

## **PART I**

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# **GREEN CHEMISTRY AND GREEN ENGINEERING IN THE MOVEMENT TOWARD SUSTAINABILITY**

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# 1

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## GREEN CHEMISTRY AND ENGINEERING IN THE CONTEXT OF SUSTAINABILITY

**What This Chapter Is About** Green chemistry and green engineering need to be seen as an integral part of the wider context of sustainability. In this chapter we explore green chemistry and green engineering as tools to drive sustainability from a triple-bottom-line perspective with influences on the social and economic aspects of sustainability.

**Learning Objectives** At the end of this chapter, the student will be able to:

- Understand the need for the development of greener chemistries and chemical processes.
- Identify sustainability principles and associate standard chemical processes with the three areas of sustainability: social, economic, and environmental.
- Identify green chemistry and green engineering as part of the tools used to drive sustainability through innovation.
- Understand the need for an integrated approach to green chemistry and engineering.

### 1.1 WHY GREEN CHEMISTRY?

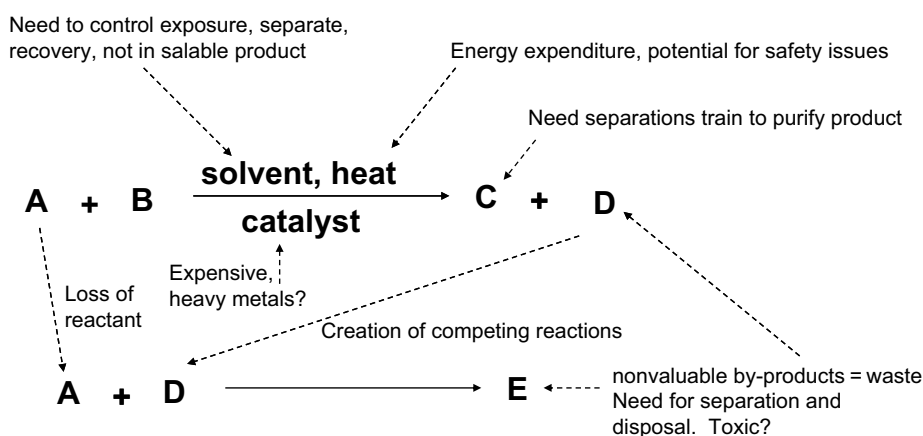


Reactant A plus reactant B gives product C. No by-products, no waste, at ambient temperature, no need for separation. Is it really that easy?

If industrial chemical reactions were that straightforward, chemists and engineers would have significantly more time on their hands and significantly less excitement and fewer long hours at work. Chemists know that this hypothetical reaction is not the case in real life, as they have less-than-perfect chemical conversions, competing reactions to avoid, hazardous materials to manage, impurities in raw materials, and the final product to reduce. Engineers know that in addition to conquering chemistry, there are by-products to separate, waste to treat, energy transfer to optimize, solvent to purify and recover, and hazardous reaction conditions to control. At the end of this first reality check, we see that our initial reaction is a much more complicated network of inputs and outputs, something that looks more like Figure 1.1.

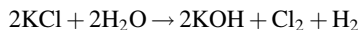
Green chemistry and green engineering are, in a very simplified way, the tools and principles that we use to ensure that our processes and chemical reactions are more efficient, safer, cleaner, and produce less waste by design. In other words, green chemistry and green engineering assist us in first thinking about and then designing synthetic routes and processes that are more similar to the hypothetical reaction depicted in equation (1.1) than to the more accurate reflection of current reality shown in, Figure 1.1.

What are the drivers in the search for greener chemistries and processes? Engineers and scientists have in their capable hands the possibility of transforming the world by modifying the materials and the processes that we use every day to manufacture the products we buy and the way we conduct business. However, innovation and progress need to be set in the context of their implications beyond the laboratory or the manufacturing plant. With the ability to effect change comes the responsibility to ensure that the new materials, processes, and designs have a minimum (or positive) overall environmental impact. In addition, common sense suggests that there is a strong business case for green chemistry and engineering: linked primarily to higher efficiencies, better utilization of resources, use of less hazardous chemicals, lower waste treatment costs, and fewer accidents.



