



Nanotechnology: Clean Energy and Resources for the Future

White Paper for
Foresight Institute

October 2002

by
Stephen L. Gillett, Ph.D.

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Revised for the Foresight Institute
November, 2002

Stephen L. Gillett, Ph.D.
Dept. of Geological Sciences
Mackay School of Mines
University of Nevada
Reno, NV 89557

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ABSTRACT.

Although resource issues have a somewhat musty feel, they have not gone away: in the case of the US and other industrialized countries, they've merely been postponed by cheap foreign sources. In fact, conventional technology is exhausting its resource base at an accelerating rate, an acceleration exacerbated by the revolution of rising expectations in the less-developed world due to the global communications revolution.

Nanotechnology is the only way to resolve this dilemma that has the prospect of providing something like a sustainable First World standard of living for the entire world. Indeed, in the author's opinion this is most critical near-term application of nanotechnology.

Resource-related applications of nanotechnology include:

- **Greatly increased energy efficiency.**

Beyond Prometheus. Energy is used grossly inefficiently at present because it is largely used as *heat*, both in Carnot-limited engines and in thermal processing to manipulate matter via phase changes. Fuels are "burned"; that's what fuels are *for*, a mindset that might be termed the "Promethean paradigm." However, burning a fuel wastes most of its energy. Utilizing chemical energy without thermalizing it, as organisms do, requires molecular structuring. A near-term technological example is fuel cells.

Focused processing. Conventional processing also creates many by-products, which add to the costs both of purification and pollution control. However, highly specific catalysts that would generate only the desired product, in emulation of biological enzymes, require nanostructuring.

Distributed fabrication. When the slogan "matter as software" begins to come true, the enormous present transportation infrastructure will slowly become obsolete, as the massive importation of raw materials into conventional factories, and their re-export as finished products, begins to be supplanted by nanoscale fabrication from local materials—again, in emulation of biological capabilities.

- **Information-intensive energy extraction**

Sensing. Ubiquitous nanoscale sensing, an extension of microtechnologies already being deployed on an experimental basis, will lead to better management of oil and geothermal reservoirs, with significant savings.

Diffuse sources. In another elaboration of existing trends, customized and ultimately distributed fabrication will make energy collection from diffuse sources much more practical. Examples include the exploitation of small-scale mechanical sources such as low-head hydropower, tidal currents, surf, and "at wellhead" geothermal power.

More importantly, cheap large-scale fabrication of nanostructured materials, which would eliminate moving parts, promise a suite of energy applications including:

- *Direct use of solar power*, via photovoltaics or artificial photosynthesis.
- *Thermoelectric materials* to exploit small thermal gradients (e.g., geothermal or marine, as in ocean thermal energy conversion);
- *Piezoelectric materials* to convert mechanical stress directly into electric potential.

Efficient energy management. Cheap nanofabrication will also lead to such things as:

- *Materials for passive energy management*, such as electrochromic or photochromic "smart windows";
- *Efficient energy conversion devices* such as non-thermal illumination sources (e.g., "white LEDs");

- *Electrosynthesis* for fuel manufacture and electricity storage;
- *Better electricity storage devices* such as intercalation batteries and high-performance "ultracapacitors."

Superstrength materials. As materials having strengths approaching the ultimate limits set by chemical bonds become available, they will make transportation considerably more efficient through savings in vehicle mass. This will have a particularly pronounced effect on near-Earth space access.

- **Molecular separation**

Element separation, whether for pollution control or resource extraction, is not intrinsically energy-intensive, as is shown by the capabilities of biosystems. The enormous energy costs of present-day pyrometallurgy largely result from the application of heat to force phase changes to exploit the partitioning of elements between phases. Biosystems achieve their efficiencies by eschewing phase changes in favor of direct molecular separation via specialized molecular machinery. Such "biomimetic" molecular separation is an obvious goal even of primitive nanotechnological systems. It will have the effect of blurring the distinction between a "pollutant" and a "resource." Such technologies will also have energy implications through making accessible low-grade sources of nuclear fuels (e.g., U, Li) and by vastly decreasing the cost and difficulty of fuel reprocessing, although concerns about control of nuclear materials become more cogent. In any event, the 5000 year-old paradigm of digging up and "cooking" anomalous geologic deposits to extract desired materials is coming to its end.

- **Change of materials mix**

As nanoscale fabrication makes accessible the ultimate materials strengths set by covalent chemical bonds, the structural metals that dominate present technology will become obsolete. If carbon becomes the "ultimate material," the carbonate rock that forms the bulk of the crustal carbon reservoir becomes an important backstop resource. Indeed, the very silicates that make up most of a rocky planet become a valuable feedstock for a mature nanotechnology.

- **Off -Earth resources**

By vastly decreasing vehicle and payload mass, nanotechnology is likely to make near-Earth space access considerably more economic in the relatively near term. This may make off-Earth resources such as solar power satellites and asteroidal metal more attractive, though nanotechnological "end runs" such as molecular separation may make such sources obsolete even as they become practical.

1. INTRODUCTION

Nearly 30 years ago *Limits to Growth*, one of the most influential books of the 20th century, was published (Meadows et al., 1972). It purported to demonstrate, by means of a computer model, the imminent collapse of industrial civilization due to the exhaustion of critical resources. It was followed shortly by the 1973 "oil crisis," which immediately lent credibility to such scenarios. However, when gas lines went away and oil prices dropped in the 80s, many people concluded the crisis was "phony"—and by implication, resource shortages were too.

