Green Chemistry

John C. Warner

President and Chief Technology Officer

Warner Babcock Institute for Green Chemistry, LLC

President

Beyond Benign

beyondbenign
a warner babcock foundation

warnerbabcock
institute for green chemistry

Asking the Right Questions

Why would a chemist
make a hazardous material?

How do we train chemists?

1984-1988 Princeton University

"Diels-Alder Reactions of Bicyclic 1,2,4-Triazines: The Conversion of Pyrimido[4,5-*e*]-1,2,4-triazines to Pyrido[2,3-*d*]pyrimidines." Taylor, E. C.; McDaniel, K. F.; Warner, J. C. *Tetrahedron Lett.*, **1987**, *28*, 1977.

"Synthesis and Structural Confirmation of 5,6-Cyclopenteno-5-deazapterin." Taylor, E. C.; Warner, J. C., *Heterocycles*, **1987**, *26*, 2673.

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Professor E. C. Taylor

"Diels-Alder Reactions of 6-Azapterins. An Alternate Strategy for the Synthesis of 5,10 Dideaza-5,6,7,8-tetrahydrofolic Acid (DDATHF)." Taylor, E. C.; Harrington, P. M.; Warner, J. C., *Heterocycles*, **1988**, *27*, 1925.

"Aromatic-Aromatic Interactions in Molecular Recognition: A Family of Artificial Receptors for Thymine that Shows Both Face-To-Face and Edge-To-Face Orientations." Muehldorf, A. V.; Van Engen, D.; Warner, J. C.; Hamilton, A. D., *J. Am. Chem. Soc.*, **1988**, *110*, 6561.

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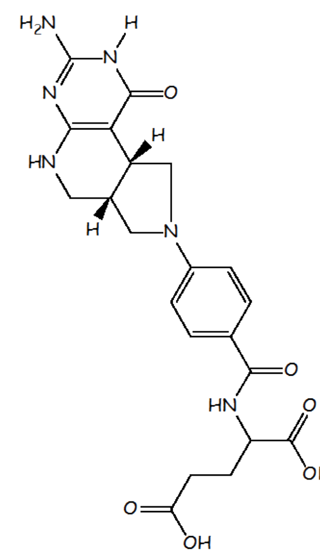
"Synthesis and Competitive Thermal Reactions of 3-[2'-(2-Propynylthio)- phenylamino]-1,2,4-triazines." Taylor, E. C.; Pont, J. L.; Warner, J. C., *J. Org. Chem.*, **1989**, *54*, 1456.

"New Synthetic Studies on Deazafolates." Taylor, E. C.; Chang, Z. Y.; Harrington, P. M.; Hamby, J. M.; Papadopoulou, M.; Warner, J. C.; Wong, G. S. K.; Yoon, C. M.; Shih, C., *Chem. Biol. Pteridines, 1989 Proc. Int. Symp. Pteridines Folic Acid Deriv.*, 9th, Meeting Date 1989, 987. Ed. by: Curtius, H.-C.; Ghisla, S.; Blau, N. de Gruyter: Berlin, Fed. Rep. Ger. **1990**.

"Pyridopyrimidines." Warner, John C. in "Miscellaneous Fused Pyrimidines" T. Delia, Ed. Part IV, vol. 24, pp 1-460 John Wiley, New York **1992**.



"Alimta"

Polaroid

1988-1997

Lloyd Taylor

"Thermographic Recording Film." Dombrowski, Edward J.; Guarrera, Donna J.; Jones, Robert L.; Mischke, Mark R.; Warner, John C.; Yang, Jiyue, US Patent 5,750,464. May 12, **1998**.
"Thermographic Recording Films." Dombrowski, Edward J.; Jones, Robert L.; Warner, John C.; Yang, Jiyue, US Patent 5,750,463. May 12, **1998**.
"Process for Fixing an Image, and Medium for Use Therin." Marshall, John L.; Shon Baker, Rita S.; Takiff, Larry C.; Telfer, Stephen J.; Warner, John C., US Patent 5,741,630. April 21, **1998**.
"Copolymers Having Pendant Functional Thymine Groups." Grasshoff, J. Michael; Taylor, Lloyd D.; Warner, John C., US Patent 5,708,106. January 13, **1998**.
"Photographic Development" Guarrera, Donna J.; Mattucci, Neil C.; Mehta, Avinash C.; Taylor, Lloyd D.; Warner, John C. US Patent 5,705,312. January 6, **1998**.
"Photographic System" Guarrera, Donna J.; Mattucci, Neil C.; Mehta, Avinash C.; Taylor, Lloyd D.; Warner, John C. PCT Int. Appl. WO 9,729,405. August 14, **1997**.
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"Low-Volatility, Substituted 2-Phenyl-4,6-bis[Halomethyl]-1,3,5-triazine for Lithographic Printing Plates." Fitzgerald, Maurice J.; Kearney, Frederick R.; Liang, Rong-Chang; Schwarzel, William C.; Guarrera, Donna, J.; Hardin, John M.; Warner, John C., US Patent 5,561,029. October 1, **1996**.
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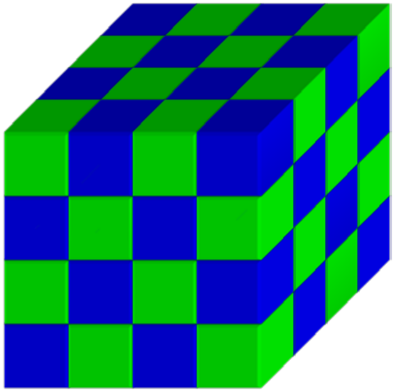
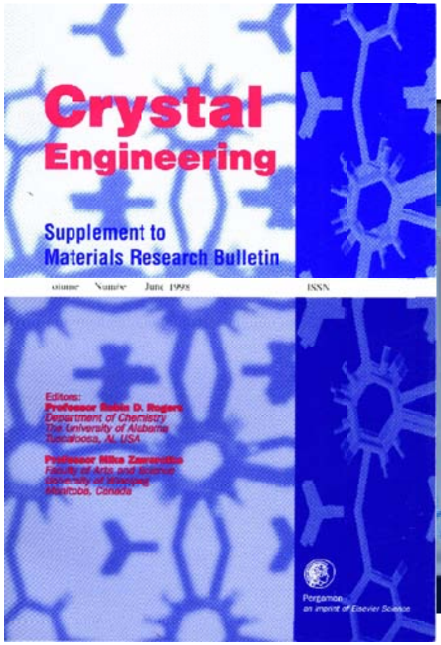
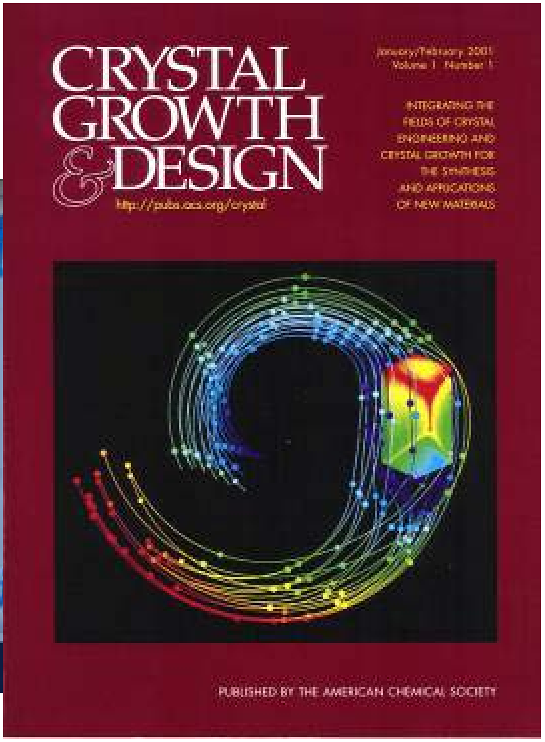
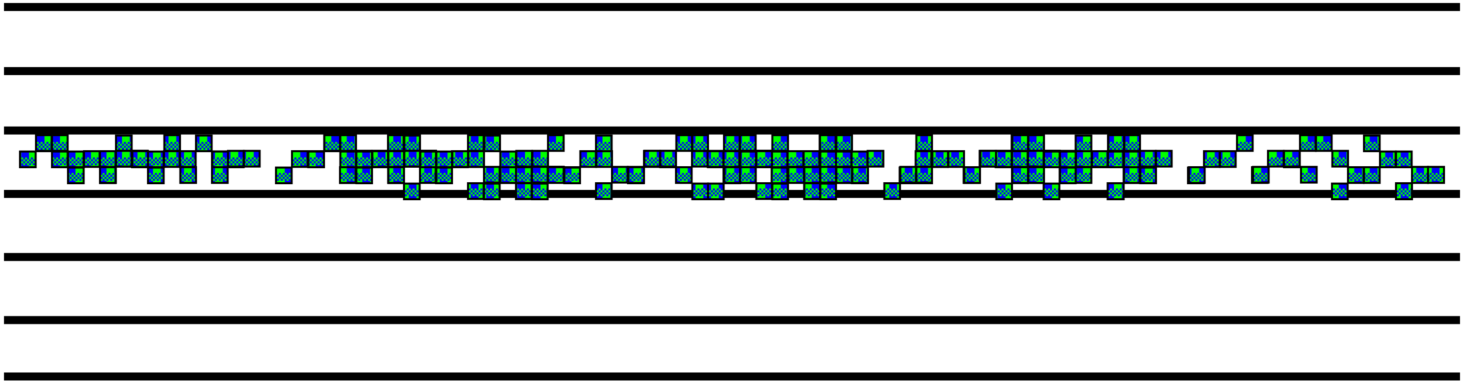
"Imaging Medium and Process." Fehervari, Agota F.; Gaudiana, Russell A.; Kolb, Eric S.; Mehta, Parag G.; Taylor, Lloyd D.; Warner, John C., US Patent 5,424,268. June 13, **1995**.
"Thermally-Processable Image Recording Materials Including Substituted Purine Compounds."Ford, M.; Guarrera, D. J.; Mischke, M.; Pai, R.; Warner, John C., US Patent 5,411,929. May 2, **1995**.
"Copolymeric Mordants and Photographic Products and Processes Containing Same." Grasshoff, J. Michael; Taylor, Lloyd D.; Warner, John C., US Patent 5,395,731. March 7, **1995**.
"Process and Composition for Use in Photographic Materials Containing Hydroquinones. Continuation in Part." Taylor, Lloyd D.; Warner, John. C., US Patent 5,338,644. August 16, **1994**.
"Process and Composition for Use in Photographic Materials Containing Hydroquinones." Taylor, Lloyd D.; Warner, John. C., US Patent 5,177,262. January 5, **1993**.

Noncovalent Derivatization









EPA Approval

Low **V**olume **E**xemption

Pre**M**anufacturing **N**otification

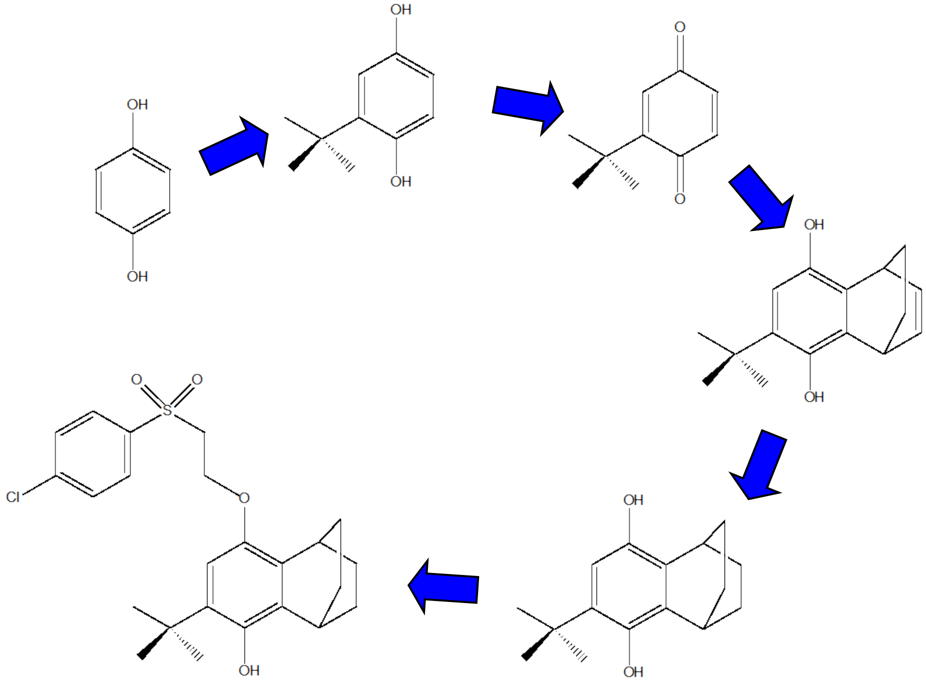
Small particles?

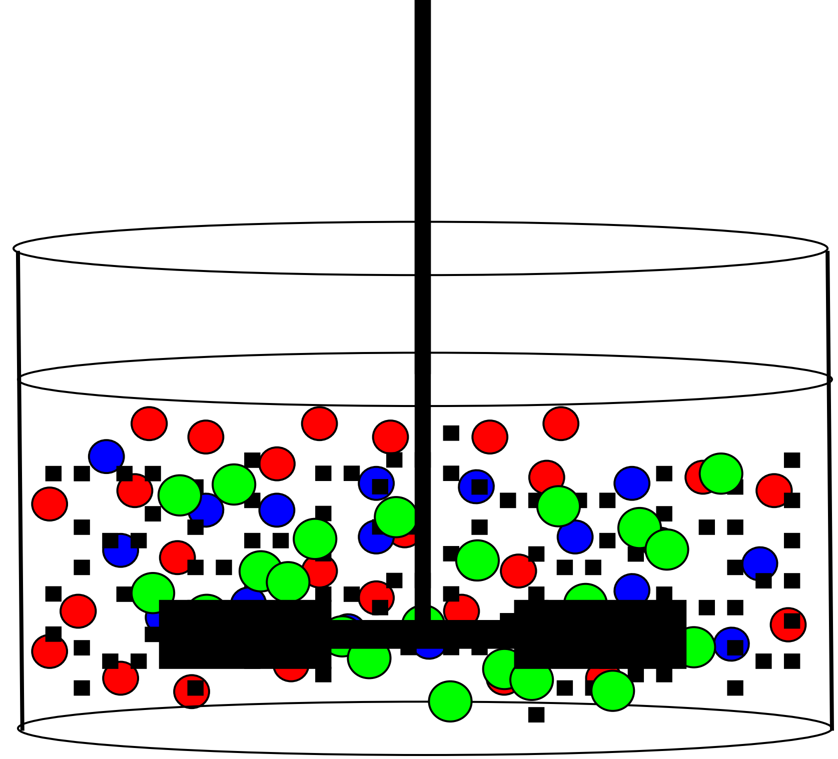
Molecular Complexes?


Polaroid
Cambridge, MA
Washington, DC
UNITED STATES
ENVIRONMENTAL PROTECTION AGENCY

Paul Anastas

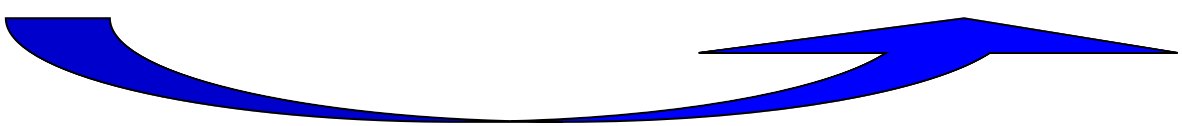
Office of Pollution Prevention and Toxics



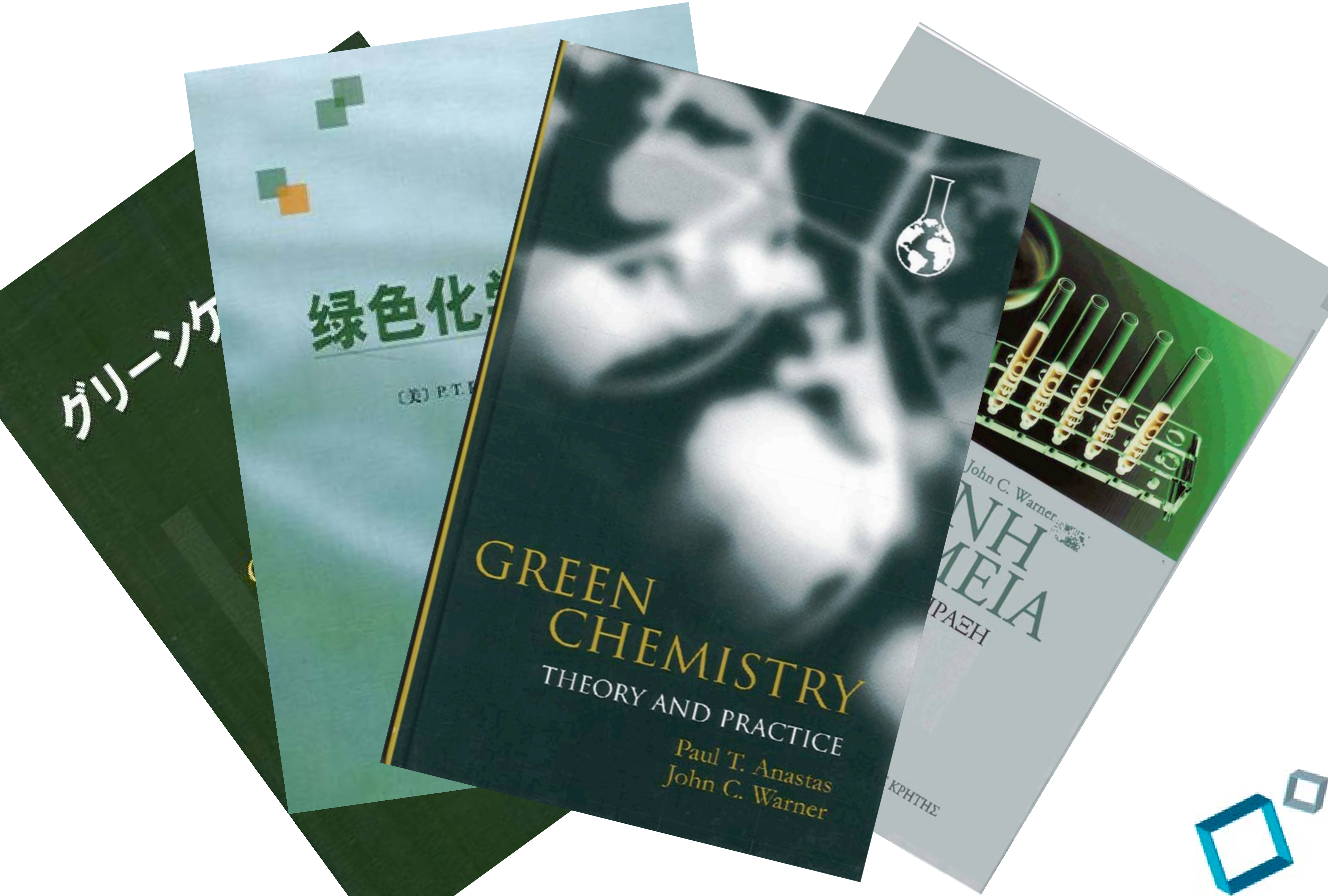


Old Technology
Several Solvents
High Energies
Hazardous Reagents

New Technology
Aqueous Conditions
Low Energies
Non-hazardous Reagents



Green Chemistry is the *design* of chemical products and processes that reduce or eliminate the *use and/or generation* of hazardous substances.