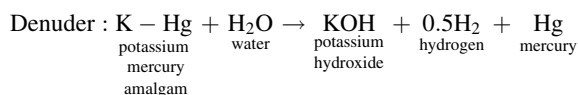
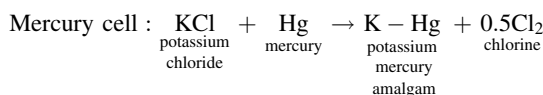
**FIGURE 1.1** Simplified vision of some of the challenges and realities of designing a chemical synthesis and process.

**Example 1.1** Potassium hydroxide is manufactured by electrolysis of aqueous potassium chloride brine,<sup>1</sup> as illustrated by the following net reaction:



How is this simple inorganic reaction different from the more complex challenges of the real world? Identify some of the green chemistry/green engineering challenges.

**Solution** The electrolysis reaction can be carried out in diaphragm, membrane, or mercury cell processes. The complexity of the reactions depend on the process that is used. Let's explore the mercury cell process, which has, historically, been the most commonly used method to produce chlorine.<sup>1,2</sup> In this case, potassium chloride is converted to a mercury amalgam in a mercury cell evolving chlorine gas. The depleted brine is recycled to dissolve the input KCl. The mercury amalgam passes from the mercury cell to the denuder. In the denuder, fresh water is added for the reaction and as a solvent for the KOH. Hydrogen gas is evolved from the reaction and mercury is recycled to the electrolysis cell:



Our simple net reaction has become a bit more complex, but it does not end there. We've not talked about a key input—energy. Electricity is required to drive the reaction forward; it represents the major part of the energy requirement for these types of reactions, and there is a need to optimize it. As a matter of fact, as of 2006 the chlor-alkali sector was the largest user of electricity in the chemical industry.<sup>2</sup>

But energy is not the only thing that we need to worry about. In addition to energy inputs, there is a need to eliminate impurities. To do that, the brine can be treated with potassium carbonate<sup>3</sup> to precipitate magnesium and heavy metals, and barium carbonate is often used to precipitate sulfates.<sup>4</sup> Also, hydrochloric acid needs to be added, as an acidic pH is required to drive the reaction to produce the desired chlorine gas, which can then be recovered from the solution, as shown in the following equilibrium reaction:



Besides using a large quantity of electricity, we have to worry about potential emissions from the reaction. Mercury is present in the reaction cell and the purged brine. Mercury emissions from the cell and the brine have long been a target for significant reduction. The purged brine is typically treated with sodium hydrosulfide to precipitate mercury sulfide, and the mercury-containing solid wastes need to be sent for mercury recovery. Other emission concerns include management of the environmental, health, and safety (EHS) challenges related to the gases in the reactions. Both the chlorine and hydrogen gas streams must be processed further. Chlorine is cooled and scrubbed with sulfuric acid to remove water, followed by compression and refrigeration. The hydrogen gas is cooled to remove water, impurities, and mercury,

followed by further cooling or treatment with activated carbon for more complete mercury removal.<sup>5</sup> In addition, hydrogen is often burned as fuel at chlor-alkali plants.

The membrane process was introduced in the 1970s and it is more energy efficient and more environmentally sustainable, which is making it the technology of choice. However, a typical mercury-based plant can contain up to 100 cells and has an economic life span of 40 to 60 years. A long phase-out is required to convert an existing mercury plant. For example, as of 2005, 48% of the European chlor-alkali capacity was mercury cell-based.<sup>2</sup>

***Additional Point to Ponder*** Chemistries and processes described in most textbooks normally don't give you all the information you need to consider the mass and energy inputs and outputs associated with a given reaction. In reality you won't always have the data you need and will have to use estimations to generate data, run experiments, perhaps use "nearest neighbor" approaches and/or make assumptions based on your experience. Sometimes, you will just have to use "simple" common sense.

