

Chemical Microengineering. I. Introduction

By Peter R. Rony

Department of Chemical Engineering

Virginia Tech

Blacksburg, VA 24061-0211

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What is Chemical Microengineering?

Chemical microengineering is defined as the study of the engineering of small chemical systems. A chemical system is defined as being "small" if at least one coordinate direction, and usually two, has/have a size smaller than one millimeter. Such systems are much easier to mathematically model than the 3-D equipment in typical large-scale chemical systems.

As taught at Virginia Tech starting in 1974, ChE 4114 is a senior elective course in chemical microengineering that includes the study of (a) the continuity-of-species equation for "small chemical systems"; (b) clever ideas and interesting gimmicks that are used in small chemical systems; and (c) interesting molecules.

Examples of Small Chemical Systems

Some examples of "small" chemical systems include:

- A biological cell in any living organism
- A leaf of a plant
- A root hair on a plant
- A sac in a human lung
- A glomerule in a human kidney
- An ion-exchange pellet
- A pellicular absorbent inside a packed, gas-liquid chromatographic column
- The thin liquid film inside a capillary chromatographic column
- An enzyme immobilized on a porous support
- A supported liquid-phase catalyst pellet
- A hollow fiber enzyme reactor
- An ion-specific electrode
- A hollow fiber
- A microcapsule
- A microdroplet within a microemulsion
- An aphron

Though a plant leaf can have a large surface area, the small leaf thickness places such a system into the chemical microengineering category. Though a capillary chromatographic column can easily exceed 10 meters in length, the small thickness of the adsorbed liquid film inside the capillary also places such a system into the chemical microengineering category. A biological cell is the finest example of a small chemical system.

To repeat: the rule of the game in chemical microengineering is that one or two coordinate dimensions of a specified chemical system is/are smaller than one millimeter in length. The list of small chemical systems is almost endless.

Quote No. 1: Basic Phenomena of General Applicability

In the context of chemical microengineering, a favorite quote is from Paul B. Weisz [2]:

"We have traced the significance of the competition between molecular reaction and molecular diffusion, as expressed by the Phi criterion, across many disciplines. It is interesting to note how researchers in many branches of the sciences have struggled with problems that arise from a basically common phenomenon, one that does not "belong" to any special discipline. We need to consider how we might best prepare ourselves and our students to understand and deal with basic phenomena of general applicability. While we continue a healthy trend to erase interdisciplinary boundaries, we must remember that any collection of items as complex as those that constitute human knowledge can only be sensibly stored, managed, or propagated with some unifying structure. Can we find structures that are orderly, basic and interdisciplinary? Can the teaching of human experience and knowledge be organized around phenomena? The diffusion-transformation interaction is but one example of a general phenomenon: there are many others. . . . each represents a general concept or phenomenon that has meaning, implications, and applicability across an enormous sector of experiences and disciplines: physical, biological, social, physiological, medical, psychological, and others. Furthermore, each can be experienced, enjoyed, and understood in some form at nearly every stage of educational development."

"Chemical Microengineering" is a course that responds to Dr. Weisz's challenge. But what phenomena would be appropriate for such a course?

Quote No. 2: Processes are Not More Complicated Than Things

Edward De Bono [2] suggests an answer:

"Up til quite recently, the world was full of things. That is to say, the most useful and respected way to look at the world was in terms of static things. These things were given very definite names and fitted into great schemes of categories and classifications and sub-classifications. Every thing had its proper place and, being a static thing, it stayed there."

"It is often felt that processes are much more complicated than things. I do not believe this is so at all. It is true that you can see cars and bicycles and boiled eggs every day, but rarely see polarization or feedback or pattern. But this may only be because one has never learned to look for them. It can be just as much fun to look for feedback in daily life as it is to look for snails in the garden or buttercups on a country wall. And one can become just as quick at recognition."