The Twelve Principles of Green Chemistry

1. Prevention. It is better to prevent waste than to treat or clean up waste after it is formed.

2. Atom Economy. Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.

3. Less Hazardous Chemical Synthesis. Whenever practicable, synthetic methodologies should be designed to use and generate substances that possess little or no toxicity to human health and the environment.

4. Designing Safer Chemicals. Chemical products should be designed to preserve efficacy of the function while reducing toxicity.

5. Safer Solvents and Auxiliaries. The use of auxiliary substances (solvents, separation agents, etc.) should be made unnecessary whenever possible and, when used, innocuous.

6. Design for Energy Efficiency. 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.

7. Use of Renewable Feedstocks. A raw material or feedstock should be renewable rather than depleting whenever technically and economically practical.

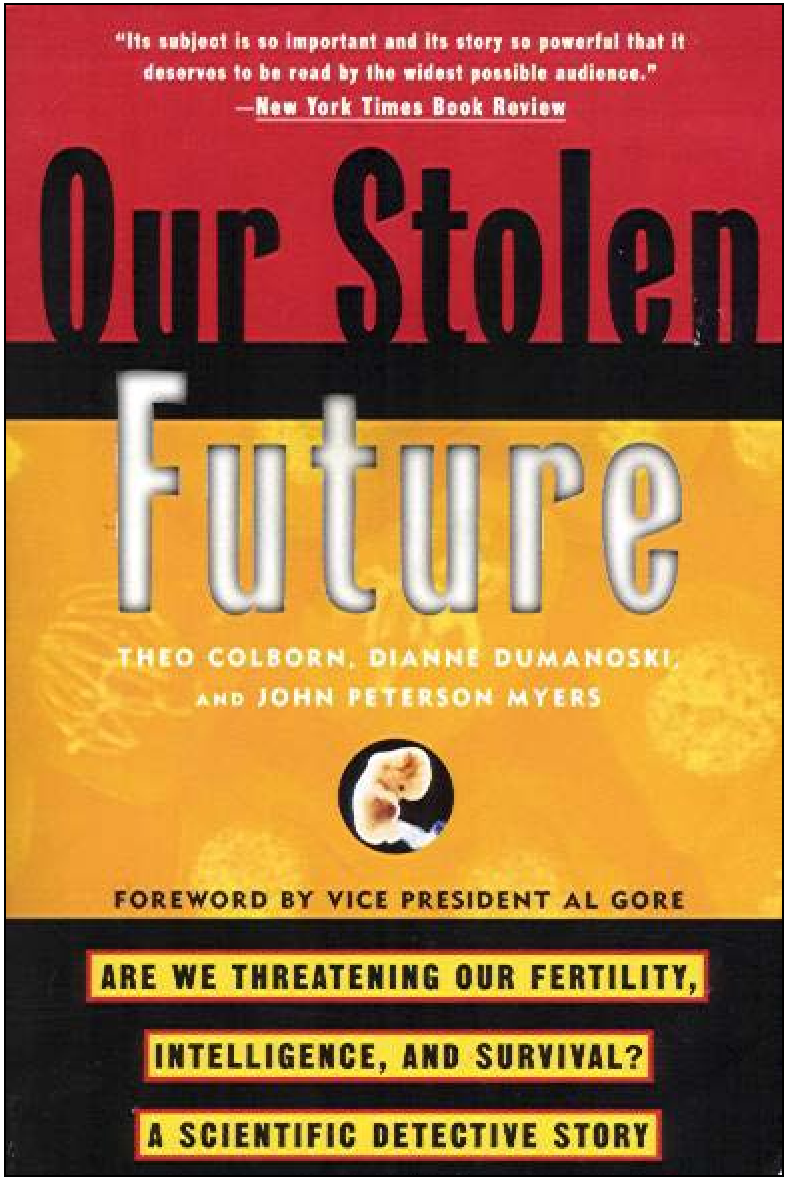
8. Reduce Derivatives. Unnecessary derivatization (blocking group, protection/deprotection, temporary modification of physical/chemical processes) should be avoided whenever possible .

9. Catalysis. Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.

10. Design for Degradation. Chemical products should be designed so that at the end of their function they do not persist in the environment and instead break down into innocuous degradation products.

11. Real-time Analysis for Pollution Prevention. Analytical methodologies need to be further developed to allow for real-time in-process monitoring and control prior to the formation of hazardous substances.

12. Inherently Safer Chemistry for Accident Prevention. Substance and the form of a substance used in a chemical process should be chosen so as to minimize the potential for chemical accidents, including releases, explosions, and fires.



I have synthesized over 2500 compounds!!!!!

I have synthesized over 2500 compounds!

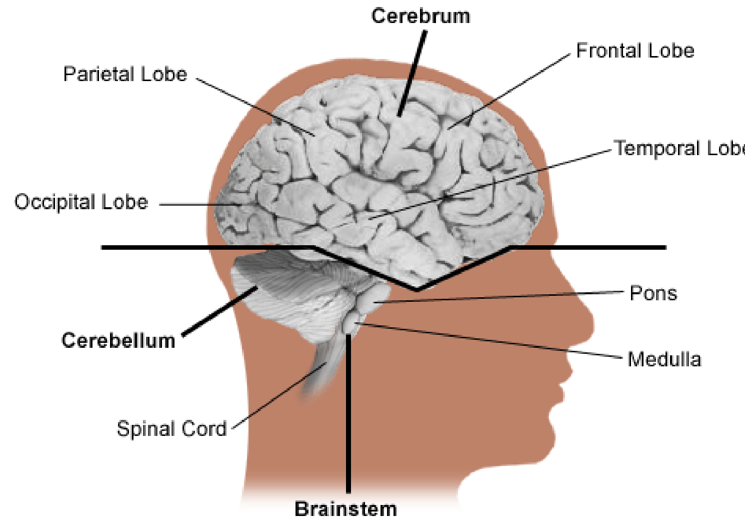
I have never been taught what makes a chemical toxic!
I have no idea what makes a chemical an environmental hazard!

I have synthesized over 2500 compounds!

I HAVE NO IDEA WHAT MAKES A CHEMICAL TOXIC!

STANFORD CANCER CENTER

Stanford Hospital & Clinics



What causes brain tumors?

The majority of brain tumors have abnormalities of genes involved in cell cycle control, causing uncontrolled cell growth. These abnormalities are caused by alterations directly in the genes, or by chromosome rearrangements which change the function of a gene.

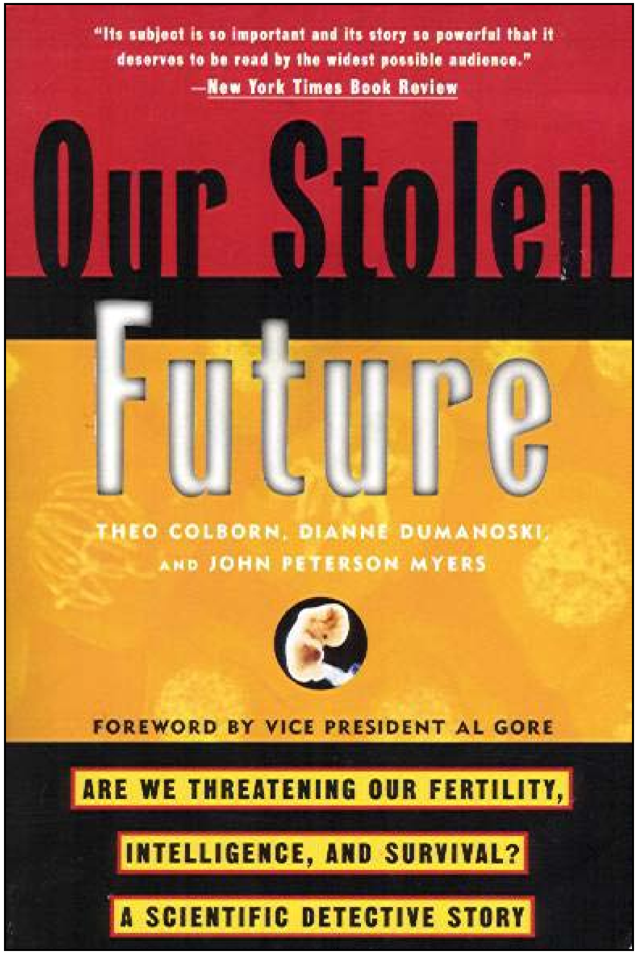
Patients with certain genetic conditions (i.e., neurofibromatosis, von Hippel-Lindau disease, Li-Fraumeni syndrome, and retinoblastoma) also have an increased risk to develop tumors of the central nervous system. There have also been some reports of people in the same family developing brain tumors who do not have any of these genetic syndromes.

Research has been investigating parents of children with brain tumors and their past exposure to certain chemicals. Some chemicals may change the structure of a gene that protects the body from diseases and cancer. **Workers in oil refining, rubber manufacturing, and chemists have a higher incidence of certain types of tumors.** Which, if any, chemical toxin is related to this increase in tumors is unknown at this time.

http://cancer.stanfordhospital.com/healthInfo/cancerTypes/brain/default

Recent scientific research has clearly demonstrated an association between organochlorines and breast cancer. An analysis of chemical plant workers in Hamburg, Germany discovered a two-fold increase in breast cancer among the women workers who had been exposed to dioxin contamination. Significantly higher levels of breast cancer have been found in separate studies of women living near organochlorine chemical plants in Minnesota and Long Island. **Other studies have revealed elevated breast cancer mortality among professional chemists.**

http://www.fwhc.org/health/xeno.htm



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Walrath, J., F. P. Li, et al. (1985). "**Causes of death among female chemists**." Am J Public Health 75(8): 883-5.

Christie, D., K. Robinson, et al. (1991). "**A prospective study in the Australian petroleum industry. II. Incidence of cancer**." Br J Ind Med 48(8): 511-4.

Persson, B., M. Fredriksson, et al. (1993). "**Some occupational exposures as risk factors for malignant lymphomas**." Cancer 72(5): 1773-8.

Berlin, K., C. Edling, et al. (1995). "**Cancer incidence and mortality of patients with suspected solvent- related disorders**." Scand J Work Environ Health 21(5): 362-7.

Persson, B. (1996). "**Occupational exposure and malignant lymphoma**." Int J Occup Med Environ Health 9(4): 309-21.

Lynge, E., A. Anttila, et al. (1997). "**Organic solvents and cancer (review).**" Cancer Causes Control 8(3): 406-19.

In 2008: (United States)

13,921 Undergraduate Degrees in Chemistry
4,708 Undergraduate Degrees in Chemical Engineering

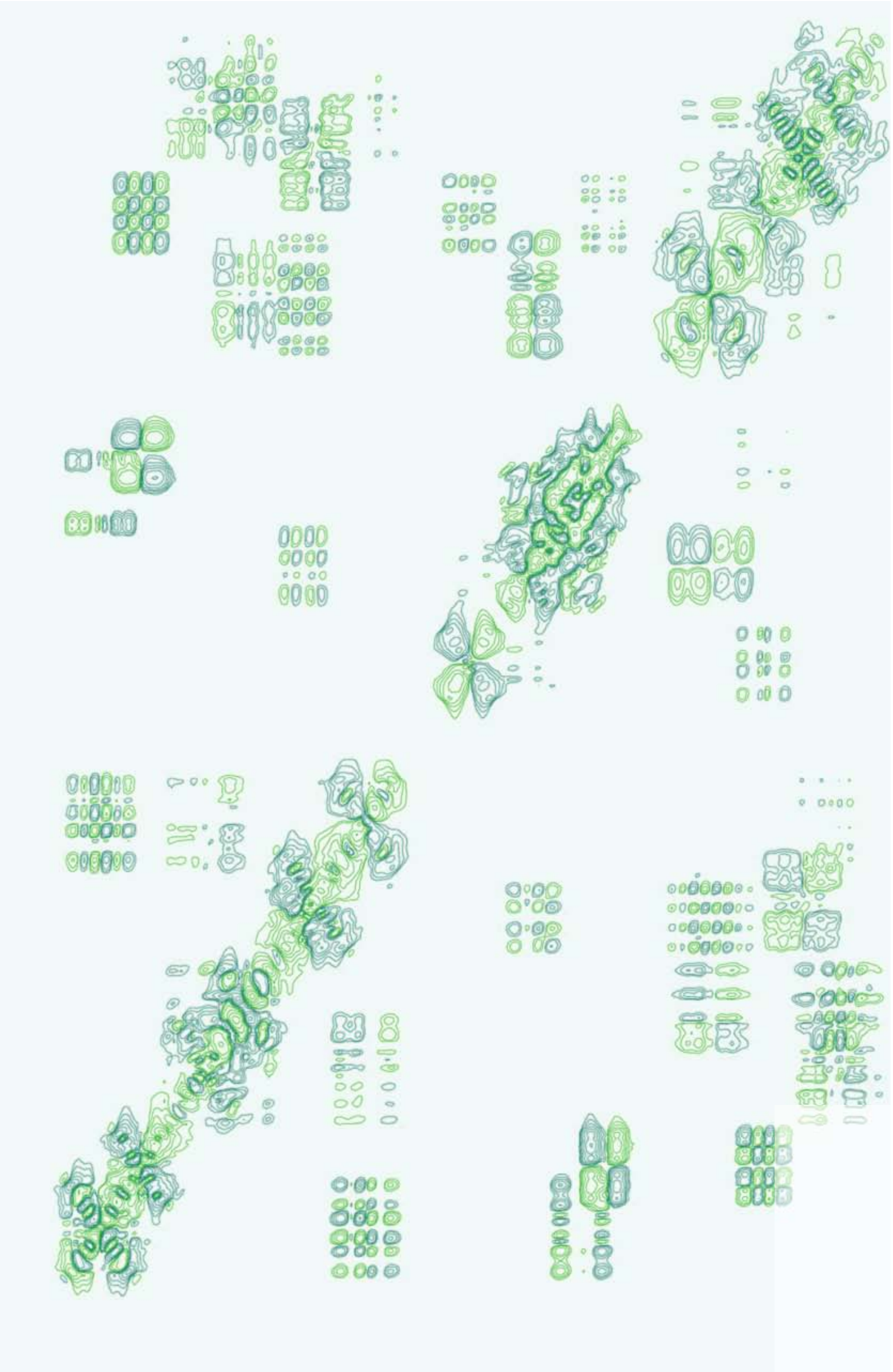
2,051 Masters Degrees in Chemistry
952 Masters Degrees in Chemical Engineering

2,362 Doctoral Degrees in Chemistry
885 Doctoral Degrees in Chemistry

50.9 % Women Undergraduate Degrees (2004)

To get a degree in Chemistry…

No universities require any demonstration of knowledge regarding toxicity or environmental impact!



Required:

Calculus
Biochemistry
Instrumentation
Independent work…

Not Required:

Toxicology
Environmental Impacts
Sustainability
Law and Policy

PHOTO BY RON SHERMAN

INCUBATOR The University of Massachusetts, Boston, houses the first Ph.D. program in green chemistry.

GREEN CHEMISTRY EARNS A PH.D.

The University of Massachusetts, Boston, now offers a Ph.D. track in green chemistry

SINCE LAST FALL, THE UNIVERsity of Massachusetts, Boston (UMB), has been accepting students into a new program called the green chemistry Ph.D. track. It is offered by the department of environmental sciences but administered by the department of chemistry.

The first of its kind in the world, the program is the brainchild of its director, UMB chemistry professor John C. Warner. Students in the program, he explains, will be trained much like other Ph.D. chemistry students, although their education will emphasize skills to design materials and processes that have minimal impact on human health and the environment. Areas of concentration include environmentally benign synthesis, environmental monitoring and detection, biodegradation, and bioremediation.

What makes the program different from anything else available so far, Warner says, is the requirement of courses in toxicology, environmental law and policy, environmental fate and transport, and industrial chemistry. Through these courses, he explains, "we broaden the students' understanding of environmental realities—such as what makes a molecule toxic, what laws have been established to govern synthetic procedures, and what happens in the environment—which conventional chemistry programs don't teach."