It wasn't, and they aren't. US oil production had peaked in 1970—not coincidentally, just before the "gas crises"—and suddenly we were at the mercy of the vagaries of foreign supplies. Despite this "wake up call," the US has made a societal choice since then to continue depending on cheap foreign oil. One result is that two numbers have been rising steadily since the early 1980s: US oil consumption, and the percentage that is imported. In 1999 the US produced 6.45×10^6 bbl/day oil (Oil & Gas Journal Databook, 1999), and imported 9.61×10^6 bbl/day (Oil & Gas Journal, 2000).

That cheap foreign oil is also limited. Duncan (2001) has developed a good case that global production of conventional oil will peak toward the end of this decade. When that happens, there will be no place left to import from. The $\sim 6 \times 10^6$ bbl/day of US domestic oil production ranks the US second among world oil producers, behind only Saudi Arabia. And it still isn't enough.

Mineral resources, obtained from geologically anomalous concentrations ("ores"), are also largely obtained from abroad. For example, the US produces no primary chromium (Papp, 2001) or manganese (Jones, 2001), both critical to steel manufacture. Meanwhile, because of a suite of reasons (high labor costs, high environmental costs, depletion of high-grade sources, an often hostile public and regulatory environment) mining in the US continues to dwindle so that the dependence on foreign sources continues to grow. For example, primary US copper production has dropped by $\sim 25\%$ since 1996, so that imports now account for about one-third of US copper demand (Edelstein, 2001).

Although the prospect of "imminent resource shortages" now has a somewhat musty feel, it's simply been postponed by cheap foreign sources. The author, who has worked professionally in resources for over 20 years, is used to the public's being out of touch with resource issues. They seem completely unaware of the utter US reliance on imported energy and minerals. But it's extremely disturbing that so many of the technical community also seem unaware of the degree to which the brave new high-tech future still relies on coal, oil, and minerals all ultimately—and messily—dug out from the Earth.

In addition, the global communications revolution is causing a worldwide revolution of rising expectations, which puts further pressure on the resource base. If nothing else, exporters now have other markets for those resources than the industrialized countries such as the US. Eventually domestic political concerns may make exporting resources politically impossible, as has already happened in many of the industrialized countries. The US no longer exports oil, for example, although it was once the world's biggest oil exporter and is still the world's second-biggest producer.

Finally, resource issues are being exacerbated by environmental concerns. As is well-known, present technology is polluting, and a major part of that pollution stems from the production and consumption of resources. Little of the material excavated from a mine ends up in finished products. Most is just waste, which is discarded in vast heaps that (at best) must be expensively reclaimed and revegetated. Reaction of some of these materials with water and air can cause further environmental degradation, as in acid-mine drainage. The extraction, transportation, and consumption of petroleum have familiar environmental hazards ranging from oil slicks to photochemical smog. Coal is abundant

and cheap, but byproducts of its combustion include acid rain and fly ash, and its mining is both dangerous and environmentally disruptive.

1.1. The Promethean Paradigm.

"The habit of neglecting or denying the possibility of technological advance is a common problem. ... Snug limits would simplify our future, making it easier to understand and more comfortable to think about. A belief in snug limits also relieves a person of certain concerns and responsibilities. After all, if natural forces will halt the technology race in a convenient and automatic fashion, then we needn't try to understand and control it.

"Best of all, this escape doesn't *feel* like escapism. To contemplate visions of global decline must give a feeling of facing harsh facts without flinching. ... Genuine courage requires facing reality, facing accelerating change in a world that has no automatic brakes."

[K. Eric Drexler \(1986, p. 166-7\)](#)

But not only is present technology exhausting its resource base while polluting the environment, it is also ludicrously inefficient and almost gratuitously dirty. No law of nature demands that things *must* be done this way.

Both the inefficiencies and the pollution come about largely through an overwhelming dependence on *heat*: on energy in its most disorganized and wasteful form. At least in Western culture, "technology" has been identified with "fire" since the legend of Prometheus. But fire turns out to be a clumsy and messy way of manipulating the world.

Other inefficiencies, and associated pollution, come about from what may be termed the "(dis)economies of scale." Because arranging matter with conventional technology is difficult, matter-organizers ("factories") have traditionally been large-scale, capital-intensive affairs to which raw materials are brought, and from which finished products are exported. This obviously requires an enormous transportation infrastructure, one of course that now subsumes the entire world. For example, bauxite, a tropical soil, is mined in Jamaica and sent to Norway for processing into aluminum (the electrolytic process for extracting aluminum requires vast amounts of electricity, and Norway has abundant cheap hydropower). Then the aluminum metal is sent around the world to be further fabricated into finished products. If the promise of distributed fabrication (section 2.2.5.) can be achieved—"matter as software"—this energy-intensive transportation network will become largely obsolete.

Another result of the present clumsy approaches to matter arranging is the unintended manufacture of unwanted byproducts. With little control over occurrences at the nanoscale, conventional synthetic processes yield a suite of molecular products, of which typically only one or two is desired. The others become waste that must be discarded or treated.

