Open-Ended Problems: A Future Chemical Engineering Education Approach. J. Patrick Abulencia and Louis Theodore.

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Nanotechnology

This chapter is concerned with nanotechnology. As with all the chapters in Part II, there are sereval sections: Overview, several technical topics, illustrative open-ended problems, and open-ended problems. The purpose of the first section is to introduce the reader to the subject of nanotechnology. As one might suppose, a comprehensive treatment is not provided although several technical topics, are also included. The next section contains three open-ended problems; the authors' solution (there may be other solutions) are also provided. The final section contains 26 problems; *no* solutions are provided here.

20.1 Overview

This overview section is concerned with—as can be noted from the chapter title—nanotechnology. As one might suppose, it was not possible to address all topics directly or indirectly related to nanotechnology. However, additional details may be obtained from either the references provided at the end of this Overview and/or at the end of the chapter.

Note: Those readers already familiar with the details associated with this topic may choose to bypass this Overview.

Nanotechnology. Everybody's talking about it. It's the new kid on the block. The financial markets and some readers don't quite know what to make of it. Although not to be found in Webster's Dictionary, it is concerned with the world of invisible miniscule particles that are dominated by forces of physics and chemistry that cannot be applied at the macro—or human—scale level. These particles, when combined, have come to be defined by some as nanomaterials, and these materials possess unusual properties not present in traditional and/or ordinary material.

Regarding the word nanotechnology, it is derived from the Greek word *nano* (for dwarf) and technology. Nano, typically employed as a prefix, is defined as one billionth of a quantity or term and is represented mathematically as 1×10^{-9} or simply as 10^{-9}. *Technology* generally refers to "the system by which a society provides its members with those things needed or desired". The term nanotechnology has come to be defined as those systems or processes that provide goods and/or services that are obtained from matter at the nanometer level, i.e., from sizes at or below one billionth of a meter. The new technology thus allows the engineering of matter by systems and/or processes that deal with atoms. One of the major problems that remain is the development of nanomachines that can produce other nanomachines in a manner similar to what many routinely describe as mass production.

Interesting, the fundamental laws of chemistry and physics work differently when particles reach the nanoscale as the powers of hydrogen bonding, quantum energy, and van der Waals' forces endow some nanomaterials with some very unusual properties. Carbon nanotubes for instance, discovered in the sooty residue of vaporized carbon rods, defy the standard laws of physics. Stronger and more flexible than steel, yet measuring about 10,000 times smaller than the diameter or a human hair, these cylindrical sheets of carbon atoms are also useful as coatings on computers and other electrical devices. Nanoparticles, another manifestation of nanotechnology, are known to foster stubborn reactions because they have an enormous surface area relative to their volume [2].

As noted above, the classical laws of science are different at the nanoscale. Nanoparticles possess large surface areas and essentially no inner mass, i.e., their surface to mass ratio is extremely high. This new "science" is based on the knowledge that particles in the nanometer range, and nanostructures or nanomachines that are developed from these nanoparticles, possess special properties, and, in conjunction with their unique behavior, can significantly impact physical, chemical, electrical, biological, mechanical, etc., functional properties. These new characteristics can be harnessed and exploited by chemical engineers to engineer "Industrial Revolution II" processes.

In addition to this overview, the chapter contains the following:

1. Early History
2. Fundamentals and Basic Principles
3. Nanomaterials
4. Production Methods
5. Current Applications
6. Environmental Concerns
7. Future Prospects