Terrence J. Collins, a chemistry professor at Carnegie Mellon University, notes that "we do not live in a sustainable civilization, sustainability meaning that what we do every day can be carried on to the indefinite future without causing damage." Collins was a recipient of the 1999 Presidential Green Chemistry Challenge Academic Award. The UMB program, he tells C&EN, is one way to call attention to the fact that "a sustainable civilization needs the intimate engagement of chemistry."

The UMB program "is timely, as there has been a distinct shift in focus in chemistry," says Janet Scott, deputy director of the Centre for Green Chemistry at Monash University, in Australia. "Even those who might not consider themselves 'green chemists' are beginning to focus on issues of sustainability and the design of benign products and processes to prevent pollution at the source. The chemical industry is beginning to demand a wider knowledge of and attention to issues of sustainability."

Mary Kirchhoff, assistant director of the Green Chemistry Institute, in Washington, D.C., agrees that the time is right for a green chemistry Ph.D. program. It might have been met with skepticism 10 years ago, when the term "green chemistry" first surfaced, she tells C&EN. Warner is the ideal person to lead such a program, she adds. "He's got the research credentials, the teaching credentials, the commitment to students, and the passion."

Particularly in organic synthesis, formal green chemistry training will force chemists to change how they think.

"One of the things that makes organic synthesis so exciting is that, if you draw a molecule, there are probably an infinite number of synthetic pathways that you can follow to make that molecule," Warner says. Traditionally, the focus has been on maximizing yields and stereoselectivities. Considerations of environmental and toxicological impact rarely come into play.

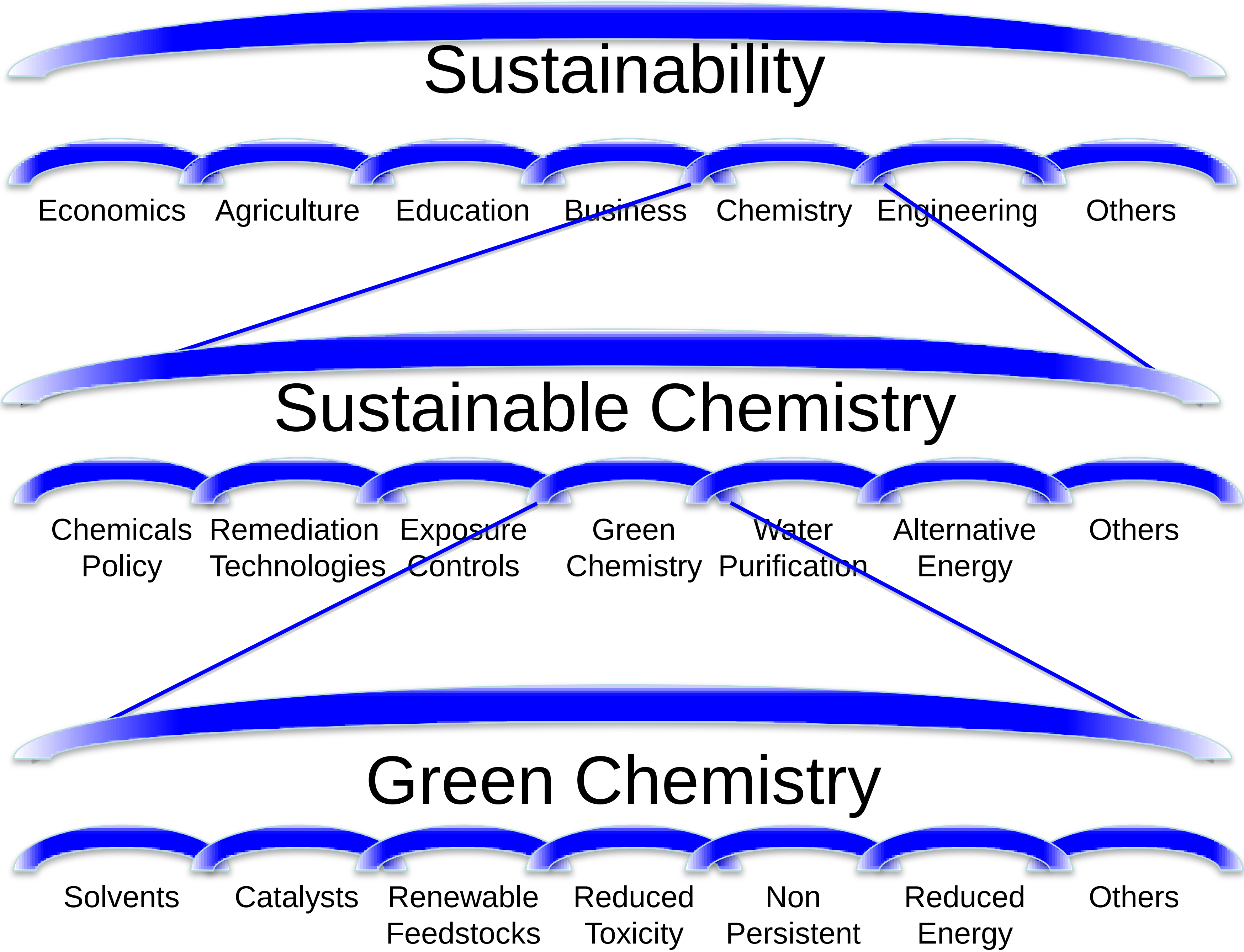
"IF ONE STEP in a synthetic sequence requires a hazardous reagent that's regulated by the federal government, that sequence could be more expensive than an alternative route that might give less yield," Warner explains. Regulatory and environmental realities often decide the economic viability of a synthetic route, he adds.

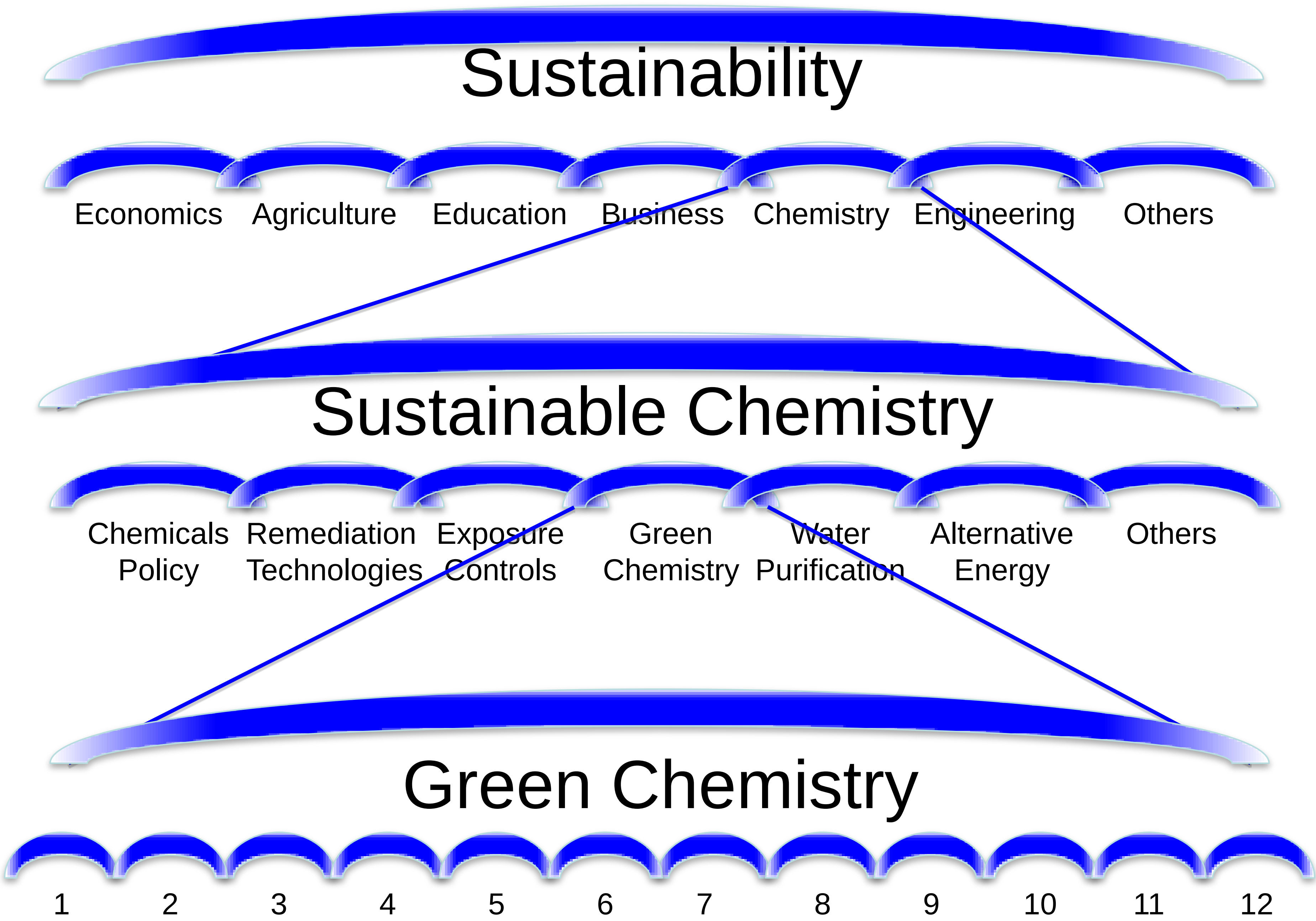
Chemists usually learn of such considerations when they're working for a company, Warner says. "Industry would like people to come in with some understanding of these issues, because there's economic benefit if processes designed in labs do not have to be reworked to satisfy regulatory requirements."

A green chemistry Ph.D. would be a big plus for chemists interested in process development, notes Berkeley Cue, vice president of pharmaceutical sciences at Pfizer Global Research & Development, Groton, Conn. "What we try to incorporate into the design of manufacturing processes—such as safety, efficient use of raw materials, minimal use of solvents, and online analysis—are aligned to the concepts that Warner and people like him are teaching," he explains. "We just didn't call it green chemistry. We called it process development."

Amy Cannon is the first student enrolled in UMB's green chemistry Ph.D. program. She's working on constructing solar energy devices in a more environmentally benign manner. Currently, she explains, producing solar cells consumes so much energy that a solar panel has to operate for years before it generates as much energy as was used to make it.

"Alternative energy is one of the most important areas in terms of sustainability," Cannon tells C&EN. Having just completed her master's degree under Warner's guidance, Cannon is passionate about green chemistry. "What could be better than this," she asks, "given that my big goal in life is to help save the world by doing what I can where I am?"—MAUREEN ROUHI


Sustainability
Economics
Agriculture
Education
Business
Chemistry
Engineering
Others
Sustainable Chemistry
Chemicals Policy
Remediation Technologies
Exposure Controls
Green Chemistry
Water Purification
Alternative Energy
Others
Green Chemistry
Solvents
Catalysts
Renewable Feedstocks
Reduced Toxicity
Non Persistent
Reduced Energy
Others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Chemicals Policy
Remediation Technologies
Exposure Controls
Green Chemistry
Water Purification
Alternative Energy
Others
Green Chemistry
1
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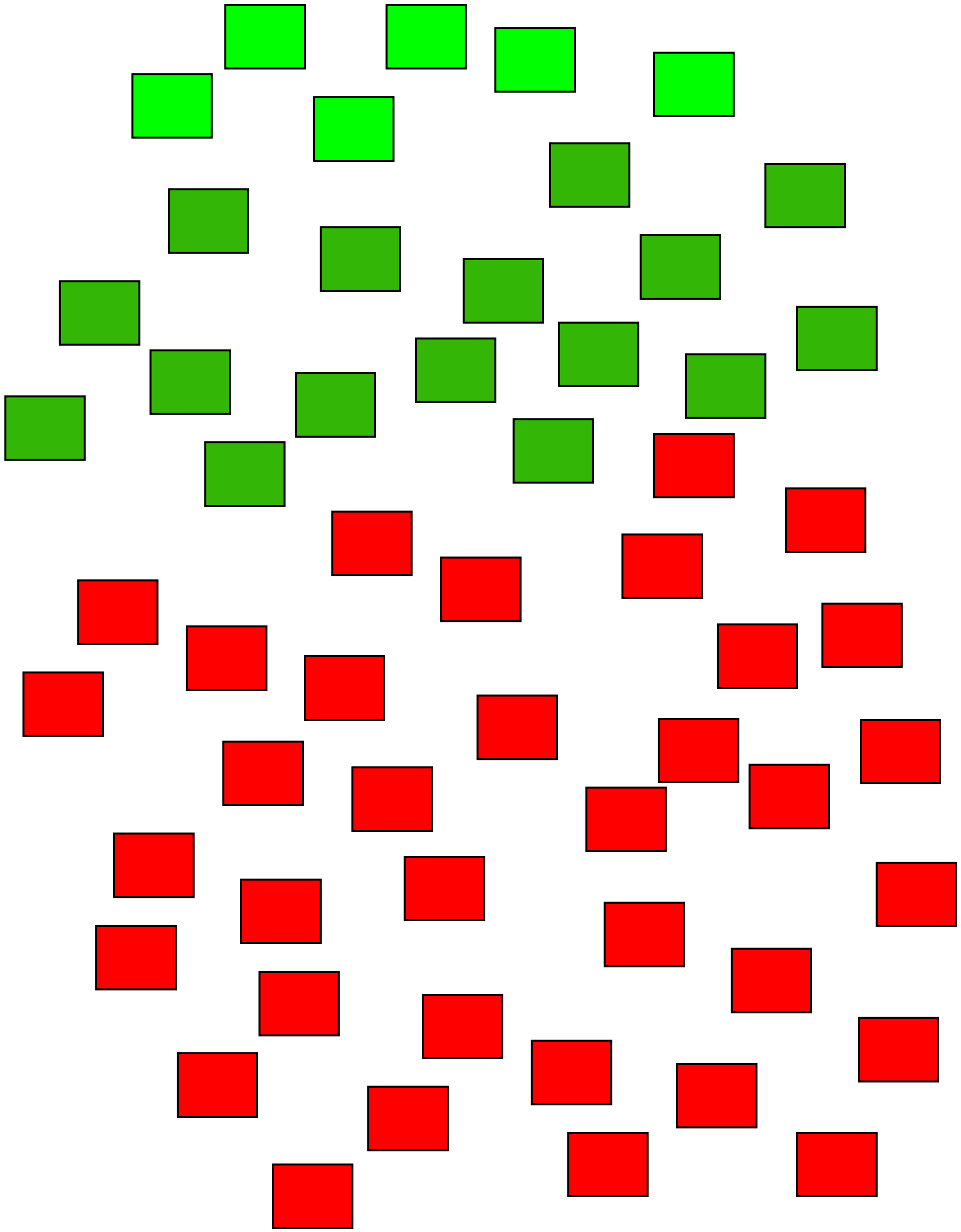
Of all the products and processes…

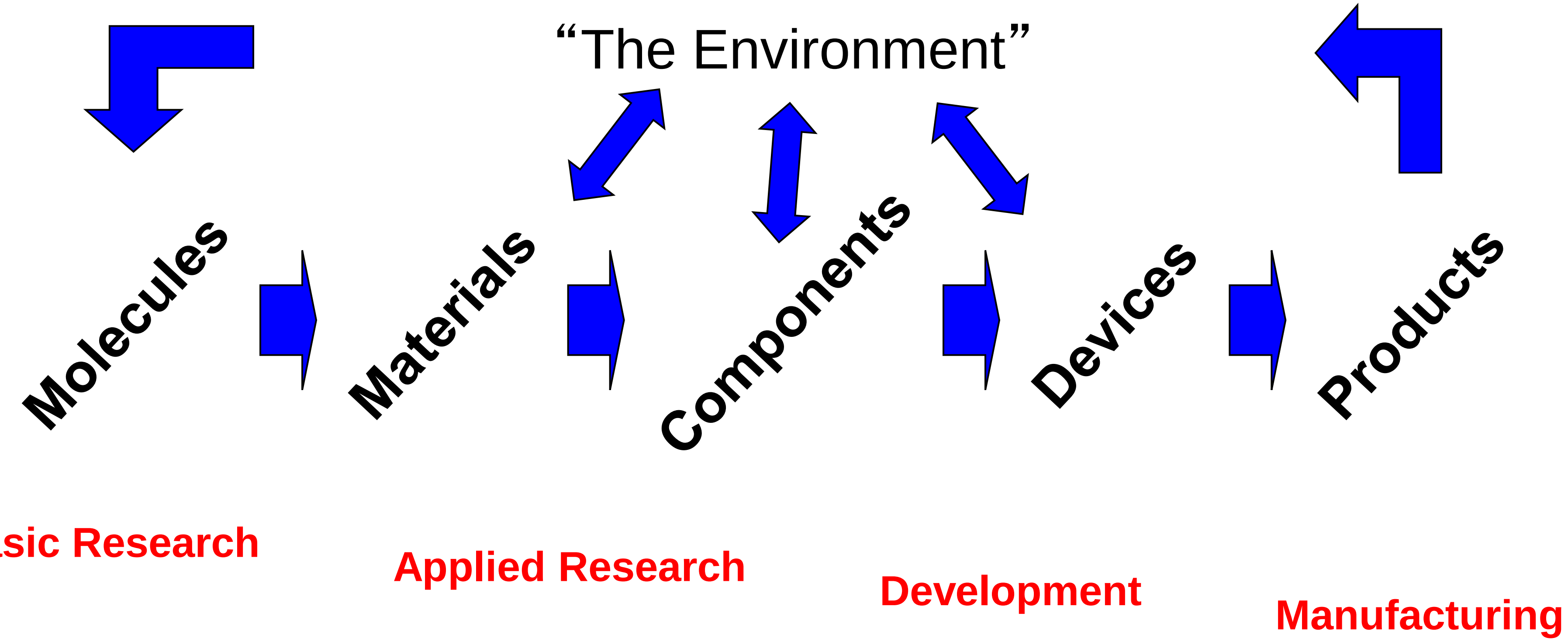
Maybe 10% are benign…

Maybe 25% have alternatives available…

65% Still have to be invented!