1.2. Beyond Prometheus.

Molecular nanotechnology (MNT), the design and construction of macroscopic materials at the molecular level, will play a major part of solving the issues of both sustainable resource extraction and byproduct mitigation. Indeed, in the author's opinion this is by far the most critical near-term application of MNT. Furthermore, MNT is the only technology that holds promise for achieving something like a

sustainable First-World standard of living for the entire world. Thus forswearing MNT is simply not an option, despite naïve calls for its "relinquishment."

The relevance of nanotechnology to resource issues falls into several broad categories. Some applications, involving proto-nanotechnology (e.g., nanostructuring by self-assembly) or even microtechnology, are already present in embryonic form. These can be expected to become more efficient and more prevalent as nanoscale control over fabrication matures. Other applications will require a more mature level of nanotechnology, even up to full-blown self-replicating molecular machines. Thus there are serious timescale issues in any discussion of MNT applications, and I have focused mostly on nearer term because of its importance. I also mention biotechnology where it seems particularly germane. After all, biotechnology merely involves exploiting natural molecular machinery, and its development costs are thereby minimized.

1.3. Applications of MNT to Resources.

For energy, the broad categories of MNT applications include:

1.3.1. Vastly improved efficiency of energy usage:

- *non-thermal energy usage*, via nanostructured devices such as fuel cells;
- *molecularly tailored catalysts*, for heightened selectivity and byproduct elimination;
- *high-strength materials*, which will decrease transportation costs, including access to space;
- *electricity storage and electrosynthesis*, both for portable power sources, and for chemical fuel generation;
- *distributed fabrication*, to minimize transportation infrastructure.

1.3.2. Information-intensive energy extraction:

- *extensive real-time sensing*, for better conventional resource extraction through (e.g.) reservoir management;
- *cheap nanofabrication*, which will make practical distributed collection from diffuse sources (e.g., artificial photosynthesis and low-head hydropower), as well as better energy management through such devices as "smart windows" and non-thermal light sources.

1.3.3. Solid-state energy generation:

- *solar power*, via photovoltaics and artificial photosynthesis;
- *thermoelectric conversion*, the direct solid-state transformation of thermal gradients into electricity;
- *piezoelectric conversion*, for direct conversion of mechanical energy into electricity.

For materials, categories include:

1.3.4. Molecular separation of elements and molecules:

- *non-thermal separation of solutes from solutions*, be they leachates, natural brines, or wastewater;

1.3.5. Change of materials mix, as high-strength covalently bonded materials replace metals in structural applications:

- "*waste as resource*," such as biowaste replacing petroleum as a source of reduced carbon compounds.
- *carbonate rocks (limestone)*, as the backstop resource of carbon on the planet;
- even *silicates*, the very stuff of a rocky planet, will become more valuable than nickel steel.

Finally, a separate note is appropriate on

1.3.6. Space-based resources:

- *space-based power systems*, through cheaper access to space and improved on-orbit fabrication.
- *space-based materials*, which will most likely be rare but important elements such as Pt.

These various points will be elaborated and illustrated below, with applications to particular energy sources sketched.

Finally, the author has tried to avoid ideological bias among different energy sources. Nanotechnology has much to offer in making practical "green" energy sources such as solar and wind. It also has much to offer in making practical sources such as nuclear power, which are considerably more controversial in some quarters. In the author's opinion, humanity can ill-afford to forego *any* energy sources, particularly on the basis of *a priori* ideological positions. In the end, choices are likely to be made on the basis of sheer economics, with due account taken of externalities.

2. NANOTECHNOLOGY AND ENERGY

Free energy—the "capacity to do work," in the formal physics definition—is the most fundamental resource. With a sufficient supply of free energy, almost anything can be carried out. The first law of thermodynamics states that energy cannot be created nor destroyed, but the critical constraint lies in the second law of thermodynamics. As usually expressed, the second law states that in an isolated system a quantity called *entropy*, with units of energy/temperature, must always increase in any spontaneous process. It can then be shown that entropy increase in turn implies that *free* energy cannot be recycled fully. Although total energy remains unchanged, less is available to carry out useful work. A certain amount is irretrievably lost, in practice generally as low-grade waste heat, which on Earth is ultimately radiated to space. (Many texts on thermodynamics and physical chemistry discuss the formulation of the thermodynamic laws at length. See [Moore, 1972, pp. 77-115](#), for example.)

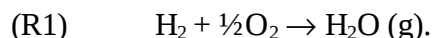
Hence, ongoing sources of free energy—or just "energy," loosely—are required for all biological and technological activity. Sunlight is the source for the biosphere. In the case of conventional technology a whole suite of sources is used, but the dominant source is fossil fuels. These have an energy density considerably higher than that of sunlight.

2.1. The Promethean Paradigm, I.

Nonetheless, energy could be used vastly more efficiently in technological processes. Present-day energy efficiencies lie anywhere from factors of several to orders of magnitude below the thermodynamic limits. In effect, the high energy densities of conventional fuels are a "brute force" compensation for the inefficiencies with which they are used.

The reason, as foreshadowed in the Introduction, is that energy is largely used as heat. "Fuels" are "burned"; that's what fuels are *for*, at least in conventional thinking. Indeed, "energy" often means just heat—a generally unexamined assumption that might be termed the "Promethean paradigm."