20.2 Early History [3]

Nanoparticles arrived on scene immediately following the Big Bang some 13 billion years ago. However, it is not clear when humans first began to take advantage of nanosized materials. It is known that in the fourth century A.D. Roman glassmakers were fabricating glasses containing nanosized metals. Michael Faraday published a paper in 1857 in the *Philosophical Transactions of the Royal Society*, which attempted to explain how metal particles affect the color of church windows. Gustav Mie was the first to provide an explanation of the dependence of the color of the glasses on the kind of metal and its size. A century later, Richard Feynman presented a lecture titled, "There Is Plenty of Room at the Bottom," where he speculated on the possibility and potential of nanosized materials. He proposed manipulating individual atoms to make new small structures having different properties. Groups at Bell Laboratories and IBM fabricated the first two-dimensional quantum cells in the early 1970s. They were made by thin-film (epitaxial) growth techniques that build a semiconductor layer one atom at a time; the work was the beginning of the development of the zero-dimensional quantum dot, which is now one of the nanotechnologies in commercial applications. In 1996, a number of government agencies led by the National Science Foundation (NSF) commissioned a study to assess the current worldwide status of trends, research, and development in nanoscience and nanotechnology. This early NSF activity provided the necessary impetus for the future for this industry to expand and flourish.

20.3 Fundamentals and Basic Principles

Matter is anything that has mass and can be physically observed. All mater is composed of *atoms* and *molecules*; it consists of a finite number of elements, often represented as *building blocks*. *Atoms* are small particles that cannot be made smaller while *molecules* are groups of atoms bound together, but possessing properties different from an atom.

The aforementioned atom is composed of a small core defined as the *nucleus* that is surrounded by *electrons*. The nucleus is composed of two types of particles: *protons* and *neutrons*; however, their is significant space between the electrons and the nucleus. Protons and neutrons are themselves made up of even smaller particles, known as quarks. One generally depicts the changes in units of the electron charge, so that the charge of an electron is written as 1^- and that of a proton is written as 1^+.

The aforementioned matter has physical and chemical properties that are related to its size, i.e., the properties of most solids depend on the size range over which they are measured. The size range can be macroscopic, microscopic, or molecular; one may view these sizes as finite, differential and molecular, respectively. The object of this chapter is to discuss these characteristics at the molecular, or nanometer level. At the macro—or large—scale range ordinarily studied in traditional fields of physics such as mechanics, electricity, magnetism, and optics, the sizes of the objects under study range from millimeters to kilometers, i.e., finite sizes. The properties that one associates with these materials are averaged properties, such as density and thermal conductivity.

When familiar materials such as metals, metal oxides, ceramics and polymers, and novel forms of carbon such as the aforementioned carbon nanotubes and fullerenes (or buckyballs) are converted/produced into infinitesimally small particle sizes (and, in the case of carbon nanotubes and buckyballs, unique structural geometries, as well), the resulting particles have an order-of-magnitude *increase* in available surface area. It is this remarkable surface area of particles in the nanometer range that confers upon them some unique material properties, especially when compared to macroscopic particles of the same material [4].

One of the hallmarks of nanotechnology is the desire to produce and use nanometer-sized particles of various materials in order to explore the remarkable characteristics and performance attributes that many materials exhibit at these infinitesimally small (particle) sizes.

20.4 Nanomaterials

Nanomaterials have their own origin with what have come to be defined as prime materials. These prime materials essentially consist of (pure) elements and compounds. The range of these elements and compounds that have been successfully produced and deployed as nanometer-sized particles include:

1. Metals such as iron, copper, gold, aluminum, nickel, and silver
2. Oxides of metal such as iron, titanium, zirconium, aluminum, and zinc
3. Silica sols, and fumed and colloidal silica
4. Clays such as talc, mica, smectite, asbestos, vermiculite, and montmorillonite
5. Carbon compounds, such as fullerences, nanotubes, and carbon fibers

Information on each of these types of materials along with the manufacturing methods (see next section) used to render them into nanoscale particles, is available in the literature [5].

Six of the major metals that have served as prime materials include the following:

1. Iron
2. Aluminum
3. Nickel
4. Silver
5. Gold
6. Copper

Five of the major mixed oxides include the following:

1. Iron oxides (Fe_2O_3 and Fe_3O_4)
2. Silicon dioxide (silica; SiO_2)
3. Titanium dioxide (titania; TiO_2)
4. Aluminum oxide (alumina; Al_2O_3)
5. Zirconium dioxide (zirconia; ZrO_2 and zinc oxide; ZnO).

Additional details on both metals and metal oxides are available in the literature [6].

20.5 Production Methods

In general, there are 6 widely used methods for producing nanoscaled particles. These are listed below.

