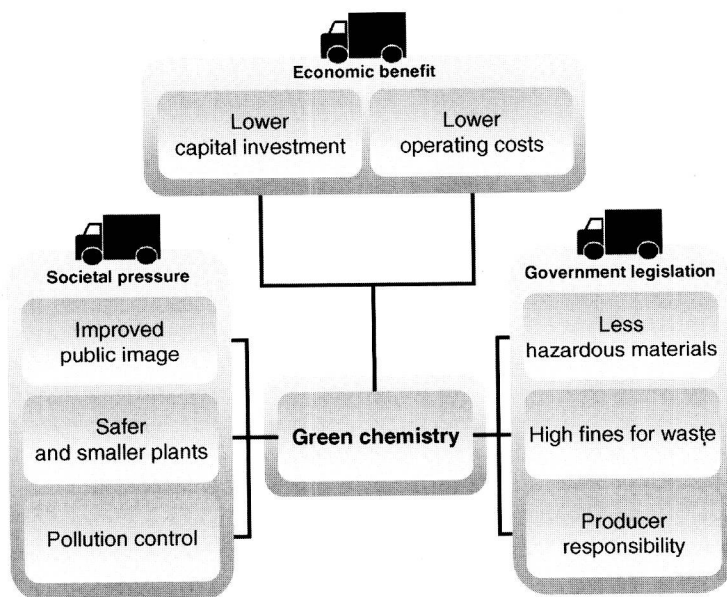


Figure 1.2 Green chemistry initiatives are driven by government legislation, societal pressure, and economic benefits.

This creates goodwill for the company, something that is difficult to quantify but undoubtedly important.

The third driver is *bona fide* economic benefit. Applying the principles of green chemistry decreases both capital investment and operating costs. If you use less (or no) solvent, and replace stoichiometric reagents with catalytic cycles, your reactor space-time yields go up. Similarly, processes running at ambient temperatures are less energy-intensive. This means doing the same work using smaller and safer equipment. Eliminating waste also eliminates the need for waste treatment and disposal. Replacing toxic reagents with benign ones saves on safety costs during transportation and storage. Thus, more and more companies are adopting green chemistry because it simply improves their bottom-line performance.

1.1.2

Quantifying Environmental Impact: Efficiency, *E*-factors, and Atom Economy

Everyone agrees that green chemistry and “green manufacture” are good things. The websites and pamphlets of all the major chemical companies emphasize their concern for the environment. They all say that their processes and products are “efficient,” “green,” and “environmentally friendly.” But how should we compare these processes? How should we judge such claims?

First, let us define some key terms. One method for quantifying a reaction’s efficiency is by examining the **reactant conversion**, the **product selectivity**, and the **product yield** over time. The reactant conversion is the fraction of reactant molecules that have transformed to product molecules (regardless of which product it is). The selectivity to product **P** is the fraction (or percentage) of the converted reactant that has turned into this specific product **P**. The yield of **P** is simply conversion \times selectivity. High conversions in short time spans mean smaller and safer reactors. Similarly, high selectivity means less waste, and simpler and cheaper separation units. Thus, conversion, selectivity, and yield are all measures of the **reaction efficiency**.

In addition, there are specific rulers for measuring the “greenness” or “eco-friendliness” of processes and products. One such measure is the ***E*-factor**, introduced by Roger Sheldon in 1994 [10,11]. A reaction’s *E*-factor is the quotient $\text{kg}_{\text{waste}}/\text{kg}_{\text{product}}$ (here “waste” is everything formed in the reaction except the desired product). The waste can be gases such as CO_2 or NO_x , water, common inorganic salts (e.g., NaCl , Na_2SO_4 , or $(\text{NH}_4)_2\text{SO}_4$), heavy metal salts, and/or organic compounds. Table 1.1 compares the production tonnage and *E*-factors of various industrial sectors. Note that the petrochemicals and the bulk chemicals sectors are the least polluting. This is surprising, as we are used to thinking of such chemicals as pollutants. In fact, *E*-factors increase substantially when going from bulk chemicals to fine chemicals and specialties. This is partly because fine-chemicals production often involves multistep syntheses, and partly because stoichiometric reagents are more often used for producing fine chemicals and pharmaceuticals.

Table 1.1 Annual production and *E*-factors in the chemical industry.

Industrial sector	Production/ton y ⁻¹	<i>E</i> -factor
Petrochemicals	10 ⁶ –10 ⁸	<0.1
Bulk chemicals	10 ⁴ –10 ⁶	1–5
Fine chemicals	10 ² –10 ⁴	5–50
Specialities/pharmaceuticals	10–10 ³	20–100

The concept of **atom economy**, introduced by Barry Trost in 1991, is similar to that of the *E*-factor [12]. Here one considers how many and which atoms of the reactants are incorporated into the products. With these two concepts, we can evaluate chemical reactions to get a quantitative result.