It turns out, however, that "burning" a fuel—i.e., converting its chemical energy into heat—discards much of its free energy, the energy available to do work. For an example, let us look at the reaction of H_2 and O_2 to form water vapor at standard temperature and pressure (STP, 1 atmosphere and 25°C):



For processes at constant pressure and temperature, typical of those at the surface of the Earth, the maximum useful work that can be obtained (or alternatively, the minimum energy cost of a thermodynamic transformation) is given by the Gibbs free energy:

$$(E1) \quad \Delta G = \Delta H - T\Delta S = \Delta U + P\Delta V - T\Delta S.$$

Here ΔH is the change in enthalpy (change in internal energy ΔU , plus any pressure-volume work $P\Delta V$ done), T is the absolute temperature, and ΔS is the change in entropy. Obviously, ΔG is a function of temperature. Since ΔH and ΔS are functions of temperature and pressure, ΔG is a function of pressure as well.

The $T\Delta S$ term, which has dimensions of energy, represents the "tithe" paid to the second law. It is a measure of the energy that is lost. Because the $T\Delta S$ term increases with temperature, the irreversible losses also are larger the higher the temperature at which reaction is carried out. Hence the maximum thermodynamic efficiency is given by $\Delta G/\Delta H$. For reaction (R1), for example, the Gibbs free energy at STP is some -228.6 kJ/mol, whereas the enthalpy is -241.8 kJ/mol. In the thermodynamic limit, therefore, some $-228.6/-241.8 \approx 95\%$ of the total reaction energy is available to do useful work.

This is far more efficient than conventional processes. Combustion heat from this reaction could instead be used to drive a heat engine. A heat engine turns some of the flow of heat from a hotter body to a cooler body into useful work, and the maximum efficiency at which it can do so is the Carnot efficiency:

$$(E2) \quad e_C = (T_h - T_c)/T_h,$$

where T_h is the absolute temperature of the hot body and T_c that of the cold. The Carnot limit can be derived rigorously from the second law of thermodynamics (e.g., [Moore, 1972, p. 78-85](#)).

For example, the heat from stoichiometric combustion of H_2 and O_2 to form one mole of water could be used to form 3.8 moles of steam at 550°C (823 K) at a pressure of $\sim 2.1 \times 10^7$ Pa (3000 psi), which are typical operating conditions for a modern steam-turbine electrical generating plant (e.g., [Peltier, 1995](#)). The limiting Carnot efficiency, assuming discharge to a reservoir at 25°C (298 K), is then only:

$$e_C = (823-298)/298 = 63.8\%.$$

In practice, however, the Carnot limit doesn't apply even theoretically. For engineering convenience the steam will be allowed to expand as nearly isentropically as possible, as part of a so-called Rankine cycle, and this expansion will do work by spinning the turbine blades. The entropy of the steam at high pressure is 177.0 J/mol K. Its enthalpy (which is just its heat content, as no chemical reactions are occurring) is 63.8 kJ/mol (Meyer et al., 1979). If this steam is expanded to a pressure of 3386 Pa (1 inch Hg, a typical value) the enthalpy at the same entropy is 38.0 kJ/mol. The limiting efficiency is then only $(63.8-38.0)/63.8 \sim 40\%$. As can be seen, the Rankine cycle is considerably less efficient than even the Carnot cycle.

A great deal of the free energy potentially available has been sacrificed by converting the chemical energy of the fuel into heat, and this conversion is *not* required by the laws of thermodynamics. These are limits set by particular technological approaches. We have had the "heat" crisis, not the "energy" crisis.

2.2. Specific Technological Approaches: MNT and Energy Efficiency.

Before sketching specific aspects of MNT applications to energy, some generalizations on the technological issues are worth highlighting:

- nanoscale structuring at an *interface* is fundamental to a great many applications, including:
 - catalyst surfaces (section 2.2.2.);
 - large-area semiconductor *p-n* junctions, critical to thermoelectric (section 2.4.1.) and photovoltaic (section 2.5.10.1.) materials;
 - nanolayered structures, such as for high-performance capacitors (section 2.2.4.1.b.), thermoelectric materials (section 2.4.1.), multijunction photovoltaics (section 2.5.10.1.), piezoelectric stacks (section 2.4.2), and sensitized photosynthetic materials (section 2.5.10.2.).
- *solid electrolytes* prove to be widely applicable:
 - critical in fuel cells (section 2.2.1.1.) and supercapacitors (section 2.2.4.1.b.)
 - relevant to intercalation batteries (section 2.2.4.1.a.), smart windows (section 2.2.6.), electrocatalysis (section 2.2.4.2.), and also to ionic separation (section 3.3.1.4.a.).

Such applications have no moving parts other than electrons and (in some cases) individual ions. They therefore seem accessible to very primitive approaches to molecular structuring such as self-assembly and *chimie douce**. I elsewhere have suggested that "near-term" nanotechnology is likely to involve molecularly structured *materials* rather than full molecular machines (Gillett, 1996a). Hence it seems fortunate that much energy-related nanotechnology seems to fall in this category. However, for

* Literally "soft chemistry," a rubric for a variety of techniques to obtain highly structured or metastable phases by low-temperature modification of host phases that does not affect the original crystal structure. These include ion exchange, replacement or alteration of surface-exposed moieties ("functionalization") by reactive reagents, and so on. *Chimie douce* methods have attracted an enormous amount of attention over the last few decades, and have resulted in the preparation of numerous materials not accessible by standard synthesis techniques (e.g., Figlarz, 1988, 1994; Gopalakrishnan, 1995; Levin et al., 1996; Rouxel, 1996).

bulk energy generation large quantities of material are required, and this remains a significant challenge to make cheaply.