1. Plasma-arc and flame-hydrolysis methods (including flame ionization)
2. Chemical vapor deposition (CVD)
3. Electrodeposition techniques
4. Sol-gel synthesis
5. Mechanical crushing via ball milling
6. Use of natural occurring nanomaterials

Naturally occurring materials, such as zeolites, can be used as found or synthesized and modified by conventional chemistry. A zeolite is a caged molecular structure containing large voids that can admit molecules of certain size and deny access to other larger molecules. They find application as catalysts as well as adsorbents and other materials [2,4,7,8].

The ongoing challenge for industry is to continue to devise, perfect, and scale up viable production methodologies that can cost effectively and reliably produce the desired nanoparticles with the desired particle size, particle size distribution, purity and uniformity in terms of both composition and structure.

To summarize, there are 6 major methods to produce nanomaterials. These are plasma arcing, flame hydrolysis, chemical vapor deposition (CVD), electrodeposition, sol gel synthesis, ball milling, and the use of natural occurring nanoparticles.

20.6 Current Applications

Present day applications include chemical products, such as plastics, specialty metals, powders, etc., computer chips, and computer systems [1]. Specific examples of nanotechnology in actual commercial use today include [4]:

1. Semiconductor chips and other microelectronics applications
2. High surface-to-volume catalysts, which promote chemical reactions more efficiently and selectively
3. Ceramics, lighter-weight alloys, metal oxides and other metallic compounds
4. Coating, paints, plastic, fillers, and food-packaging applications
5. Polymer-composite materials, including tires with improved mechanical properties
6. Transparent composite materials such as sunscreens containing nanosized titanium dioxide and zinc oxide particles

7. Use in fuel cells, battery electrodes, communication applications, photographic film developing, and gas sensors
8. Nanobarcodes
9. Tips for scanning probe microscopes
10. Purification of pharmaceuticals and enzymes

A host of other applications are certain to emerge in the future.

20.7 Environmental Concerns [9,10]

Any technology can have various and imposing effects on the environment and society. Nanotechnology is no exception, and the results of these effects will be determined by the extent to which the technical community manages this technology. This is an area that has, unfortunately, been seized upon by a variety of environmental groups.

An environmental implication of nanotechnology has been dubbed by many in this diminutive field as "potentially negative". The reason for this label is as simple as obvious. The technical community is dealing with a significant number of unforeseen effects that could have disturbingly disastrous impacts on society. Fortunately, it appears the probability of such dire consequences actually occurring is near zero…but *not* zero. This finite, but differentially small, probability is one of the reasons this section was included in this chapter; and it is the key topic that is addressed in the material to follow.

Air, water, and land (solid waste) emissions from nano-technology operations in the future, as well as companion health and hazard issue are a concern. These issues arose earlier with the Industrial Revolution, the development/testing/use of the atomic bomb, the arrival of the internet, Y2K, etc.; and, all were successfully (relatively speaking) resolved by the engineers and scientists of their period.

To the authors' knowledge there are no documented nano human health hazards. Statements in the literature refer to *potential* health problems. The authors have also speculated on the need for future nanoregulations (see next paragraph and problem 2 in a later section). Suggestions and potential options are provided [11] while noting that the ratio of pollutant nanoparticles (from conventional sources such as power plants) to engineered nanoparticles being released into the environment may be as high as a trillion to one, [12] i.e., 10^{12}:1. If this be so, the environmental concerns for nanoparticles can almost certainly be dismissed.

Current environmental regulations, as they apply to nanomaterial, are provided by Stander and Theodore [13]. Many environmental concerns are addressed by existing health and safety legislation. Most countries including the U.S. require a health and safety assessment for any new chemical before it can be marketed. In addition, the European Union (EU) recently introducing the world's most stringent labeling system. Prior experience with materials such as PCBs and asbestos, and a variety of unintended effects of drugs such as thalidomide, mean that both companies and governments have incentives to keep a close watch on potential negative health and environmental effects [14].