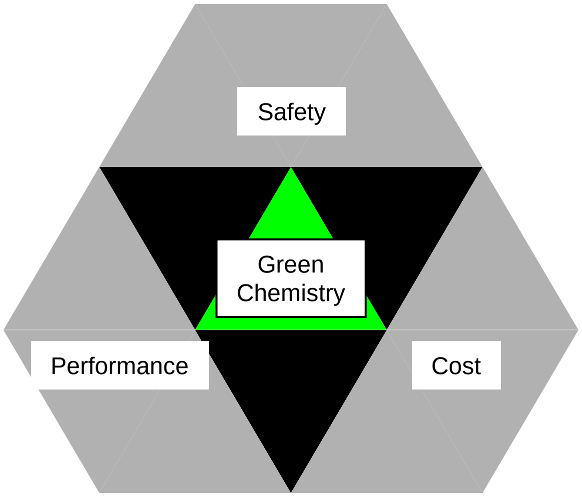
Where do products come from?

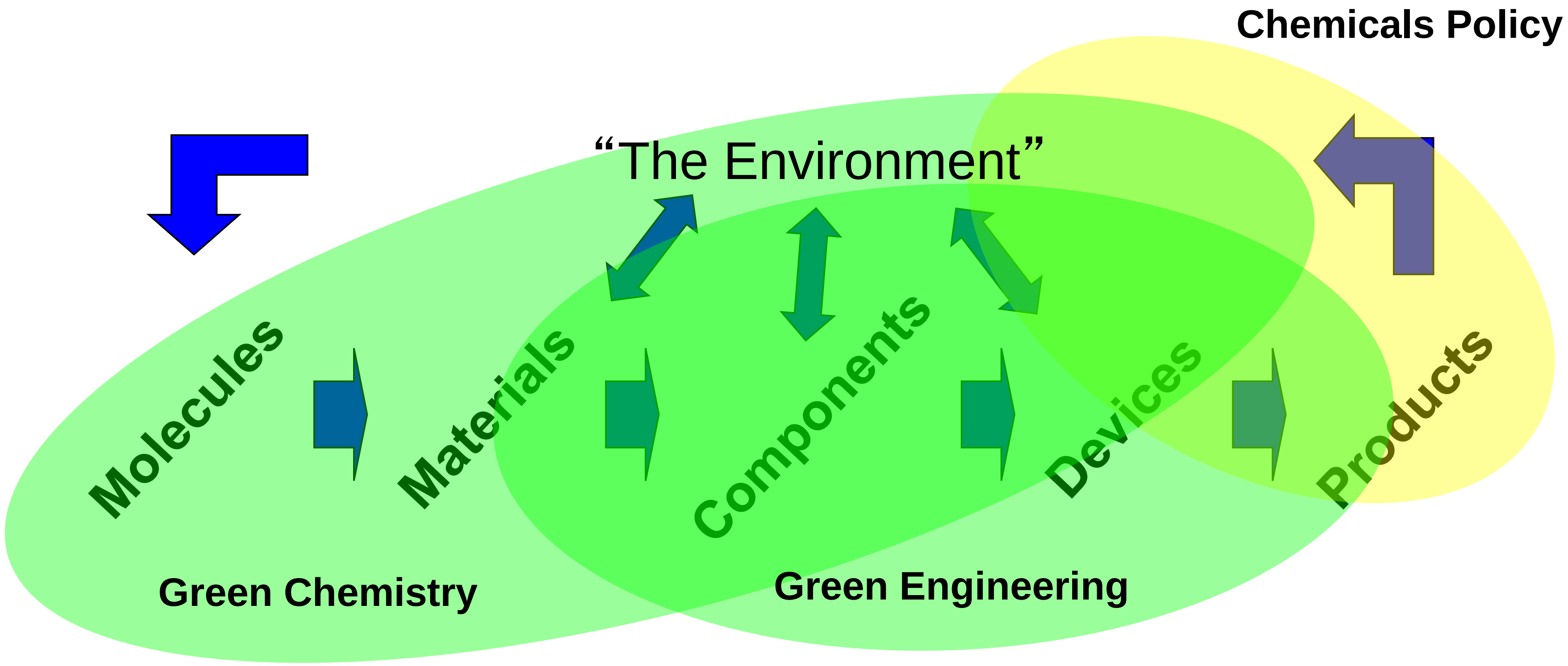


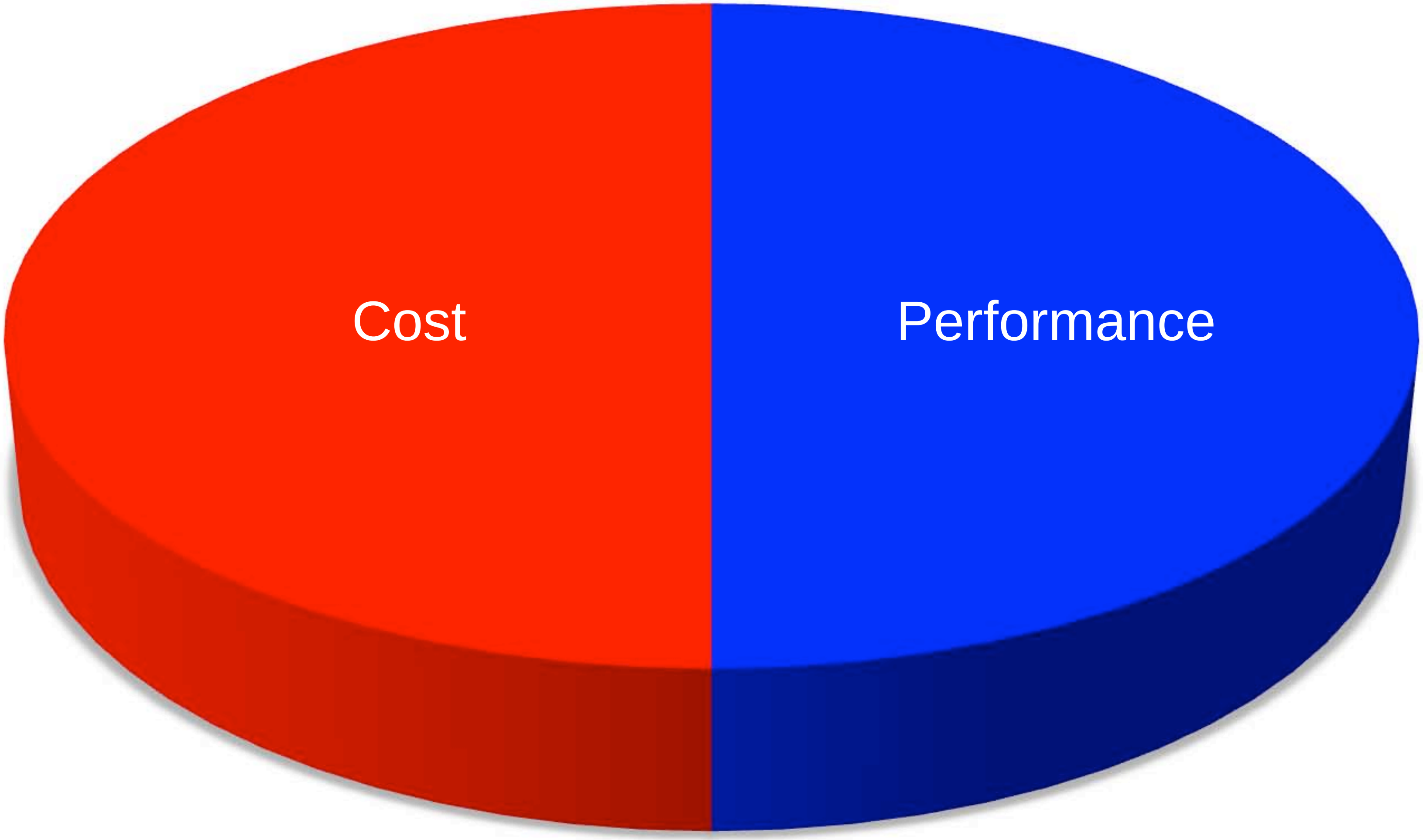
Performance

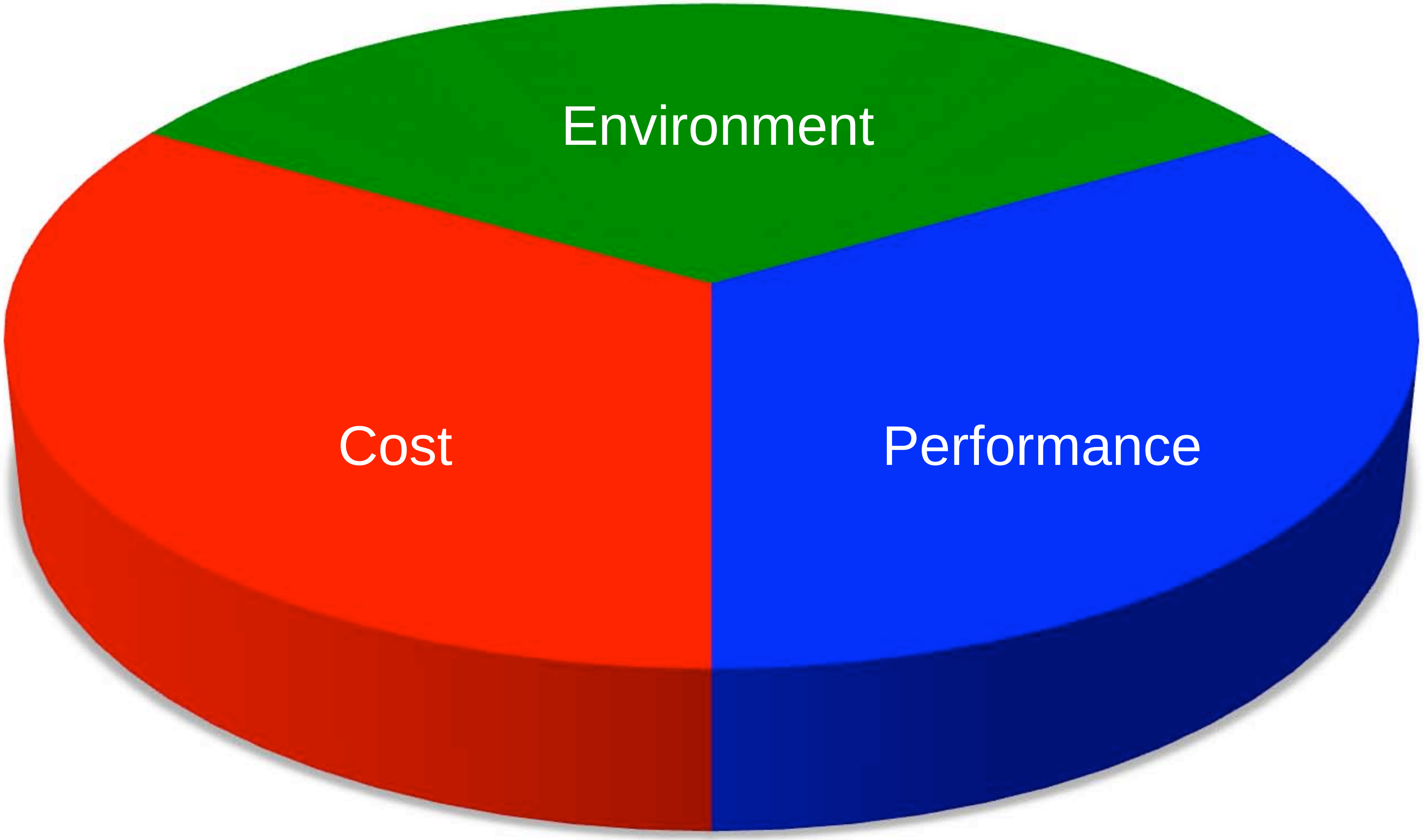
Economics

Social Implications




Chemicals Policy
"The Environment"
Molecules
Materials
Components
Devices
Products
Green Chemistry
Green Engineering