## 1.2 GREEN CHEMISTRY, GREEN ENGINEERING, AND SUSTAINABILITY

The modern understanding of sustainability began with the United Nations World Commission on Environment and Development's report *Our Common Future*,<sup>6</sup> also known as the *Brundtland Report*. The Brundtland Commission described *sustainable development* as "development that meets the needs of the present without compromising the ability of future generations to meet their own needs." What does this actually mean? This definition doesn't give us many clues or supply much practical guidance as to how to implement sustainable development or move toward more sustainable activities, but it does provide us with a powerful aspiration. It has been up to society collectively and up to us as individuals to develop guidance and tools that will help us to design systems and processes that have the potential to achieve the type of development described in the definition.

The first thing to remember is that sustainability or sustainable development is a complex concept with which many people are still attempting to come to terms. In 1998, John Elkington, one of the early innovators of sustainable development, coined the phrase *triple bottom line*.<sup>7</sup> Elkington did this in an attempt to make sustainable development more understandable and palatable to business people, to encourage them to see it as a logical extension of the traditional business focus on economic performance. By using this term, Elkington was trying to highlight the need to consider the intricate interrelationships among environmental, social, and economic aspects of human society and the world. In a way, sustainability can be seen as a very delicate balancing act among these three factors, and not always with a strong one-to-one relationship. Table 1.1 provides a summary of several approaches to sustainable development principles. It should be noted that the Carnoules statement includes an organizational principle framework, in addition to the overarching social aspects widely recognized to be an integral part of sustainability. This organizational principle is useful when relating the operational aspects of sustainability within the sphere of controls defined by company culture and policy.

When talking about sustainability, one cannot focus on only a single aspect, as this necessarily limits and biases one's view. For a system to be sustainable, there is the need to balance, insofar as possible, social, economic, and environmental aspects, ideally having each area "in the black," that is, with no single aspect optimized to the detriment of the others.



**TABLE 1.1 (Continued)**

| Alcoa <sup>8</sup>   | International Chamber of Commerce <sup>9</sup>   | Chemical Associations <sup>10</sup>  | Carnoules Statement <sup>11</sup>  | Hanover Principles <sup>12</sup>  | Natural Step <sup>13</sup>  | UN Global Compact <sup>14</sup>   |
|--|--|--|--|---|---|---|
| Increased transparency and collaboration in community-based EHS initiatives. | <p><i>Employee education:</i> To educate, train, and motivate employees to conduct their activities in an environmentally responsible manner.</p> <p><i>Prior assessment:</i> To assess environmental impacts before starting a new activity or project and before decommissioning a facility or leaving a site.</p> <p><i>Products and services:</i> To develop and provide products or services that have no undue environmental impact and are safe in their intended use, that are efficient in their consumption of energy and natural resources, and that can be recycled, reused, or disposed of safely.</p> <p><i>Customer advice:</i> To advise and, where relevant, educate customers, distributors, and the public in the safe use, transportation, storage, and disposal of products provided; and to apply similar considerations to the provision of services.</p> | <p><i>Process safety:</i> We will assess and manage the risks associated with our processes.</p> <p><i>Product stewardship:</i> We will assess the risks associated with our products and seek to ensure that these risks are properly managed throughout the supply chain through stewardship programs involving our customers, suppliers, and distributors.</p> <p><i>Resource conservation:</i> We will work to conserve resources and reduce waste in all our activities.</p> <p><i>Stakeholder engagement:</i> We will monitor our HS&amp;E performance and report progress to stakeholders; we will listen to the appropriate communities and engage them in dialogue about our activities and our products.</p> | <p>Access to education.</p> <p>Identity and self-realization.</p> <p>Security.</p> <p>Equitable access to food, drinking water, and natural resources.</p> <p>Healthy and secure shelter.</p> <p>Readjusted demand for resource consumption, and the environmental impact of household consumption.</p> <p>Secure environmental quality for the health of human beings.</p>  | <p>Accept responsibility for the consequences of design decisions on human well-being, the health of natural systems, and their right to coexist.</p> <p>Create safe objects of long-term value. Do not burden future generations with requirements for maintenance or vigilant administration of potential danger due to the careless creation of products, processes, or standards.</p> <p>Eliminate the concept of waste. Evaluate and optimize the full life cycle of products and processes to approach the state of natural systems in which there is no waste.</p> <p>Rely on natural energy flows. Human designs should, like the living world, derive their creative forces from perpetual solar income. Incorporate this energy efficiently and safely for responsible use.</p> | <p>In a sustainable society, nature's productivity should not be diminished in either quality or quantity, nor should more be harvested than can be recreated.</p> <p>System condition 4: We must be fair and efficient in meeting basic human needs.</p> <p>In a sustainable society, basic human needs must be met with the most resource-efficient methods possible, including the just distribution of resources.</p> | <p>To encourage the development and diffusion of environmentally friendly technologies.</p> |
|  |  |  | <b>Economic Principles</b>   |   |   |   |
|  |  |  | <p>Sufficient supply and goods and services</p> <p>Efficient wealth creation</p> <p>Economic system's evolution and competitiveness</p> <p>Enhance the distributational justice (equity principle)</p> <p>Efforts (paid and unpaid) should be devoted fairly to generate sustainable incomes.</p> <p>Provide opportunities for paid labor to all willing and able to work.</p> <p>Increase knowledge intensity.</p> <p>Refocus innovation and adapt its speed to societal demands.</p> |   |   |   |