It is very difficult to predict future nanoregulations. In the past, regulations have been both a moving target and confusing. What can be said for certain is that there will be regulations, and the probability is high that they will be contradictory and confusing. Past and current regulations provide a measure of what can be expected. And, it is for this reason that this section is included in this chapter. Detailed analysis of various U.S. and EU laws and regulations are available in the literature [15–19].

20.8 Future Prospects [6,8,20,21]

Ranking high among the challenges is the ongoing need to develop and perfect reliable techniques to produce (and mass produce) nanoscaled particles that have not only the desirable particle sizes and particle size distributions but also a minimal number of structural defects and produce acceptable purity levels since these latter attributes can drastically alter the anticipated behavior and properties of the nanoscaled particles. Experience to date indicates that scale-up issues associated with moving today's promising nanotechnology-related development from laboratory and pilot scale demonstrations to full scale commercialization can be considerable [6].

Most believe nanotechnology will have its major impact on war, crime, terrorism, and the massive companion industries, particularly security and law enforcement. The military has a significant interest in nanotechnology, including such areas as optical systems, nanorobotics, nanomachines, "smart" weapons, nanoelectronics, virtual reality, massive memory, specialty materials for armor, nanobased materials for stopping bullets, and bionanodevices to deter and destroy chemical and biological agents. Most of this activity is concerned with protection against attack and minimizing risk to military personnel, e.g., devices that may be able to repair defective airframes or the hulls of ships before major problems develop. But make no mistake, the rush is on (as with development of the atomic bomb) to conquer this technology; the individual or organization or country that successfully conquers this technology will almost certainly conquer the world. Society, as well as the technical community, has to understand that the misuse of this new technology can lead to and cause catastrophic damage; alternately, nanotechnology could be used to provide not only sophisticated sensor and surveillance systems to identify military threats but also weapons (or the equivalent) that will eliminate these threats [20].

Regarding crime, the techniques of nanoscience will have a lot to offer forensic investigations, both for biological analysis, and materials and chemical studies. Portable instruments with sophisticated nanosensors will be able to perform accurate high level analyses at crime sites. These instruments should greatly improve conviction rates and the ability to locate real clues. Nanotechnology will also stop money laundering by imprinting every computer digit [21].

Nanotechnology may open up new ways of making computer systems and message transfers secure using special hardware keys that are immune to any form of hacking. Very few current computer protection systems are able to keep out determined hackers. Nanoimprinting, which already exists, could be used to make "keys" or even special nano-based biosensors coded with a dynamic DNA sequence. Nano-imprinting is already used to make bank notes virtually impossible to forge by creating special holograms in the clear plastic; forgery would be possible only if the master stamps were actually stolen, but then a new hologram could be made [20].

In addition, nanoparticle-related developments are being actively pursued to improve fuel cells, batteries, solar devices, advanced data-storage devices such as computer chips and hard drives, magnetic audio and videotapes, and sensors and other analytical devices. Meanwhile, nanotechnology-related developments are also being hotly pursued in other medical applications, such as the development of more effective drug-delivery mechanisms and improved medical diagnostic devices, to name just a few.

A detailed and expanded treatment of nanotechnology is available in the following three references.

1. Adapted from, L. Theodore and R. Kunz, *Nanotechnology: Environmental Implications and Solutions*, John Wiley & Sons, Hoboken, NJ, 2005 [6].
2. Adapted from, L. Theodore, *Nanotechnology: Basic Calculations for Engineers and Scientists*, John Wiley & Sons, Hoboken, NJ, 2006 [8].
3. L. Theodore, *Chemical Engineering: The Essential Reference*, McGraw-Hill, New York City, NY, 2014 [21].

20.9 Illustrative Open-Ended Problems

This and the last section provide open-ended problems. However, solutions *are* provided for the three problems in this section in order for the reader to hopefully obtain a better understanding of these problems which differ from the traditional problems/illustrative examples. The first problem is relatively straightforward while the third (and last problem) is somewhat more difficult and/or complex. Note that solutions are not provided for the 26 open-ended problems in the next section.

Problem 1: Briefly define and discuss present-day atomic theory [8].

