Fundamental and Applied Science, Academia and Industry, a Creative Tension in Today's Chemistry

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Abstract: The scale of the chemical production is immense, obviously of benefit to human beings, as well as being profitable. At the beginning of many successful commercial chemical processes there often lies fundamental science, whether done at universities, or in progressive industrial laboratories. A rationale for encouraging basic science is presented. The scale of chemical processes inherently leads to problems, to ourselves and the environment. Two examples are given of new, environmentally sensitive developments in the field of synthetic polymers. After a brief survey of the way commercialization is encouraged within academia, a concern about its effects for education is voiced. The tension in contemporary chemistry, between "pure" and applied science, between academia and industry, is approached through questions which can be asked about work in the author's research group, on benzene nanothreads.

The scale of chemical industrial activity

The world requires chemical transformation of natural materials on an incredible scale. This can be illustrated in a number of ways. For example, world chemicals sales in 2015 are estimated near 3.8 x 10^{12} Euros.[1] You can be sure that sums of this magnitude are received for substances that are of use to someone. Another perspective is obtained by looking at the mass of the chemicals produced. Figure 1 shows 2010 United States chemical production volumes.[2] The units are millions of pounds.

Table 3-1. U.S. Production Volumes in 2010 of 74 Chemicals Selected for the Bandwidth Analysis

Chemical	2010 Production (Million lb/Year)	Chemical	2010 Production (Million lb/Year)
Acetic Acid	4,366	Methanol	2,024
Acetic Anhydride	1,798[a]	Methyl Chloride	1,330[c]
Acetone	3,178	Methyl Methacrylate	1,529
Acrylic Acid	2,723	Methyl tert-Butyl Ether	3,386
Acrylonitrile	2,505	Monoammonium Phosphate	9,245
Aluminum Sulfate	1,906[a]	Nitric Acid	15,280
Ammonia	22,691	Nitrobenzene	[illegible]
Ammonium Nitrate	15,166	Nitrogen	69,609[b]
Ammonium Phosphates (Other)*	3,053	Oxygen	58,287[a]
Ammonium Sulfate	5,729	Phenol	[illegible]
Aniline	2,348	Phosphoric Acid	20,678
Benzene	13,274	Polycarbonate	1,862[c]
Bisphenol A	1,610	Polyester	2,525
Butadiene	3,484	Polyethylene Terephthalate	[illegible]
Butylenes	2,110	Polyethylene, High Density	16,889
Calcium Carbonate	24,282	Polyethylene, Linear Low Density	13,787
Calcium Chloride	2,204[a]	Polyethylene, Low Density	6,741
Caprolactam	1,530	Polypropylene	17,258
Carbon Black	3,415[a]	Polystyrene	5,055
Carbon Dioxide	17,365[a]	Polystyrene, High Impact	1,873[c]
Chlorine	21,465	Polyurethane	4,143
Cumene	7,626	Polyvinylchloride	14,019
Cyclohexane	3,452	Propylene	[illegible]
Cyclohexanone	3,031[a]	Propylene Oxide	4,470
Diammonium Phosphate	[illegible]	Soda Ash (Sodium Carbonate)	23,373
Ethanol	66,080	Sodium Hydroxide	16,581
Ethylbenzene	9,349	Sodium Hypochlorite	11,589[a]
Ethylene	52,864	Sodium Silicates	2,624
Ethylene Dichloride	19,426	Styrene	9,179
Ethylene Glycol	2,867	Sulfur	[illegible]
Ethylene Oxide	5,876	Sulfuric Acid	71,687
Formaldehyde	3,050[b]	Terephthalic Acid	[illegible]
Hydrogen	6,591	Urea	11,292
Hydrochloric Acid	7,840	Vinyl Acetate	3,054
Hydrogen Peroxide	852	Vinyl Chloride	14,159
Isobutylene	8,769	Xylenes, Mixed	13,869
Isopropanol	1,662	Xylenes, Paraxylene	7,520
Subtotal			903,270
Total Sector-Wide			2,400,000

Figure 1. Chemical production in USA in 2010. Boxes surround chemicals produced in greatest amount. Source: US Department of Energy.