De Bono's first list of process concepts includes the following items:

*to feedback
to manage
to forecast
to optimize
to control
to permit
to catalyze
to transfer
to convert
to sample
to oscillate
to filter
to polarize
to trigger off*

to extrapolate
to amplify
to regenerate
to communicate"

Quote No. 3: Some Phenomena and Processes in Chemical Microengineering

In chapter 4 of a supplementary ACS "sourcebook for physical chemistry teachers", Rony suggests the following lists of phenomena and processes [3] for a chemical microengineering course:

"In the spirit of the comments of Weisz and de Bono, what are the phenomena and processes associated with applications of the continuity-of-species equation? First are the processes, which can be expressed as verbs:

to diffuse
to distribute
to convect (to undergo convection)
to partition
to separate
to react
to catalyze
to accumulate
to undergo a diffusion-controlled reaction
to equilibrate
to undergo a convection-controlled reaction

"Second are the phenomena, which can be expressed as nouns:

diffusion
partitioning
convection
separation (diffusion-controlled convection)
reaction (chemical kinetics)
accumulation
catalysis
equilibration
diffusion-controlled reaction
distribution
convection-controlled reaction"

In chemical microengineering we demonstrate an intellectual framework in which a discussion of such phenomena and processes can occur naturally. Such topics are also appropriate in a physical chemistry course, which is why chapter 4 was written for the 1988 American Chemical Society sourcebook for physical chemistry teachers.

Example Categories of Clever Ideas and Gimmicks

In addition to identifying appropriate chemical microengineering processes and phenomena, we have also identified an eclectic group of principles that we call "chemical microengineering gimmicks":

- 2-dimensional equilibria
- Linear multistate chemical systems

- Pulse chromatography
- Affinity chromatography
- Gel permeation chromatography
- Porous solids/high interfacial areas
- Molecular anchoring
- Molecular barriers
- Molecular arrays
- Molecular recognition
- Extent of separation index
- Diffusion-controlled reaction
- Convection-controlled reaction (reactor)
- Dimensionless groups
- Catalysis
- Molecular carriers and facilitated diffusion
- Molecular isolation
- Molecular confinement
- Molecular protection
- Molecular inhibition
- Molecular bookkeeping
- Timed-release
- Countercurrent flow
- Combinatorial chemistry
- Short diffusion path lengths
- Use convection rather than diffusion to move molecules
- Microcapsules
- Microemulsions
- Aphrons
- Hollow fibers
- Liquid membranes
- Molecular tags
- Molecular amplification
- Molecular oscillators
- Molecular self assembly
- Molecular layers
- Molecular feedback
- Nanotubules
- Molecular sieves
- Molecular sensors
- Oscillogenic instruments

Example Categories of Interesting Molecules

The skills of chemists in creating interesting molecules is accelerating. Such molecules can be organized according to the categories of molecular topology, molecular machines, and molecular electronics. Molecular topology provides the greatest selection of interesting molecules, which include:

- Molecular cages (clathrates)
- Molecular claws (chelates)
- Molecular tubes

- Molecular geodesic domes
- Molecular channels
- Molecular separators
- Molecular spirals

Possible examples of molecular machines include:

- Molecular brushes
- Molecular zippers
- Molecular bearings
- Molecular drills
- Molecular handles
- Molecular chains

The synopsis to the article, "Computing with Molecules", by Reed and Tour [7], reads as follows:

"Researchers have produced molecules that act like switches, wires and even memory elements. But connecting many of the devices together presents enormous challenges". A remarkable figure from this article is the plot of Conductance (0.00 to 0.10 microSiemens) versus Voltage (-5 to +5 Volts) for a single benzene para-dithiol molecule bonded between two gold tips. The molecule could sustain a current of approximately 0.2 microAmpere at five Volts, or Teraelectrons per second in single file through the benzene dithiol. Although more complex logic circuits may be difficult to create, single molecules that exhibit the following examples of molecular electronics may be possible, even likely, to synthesize"

- Molecular switch
- Molecular diode
- Molecular conductor
- Molecular superconductor
- Molecular memory
- Molecular transistor
- Molecular wire
- Molecular amplifier
- Molecular address
- Molecular AND gate
- Molecular OR gate
- Molecular RAM
- Molecular ROM
- Molecular communications

Why Now?