Solution: In ancient Greek philosophy, the word *atomos* was used to describe the smallest bit of matter that could be conceived. This "fundamental particle" was thought of as indestructible; in fact, atomos means "not divisible". Knowledge about the size and nature of the atom grew slowly throughout the centuries.

As discussed in the Overview, the atom consists of three subatomic particles: the *proton*, *neutron*, and *electron*. The charge of an electron is -1.602×10^{-19} C (coulombs), and that of a proton is $+1.602 \times 10^{-19}$ C. The quantity -1.602×10^{-19} is defined as the *electronic charge*. Note that the charges of these subatomic particles are expressed as multiples of this charge rather than in coulombs. As noted, the charge of any electron is 1−, and that of a proton is 1+. Neutrons carry no charge, i.e., they are electrically neutral. Since an atom has an equal number of electrons and protons, it has zero or no net electric charge.

Both the protons and neutrons reside in the nucleus of the atom, which is extremely small. Most of the atom's volume is the space in which the electrons reside. The external electrons are attracted to the protons in the nucleus because of their opposite electrical charge.

Problem 2: Provide a general overview of nanotechnology environmental regulations.

Solution: Completely new legislation and regulatory rulemaking may be necessary for the environmental control of nanotechnology. However, in the meantime, one may speculate on how the existing regulatory framework might be applied to the nanotechnology area as this emerging field develops over the next several years.

Commercial applications of nanotechnology are likely to be regulated under TSCA, which authorizes the U.S. EPA to review and establish limits on the manufacture, processing, distribution, use, and/or disposal of new materials that EPA determines to pose "an unreasonable risk of injury to human health or the environment." The term *chemical* is defined broadly by TSCA. Unless qualifying for an exemption under the law (a statutory exemption requiring no further approval by EPA), low-volume production, low environmental releases along with low-volume releases, or plans for limited test marketing, a prospective manufacturer is subject to the full-blown procedure. This requires submittal of said notice, along with toxicity and other data to EPA at least 90 days before commencing production of the chemical substance [13].

Approval then involves recordkeeping, reporting, and other requirements under the statute. Requirements will differ, depending on whether EPA determined that a particular application constitutes a "significant new use" or a "new chemical substance." The EPA can impose limits on production, including an outright ban when it deemed necessary for adequate protection against "an unreasonable risk of injury to health or the environment". The EPA may revisit a chemical's status under TSCA and change the degree or type of regulation when new health/ environmental data warrant [13].

Workplace exposure to a chemical substance and the potential for pulmonary toxicity is subject to regulation by OSHA, including the requirement that potential hazards be disclosed on a MSDS (Material Safety Data Sheet). (An interesting question arises as to whether carbon nanotubes, chemically carbon but with different properties because of their small size and structure, are to be considered the same as or different from carbon black for MSDS purposes.) Both governmental and private agencies can be expected to develop the requisite threshold limit values (TLVs) for workplace exposure. Also, the EPA may once again utilize TSCA to assert its own jurisdiction, appropriate or not, to minimize exposure in the workplace. This is almost definitely wishful thinking given the past performance of similar bureaucratic agencies. Adding to the dilemma is the breadth of the nano field and the lack of applicable toxicology and epidemiology data [22].

Another likely source of regulation would fall under the provisions of the Clean Air Act (CAA) for particulate matter less than 2.5 μm ($PM_{2.5}$). Additionally, an installation manufacturing nanomaterials may ultimately become subject as a "major source" to the CAA's Section 112 governing hazardous air pollutants (HAP) [13].

Wastes from a commercial-scale nanotechnology facility would be classified under RCRA, provided that it meets the criteria for RCRA waste. RCRA requirements could be triggered by a listed manufacturing process or the act's specified hazardous waste characteristics. The type and extent of regulation would depend on how much hazardous waste is generated and whether the wastes generated are treated, stored, or disposed of on site [6,13].