As an example, let us consider the stoichiometric oxidation of diphenylmethanol to benzophenone, one of the most commonly used photosensitizers in photochemistry (Figure 1.3). We will evaluate this reaction using the measures of product yield, product selectivity, *E*-factor, and atom economy. In this reaction, three equivalents of diphenylmethanol react with two equivalents of chromium trioxide and three equivalents of sulfuric acid, giving three equivalents of benzophenone. First, let us see how the reaction measures with respect to product yield and selectivity. Assume that this is an ideal chemical reaction which goes to completion, so one obtains 100% yield of the product, benzophenone. If no other (organic) by-product is obtained, the product selectivity is also 100%. This is all well and good, and indeed for many years this has been the way that chemical processes were evaluated, both in academia and in the (fine-) chemical industry.

However, examining the *E*-factor for this reaction, we see that for every three moles of benzophenone we produce one mole of chromium sulfate and six moles of water. The molecular weight of benzophenone is 182.2 g mol⁻¹, so every kilogram of benzophenone contains 5.48 moles of benzophenone. This means that for every kilogram of benzophenone we generate 5.48/3 = 1.83 moles (or 0.717 kg) of

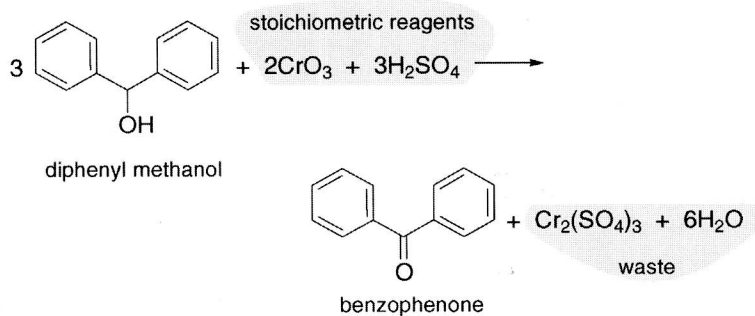
**Figure 1.3** Oxidation of diphenylmethanol to benzophenone using chromium trioxide and sulfuric acid.

Table 1.2 Hazard quotient (Q) values for some common chemical by-products.

Compound	Q -value	Compound	Q -value
Nitrogen gas	zero	acids	medium
Carbon dioxide	low	bases	medium
Water	low	heavy-metal salts	high
NaCl	low	CFC gases	high
Nonmetal salts	medium	persistent materials	high

chromium sulfate and 10.98 moles (or 0.197 kg) of water. The overall E -factor is therefore given by Eq. (1.1).

$$E\text{-factor} = \frac{\text{kg}_{\text{waste}}}{\text{kg}_{\text{product}}} = \frac{0.717 + 0.197}{1} = 0.914 \quad (1.1)$$

Nearly a whole kilogram of waste for every kilogram of product! Remember, this is for the ideal case of 100% yield and 100% selectivity. In real life, the E -factor is usually much higher, because product yields are less than 100% and the reagents are often used in excess. Furthermore, in many cases one needs to neutralize acid or base side-products, so the overall waste amounts are even higher.

The E -factor and atom economy can be used for comparing reaction alternatives, but we should remember that there are different types of “waste”. The reaction example above has two by-products: chromium sulfate and water. Obviously, water is “good waste”, while chromium sulfate is “bad waste”, so evaluating a synthetic protocol on the basis of only the amount of waste produced is insufficient. To solve this problem, Sheldon put forward the concept of the **environmental quotient** (EQ) [10]. By multiplying the E -factor by Q , an arbitrarily assigned hazard quotient, this measure takes both the amount and the nature of the waste into account. Table 1.2 shows some possible Q -values for different by-products. Assigning absolute Q -values to waste streams is difficult, because cases differ according to location and type of waste. Nevertheless, the EQ gives a better measure of the environmental impact of a process than the E -factor or the atom economy alone.

1.1.3

Just How “Green” is this Process?

Some processes and products seem more eco-friendly than others. Often this is because we see only part of the process. An overall environmental impact analysis should take into account not only the chemical reactions, but also the hazards and consequences of acquiring and transporting the raw materials. Additionally, it should factor in the overall energy demand. A reaction can have 100% atom economy, yet still be problematic because of hazardous reagents. Adding Br_2 , HF , or HCN to a double bond, for example, is “clean” from the atom economy perspective, but storing