Cost
Performance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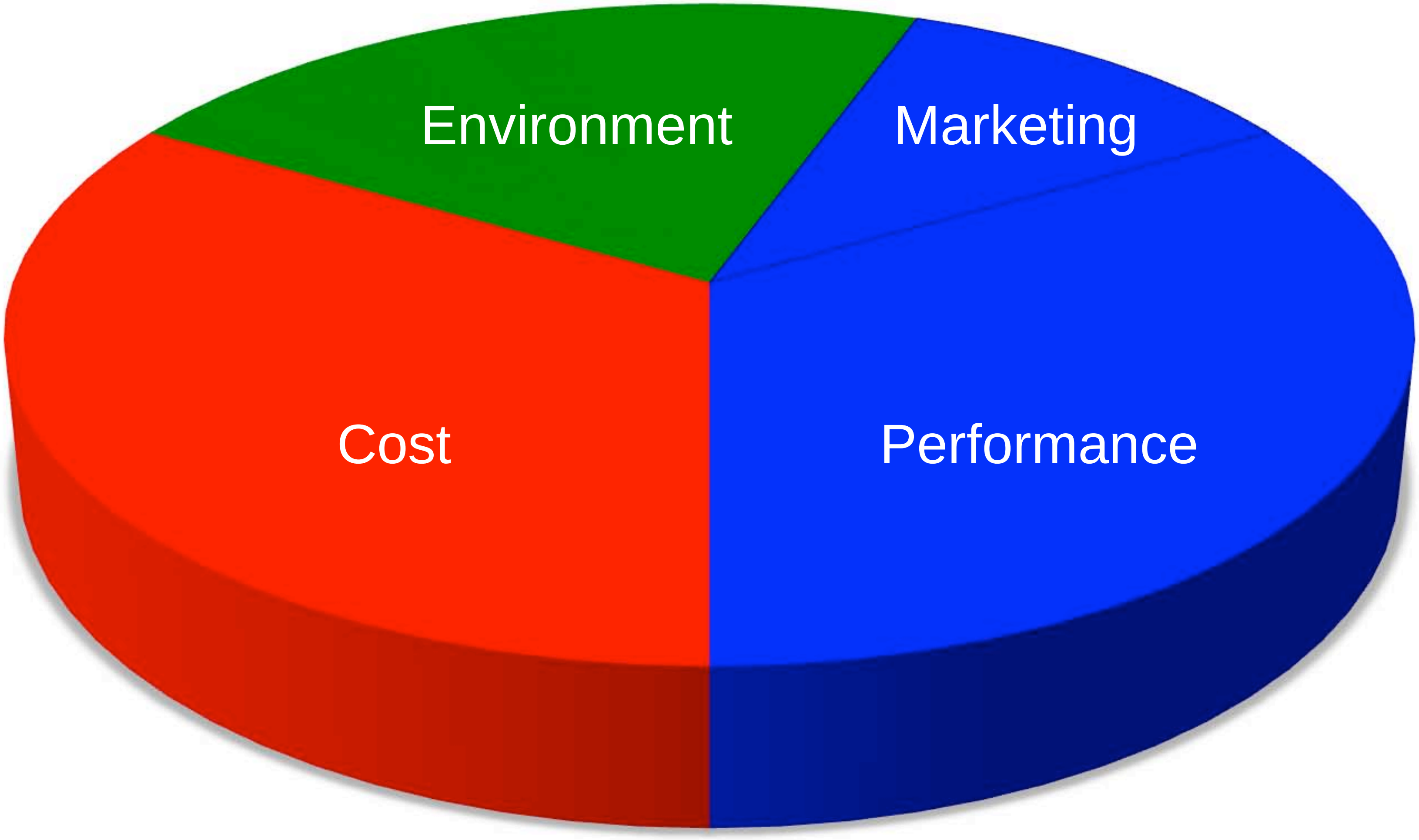
Environment
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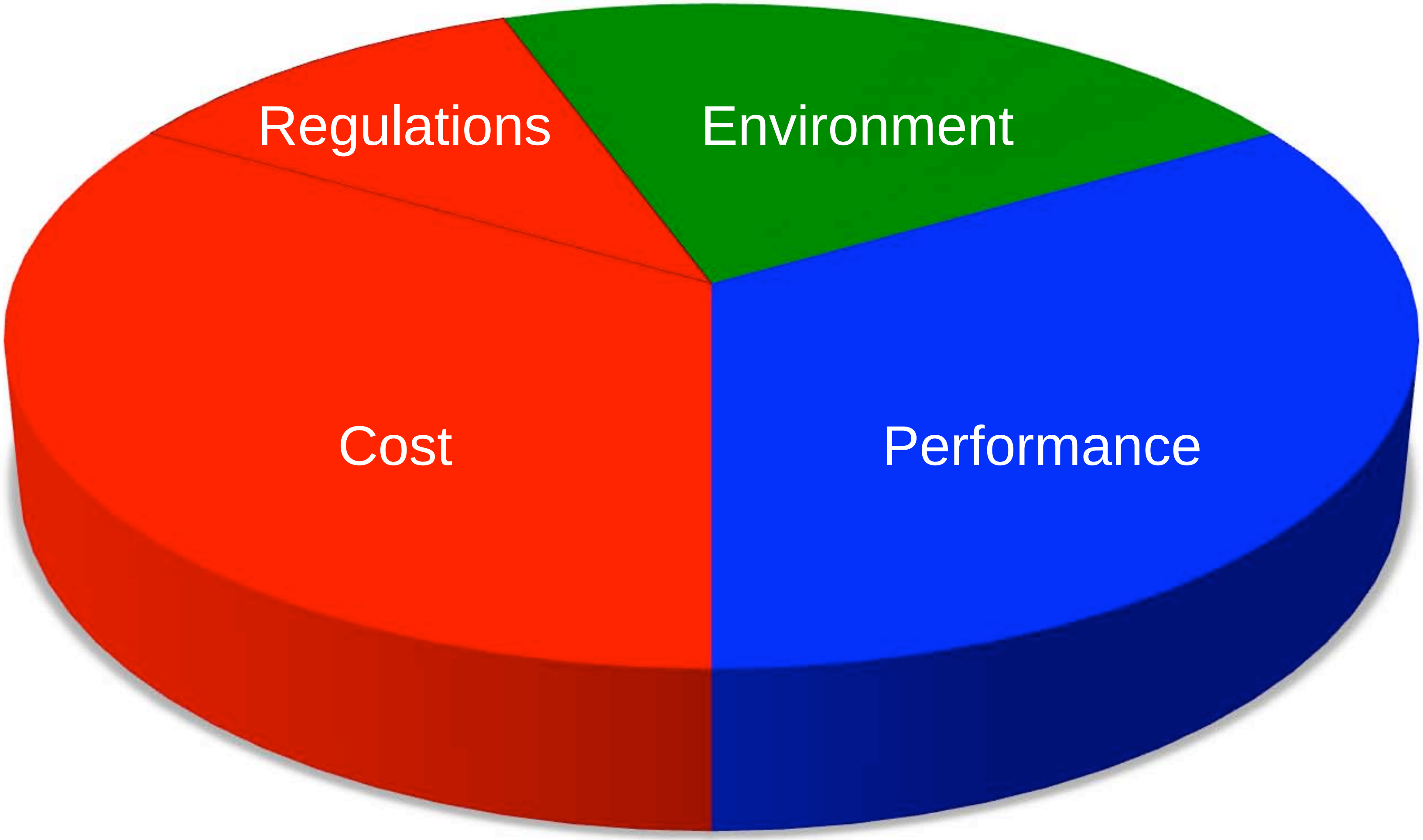
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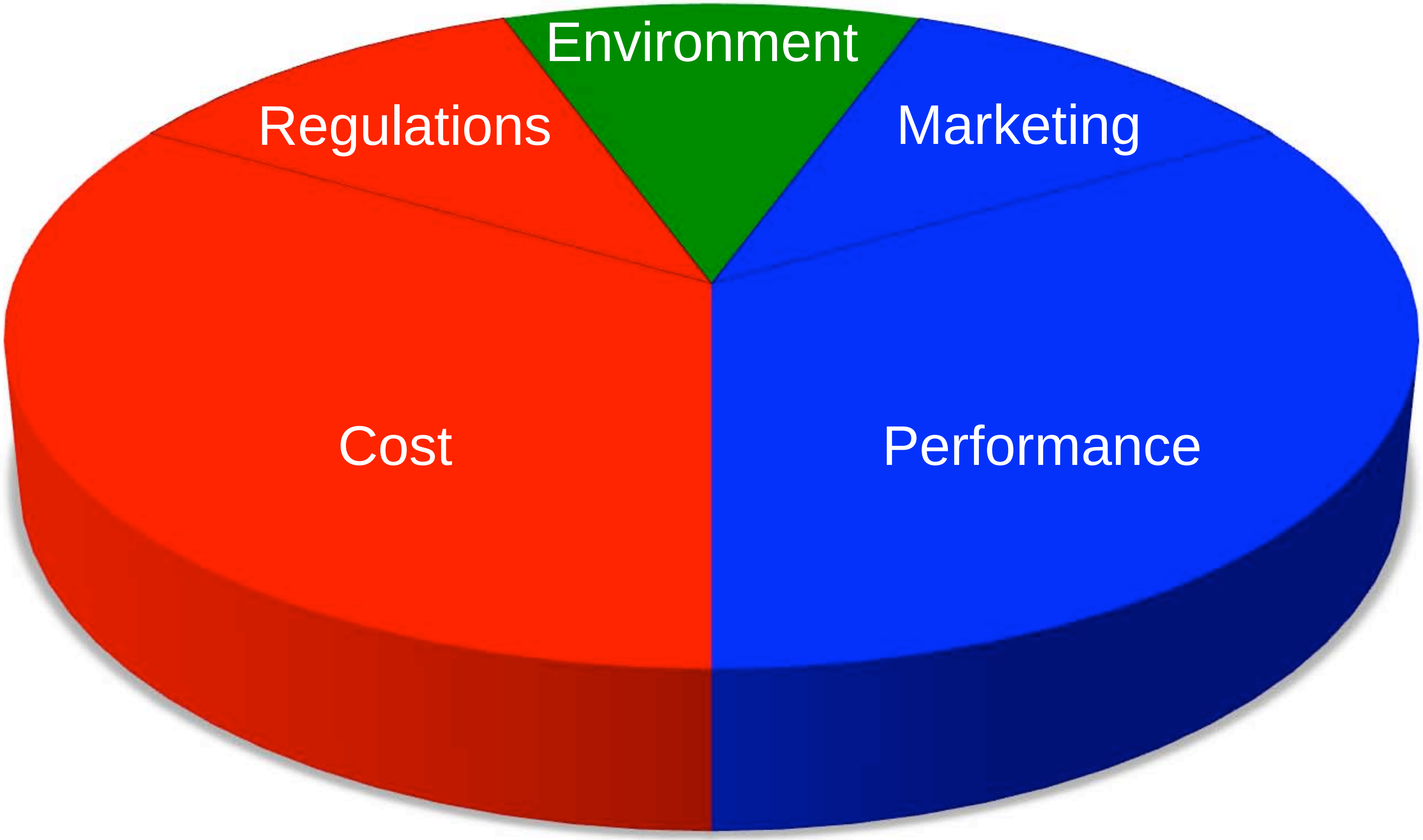
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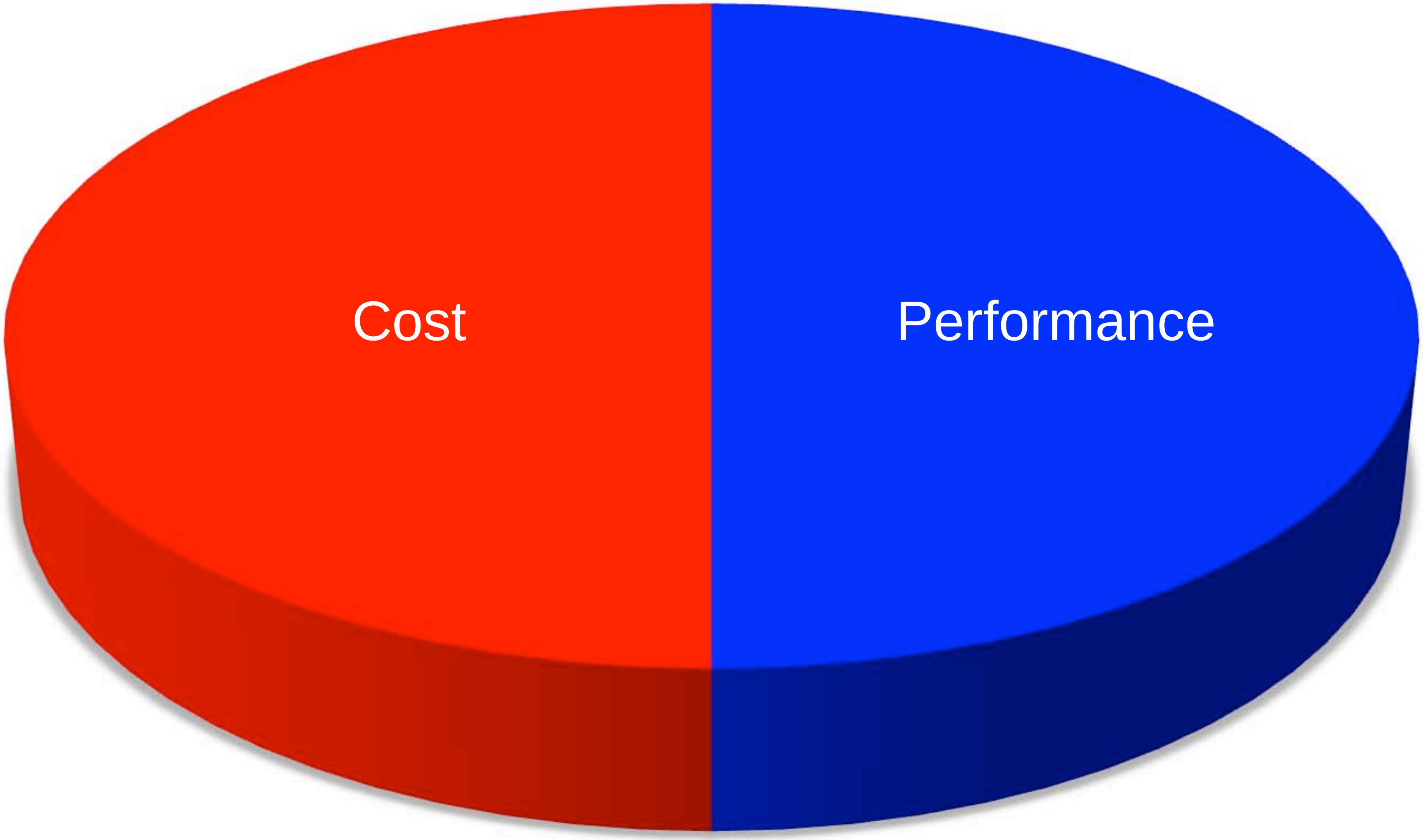
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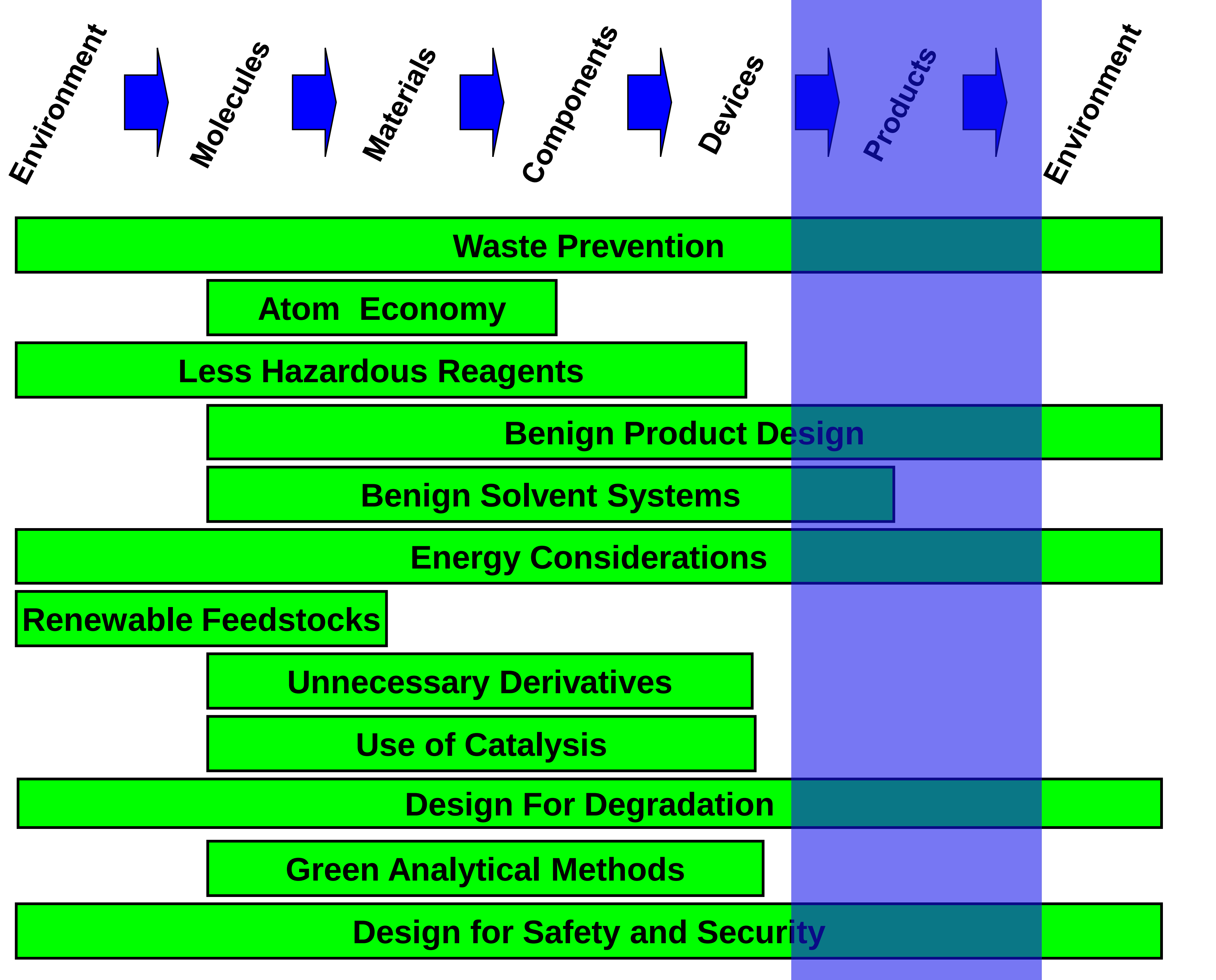
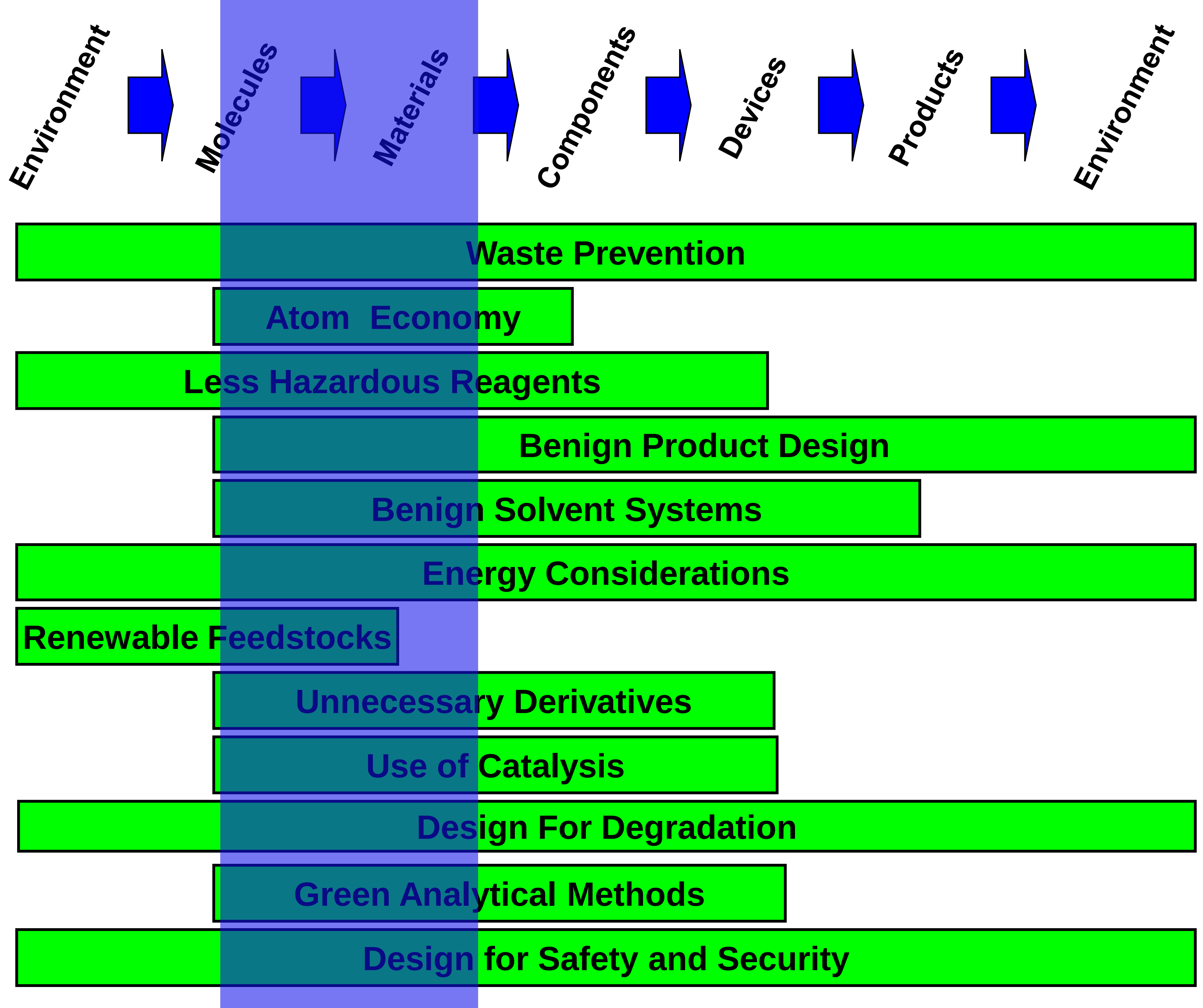

Environment
Molecules
Materials
Components
Devices
Products
Environment
Waste Prevention
Atom Economy
Less Hazardous Reagents
Benign Product Design
Benign Solvent Systems
Energy Considerations
Renewable Feedstocks
Unnecessary Derivatives
Use of Catalysis
Design For Degradation
Green Analytical Methods
Design for Safety and Security



Environment
Molecules
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Components
Devices
Products
Environment
Waste Prevention
Atom Economy
Less Hazardous Reagents
Benign Product Design
Benign Solvent Systems
Energy Considerations
Renewable Feedstocks
Unnecessary Derivatives
Use of Catalysis
Design For Degradation
Green Analytical Methods
Design for Safety and Security

Golf Metaphor:

Measurable Attributes

How far can the golfer drive?

How straight can the golfer hit?

How accurate is the golfer's short game?

How well does the golfer get out of traps?

How consistent is the golfer?

Golf Metaphor:

Adjustable Components

How does the golfer grip the club?

How does the golfer hold their shoulders?

How does the golfer place their feet?

How does the golfer swing the club?

How well does the golfer pick their clubs?

Chemists have ALWAYS cared about Human Health and the Environment.