|  |   |  |   |
|--|---|--|---|
| <p><i>Facilities and operations:</i> To develop, design, and operate facilities and conduct activities taking into consideration the efficient use of energy and materials, the sustainable use of renewable resources, the minimization of adverse environmental impact and waste generation, and the safe and responsible disposal of residual wastes.</p> <p><i>Research:</i> To conduct or support research on the environmental impacts of raw materials, products, processes, emissions, and wastes associated with the enterprise and on the means of minimizing such adverse impacts.</p> <p><i>Precautionary approach:</i> To modify the manufacture, marketing, or use of products or services or the conduct of activities, consistent with scientific and technical understanding, to prevent serious or irreversible environmental degradation.</p> | <p><i>Management systems:</i> We will maintain documented management systems which are consistent with the principles of responsible care and which will be subject to a formal verification procedure.</p> <p><i>Past, present, and future:</i><br/>Our responsible care management systems will address the impact of both current and past activities.</p> | <p><b>Organizational Principles</b></p> <p>Ensure structural change to reflect the need for societal development.</p> <p>Improve societal interchange, communication, and intercultural learning.</p> <p>Protect cultural diversity</p> <p>Achieve distributional fairness and justice, equity and sufficiency.</p> <p>Develop anticipatory capacities for the democratic process.</p> | <p>Understand the limitation of design. No human creation lasts forever and design does not solve all problems.</p> <p>Those who create and plan should practice humility in the face of nature. Treat nature as a model and mentor, not as an inconvenience to be evaded or controlled.</p> <p>Seek constant improvement by the sharing of knowledge.</p> <p>Encourage direct and open communication among colleagues, patrons, manufacturers, and users to link long-term sustainable considerations with ethical responsibility, and reestablish the integral relationship between natural processes and human activity.</p> |
| <p><b>Social Principles</b></p> <p><i>Ethical trade:</i> to ensure that all business, wherever companies trade, is conducted to the highest global ethical standards.</p> <p><i>Public understanding:</i> to play their part in helping people understand and appreciate relevant science and technology.</p> <p><i>Part of the community:</i> to play an active role in their communities by interacting with schools, local government, and other bodies.</p>  |   |  |   |

(continued)