The author has observed a significant evolution of research interests in the Virginia Tech ChE department, between 1970 to 2000, probably typical of research trends in ChE departments nationwide. In 1970, the focus of research was on traditional, chemical engineering topics, most of which had a negligible chemistry or biochemistry component. By 2000, at least two-thirds of the Virginia Tech faculty are engaged in research projects that have a chemical-microengineering flavor. It is likely that this trend in research interest will filter down to the undergraduate curriculum.

Quote No. 4: Microengineering Beyond the Electronics Domain

Another favorite quote is from Thomas Hirschfeld [5]:

"Mainly, however, microengineering beyond the electronics domain gives us the possibility of designing objects in an entirely new fashion since the significance of the physical and chemical principles involved changes as the scale of the system decreases. In an attempt to learn from experience, we have kept in mind that the biological world has been designing on the micrometer scale for eons and, thus, furnishes us with some impressive examples of microengineering. . . ."

"We have undertaken a systematic study of the physics, chemistry, and engineering of the microscopic domain. To do this, we have had to bring together a number of fields that initially do not appear to have much in common. The obvious starting point was microelectronics and its fabrication technology. However, unless we were to build everything out of silicon and only in two dimensions, we could not stop there. We soon realized that microscopic sizes are the normal design range of the biological world, and, after a billion years or so, nature has accumulated considerable expertise in this area. Through a careful search of the molecular biology and entomology literature, we identified a number of useful biological devices and design principles that can be incorporated in our microengineered devices."

"This leads directly to the first major technical task in microengineering-identifying the scaling laws. The scaling laws describe the variation in the relative importance of different phenomena as things change in size. For example, weight increases with the cube of a linear dimension but strength increases only with the square. . . ."

Quote No. 5: The Century of Biology

Equally appropriate here is a quote by John Carey [6]:

"New research technologies are vastly accelerating the pace of discovery in biology, driving forward not only medicine but also industry, environmental cleanup, and agriculture. Scientists are unlocking biochemical pathways in cancer, clogged arteries, and Alzheimer's disease. Not only are they understanding life, they're manipulating it. They are slipping new genes into people to treat disease and genetically engineering plants and animals to boost yields or transform them into bio-factories of plastics and drugs."

"Add it all up, and just as information technology undergirds today's booming economy, biology may drive tomorrow's. In fact, biology could transform information technology through such developments as DNA-based computers and software that repairs flaws as nature does. "We are now starting the century of biology," says J. Craig Venter, president of the Institute for Genomic Research and pioneering gene finder."

Clearly, the biological-system-based component of the 21st-century chemical engineering curriculum, will need to significantly expand from its current base of almost zero. One example of such expansion is the inclusion of a semester or two of biochemistry, perhaps supplemented by a biochemistry lab course.

A course in chemical microengineering provides an additional opportunity to discuss important principles of biological systems in the context of chemical engineering.

Cross - Fertilization Between Chemistry and Chemical Engineering

The author participated in a 1980 workshop on "Cross - Fertilization between Chemistry and Chemical Engineering", sponsored by the ACS Education Commission, *"which expressed concern about introductory physical chemistry courses and recommended that a study of the situation be made."* The author contributed the 36-page Chapter 4 to the resulting product of this workshop, namely, a paperback ACS publication entitled "Essays in Physical Chemistry:

A Sourcebook for Physical Chemistry Teachers" [3]. One day, the typical physical chemistry course may incorporate topics related to the continuity-of-species equation. The topic is as relevant to chemists as are other physical-chemistry theoretical topics, including quantum mechanics, statistical mechanics, chemical kinetics, and thermodynamics.

What Next?

This article is the first of a series of planned articles in CACHE News Online that explore various aspects of a Chemical Microengineering senior elective course for undergraduates. The author has taught such an elective course, off and on, since 1974 with the hope that it would attract a multidisciplinary undergraduate audience. In 26 years, the course's single interdisciplinary student was Dr. Yoel Sasson, a post-doctoral researcher from the Hebrew University of Jerusalem. Dr. Sasson learned the principle of phase-transfer catalysis during the 1970's version of the chemical microengineering course, and has become since that time an international expert on the subject [8].

Subsequent CACHE News Online articles will explore items from the listings contained in this paper.

References

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