2.2.1. MNT vs. *Prometheus*.

As might be expected, transforming chemical energy without thermalizing it requires controlling the reactions at the nanoscale. (Nearly the only advantage of fire is that it's simple.) Thus MNT promises to make such transformations considerably more practical.

As usual, biosystems are far ahead of technology. Even though organisms are loosely spoken of as "burning" food for energy, biological systems are not heat engines and so are not Carnot-limited. Rather than converting the energy of chemical fuel (i.e., food) to heat, and converting only some of that heat to work as it flows to a cooler body, living things oxidize their fuel non-thermally, via a cascade of molecular-scale mechanisms that approach the reversible limit set by the difference in free energy. Since they carry out their chemical processes isothermally in the range 25-40°C or so, the irreversible losses are also much lower (that is, the TΔS term is much smaller).

2.2.1.1. Fuel cells. Probably the best example of a technological non-thermal conversion device is a fuel cell, which transforms chemical energy directly into electricity (e.g., [Kantha & Grimes, 1994](#)). Fuel cells first attracted attention in the 19th century, but although practical fuel cells have been around since the 1960s, only recently have they begun attracting serious attention outside high-value niche markets such as spacecraft. They have been beset with two problems: high cost due to fabrication issues and limited lifetimes, and restriction to hydrogen as the fuel.

In large part both problems stem from the limited current capabilities in nanofabrication. As might be expected, converting chemical energy to electricity without thermalizing it requires nanostructuring. In fact, the failure of 19th century attempts to convert coal electrochemically into electricity, as well as the long delay in commercializing fuel cells, probably stem from the need for cheap nanofabrication.

The two main nanofabrication issues are first, better catalysts, which ideally would be

- tolerant of common contaminants such as CO and sulfur species;
- work at room temperature;
- work with C-containing fuels, not just hydrogen;
- cheap!

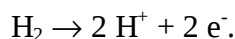
Unsurprisingly, no current catalysts fit these desiderata, most especially the last.

The second issue is better solid electrolytes. As described below, fuel cells require that ions be conducted between anode and cathode to compensate the electron flow in the external circuit, and ideally this flow would occur in the solid state.

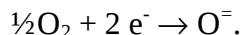
These two issues will be elaborated below.

2.2.1.1.a. Fuel cell catalysts. The nanotechnological prospects for catalysts are overviewed in the next section. Here just the issues relevant to fuel cells are highlighted.

Fuel molecules in a fuel cell must be ionized to react. Indeed, the fuel cell can be thought of as intercepting the electrons transferred during the oxidation reaction to do useful work. Hence one catalyst must promote ionization of fuel at the anode, e.g.:



while at the cathode another must promote the reduction of dioxygen by electrons with as low an overvoltage as possible:



Platinum-group metals (PGMs) are usually used at the anode because of their high activity (Hamnett, 1996). They obviously add significantly to the cost, however. Hence catalyst usage must be minimized, which at least involves nanostructuring of the interface so that precious-metal atoms are deployed most effectively. Even better, of course, would be the development of alternative catalysts not using rare elements. The current catalysts are also susceptible to "poisoning" (deactivation through impurities that bind to and block the active sites), particularly CO and sulfur compounds. For this reason even current "low temperature" fuel cells run at temperatures significantly above ambient (>70°C up to several hundred °C, depending on the electrolyte), as the poisoning agents tend to desorb at higher temperatures. However, not only is high temperature operation considerably less convenient, it also imposes an additional thermodynamic cost in lessened efficiency.

At the cathode, cheaper catalytic materials (e.g., transition metal oxides) can be used, but rapid reaction without the use of high overvoltage is still a limiting factor, especially near room temperature (e.g., Hamnett, 1996).

Because they use specific molecular mechanisms, non-thermal converters like fuel cells are also much more "picky" about their reactants than is combustion, as is indeed shown by their sensitivity to catalytic poisoning. In particular, fuel cells that could use carbon-containing fuels (e.g., CH₄, CH₃OH) would be much more adaptable to the current mix of fuels. Liquid carbon-containing fuels are also considerably easier to store and handle than H₂. Hydrogen is particularly inconvenient for transportation applications because H₂ storage imposes a substantial weight penalty.

Alcohol fuels would be particularly attractive because they are common products of bio- and technological syntheses. They also are more reactive than hydrocarbons, which makes the catalysis less demanding. Furthermore, because they are water-miscible they are less convenient for combustion engines. Purifying ethanol derived from fermentation, for example, is a major expense for ethanol to be used as fuel. Indeed, if purification is carried out thermally (!), by distillation, there is probably a net energy cost (Giampetro et al., 1997). This issue would vanish if diluted ethanol could be used directly in a fuel cell.

Unfortunately C-tolerant fuel cells are still experimental. No catalyst that can activate C-C bonds at room temperature has yet been found, which precludes the use of conventional hydrocarbon fuels (Hamnett, 1996). Poisoning by CO and H₂S are also more serious issues. Hibino et al. (2000) demonstrated a "low-temperature" (773 K) solid-oxide fuel cell that is CO tolerant and can operate on small multicarbon hydrocarbons such as propane, but its "low-temperature" operation is merely relative.