The boxes outline the chemicals made in greatest amounts – ethanol, nitrogen, oxygen (yes, these two need to be separated from the air), the common plastics, grouped together, and sulfuric acid. These chemicals are each made in some 70 billion pounds in the US per year, and worldwide probably 4-5 times as much. The ethanol is made largely not to be consumed, but as a biofuel. Some of these substances are familiar, but you would be hard pressed to find a bottle of sulfuric acid on your Lawson store shelves. It is the ultimate transformer – made in gigantic volume to be used in the making of other chemicals. Note also that sulfuric acid is deadly dangerous. But you have not heard much about anyone in the world killed in the production of such vast quantities of sulfuric acid. Very dangerous substances – concentrated sulfuric acid, hydrogen, HCN – can be handled safely industrially.

No one makes such amounts of chemicals for fun – they are made to be sold, to be used. The use encompasses every part of our daily existence, and every industry – from toothpaste to automobiles, from hair coloring to a colored sock.

I would like to tell you the story of one chemical, and this is the most common and essential fertilizer, ammonia. Imagine a lovely *kaiseki* cuisine dish, a swirl of cut scallions above a mussel arranged on a small bed of rice, with drops of a complex sauce over it. The ingredients are animal and vegetable, and ultimately the animal comes from the vegetable realm. The essential benefit to our bodies (not ignoring the aesthetic/spiritual aspects of this cuisine) derives from the carbohydrates and proteins and vitamins in the ingredients. Absolutely critical for our life are the nitrogen atoms in that food. For all proteins and nucleic acids in us have N in them. We breathe in N_2 gas, 78% of atmosphere. And breathe it out again, not taking an atom from that N_2. We, the supposed pinnacle of evolution, can't use the N_2 we breathe in. But lowly bacteria, symbiotic with the roots of leguminous plants can. They accomplish the transformation of atmospheric nitrogen into ammonia with a remarkable enzyme, nitrogenase. The active part of the natural, biological molecule involved, is a cluster of some sulfurs, 7 Fe atoms, 1 molybdenum (!) and a carbon at the middle.

Some nitrogen comes into the food chain also from nature's own, perfectly natural acid rain after storms – lightning causes nitrogen and oxygen in the atmosphere to combine, eventually leading to nitrates in the soil. Ammonia and nitrates go into plant-origin amino acids, supplying the essential nitrogen in us.

The work of bacteria, as well as lightning combining N_2 and O_2 in the atmosphere, is responsible for about half the N atoms we need. The rest come from a remarkable industrial process more than a hundred years old, the Haber-Bosch process. In it, hydrogen (ultimately from CH_4 in natural gas) and atmospheric nitrogen are combined to produce ammonia.

Half the nitrogen atoms in your bodies have seen the inside of a Haber-Bosch factory. Or, half the people in this world are alive because of the Haber-Bosch process.

Let's move to a material we all know, produced in vast quantity, and a signpost of the contemporary world: plastics. 2 million plastic (polyethylene) bottles are used every 5 minutes in US. The staggering consumption of plastic in the world has associated problems, to which I will return.

Fundamental and applied chemistry

The Haber-Bosch process, or the manufacture of plastics on the scale mentioned, are clearly industrial and commercial activities on a vast scale. They have long moved from discovery to production. But was their discovery, the first steps leading to them, the result of basic or fundamental or pure research? The descriptors I have used imply demarcations or divisions, compartmentalization, in the activity of many-faceted human beings and human enterprises. Words such as "fundamental" or "applied" are clearly problematic -- they take away from humanity and creativity. Yet it is interesting to seek a distinction, while fully aware of the limitation in our language.