**TABLE 1.1 (Continued)**

| Alcoa <sup>8</sup>  | International Chamber of Commerce <sup>9</sup>  | Chemical Associations <sup>10</sup>   | Carnoules Statement <sup>11</sup> | Hanover Principles <sup>12</sup> | Natural Step <sup>13</sup> | UN Global Compact <sup>14</sup> |
|---|---|---|-----------------------------------|----------------------------------|----------------------------|---------------------------------|
| <p><i>Contractors and suppliers:</i> To promote the adoption of these principles by contractors acting on behalf of the enterprise, encouraging and, where appropriate, requiring improvements in their practices to make them consistent with those of the enterprise; and to encourage the wider adoption of these principles by suppliers.</p> <p><i>Emergency preparedness:</i> To develop and maintain, where significant hazards exist, emergency preparedness plans in conjunction with the emergency services, relevant authorities, and the local community, recognizing potential transboundary impacts.</p> <p><i>Transfer of technology:</i> To contribute to the transfer of environmentally sound technology and management methods throughout the industrial and public sectors.</p> | <p><i>Employability:</i> to ensure that all employees have access to training and development opportunities to enable them to fulfill their role in the organization and to keep them up to date with the labor market.</p> <p><i>Equality of treatment and opportunity:</i> to ensure that all employees are free from discrimination and have the opportunity to develop their careers and themselves, subject only to business needs and personal ability.</p> | <p><i>Participation:</i> to ensure that all employees have access to the information needed for them to do their job, be consulted about matters that affect them, and have the opportunity to participate, to the appropriate level, in the management of their company.</p> <p><i>Balance between work and life:</i> to provide all employees with the opportunity to balance the requirements of their work and their life outside work so as to enhance work effectiveness and personal well-being.</p> |                                   |                                  |                            |                                 |

*Contributing to the common effort.* To contribute to the development of public policy and to business, governmental and intergovernmental programs, and educational initiatives that will enhance environmental awareness and protection.

*Openness to concerns:* To foster openness and dialogue with employees and the public, anticipating and responding to their concerns about the potential hazards and impacts of operations, products, wastes, or services, including those of transboundary or global significance.

*Compliance and reporting:* To measure environmental performance; to conduct regular environmental audits and assessments of compliance with company requirements, legal requirements, and these principles; and periodically to provide appropriate information to the board of directors, shareholders, employees, the authorities and the public.

## **Economic Principles**

*Sustainable profitability:* generating profits to satisfy shareholders' expectations and to invest in the future through R&D, capital expenditure, and employee development.

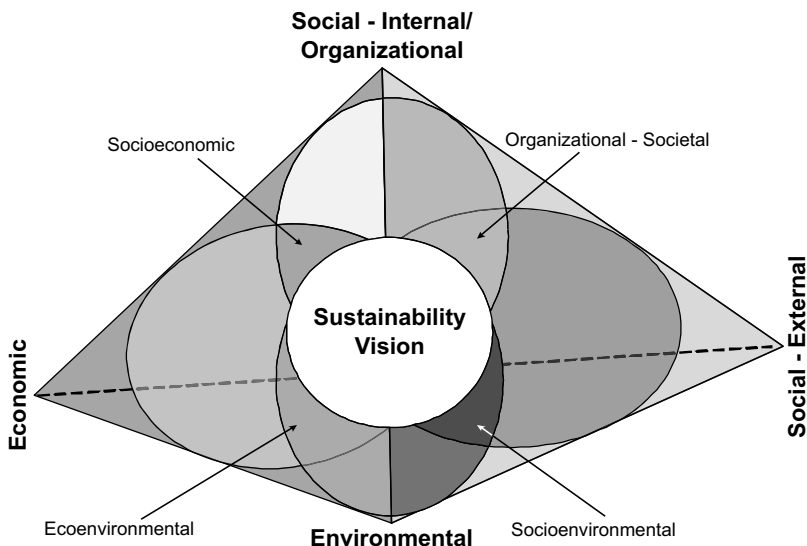
*Competitiveness:* achieving long-term competitiveness through the spread of international best practice, in a climate of fair competition

*Innovation:* continuing to research, develop, and market innovative products that help improve economic well-being and quality of life.

