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Guest Editor's Note:

Green Chemistry

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Green chemistry means we prevent waste rather than clean it up. Design nonhazardous and sustainable chemical processes and products. In the recent Paris Accord 185 countries and the European Union agreed to control emissions of carbon dioxide. Now we will see innovations in chemicals and renewable energy. The transition from fossil-fuel-based society to one that relies more on renewable energy will require new methods. Buildings and transportation industries will require new materials. Governments and industry will have to work together to make the Paris Accord work. Who will take the leading role in this? Chemists and Chemical Engineers. We can make chemistry safe and energy efficient while saving time and money. Green Chemistry will be the way to make our future better. The Principles of Green Chemistry were outlined by Paul Anastas and John Warner in their book Green Chemistry: Theory and Practice. Read this and think carefully how you can apply the principles to your company and research. Most of what I write here comes from many leading researchers in the field especially John Constable and of the Green Chemistry Institute of the American Chemical Society.

Prevent pollution and toxic materials at the source. Don't clean it up later. This is the essence of Green chemistry. Say you start a job with a company that makes a product to clean floors. Really think about the reaction they use to make this. How many kilos of everything go into making one kilo of product? Can you think of a way to make the product from less starting material? Do you need so much solvent? Must you really heat the reaction mixture? Is it just "the way we always did it"? Rather than pushing the reaction by using molar excess of reagent can we "pull" the reaction forward by removing a product from the reaction mixture? What happens to the waste?

Atom economy, which was developed by Barry Trost, asks the question "what atoms of the reactants are incorporated into the final desired product(s) and what atoms are wasted?". This was a significant advance over simple per cent yield calculations. A different measure of waste has been used called the E-factor, was described by Roger Sheldon, which relates the weight of waste coproduced to the weight of the desired product. More recently, the ACS Green Chemistry Institute Pharmaceutical Roundtable (ACS GCIPR) has favored process mass intensity, which expresses a ratio of the weights of all materials (water, organic solvents, raw materials, reagents, process aids) used to the weight of the active drug ingredient (API) produced. This is an important roundtable focus because of the historically large amount of waste coproduced during drug manufacturing—more than 100 kilos per kilo of API in many cases. However, when companies apply green chemistry principles to the design of the API process, dramatic reductions in waste are often achieved.

Wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment. It may not be practical or possible to avoid using substances that are toxic. Reactive chemicals afford reactions that are kinetically and thermodynamically favorable. We must stop and reconsider each chemical process. Use our chemical education and background to replace toxic chemicals and large quantities of solvents. For the synthetic organic chemist, effecting a successful chemical transformation in a new way or with a new molecule is what matters. I have heard arguments, as "all the other stuff in the flask is just there to make the transformation possible". We must ask chemists to broaden their definition of what constitutes good science. When we ignore all the other “stuff,” we pay a high price and it’s a price we need to stop paying.

It is quite challenging to maintain function and efficacy while minimizing toxicity of reactants, products, and processes. It requires an understanding of not only chemistry but also toxicology and environmental science. We need to meet with and understand our toxicology colleagues. Highly reactive chemicals are often used by chemists to manufacture products because they are quite good at causing molecular transformations. However, they are also very good at reacting with biological targets like humans.

Hazard is a design flaw and must be addressed at the beginning of molecular design. The intrinsic hazard of elements and molecules is a fundamental chemical property that must be characterized, evaluated and managed. When you place a product in the hands of a consumer, you must realize they will put on their hands. They may even try to eat it. Broaden your area of study. If you are a chemist who has studied some biology, you are a more valuable worker. You are worth more to your company if you can bridge the conversation between chemists, toxicologists, biologists, and money managers. The field of toxicology is changing rapidly, incorporating and applying the advancements made in molecular biology to reveal the mechanisms of toxicity.

The use of solvents and separation agents should be made unnecessary wherever possible and, innocuous when used. We used to think solvents did not matter. Use whatever does the job and boil it off or put it down the drain. Why did we think this way? The first principle you learn in general chemistry is that matter is never destroyed. Under the principle of the Conservation of Mass it may change form, but it is always with us. We pour it out of a bottle into a flask. Run the reaction. Then boil it off to……where?……..to my neighborhood. We all get to breathe it. In many cases, reactions wouldn't proceed without solvents and/or mass separation agents. To say that they don't matter, or that it's only the chemistry of the important reagents that counts is not just a logical fallacy, it's chemically incorrect. Solvents and separation agents provide for mass and energy transfer and without this, many reactions will not proceed. Solvents account for about 75% of the environmental impacts of a standard batch chemical operation. Another thing to think about. When you buy a bottle of solvent, you pay for it three times. 1. Purchase it. 2. Pay a technician to separate it from your product. and 3. You pay to dispose of it. Solvents are alternately heated, distilled, cooled, pumped, mixed, distilled under vacuum, filtered, etc. It takes a great deal more heat to warm up 100 liters than 1 liter. And that's before they may or may not be recycled. If they're not recycled, they are often incinerated. Solvents contribute the greatest concern for process safety issues because they are flammable and volatile, or under the right conditions, explosive. They also generally drive workers to put on personal protective equipment. The object is to choose solvents that make sense chemically, reduce the energy requirements, have the least toxicity, have the fewest life cycle environmental impacts and don't have major safety impacts.