Most modern plastics are the outcome of basic research. Take nylon, a remarkable, strong fiber, a polymer of hexamethylene and adipic acid. It was synthesized in DuPont's laboratories in 1935 by Wallace Carothers. Carothers' work in linear polymers began as an unrestricted foray into the unknown, with no practical objective in mind. But the research was in a new field in chemistry and Du Pont believed that any new chemical breakthrough would likely be of value to the company. It was.

Polyethylene was known from 1898, with industrial production beginning in the 1930s. But a breakthrough was needed for production in the volume we see, and this occurred with the help of a catalyst that allows the polymerization to proceed at mild temperatures and pressures. This was done in 1950s by Karl Ziegler, who developed in fundamental research a catalytic system based on titanium halides and organoaluminium compounds. and by Giulio Natta who gave us a way to highly ordered polyethylene.

In 1939, Abraham Flexner, the first President of the Institute for Advanced Study in Princeton, where Einstein and Oppenheimer worked, wrote a remarkable essay, “The Usefulness of Useless Knowledge”. It is worthwhile to quote from that essay:

“*Institutions of learning should be devoted to the cultivation of curiosity and the less they are deflected by considerations of immediacy of application, the more likely they are to contribute not only to human welfare but to the equally important satisfaction of intellectual interest which may indeed be said to have become the ruling passion of intellectual life in modern times.”*

I am not for a moment suggesting that everything that goes on in laboratories will ultimately turn to some unexpected practical use or that an ultimate practical use is its actual justification. Much more am I pleading for the abolition of the word “use”, and for the freeing of the human spirit.”[3]

Flexner was wise enough to see the mutual interaction of fundamental and applied science. So he continues:

“*Not infrequently the tables are turned, and practical difficulties encountered in industry or in laboratories stimulate theoretical inquiries which may or may not solve the problems by which they were suggested, but may also open up new vistas, useless at the moment, but pregnant with future achievements, practical and theoretical.”*

Problems of scale and taking environmental issues into account

It’s obvious that any advance in our standard of living, of the kind that contemporary chemical industrial activity has enabled, is introduced for good reasons. And yet may have effects that we cannot anticipate, effects that become apparent only when that advance becomes widely distributed. So it is with plastics. Plastics are strong and durable. They are too durable. Plastics are inexpensive, lightweight. They have come to clutter our environment, found on the high seas, in deserts. Is this a reason not to introduce them, not to use them? Opinions differ. Clearly the introduction of any material into the environment should be accompanied by a precautionary investigation of its effects, both material and social, on our health, on that of the environment. Sadly, this is not done in sufficient measure. And sometimes the effects just cannot be estimated.

It is possible to direct fundamental research toward desirable environmental goals. Here is one example: In 2003 and 2005, Geoffrey Coates, a brilliant colleague of mine, and his coworkers came up with a catalyst for a remarkable process for making a polymer from CO_2 and another molecule, a so-called epoxide.[4] The polymer contains 44% by weight of CO_2. Another process uses an epoxide that can be made from orange peels. The papers behind what made it possible, the cobalt-containing catalyst shown in Figure 2, were published in the prime fundamental chemistry journals of this world. They were followed up by development; commercialization is very much underway.

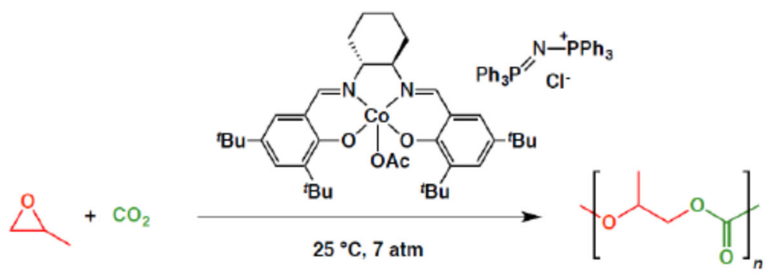

Figure 2. The catalyst and polymerization process of Coates and coworkers.

There is much interest in polymers made entirely from renewable resources, as is done in the reaction just mentioned. So Showa Denko K. K. has come up with a polymer Bionolle™, an aliphatic polyester resin that begins life in ethanol, and while having desirable strength is entirely biodegradable in arelatively short time scale in compost.[5]

The environment can be served better, as these examples show.