*Wealth generation:* generating wealth, thereby sustaining employment, improving the UK's trade balance, and contributing to government revenue to fund public expenditure.

*Economic growth:* continuing their key role in supporting sustained UK economic growth throughout the entire manufacturing supply chain.

*Resource efficiency:* making the most efficient use of resources, whether they be land, water, raw materials, or energy.



**FIGURE 1.2** Spheres of action of sustainability.

One of the most puzzling, challenging, and exciting characteristics in the study of sustainability is the inherent complexity of the concept. There are synergies, trade-offs, a variety of shared values of what constitutes a sustainable practice, and so on. Figure 1.2 displays those interrelations graphically.

Green chemistry and green engineering represent some of the many concepts, tools, and disciplines that come into play in helping to move society toward more sustainable practices. They do this by focusing scientists and engineers on how to design more environmentally friendly, more efficient, and inherently safer chemistries and manufacturing processes. However, some might suggest that when talking about green chemistry and green engineering in the context of sustainable development, we can honestly say simply that the primary focus area is what has come to be known as *environmental sustainability*. Is this really true? Whereas green chemistry and green engineering may be seen as being related primarily to the environmental aspects of sustainability, they also have strong ties to the eco-environmental (or eco-efficiency) sub-area of sustainability by virtue of the fact that they include resource conservation and efficiency. By the same token, green chemistry and green engineering are related to the social aspects of sustainability because they promote the design of manufacturing processes that are inherently safer, thereby ensuring that workers and residential neighborhoods close to manufacturing sites are protected.

**Example 1.2** Explain how reaction (1.1) relates to the three aspects of sustainability.

**Solution** Several of the issues related to green chemistry and green engineering were highlighted in the solution to Example 1.1. Table 1.2 provides examples of how they relate to the three aspects of sustainability.

**TABLE 1.2 Issues Related to Sustainability**

| Environmental   | Social   | Economic   |
|---|--|--|
| Mercury emissions from a cell and in the purged brine | Worker safety issues related to chlorine and hydrogen management     | Jobs and wealth created by a potassium chloride plant                                    |
| Energy consumption                                    | Safety and well-being of communities adjacent to manufacturing plant | Economic resources needed to operate the plant in a safe and efficient manner            |
| Water consumption                                     |  |  |
| Emissions released during energy production           | Potential for process accidents, incidents, and lost-time injuries   | Investment that will be necessary to replace mercury cells for an alternative technology |
| Fugitive chlorine emissions                           |  |  |
| Waste management of carbonate precipitates            | Issues related to safely transporting chlorine                       | Supply chain implications for other products that utilize KCl or chlorine                |
| Environmental impacts resulting from mercury mining   | Working conditions in mercury mines to extract the metal             |  |

**Additional Point to Ponder** Most textbook examples and problems have only one correct answer, although many examples have several possible answers. In real-world manufacturing processes, it is common to have difficulties in defining what the true problem is—and when this is defined, several “not-quite-optimal” answers may be found. When this happens, a decision must be made that accounts for or balances all the important factors and, hopefully, leads to the optimal or “best” answer.

### 1.3 UNTIL DEATH DO US PART: A MARRIAGE OF DISCIPLINES

What does it mean to have an integrated perspective between green chemistry and green engineering? Just imagine the following not-so-hypothetical scenario. A chemist works at a large company and after years of hard work discovers a novel synthesis to produce a valuable material. At this point, hundreds of engineering questions are formulated and need to be addressed, such as:

- What is the best design for the reactor? Which material?
- Does the reaction need to be heated? Cooled? How fast are heating and cooling transferred?
- What types of separation processes are needed?
- How could the desired purity be achieved?
- How fast is the reaction? Is there a risk of an exothermic runaway?
- What can possibly go wrong? How can we prepare for problems?