Energy requirements should be recognized for their environmental and economic impacts and should be minimized. Synthetic methods should be conducted at ambient temperature and pressure. Most if not all the attention that energy gets from chemists is devoted to heating, cooling, separations, electrochemistry, pumping and reluctantly, to calculations related to thermodynamics. Our textbooks make it clear that it is just a given that we need to heat or cool or shove electrons into the reaction to make or break bonds. That may or may not be true. If you think about where most chemists are trained around energy, it's around ΔH in the Gibbs Free Energy equation. Heats of formation, heats of vaporization, enthalpy, exothermic reactions, etc; these are what we think about. The interesting thing is that nature largely works with ΔS. However, getting back to the laboratory bench and the production plant it is not the reaction that uses the most energy. Most is used in solvent removal to set up for the next reaction, or to remove one solvent and replace it with another, or to isolate the desired product, or to remove impurities. This doesn't mean that energy isn't important, it is just important in areas where most chemists are not focused. We have to refocus and consider all aspects of the chemical reaction of interest. Look at the reagents we have chosen, the size of the reaction vessel, heating requirements, and solvent choice.

A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable. Either stop burning petroleum or find different renewable feedstocks. The concept of making all our future fuels, chemicals and materials from feedstocks that never deplete is an interesting one. Mankind currently removes fossil fuels, coal, oil and natural gas from the ground and extracts minerals for profit until they are gone. When you look at crude oil, do you see food, medicine, clothing? You should. What I see is all those lovely organic compounds waiting to make new shirts and anti-headache medicine. We will get some of our feedstock from air in the form of carbon dioxide and methane. What about all those plants growing all over our countryside? Nature produces about 170 billion tons of plant biomass annually, of which we currently use about 3.5 % for human needs. It is estimated that about 40 billion tons of biomass, or about 25 % of the annual production, would be required to completely generate a bio-based economy. The technical challenge in the use of such renewable feedstocks is to develop low energy, non-toxic pathways to convert the biomass to useful chemicals. We want to be sure not to generate more carbon than is being removed from air, the difference between C(in) from the air, and C(out) from the energy used, is the carbon footprint ΔC. Carbon footprints by design should be positive such that C(in) >> C(out). This leads in a natural way to the reduction of global warming gasses. In the past 10 years, significant advances have been made in the development of fuels, chemicals and materials from renewable feedstocks. These have included

1. biodiesel from plant oils and algae
2. bioethanol and butanol from sugars and lignocellulose
3. plastics, foams and thermosets from lignin and plant oils
4. electronic materials from chicken feathers

Our future is bright due to the ongoing collaborations between several disciplines involving biotechnology, agronomy, toxicology, physics, engineering and others. New fuels, chemicals and materials are being derived from renewable feedstock with minimal impact on human health and the environment. Chemists and chemical engineers need to learn a little biochemistry. There are microbes that exist or can be genetically engineered to turn biomass into many useful compounds. The future is wide open for new companies to use renewable feedstocks to make useful chemicals.

Catalytic reagents (as selective as possible) are superior to stoichiometric reagents. A catalyst is defined as "a substance that changes the velocity of a reaction without itself being changed in the process". It lowers the activation energy of the reaction and is not consumed. This means that, in principle at least, it can be used in small amounts and be recycled indefinitely, that is it doesn't generate any waste. Catalytic hydrogenations are widely applied in the petrochemical industry, where the use of other reductants is generally not economically viable. It is only in the last two decades that catalysis has been widely applied in the pharmaceutical and fine chemical industries. This minimizes the enormous amounts of waste generated by the use of stoichiometric inorganic reagents. When you propose a new reaction scheme, see whether a catalyst will help? What kinds of catalyst? Consider heterogeneous, homogeneous, organocatalysts and, more recently, Nature's own exquisite catalysts: enzymes. Enzymes are particularly effective at catalyzing highly selective processes under mild conditions. They are expected to play an important role in the transition from a chemical industry based on non-renewable fossil resources to a more sustainable biomass economy.

Chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not persist in the environment. When you make a chemical product, consider what will happen to it seven generations into the future. The principle of designed degradation will become more and more important in the future. Persistence of chemicals in the environment is caused by properties such as volatility or sorption to particles. Regulators have established criteria (half-lives in water, soil, air) that define persistence used to identify chemicals as PBT (Persistent, Bioaccumulative, Toxic). Recycling and composting will become far more important in our future. New companies will form to take advantage of the great amounts of products that may be recycled. Jobs will be created as the recycled materials must be sorted and sold. New products can be made. Think about the role entropy plays. Instead of expending work to bring atoms together from a scattered source, recycling chemicals uses molecules that already exist. Instead of digging elements out of the ground, consider certain products like mobile phones as small mines-sources of those elements. The lanthanides are called "rare earths" for a reason. A new type of recycling is on the horizon. Many companies are getting interested in taking back their products when we trade them in. It will be normal that TVs, phones, computers will be returned to the manufacturer when we are finished with them. Recycling manufactured products creates jobs and greatly helps the economy.

Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances. Real-time feedback is essential in proper functioning chemical processes. Analysis can also be performed in a chemical plant, a subdiscipline known as process analytical chemistry. Such analysis can detect changes in process temperature or pH prior to a reaction going out of control or poisoning a catalyst. Other events can be detected before a major incident occurs. The effective application of process analytical chemistry directly contributes to the safe and efficient operation of chemical plants worldwide. We need to monitor exactly what is present during production of a chemical. What has been left in the water layer; what has leaked into the air? What % of the chemical is flowing through the pipe? Do we need to draw samples and take them back to the lab? Can we use a probe to take measurements during the reaction? It can be something simple like pH, concentration of chloride ion, etc.

Green Chemistry’s primary focus is to make the environment safer. The public may have a short exposure, and we must measure the effects of that exposure. A researcher, a teacher, or a production worker may be exposed to for many years. Materials and processes that are safer for the environment also are likely to be safer for all of the people who may come in contact with it. When we work together to achieve the goals of safer chemistry, we all benefit. It will no longer be called green chemistry. In the future it will just be smart and profitable chemistry.