Commercialization

Potential commercialization of the outcomes of their basic research is certainly on the minds of many of our researchers. Why not? The mix of potential benefit to humanity and personal profit is a powerful incentive to creativity. Universities, now fully aware of potential benefit to them, have created the support infrastructure for this to happen – help in patenting discoveries, incubators for scaling up and development.

Our professional societies are very much concerned with facilitating the prospect as well. Here for instance are the highlights of a recent report by Mark Cesa of the American Chemical Society (ACS) Committee on Science on "Building strategic industry-university partnerships in the field of Advanced Materials":[6]

Objective setting: Develop a shared vision that sets clear mutual objectives for the strategic partnership and the problems to be addressed, including key research challenges.

Leadership: Identify leaders on both sides who are capable of crossing boundaries and building trust between business and academia.

Type of research: Design a research program that is commercially relevant, precompetitive, and long-term. R&D can span from basic research to technology development.

Partnership principles: Define, fund, and staff the research jointly, including in-kind contributions, to share risk and incentivize collaboration

Intellectual property: Establish a clear agreement for the use of resultant intellectual property

Communication: Dissolve boundaries between entities by facilitating frequent communication among researchers and managers.

Outcomes: Set timelines and outcome-oriented milestones to track and gauge progress and results.

These general rubrics will be followed up by case studies in the report of the ACS Committee. I note the "managerial tone" in these recommendations; it's not how fundamental research is done in universities, but derives from the industrial side of the collaboration. Perhaps it has to be that way.

The fundamental research is often accomplished with government agency support, and so innovators in academia must walk carefully when they discover something of commercial value – there are legal interests involved of the professor, of the university, and the government granting agency. The legal picture varies from country to country, and, as fascinating as it is in its own right, cannot be done justice to in this brief account.

Some educational concerns with commercialization

I do want to raise a potential problem, which is the effect of a university research and education environment that encourages commercialization on the educational experience of a graduate student.

The problem is best framed by two quotes from students in an essay by Brian Coppola on "The Technology Transfer Dilemma: Preserving morally responsible education in a utilitarian entrepreneurial academic culture."

"*Four years ago, one of my former students asked, "Do you know how we tell what kind of mood the boss is going to be in? Well, we check the stock market page to see how his company is doing that day."*

Two years ago, another former undergraduate student wrote to me worried about his future. Although he was excited to enter the job market, he could not talk about his unpublished results because he was bound by non-disclosure until the patents made their way through the system. Adding to his dilemma, any delay of publication gave the group a lucrative head start on subsequent research."[7]

If a professor owns a company, and former graduate students run it, does this affect the educational process? Does it influence the attitude of the current students of that professor toward their research?

We should be sensitive to potential distortions of the educational process that come from commercialization. But also we should recognize that it is possible to be entrepreneurial, to obtain patents, and yet assure that one's students' education is guided only by a search for understanding and reliable knowledge, and not potential profit.

So I would add to the list of steps encouraged by that ACS Committee mentioned in the previous section, this:

> "Preserve the integrity of the educational process: Throughout, discuss ethical and social responsibility questions."

I want to finish with a story from our own work, which will allow me to pose at its end some questions that epitomize the tension I mention in the title of my talk.

A case study from our own work

Benzene has been subjected to high pressure for >100 years, yielding intractable amorphous solids. Until 2014, when a group at Penn State led by John Badding carried out a slow pressurization, and obtained a striated material with molecular lines only 6.5 Angstroms thick.[8] On sonication one got individual, worm-like, long nanothreads. What are they? Well, various physical measurements showed the material had composition CH, and consisted mostly of four-coordinate carbon – a completely saturated polymer of benzene.