Problem 3: Your consulting firm has received a contract to develop, as part of research study, a mathematical model describing the concentration of a nanochemical in a medium-sized ventilated laboratory room. The following notation/data (SI) units are provided:

V = volume of room, m^3
v_0 = volumetric flow rate of ventilation air, m^3/min
c_0 = concentration of the nanochemical in ventilation air, gmol/m^3
c = concentration of the nanochemical leaving ventilated room, gmol/m^3
c_i = concentration of the nanochemical initially present in the ventilated room, gmol/m^3
r = rate of appearance of disappearance of the nanochemical in the room due to reaction and/or other effects, gmol/m^3·min.

As an authority in the field, you have been requested to:

1. Obtain the equation describing the concentration in the room as a function of time.
2. Calculate the minimum air ventilation flow rate containing 10ng/m^3 nano-particles flowing into the room to assure that the nanoagent concentration does not exceed 35.0 ng/m^3. The nanoagents are appearing (internally) in the laboratory at a rate of 250 ng/min. Assume steady-state conditions.
3. Comment on the validity and limitations of both the model (1) and calculated results (2).

Solution: 1. Use the laboratory room as the control volume. Apply the concentration law for mass (see also chapter 3) to the nanochemical.

$$\begin{Bmatrix} rate\ of\ mass \\ in \end{Bmatrix} - \begin{Bmatrix} rate\ of\ mass \\ out \end{Bmatrix} + \begin{Bmatrix} rate\ of\ mass \\ generated \end{Bmatrix} = \begin{Bmatrix} rate\ of\ mass \\ accumulated \end{Bmatrix} \tag{20.1}$$

Employing the notation specified in the problem statement gives:

$$\begin{aligned}
&\{\text{rate of mass in}\} = v_0 c_0 \\
&\{\text{rate of mass out}\} = v_0 c \\
&\{\text{rate of mass generated}\} = rV \\
&\{\text{rate of mass accumulated}\} = \frac{\mathrm{d}c}{\mathrm{d}t}
\end{aligned} \tag{20.2}$$

Substituting above gives

$$v_0 c_0 - v_0 c + rV = \frac{\mathrm{d}c}{\mathrm{d}t} \tag{20.3}$$

If the laboratory room volume is constant, *V* may be taken out of the derivative term. This leads to

$$\frac{v_0}{V}\left(c_0 - c\right) + r = \frac{\mathrm{d}c}{\mathrm{d}t} \tag{20.4}$$

The term V/v_0 represents the average residence time the nanochemicals reside in the room and is usually designated as τ. The above equation may then be rewritten as

$$\frac{\mathrm{d}c}{\mathrm{d}t} = \frac{c_0 - c}{\tau} + r \tag{20.5}$$

2. The applicable model for this case is:

$$v_0\left(c_0 - c\right) + rV = V\frac{\mathrm{d}c}{\mathrm{d}t} \tag{20.6}$$

Under steady-state conditions, $\mathrm{d}c/\mathrm{d}t = 0$.

$$v_0\left(c_0 - c\right) + rV = 0 \tag{20.7}$$

Pertinent information incudes

$$\begin{aligned} rV &= 250 \text{ ng/min} \\ c_0 &= 10 \text{ ng/m}^3 \\ c &= 35 \text{ ng/m}^3 \end{aligned}$$

Substituting into equation 20.7 gives

$$\begin{aligned} v_0 &= \frac{-rV}{c_0 - c} \\ &= \frac{-rV}{c - c_0} \\ &= \frac{250}{35 - 10} \\ &= 10 \text{ m}^3/\text{min} = 353\text{ft}^3/\text{min} \end{aligned}$$

3. There were two assumptions in the development. The assumption that the room volume is constant is reasonable. However, the development also assumes that room contents are perfectly mixed (similar to a continuous stirred tank reactor, i.e., CSTR) and this can significantly impact the analysis and results [2,3].

This open-ended problem will be revisited in Part III, Chapter 26, Environmental Health and Hazard Risk; Term Projects 26.4-26.5.

20.10 Open-Ended Problems

This last section of the chapter contains open-ended problems as they relate to nanotechnology. No detailed and/or specific solution is provided; that task is left to the reader, noting that each problem has either a unique solution or a number of solutions or (in some cases) no solution at all. These are characteristics of open-ended problems described earlier.