Risk = Exposure x Hazard

The cost of using hazardous materials:

Storage
Transportation
Treatment
Disposal
Regulatory Costs
Liability
Worker Health and Safety
Corporate Reputation
Community Relations
New Employee Recruitment

Traditional Processes

Green Alternatives

"The Incorporation of Hazard Reduction as a Chemical Design Criterion in Green Chemistry" Anastas, Nicholas; Warner, John C. *J. Chem. Health and Safety* **2005**, *12(2)*, 9-13.

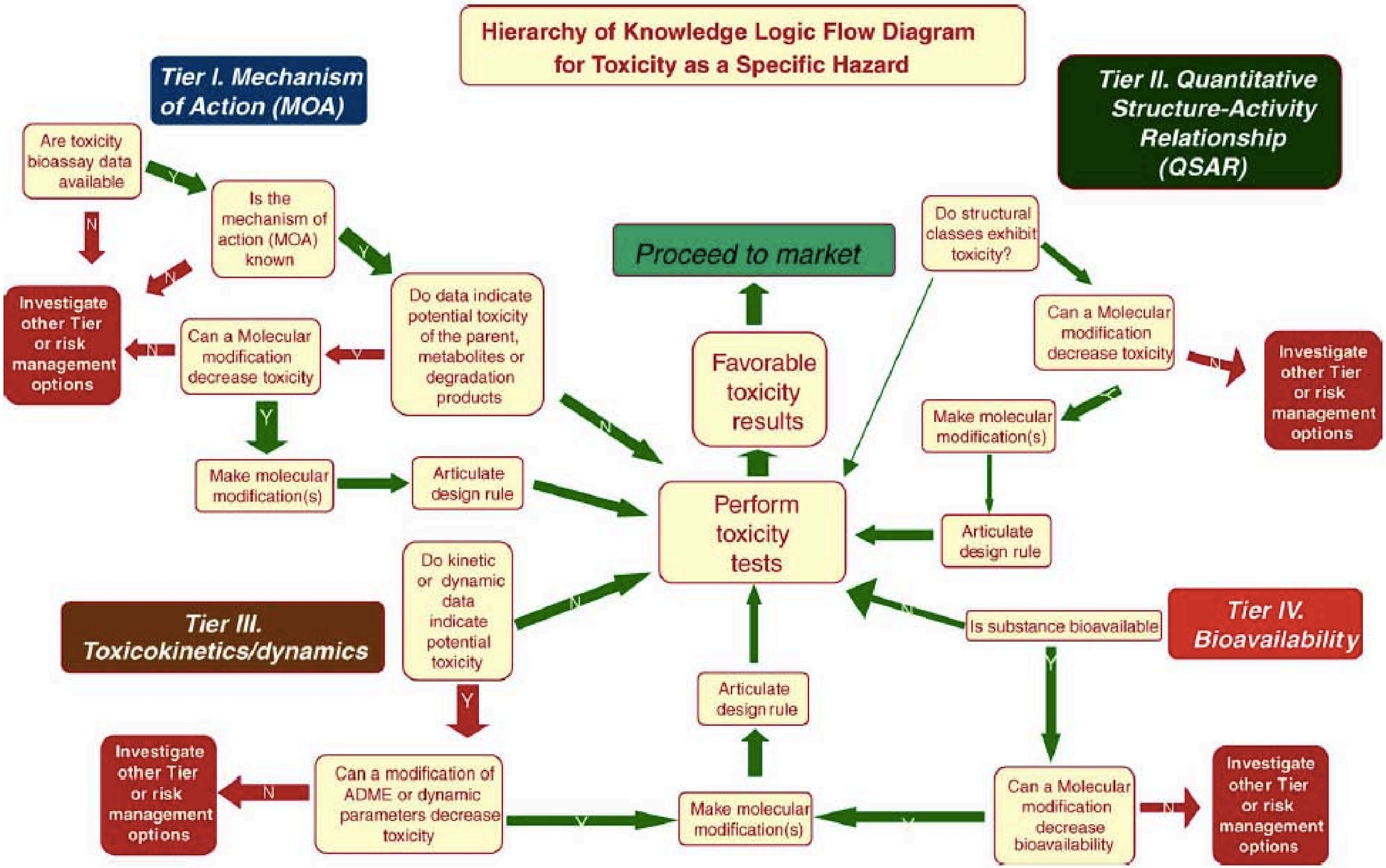
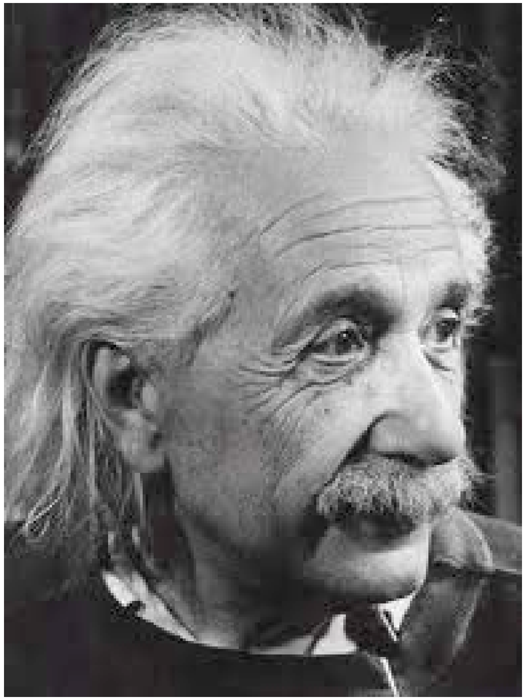
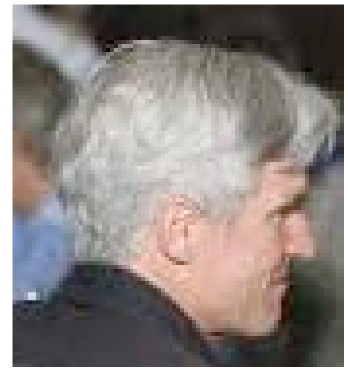


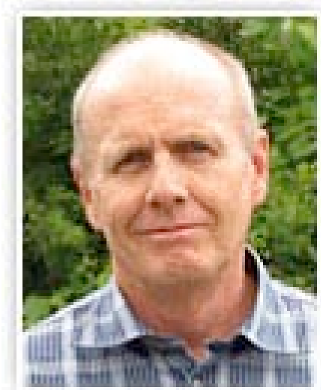
Figure 1. Hierarchy of Knowledge Logic Flow Diagram for Toxicity as a Specific Hazard.

Problems cannot be solved at the same level of awareness that created them.



Albert Einstein





John Warner Amy Cannon Jim Babcock Bill Kunzweiler

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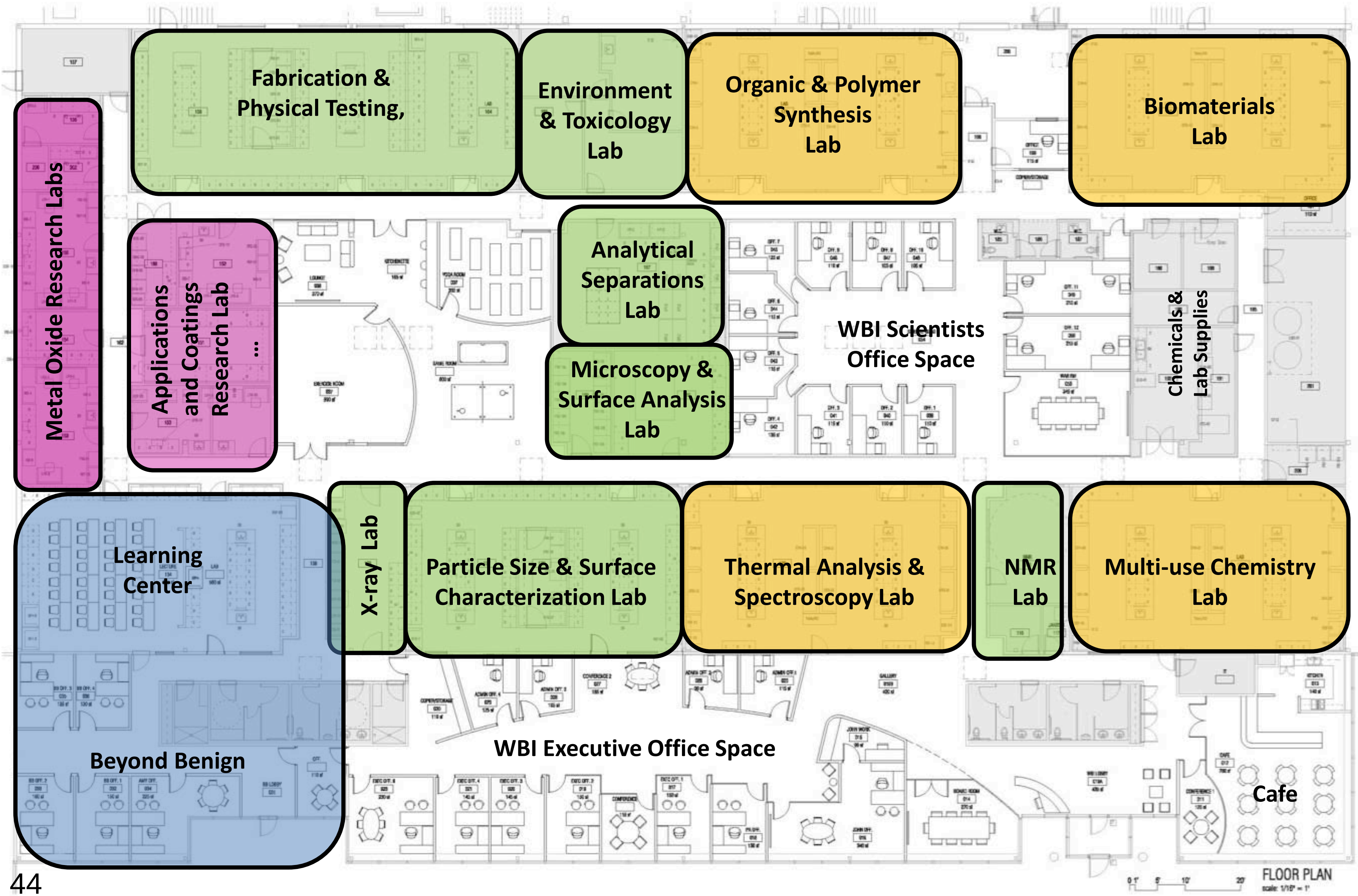
institute for green chemistry

100 Research Drive, Wilmington, Massachusetts



Fabrication &
Physical Testing,
Environment
& Toxicology
Lab
Organic & Polymer
Synthesis
Lab
Biomaterials
Lab
Metal Oxide Research Labs
Applications
and Coatings
Research Lab
…
Analytical
Separations
Lab
Microscopy &
Surface Analysis
Lab
WBI Scientists
Office Space
Chemicals &
Lab Supplies
Learning
Center
X-ray Lab
Particle Size & Surface
Characterization Lab
Thermal Analysis &
Spectroscopy Lab
NMR
Lab
Multi-use Chemistry
Lab
Beyond Benign
WBI Executive Office Space
Cafe
FLOOR PLAN

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Dr Amy Cannon
Executive Director

K-12

- Curriculum Development and Teacher Training
  - Green Chemistry
  - Green Math & Engineering
  - Biotechnology
  - Forensics
  - Watershed Science

Community

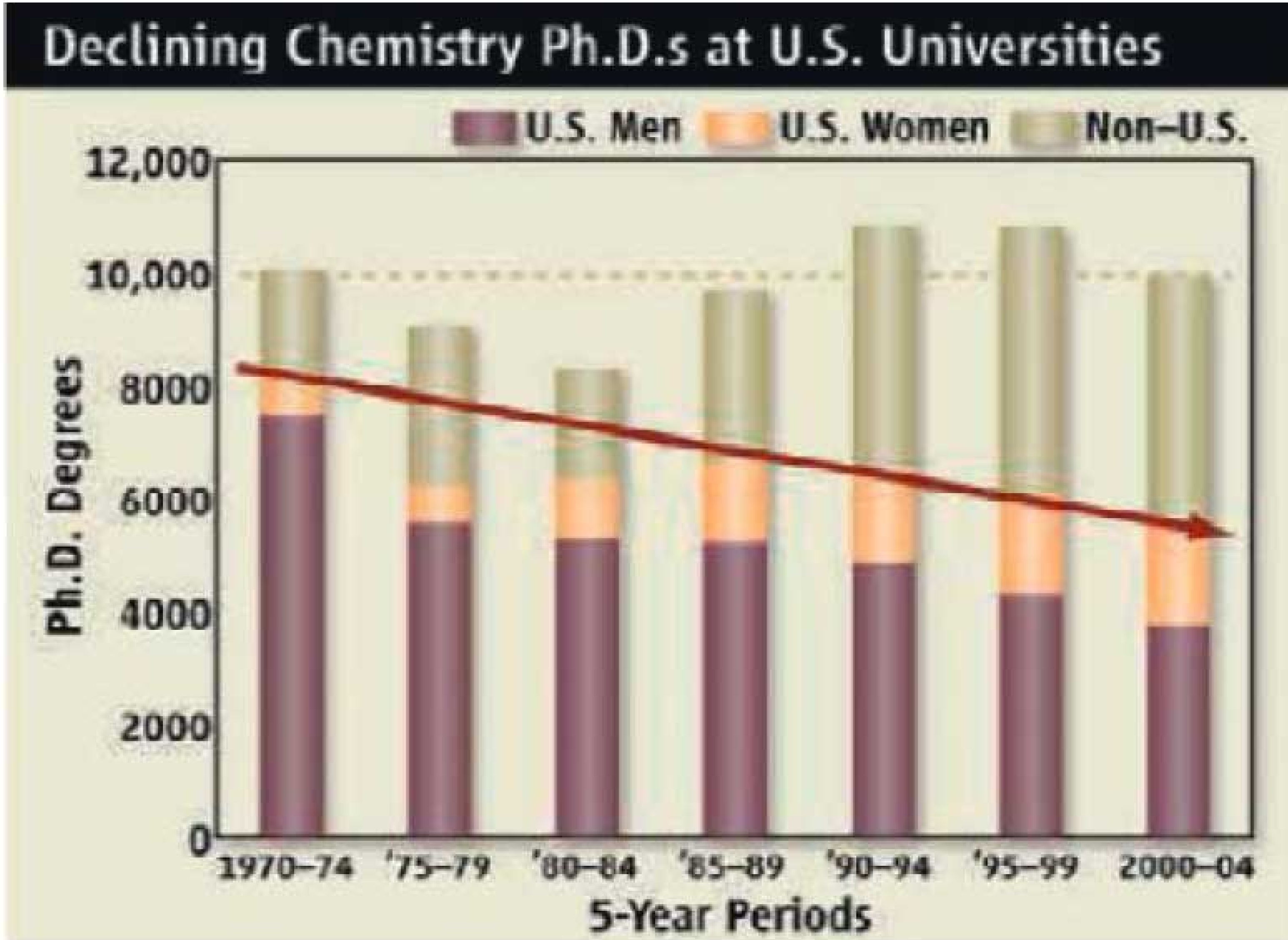
- K-12 and Community Outreach
  - K-12 classroom visits
  - Community events
  - Informational/promotional events
- Community Building (Regional and International)

Workforce Development

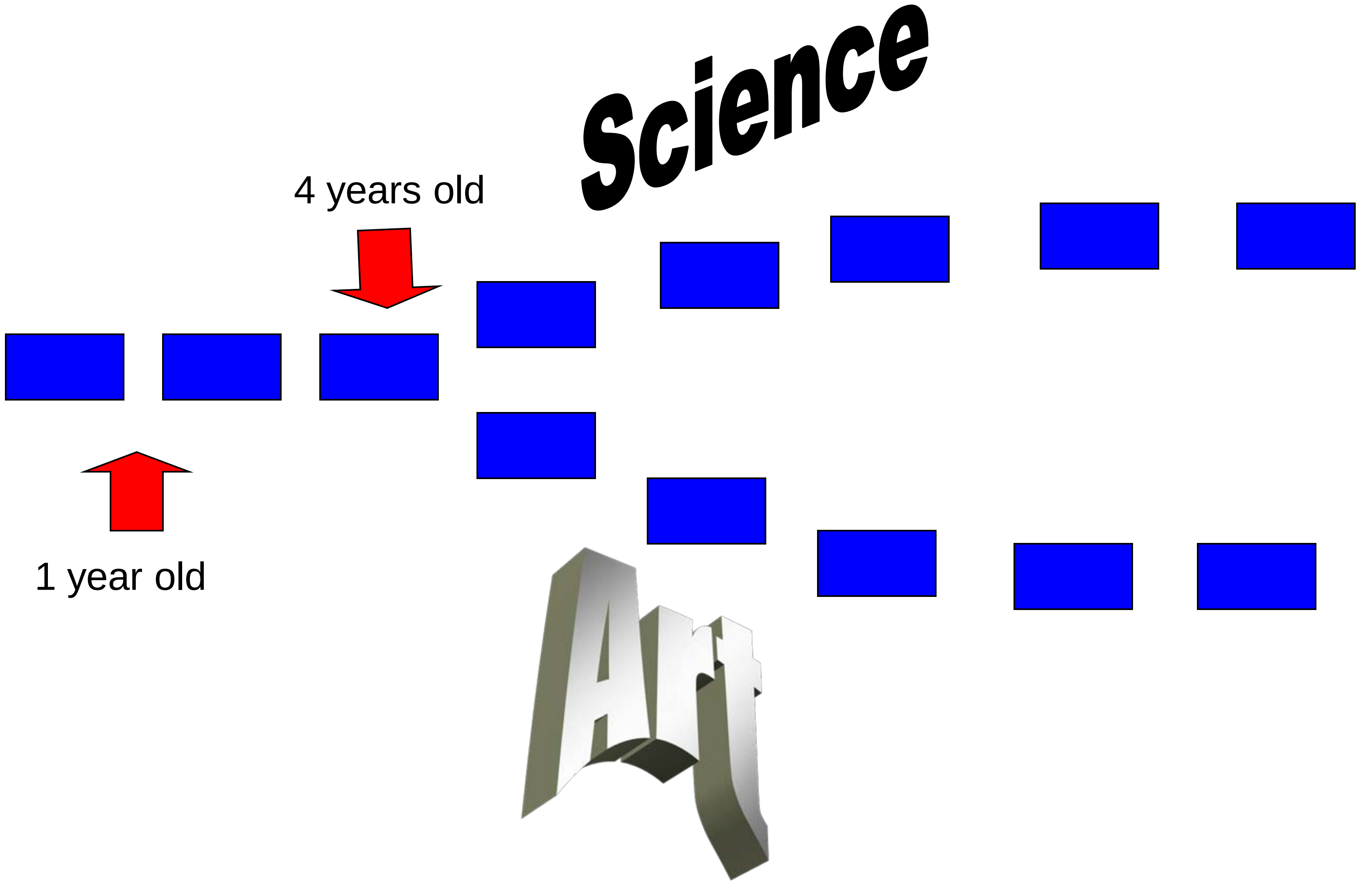
- Curriculum Development and Training
  - Academia
  - Technical Training