Three suggestions were already in the literature (Figure 3) – Vince Crespi and coworkers had suggested a hydrogenated natotube,[9] as at left. Xiaodong Wen and I and Neil Ashcroft obtained another linear polymer from a computational study of benzene under compression,[10] and Dirk Trauner came up with the idea of a polytwistane, at right.[11] In all of these, if you look carefully, you can see the benzene rings, now polymerized into a completely saturated polymer, still CH in composition.

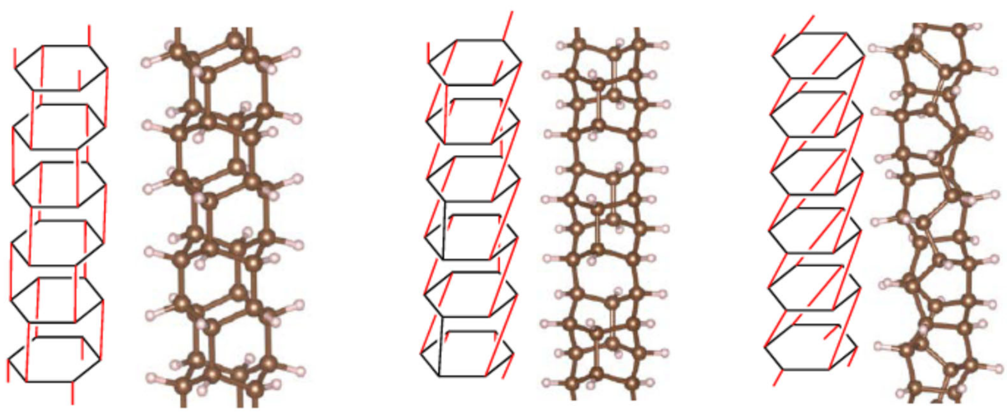

Figure 3. Three proposed regular benzene polymers.

So what are the real nanothreads made by the Penn State group? The world of theoreticians (that's the people who proposed the regular, repeating polymers in Figure 3) is always as simple as possible. The world of nature is… as complicated as it need be. The nanothreads are a polymer disordered along its length, a polymer of benzene for sure, but one made up from pieces of the regular polymers suggested.

We next wanted to study how these polymerizations could take place. One starts out from the crystal structure of solid benzene. In the first steps of polymerization two carbons become saturated, then four, then all six. Bo Chen in my group is currently studying the mechanism of the polymerization. Things are not simple. For every degree of saturation -- two, four, or six – there is not one polymer but many isomeric forms. In a heroic first step, Bo Chen has produced a road map for polymerization – the 12 lowest energy nanothreads can made by intricate, overlapping paths from 7 degree four polymers, and these in turn come from 4 degree two polymers.[12] Which come from crystalline benzene. He is now looking at the activation energies for all these processes, under pressure. Stay tuned.

I could tell you so much more about this beautiful set of materials, new polymers in the process of formation. But let me return to the theme of this lecture through several questions about what will happen next in this project.

Will we find out how benzene polymerizes under pressure?

Will our collaborators be able to make stereochemically pure nanothreads?

The answer to the first question is "maybe", to the second " surely", given my infinite faith in the abilities of organic chemists. Both questions are fundamental, basic research questions, best carried out at a university of research institute, but could be accomplished in an industrial setting as well, though likely only in large company research laboratories.

The next two questions are:

Will they be strong? Will they be useful in other ways?

Will they be a commercial product?

These questions bridge to commercialization and industry. The first question is one to be studied in an academic setting or an industrial one. The third one , *" Will they be a commercial product?"* depends so much on matters quite far removed from science – will the nanothreads fill a need? innovate? find a market?

The last questions I ask is

If our collaborators start a company, will that affect how they interact with their students? Will potential commercialization influence my colleagues's future research?

These are clearly questions of psychology, educational practice, and ethics.

The totality of these questions, the different directions they take from the starting point of a current discovery, illustrate the tension between fundamental and applied research, between academia and industry in chemistry. At the end, we will have a significant advance in our understanding of how this (small) part of the universe works, some educated and creative young scientists, and, perhaps, just perhaps, a new class of polymers with useful properties.

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