The C-H bond is also difficult to activate electrocatalytically, but an experimental fuel cell using CH₄ has been demonstrated (Bergens et al., 1994). However, methanol is both more reactive and, being liquid, more convenient than methane. Unlike ethanol, it also has no C-C bonds. Hence the so-called "direct methanol" fuel cell has received a great deal of attention (e.g., Goodenough, 1992; Hamnett, 1997). Unfortunately, with present catalysts the most practical direct-methanol fuel cell requires methanol vapor, so that it still operates at elevated temperatures.

2.2.1.1.b. *Fuel cell electrolyte.* All fuel cells also require an electrolyte between the cathode and anode to conduct ionic species so that they can react, and fuel cells are commonly classified by the nature of this electrolyte (Figure 1). Liquid electrolytes have been used in "traditional" fuel cells. Examples include the "classical" alkaline cell, used on the Apollo missions, in which the electrolyte is aqueous KOH operating at $\sim 70^\circ\text{C}$ (Hamnett, 1996). Phosphoric acid and molten carbonate fuel cells are not poisoned by CO_2 as is the alkaline cell, but they also operate at considerably higher temperatures.

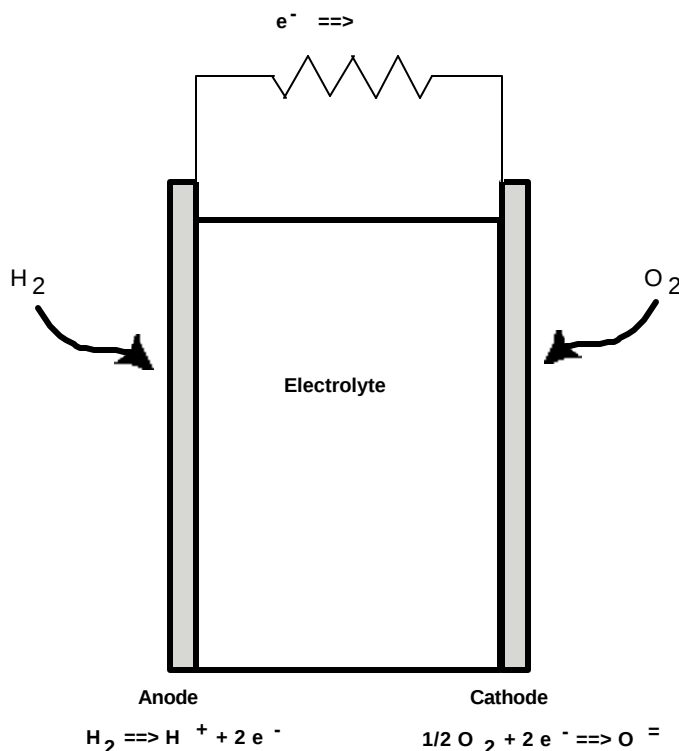


Figure 1.

Figure 1: Fuel cell. Fuel cells convert the energy of a redox reaction directly into electricity, in essence by intercepting the flow of electrons from the oxidant to the reductant to drive an electrical circuit. For illustration, in this diagram the reductant (fuel) is H_2 while the oxidant is atmospheric O_2 , but conceptually any fuel would work similarly. The practical issue lies in the electrodes, which must catalyze the ionization of oxidizer and fuel without significant degradation. In any fuel cell, an ionic flow in the electrolyte must also compensate the external electron flow.

Although they have the virtue of simplicity, liquid electrolytes have serious deficiencies. Corrosion of the electrodes places major constraints on their possible compositions, and high temperature operation also decreases thermodynamic efficiency. Containing hot, corrosive liquid also does not decrease the engineering difficulties.

All-solid-state fuel cells are thus attractive. They require a *solid electrolyte*, a substance that conducts ions while remaining in the solid state (e.g., [Rickert, 1982](#)). Present-day fuel cells operating near room temperature that use H_2 incorporate a proton-permeable membrane, which conducts protons from anode to cathode. The material used in commercial units is Nafion, a solid fluorocarbon polymer. It is hardly ideal, being expensive and subject to degradation through dehydration. As with any conventional polymer, too, there is hardly nanoscale control in its synthesis. The membrane pores are not uniform in size or distribution, and the surface active sites involved in proton binding and release are haphazardly exposed. Thus there is much effort directed toward finding alternative proton-conducting materials ([Peled et al., 1998](#)).

Other solid electrolytes are 3-D crystal structures. These work by having many ionic site vacancies: under the influence of an electric field an adjacent ion can hop into the vacancy, leaving a new vacancy behind. Thus in effect the vacancy moves, analogous to the motion of a "hole" in a semiconductor. Obviously (and unfortunately), however, this hopping works best at high temperature, where the thermal motion of the ions makes them easier to move. For example, one of the most practical solid electrolytes is presently doped ZrO_2 , the basis of so-called "solid-oxide" fuel cells, but it is only effective $>600^\circ C$ (e.g., [Rickert, 1982](#)). The crystal fundamentally consists of close-packed O^{2-} ions, which include the Zr^{4+} cations in the interstices. Substitution of (e.g.) $\sim 10\%$ Y^{3+} , instead of Zr^{4+} , however, leaves some O^{2-} sites vacant to preserve charge balance. Oxygen anions can therefore migrate toward the anode. In this case, too, the oxygen anions are obviously the mobile species.