There are comments associated with some, but not all, of the problems. The comments are included to assist the reader while attempting to solve the problems. However, it is recommended that the solution to each problem should initially be attempted *without* the assistance of the comments.

There are 26 open-ended problems in this section. As stated above, if difficulty is encountered in solving any particular problem, the reader should next refer to the comment, if any is provided with the problem.

The reader should also note that the more difficult problems are generally located at or near the end of the section.

1. Describe the early history associated with nanotechnology.
2. Discuss the recent advances in nanotechnology.
3. Select a refereed, published article on nanotechnology from the literature and provide a review.
4. Provide some normal everyday domestic applications involving the general topic of nanotechnology.
5. Develop an original problem on nanotechnology that would be suitable as an illustrative example in a book.
6. Prepare a list of the various technical books which have been written on nanotechnology. Select the three best (hopefully, it will include a book written by one of the authors) and justify your answer. Also select the three weakest books and, once again, justify your answer.
7. Describe nanotechnology in layman terms.
8. Consider how to integrate pure nanomaterials into the periodic table.
9. Outline how to determine the number of potential nanomaterials that could possibly be derived from the 112 elements.
10. Describe, in technical detail, the different between true density, actual density, and bulk density.
11. Describe, in layman terms, the difference between true density, actual density, and bulk density.
12. Describe the impact of different shaped particles on true density, actual density, and bulk density.
13. Develop equations describing the area and volume of various shaped particles.

    Comment: Consider a sphere and cube initially and continue on from there. Also, refer to the literature [8].
14. Describe some of the procedures that are available to estimate the physical properties of nanomaterials.
15. Describe some of the procedures that are available to estimate the chemical properties of nanomaterials.
16. Attempt to develop an improved method to describe submicron particle behavior in air.
17. The bulk of material on the Cunningham Correction Factor (CCF) is based on particle behavior in air [7]. Quantitatively discuss how the CCF would be affected by other gases.

18. Develop equations describing the particle collection efficiency as a function of particle size for various air pollution control devices, e.g., baghouses, electrostatic precipitators, cyclones, etc.

    Comment: Refer to the literature [7] for additional details.
19. Discuss in layman terms the difference between collection efficiency and penetration.

    Comment: Refer to the literature [7] for additional details.
20. Refer to Problem 3 in the previous Section. Develop describing equations for the ventilation system if the nanomaterial is undergoing a reaction. Present the equations for reaction mechanisms of your choice.

    Comment: Refer to the literature [8] for additional details.
21. Refer to Problem 3 in the previous Section. Develop describing equations for the ventilation systems if the nanomaterial is being introduced into the system for different time-variable flowrates. Present the equations for reaction mechanisms of your choice.
22. Provide calculational procedures to estimate nanoparticle emissions from line and area sources [7].
23. As discussed in the Overview, there are six widely used methods for producing nanoscaled particles of various materials. These are listed below:
    - Plasma-arc and flame-hydrolysis methods (including flame ionization)
    - Chemical vapor deposition (CVD)
    - Electrodeposition techniques
    - Sol-gel synthesis
    - Mechanical crushing

    Promising technologies

    Describe these methods in layman terms.
24. Size distributions of nanoparticles are often characterized by a “mean” particle diameter. Although numerous “means” have been defined in the literature, the most common are the arithmetic mean and the geometric mean. The arithmetic mean diameter is simply the sum of the diameters of each of the particles divided by the number of particles measured. The geometric mean diameter is the *n*th root of the product of the *n* number of particles in the sample. In addition to the arithmetic and geometric means, a particle size distribution may also

be characterized by the "median" diameter. The median diameter is that diameter for which 50% of the particles are larger in size and 50% are smaller in size. Another important characteristic is the measure of *central tendency*. Is it sometimes referred to as the dispersion or variability. The most common term employed is the standard deviation. Present at least two other methods of describing particle size distributions [7,20]

25. Briefly describe the regulatory processes that opponents of nanotechnology could pursue in the future and comment whether (in your judgment) their efforts will be successful.
26. Determine the number of four, five, and six element chemical compounds that can theoretically be generated from a pool of 112 elements. Assume each element counts only once in the chemical formula. An example of a three-element compound is H_2SO_4 (sulfuric acid), or CH_3OH (methanol). An example of a four-element compound is $NaHCO_3$. Also perform the calculations if the element appears twice in the chemical formula. Comment on the results.