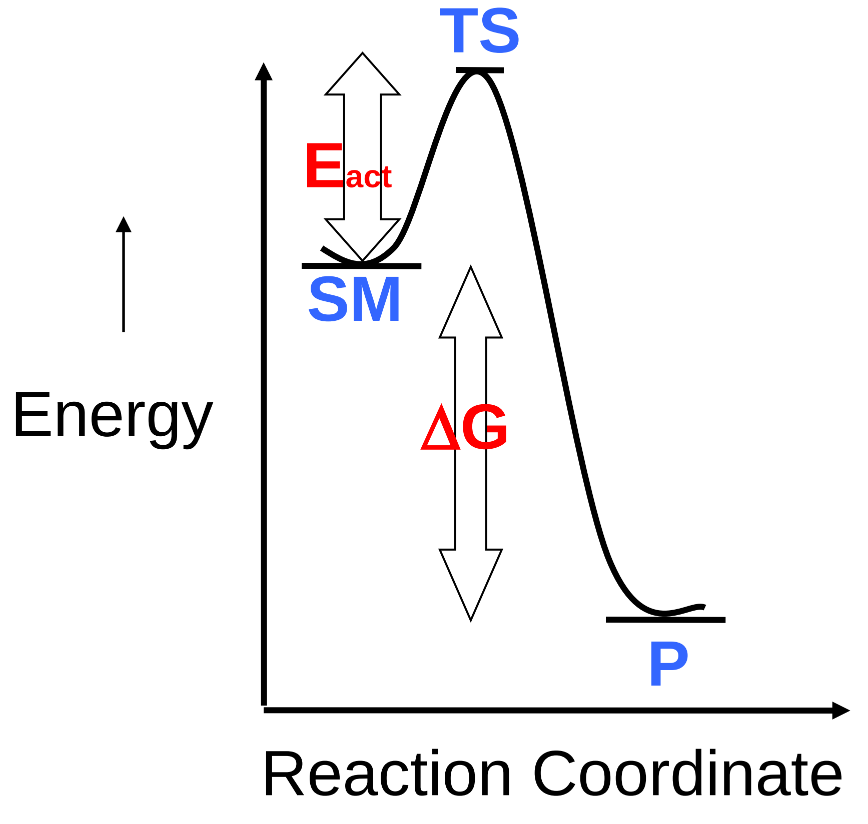
The Green Chemistry Commitment: The Call for Systematic Change

- *Changing Practices:* Implementing green chemistry laboratory exercises throughout the chemistry curriculum
- *Changing Curriculum:* Green Chemistry introduced and integrated throughout chemistry courses and/or courses on Green Chemistry will be offered as a requirement course for chemistry majors. Additional courses in environmental science, environmental fate and transport, and/or environmental law and policy will be made available to students as elective courses.
- *Teaching Toxicology:* Toxicology/environmental health sciences course for chemistry majors introduced as a core course, leading to the course becoming a requirement for chemistry majors.
- *Reaching Out:* Green Chemistry incorporated into Service Learning and Outreach programs to connect with communities and advance awareness of green chemistry throughout the region.
- *Integrating Research:* Green Chemistry will be integrated into research projects and research programs as part of the chemistry program.



Declining Chemistry Ph.D.s at U.S. Universities
U.S. Men
U.S. Women
Non–U.S.
12,000
10,000
8000
6000
4000
2000
0
Ph.D. Degrees
1970–74
'75–79
'80–84
'85–89
'90–94
'95–99
2000–04
5-Year Periods


Science
4 years old
1 year old
Art


TS
E_{act}
SM
ΔG
P
Energy
Reaction Coordinate

D'earth, UVa musicians explore chemistry through jazz.

ABOUT | GREEN CHEM 101 | INNOVATION | BENCHMARKING | COLLABORATIONS | IN THE NEWS | COMMENTARY

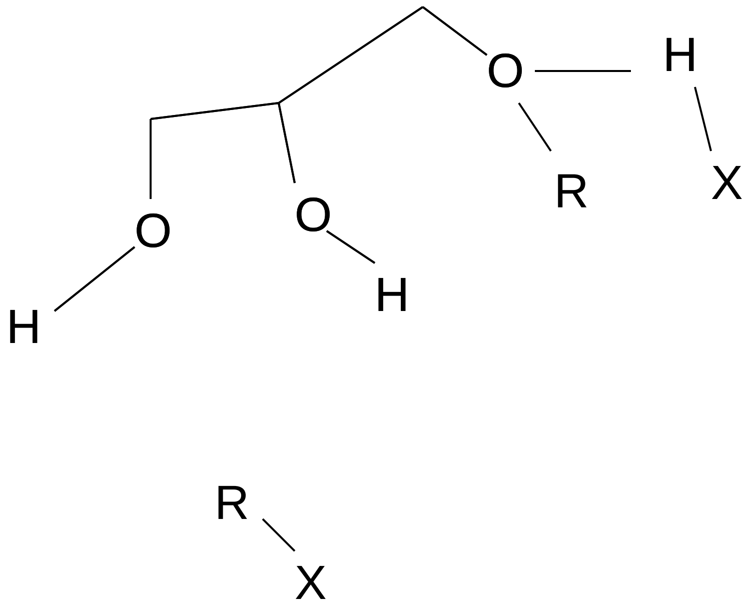
- 

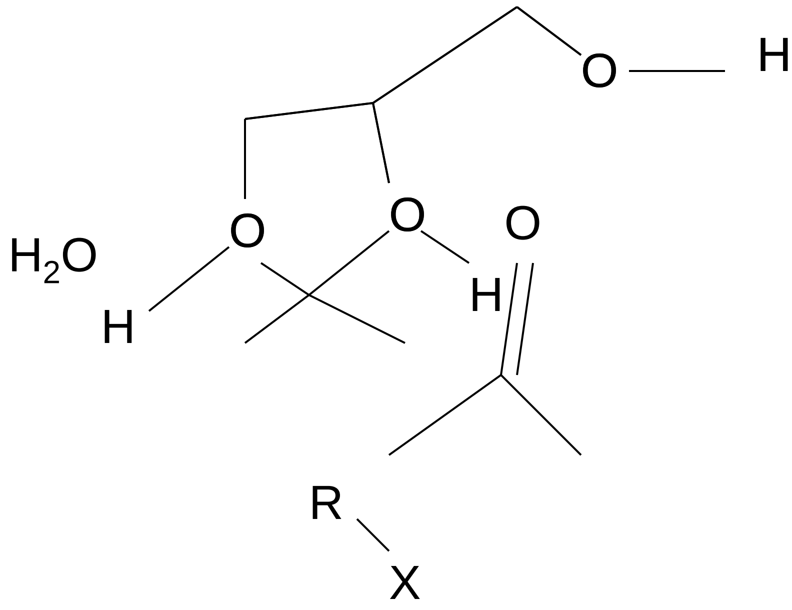
John D'earth (right) leads the University of Virginia Jazz Ensemble. His new composition, "Green Chemistry," is on this weekend's program. Credit: Sena Aydin

Creating Chemistry

Organic Synthesis

Creating molecules…





H
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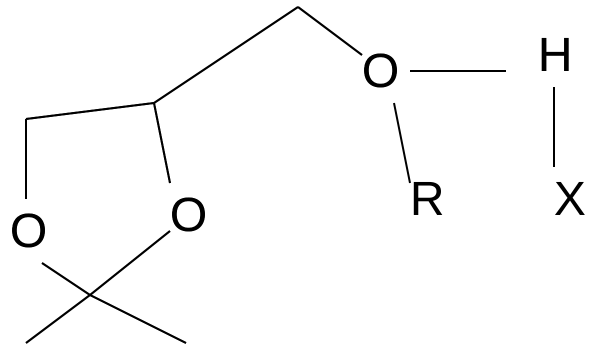
H₂O
H
H
R
X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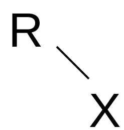
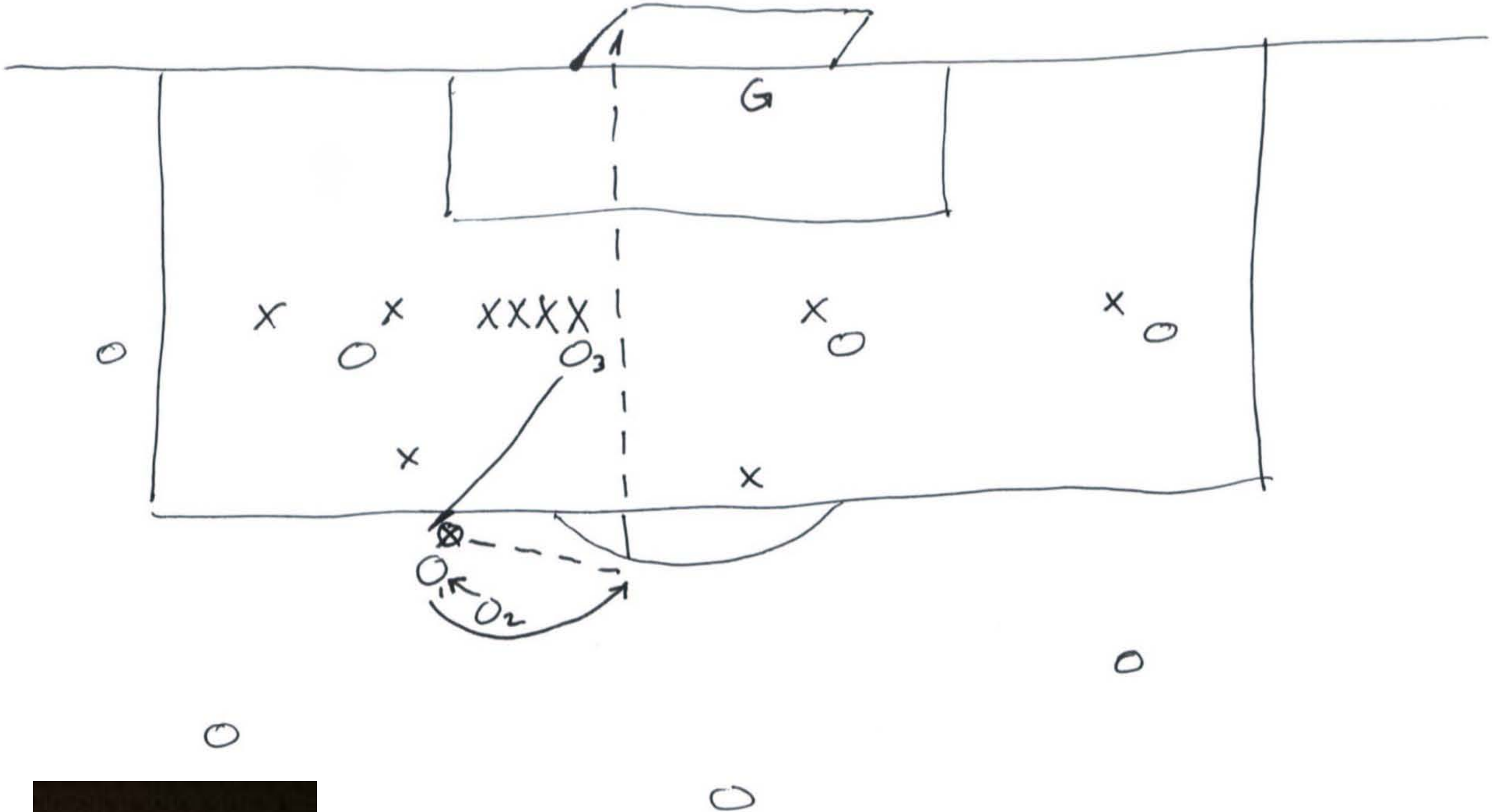
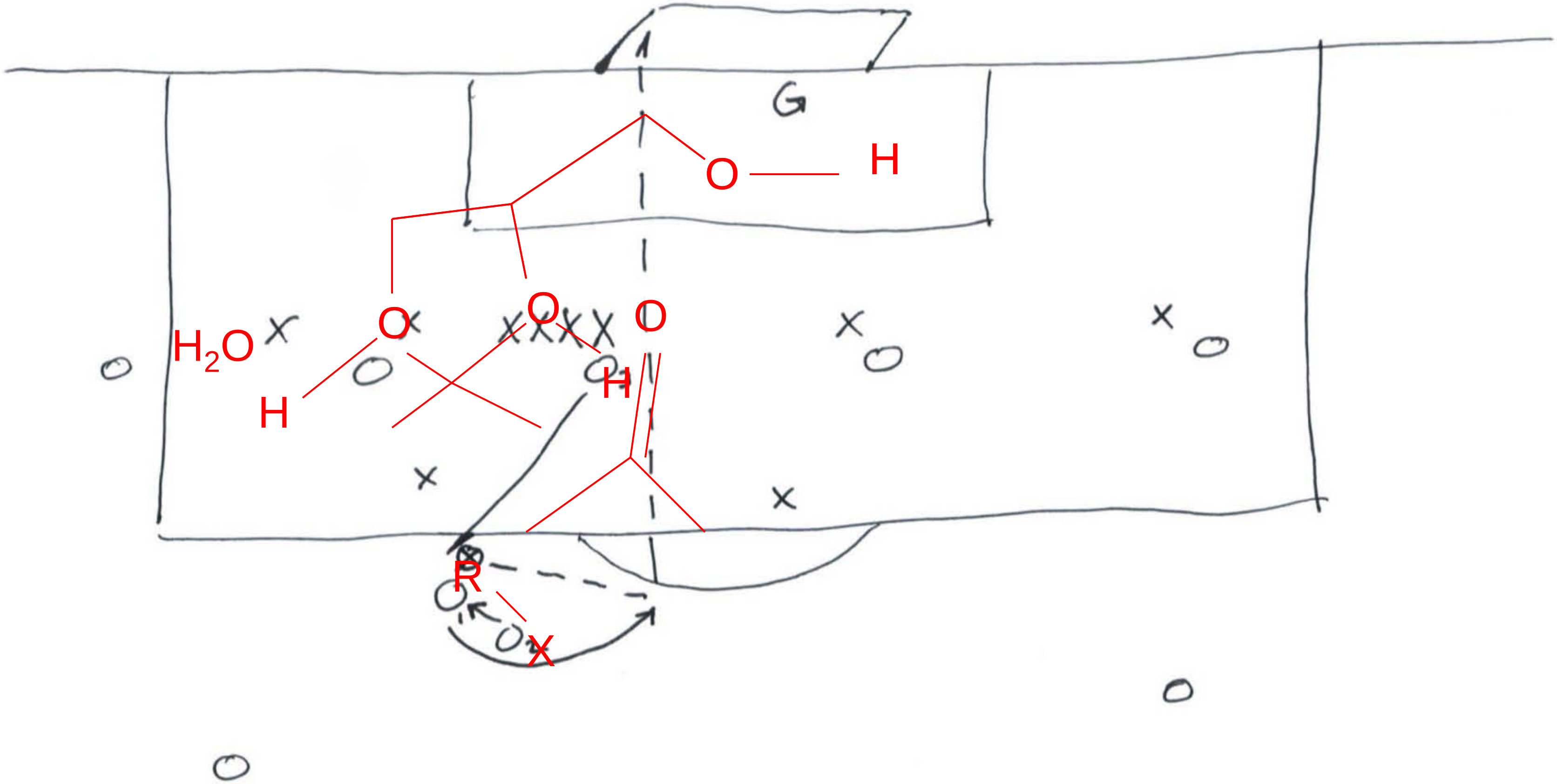