Such high-temperature operation obviously severely limits potential applications, and as mentioned decreases the ultimate thermodynamic efficiency substantially. However, a large number of void-bearing crystalline structures is known, such as the *zeolites*, open frameworks based on corner-sharing SiO_4 and AlO_4 tetrahedra. Such "molecular sieve" materials, in which the crystal structure is traversed by molecular or supramolecular-scale channels, may provide alternative solid electrolytes for cations, especially for small cations such as H^+ . Unfortunately, currently accessible structures are impractical, as they have conductivities several orders of magnitude lower than alternative ionic conductors (e.g., [Kelemen et al., 1989](#)). Part of the problem, however, is that the zeolites tested were polycrystalline aggregates consisting of tiny ($\sim 1\ \mu m$) unoriented crystals, so the bulk conduction properties probably reflect a great deal of grain-boundary and surface effects. Hydration of the cations can also increase their effective size and thus decrease their mobility significantly ([Rees, 1978](#)).

Perhaps more promising are open frameworks formed by redox-active elements such as W. These are already known to take up ions, including H^+ , in some cases. Reduction of framework ions draws in such small counterions to maintain charge balance. Such intercalation is the basis of lithium batteries (section 2.2.4.1.a.) and electrochromism (section 2.2.6.), and it seems directly relevant to solid electrolytes. Zeolites cannot work in this way, because neither Si nor Al has oxidation states separated by a single electron.

In any case, nanoscale fabrication of solid electrolytes, such as megascopic single crystals, is likely to be important for practical low-temperature fuel cells.

2.2.2. Catalysis.

Catalysts, of course, cause a thermodynamically favorable reaction to occur under circumstances where it otherwise wouldn't. They do so by decreasing the activation energy to reaction via molecular-scale interactions.

Three parameters, which are commonly independent, describe catalysts: their *activity*, or how effective they are at promoting a desired reaction; their *selectivity*, or the degree to which they promote the desired reaction only; and their *stability*, or resistance to degradation while operating. All are important for energy efficiency. Activity is important for minimizing the amount of catalyst required. Selectivity is even more important, because the greater the degree to which the desired product is formed, the fewer the unwanted by-products, and thus the less the purification and disposal costs. Finally, a practical catalyst must remain active over millions of catalytic cycles before requiring replacement or reactivation.

Homogeneous catalysts are mixed in with the reactants. Because they are molecular, they can be highly selective, but they have the serious disadvantage of being difficult to separate from the reacting fluid. *Heterogeneous* catalysts are solids, with catalysis taking place at the interface between the solid and the fluid phase containing the reactants. They are considerably easier to use because the catalytic surface (which commonly is a high-surface area solid fixed in place) is separate from the reactants and products. Heterogeneous catalysis is intrinsically more complicated, however, because the selectivity and activity are intimately bound up with atomistic details of the surface structure. Often the very nature of the "active sites," where catalysis occurs, is uncertain. Traditionally, therefore, catalysis is an "art" that relies on a host of empirical observations with limited understanding of the actual molecular mechanisms.

This is changing, as understanding continues to improve at a molecular scale (e.g., [Somorjai, 1984, 1986, 1990](#); [Bond, 1993](#)). For example, electronic modification of the catalytic surface by adatoms, which is critical both in poisoning and "promotion" of catalytic activity, has been modeled (e.g., [Feibelman & Hamann, 1985](#); [Maclaren et al, 1986](#)), and the mechanisms of catalyst activity are now the subject of detailed modeling at the molecular level (e.g., [Catlow & Thomas, 1992](#)). Despite such improvements, the empirical basis of practical catalysts has hardly vanished. [Schlögl \(1993\)](#) called practical catalysis "still magic," which occasioned a heated discussion ([Thomas & Zamaraev, 1994](#)).

Even if the catalytic mechanisms are understood, with conventional fabrication techniques there's little nanoscale control over structures that direct those mechanisms. Hence conventional syntheses, although not quite at the eye-of-newt-by-the-light-of-the-full-Moon level, are empirical recipes that commonly are poorly reproducible. In many cases one batch of catalyst differs enough from the next that the chemical processes have to be adjusted for each new batch (R. Phair, pers. comm., 1997).

[Zuburtikudis & Saltsburt \(1992\)](#) used conventional microtechnological techniques to prepare well-characterized catalytic surfaces, the idea being to isolate the variables relevant to catalytic activity. Although their study had an experimental focus, being able to structure catalyst surfaces directly at the nanoscale would obviously be extremely attractive. This is another obvious near-term application of nanofabrication techniques that fall short of full molecular machinery. Indeed, fabrication of "high technology" catalysts has been proposed using extensions of conventional microtechnology techniques ([Ribeiro & Somorjai, 1994](#)). The structuring of catalyst surfaces could also be an application of the primitive "molecular looms" I have previously suggested ([Gillett, 1996a](#)). Catalysts have a strong "multiplier effect" because each catalytic site is used repeatedly. Hence even a modest amount of nanostructuring, such as might be carried out by ganged scanning-probe microscopes, could yield a useful amount of product. The short-term potential thus seems especially high.

One last issue of great practical importance is worth mentioning. Most complex compounds, such as pharmaceuticals, occur in "mirror-image" ("chiral") forms, and generally only one "handedness" is biologically active. Indeed, the other so-called "enantiomer" is commonly toxic or otherwise

undesirable. Hence, there is currently enormous interest in chiral-selective syntheses, an especially high-value market since it is focused on pharmaceuticals.