References

1. L. Theodore, *Nanotechnology I*, The Williston Times, East Williston, NY, April 16, 2004.
2. R. D'Aquino, personal communication, to L. Theodore, Bronx, NY, 2005.
3. Adapted from, C. Poole and F. Owens, *Introduction to Nanotechnology*, John Wiley & Sons, Hoboken, NJ, 2003.
4. S. A Shelley with G. Ondrey, *Nanotechnology- The Sky's the Limit*, Chemical Engineering, New York City, NY, December 2002.
5. A. Boxall, Q. Chaudhry, A. Jones, B. Jefferson, and C.D Watts, *Current and Future Predictions of Environmental Expose to Engineered Nanoparticles*, Central Science Laboratory, Sand Hutton, UK, 2008.
6. Adapted from, L. Theodore and R. Kunz, *Nanotechnology: Environmental Implications and Solutions*, John Wiley & Sons, Hoboken, NJ, 2005.
7. L. Theodore, *Air Pollution Control Equipment Calculations*, John Wiley & Sons, Hoboken, NJ, 2008.
8. Adapted from, L. Theodore, *Nanotechnology: Basic Calculations for Engineers and Scientists*, John Wiley & Sons, Hoboken, NJ, 2006.
9. M.K. Theodore and L. Theodore, *Major Environmental Issues Facing the 21st Century*, (originally published by Prentice-Hall), Theodore Tutorials, East Williston, NY, 1996.

10. G. Burke, B. Singh, and L. Theodore, *Handbook of Environmental Management and Technology*, 2^{nd} edition, John Wiley & Sons, Hoboken, NJ, 2000.
11. L. Theodore, *Waste Management of Nanomaterials*, USEPA, Washington, DC, 2006.
12. Personal notes, L. Theodore, 2006.
13. L. Stander and L. Theodore, *Environmental Regulatory Calculations Handbook*, John Wiley & Sons, Hoboken, NJ, 2010.
14. National center for Environmental Research, *Nanotechnology and the Environment: Applications and Implications*, STAR Progress Review Workshop, Office of Research and Development, National Center for Environmental Research, Washington, DC, 2003.
15. D. Fiorino, *Voluntary Initiatives, Regulations, and Nanotechnology Oversight: Charting a Path*, Woodrow Wilson International Center for Scholars, Washington, DC, U.S.A, November 2010.
16. L. Breggin, R. Faulkner, N. Cheel, K. Prendergrass, and R. Porter, *Securing the Profits of Nanotechnologies: Towards Transatlantic Regulatory Cooperation*, Chatham House: London, UK, September, 2009.
17. Laws and Regulations; U.S EPA: Washington, DC, U.S.A, available online: http://www.epa.gov'lawsregs/laws/index.html (accessed on 23 November 2010).
18. L. Bergeson, *Nanotechnology Trend Draws Attention of Federal Regulators*, Manufacturing Today, location unknown, March/April 2004.
19. L. Bergeson, B. Auerbach, *The Environmental Regulation Implications of Nanotechnology*, BNA Daily Environment Reporter, pp. B-1-B-7, location unknown April 14, 2004.
20. L. Theodore, *Nanotechnology II*, The Williston Times, East Williston, NY, April 23, 2004.
21. L. Theodore, *Chemical Engineering: The Essential Reference*, McGraw-Hill, New York City, NY, 2014.
22. L. Theodore and R. Dupont, *Environmental Health and Hazard Risk Assessment: Principles and Calculations*, CRC Press/Taylor & Francis Group, Boca Raton, FL, 2012.
23. L. Theodore, *Chemical Reactor Analysis and Applications for the Practicing Engineer*, John Wiley & Sons, Hoboken, NJ, 2012.