- Are there inherent hazards in the materials?
- Are there any incompatibilities with materials?
- How much waste is produced? How toxic is it? Can it be avoided?
- Where should the reactants be procured? Is it more efficient to make them or to buy them?
- How much would this process cost?
- What types of preparations and skills would future operators need?

Imagine how difficult it would be to answer these and other questions if the chemist doesn't work closely with a chemical engineer. How efficient would the final process be? To truly understand the impacts of this novel chemistry in the real-world manufacturing environment, the chemist will need to involve engineers beginning at the earliest stages of development.

Similarly, a chemical engineer working on transforming a laboratory synthesis into a scalable, effective production process will need to collaborate closely with a chemist to understand how the chemical synthesis might be changed. A myriad of chemically related questions must be answered to design and scale-up a good manufacturing process:

- What function is the solvent performing in the reaction?
- Are there alternative reaction pathways that can be used to:
  - Avoid uncontrollable exotherms?
  - Substitute reactant A for B to avoid safety issues?
  - Eliminate hazardous reagents?
- If we recirculate part or all of the reaction mother liquors, how much of material X can be tolerated by the reaction system before we are not able to do this?
- Are there any reactivity issues by introducing solvent Y as a mass separating agent?
- What are the potential side reactions?
- Are there any alternative catalytic methods that we might be able to use?

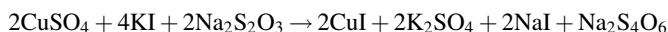
The decisions that are made in the design of synthetic chemistry pathways affect and either enable or restrict the engineering opportunities, and vice versa. Chemists and chemical engineers should operate in an integrated fashion if the goal is to design an efficient process, in the widest sense of the term and in the context of green chemistry and engineering.

Hopefully, we have made a good case for integrating green chemistry and green engineering, but our effort to integrate disciplines is not over. Carrying on with our original scenario, the chemist and engineer have successfully identified a chemical they want to make and the synthetic route or pathway to be used to make it, and have some idea of the critical process parameters that they need to focus on if they are to optimize the process from a green chemistry and green engineering perspective. So, is anything missing? What about knowledge of how the various reactants, reagents, catalysts, solvents, by-products, and so on, used in the process affect living organisms and the environment? One might be tempted to ask who really cares about such things, since most of the materials may be consumed in the process and the product we are making is a valuable material that others need or want.

These questions are not merely rhetorical; the answers are very important for current and future generations. Human beings have and continue to affect the world in very significant ways, and it is critical that all chemists and engineers understand how material choices, process designs, energy use, and so on, affect the world. Chemists and engineers need to design and choose synthetic strategies that minimize the potential for causing short-, medium-, and long-term harm not only to humans, but to other environmental organisms as well. To do this correctly, they need to collaborate with toxicologists and environmental, health, and safety professionals to discuss and develop appropriate options for syntheses. In short, a host of disciplines are required to bring a product to market appropriately and successfully and to ensure that this is done in a sustainable fashion. It is no longer acceptable practice for chemists to isolate themselves in a laboratory and design reactions that are chemically interesting but, because it is expedient to do so, utilize reagents, reactants, and solvents that are inherently hazardous.

## PROBLEMS

- 1.1 How do green chemistry and green engineering differ from chemistry and engineering?
- 1.2 Examples 1.1 and 1.2 refer to the environmental, health, and safety challenges related to mercury, chlorine, and hydrogen. What are those challenges?
- 1.3 The primary route for making copper iodide is by reacting potassium iodide with copper sulfate:



Identify potential green chemistry and green engineering challenges of the reaction.

- 1.4 From a sustainability framework, identify environmental, social, and economic impacts derived from the chemistry shown in Problem 1.3.
- 1.5 Using reaction system of example (1.1), provide some examples of how the chemistry can affect decisions made in engineering.
- 1.6 What are some potential barriers for an effective, close collaboration between a chemist and an engineer when designing a novel process. Provide some ideas on how to circumvent these obstacles.

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