R
X

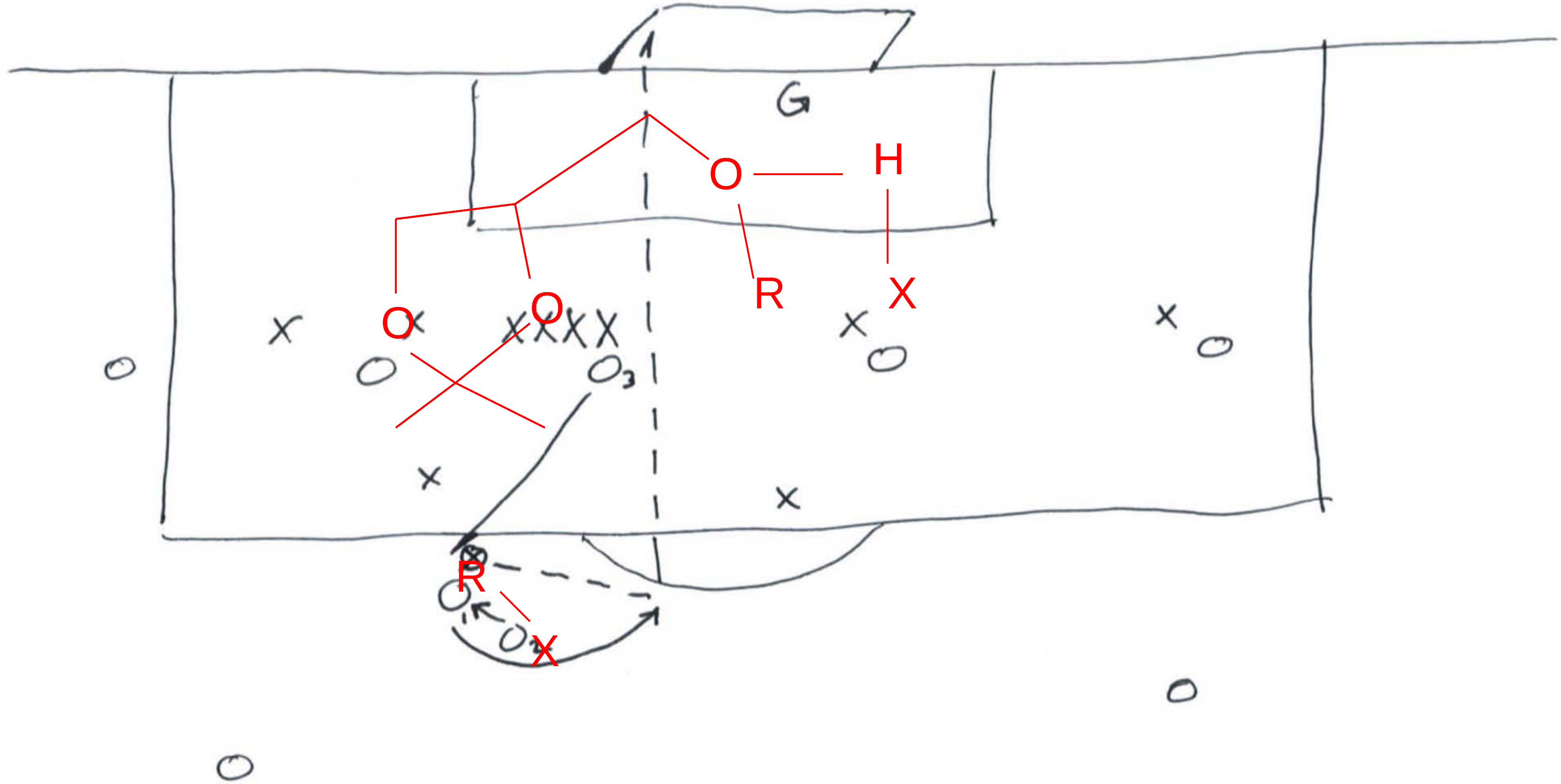


WHAT ARE YOU DOING AFTER THE GAME ?

Ed Cannon
Athletic Director
St. Anselm

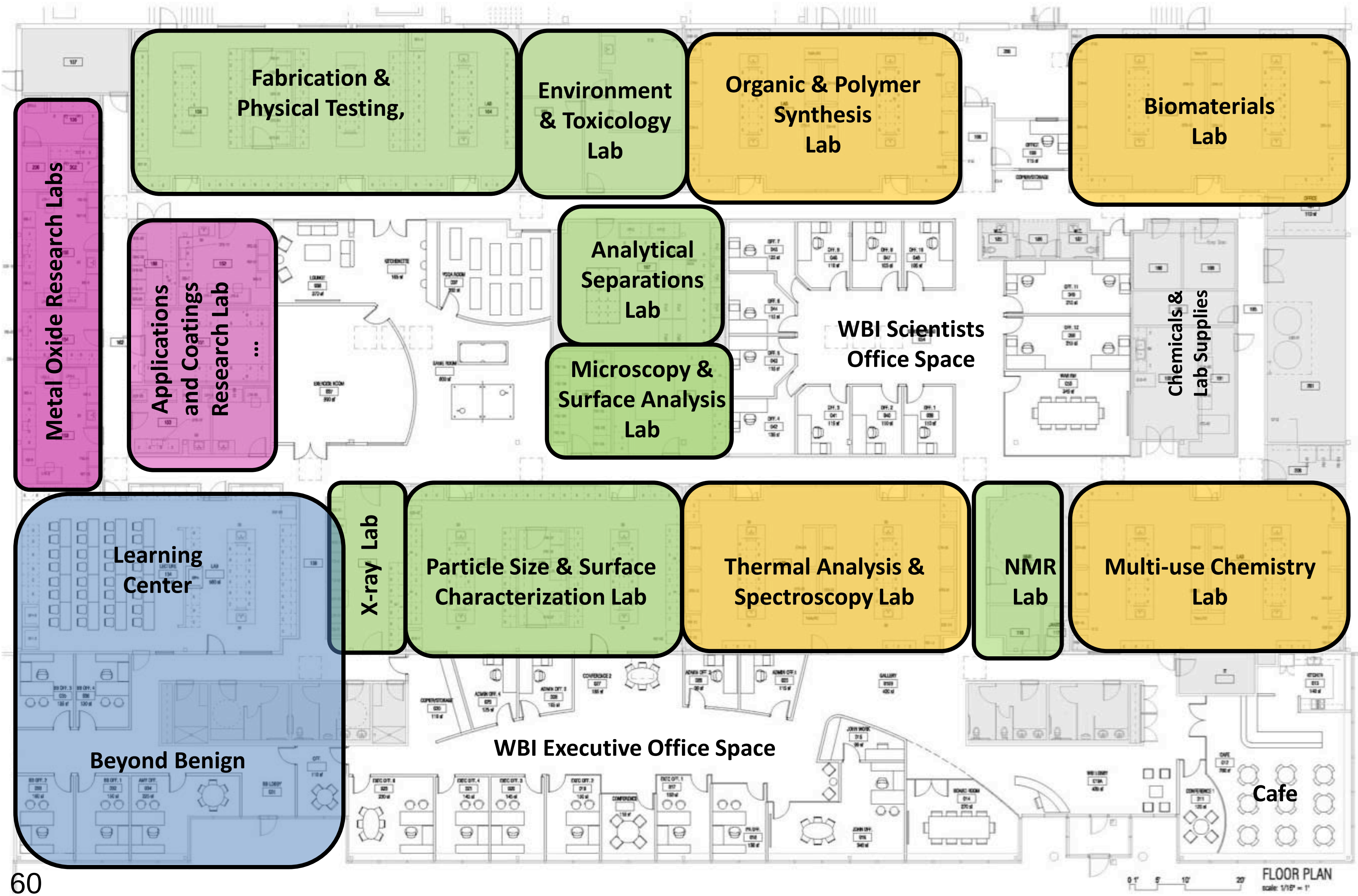


WHAT ARE YOU
DOING AFTER
THE GAME?



WHAT ARE YOU
DOING AFTER
THE GAME ?

Green Chemistry is a set of handcuffs that slow productivity!



Fabrication & Physical Testing,
Environment & Toxicology Lab
Organic & Polymer Synthesis Lab
Biomaterials Lab
Metal Oxide Research Labs
Applications and Coatings Research Lab …
Analytical Separations Lab
Microscopy & Surface Analysis Lab
WBI Scientists Office Space
Chemicals & Lab Supplies
Learning Center
X-ray Lab
Particle Size & Surface Characterization Lab
Thermal Analysis & Spectroscopy Lab
NMR Lab
Multi-use Chemistry Lab
Beyond Benign
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Cafe
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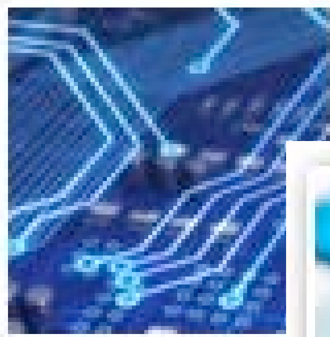
Industry Sectors

Energy, Natural Resources and Environment

Industrial Chemicals and Materials



Industrial Products

Pharmaceuticals and Biotechnology

Personal Care & Cosmetics

Retail, Consumer, Supply Chain

Core Technologies

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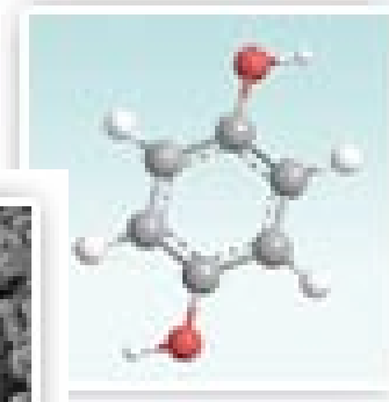
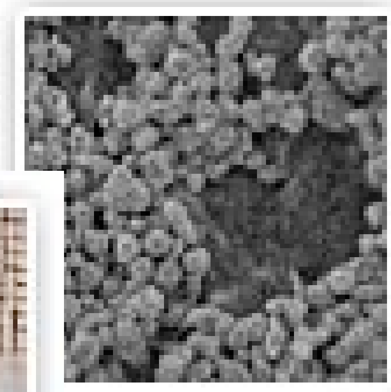
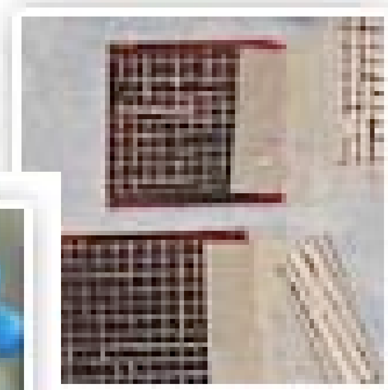
Non-covalent Derivatization & Formulation Science



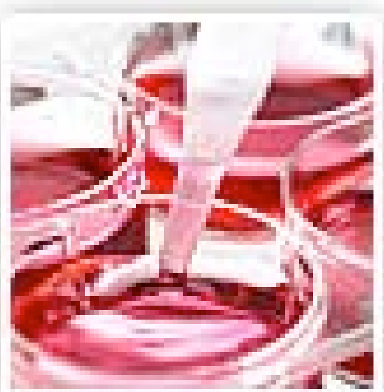
Metal Oxides Nanotechnology





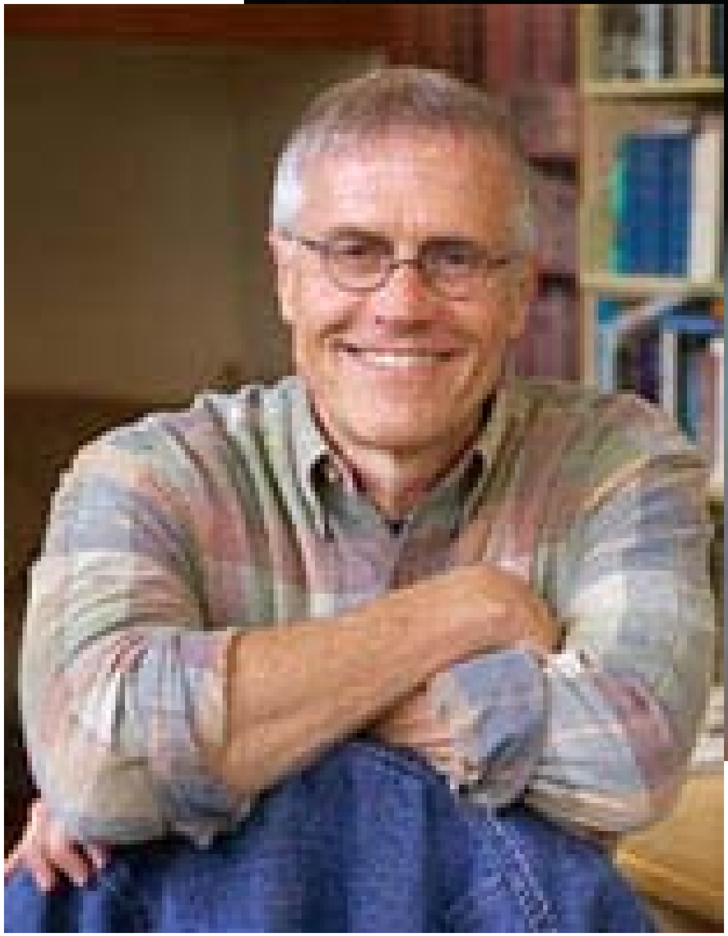
Films, Coatings and Surfaces

Organic/Polymer Synthesis & Engineering



Non Animal Toxicology Testing

Ultra Low Cost Non-Toxic Solar

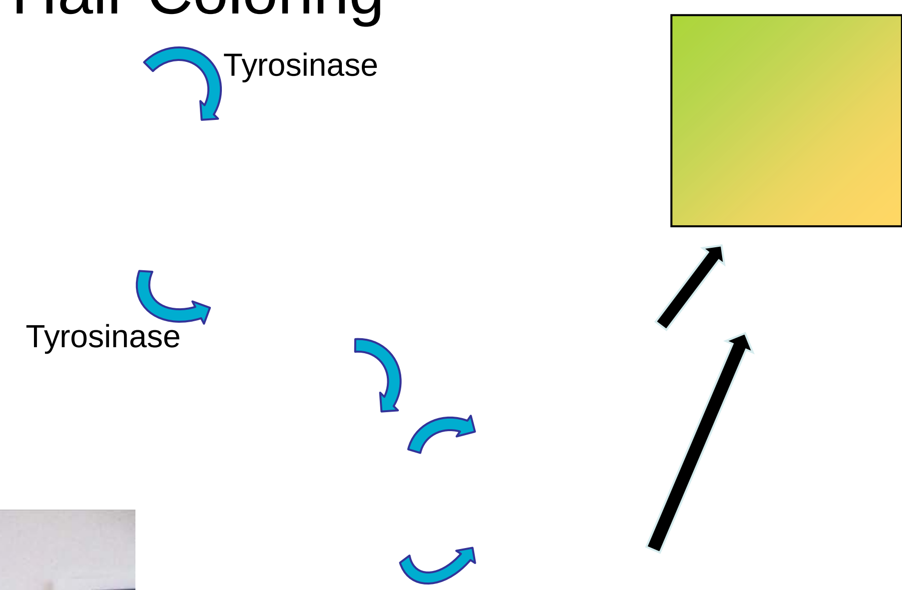


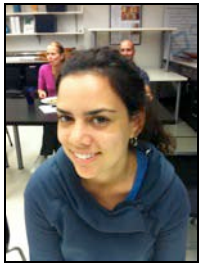
Paul Hawken

Janine Benyus

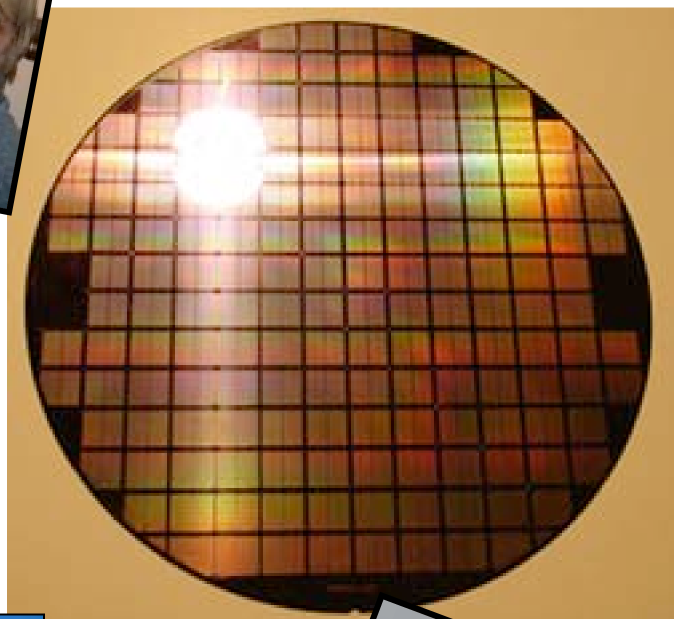
John Warner

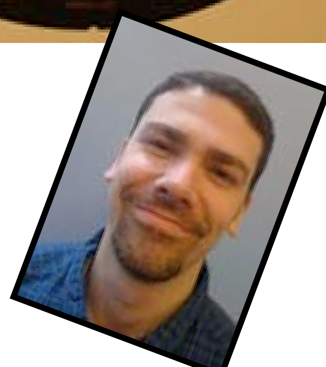
Nontoxic, Environmentally Benign Hair Coloring

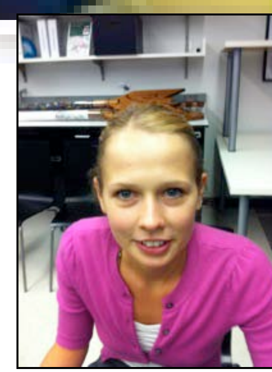


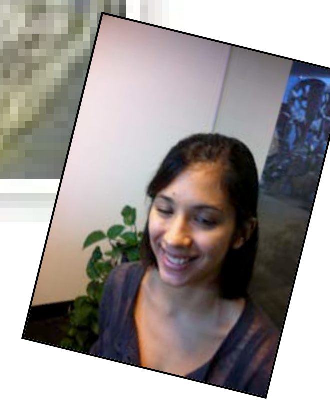


Water Based Non Toxic Photoresist Cleaning Solutions

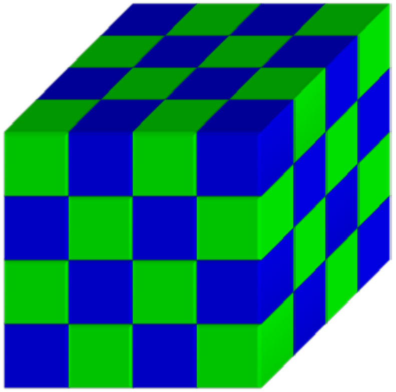








Increased Bioavailability for a Parkinson’s Disease Drug



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john.warner@warnerbabcock.com
www.warnerbabcock.com