2.2.3. *High-strength materials.*

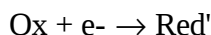
A result from elementary materials science is that macroscopic materials are far weaker, typically by 1-2 orders of magnitude, than would be inferred from the strength of the chemical bonds making them up. The reason is that macroscopic materials are dominated by microscale and nanoscale flaws, from crystal dislocations to intracrystalline grain boundaries, and these flaws control the macroscopic strength (section 3.5.1.). One of the most promising applications of nanofabrication is the construction of materials that are essentially defect-free at the atomic level, such that their strength approaches the limit set by chemical bonds. (Such capabilities will also have profound implications for the mix of desired raw materials, as discussed at length in section 3.5.1.) Because strong materials involve no molecular moving parts, they are also likely to be accessible in the nearer term as their fabrication need not be carried out by full-blown molecular machines.

The stronger a material, the less required for a given application. This mass savings is likely to have its greatest effect on transportation by decreasing the weight of vehicles. Even though the sheer volume of transportation, particularly for bulk commodities, is likely to dwindle as nanotechnology matures, travel is unlikely to vanish. At least in the relatively near term, moreover, high-strength materials will also be useful for such macroscopic moving parts as turbines.

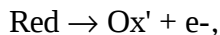
2.2.4. *Energy storage.* The storage of electricity is a particularly pressing problem. It consists of two parts, of which the first is the less important:

2.2.4.1. *Portable power sources.* The inadequacy of current batteries for powering the welter of new portable electronic (and electric) devices is well known. Nanotechnological fabrication can probably contribute here.

2.2.4.1.a. *Batteries.* A battery is an electrochemical device that generates DC through a coupled set of redox reactions. The positive electrode is reduced:

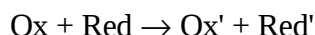


while the negative electrode is oxidized:



the electron transfer being responsible for the generated current. If the battery is reversible, application of current in the opposite direction regenerates the original species Ox and Red from Red' and Ox', respectively.

In the reversible limit, the energy obtained is the Gibbs free energy for the reaction:



which is also equal to the charge Q transferred times the change in potential, in volts:

$$(E3) \quad \Delta G = Q\Delta V.$$

For real substances $\Delta V < \sim 4$ V (e.g., [Conway, 1991](#)).

Intercalation-based batteries, generally using the small Li^+ ion, have attracted a great deal of attention in recent years because of their higher energy densities. In such batteries, at least one redox-active electrode has an open crystal structure with voids capable of intercalating Li^+ ions. In so-called "rocking chair" batteries (e.g., [Tarascon & Guyomard, 1993](#); [Thackeray et al., 1995](#); [Exnar et al., 1997](#)), both electrodes can take up Li^+ . During discharge Li^+ is expelled from one electrode and taken up by the other.

In commercial batteries, for example, oxidation of Co in LiCoO_2 expels Li^+ , which is taken up in a graphite anode. Recharge of the battery involves re-reduction of Co with concomitant take-up of Li^+ . In effect an intercalation electrode greatly boosts the surface area at which redox reaction can take place, which improves energy storage while also maintaining recharge capability.

Many fabrication issues arise with such batteries. Obviously a redox-active crystal structure capable of *reversibly* intercalating small ions is required. One mechanism for degradation of such batteries is by irreversible changes in the crystal structure on deintercalation, through mechanisms whose molecular details remain somewhat obscure. The crystal structure must also be fabricated with near-nanoscale precision. LiCoO_2 turns out to be accessible with conventional fabrication methods, but others would be attractive if they could be synthesized reproducibly (e.g., [Koksbang et al., 1996](#)). Overall, it seems that a capability of fabricating such structures with nanoscale control would make such batteries cheaper and more practical.

2.2.4.1.b. *Capacitors.* A capacitor is, of course, an alternative way to store electricity. The energy of a capacitor is given by:

$$(E4) \quad E = \frac{1}{2}CV^2 = \frac{1}{2}QV,$$

where C is the capacitance, V the voltage, and Q the charge. Thus, for a given charge and voltage, a capacitor stores half as much energy as a battery ([Conway, 1991](#)). For a parallel plate capacitor, the capacitance is given by:

$$(E5) \quad C = \epsilon_0 \kappa A/d,$$

where ϵ_0 is the permittivity of free space, κ is the dielectric constant of the spacing material, A is the plate area, and d is their separation (all SI units). Obviously, increasing capacitance requires increasing A and/or κ , and/or decreasing d .

Even though capacitors are less efficient than batteries at energy storage *at the same voltage*, the voltage of batteries is limited by the potential of redox reactions. Capacitors are less limited: by equation (E4) the energy storage goes up as the square of the voltage. However, the voltage across a capacitor cannot increase arbitrarily because at some voltage the capacitor "breaks down" through charge crossing the gap d . Capacitors thus involve a tradeoff between a larger d to maximize the breakdown voltage, and a smaller d to increase capacitance. In electrolytic capacitors, for example, a thin oxide film is formed atop a metal foil by electro-oxidation, and this film serves as the

dielectric. The thicker the film, the more resistant the capacitor to breakdown, but the smaller its capacitance. In any case, d must be large enough that electron tunneling is unimportant.

Improved dielectrics provide both a way to boost the dielectric constant and minimize d . Interest in better dielectrics was inspired decades ago by ferroelectric materials such as BaTiO_3 . This compound has a distorted perovskite structure (Figure 2), which consists of apex-sharing TiO_6 octahedra with the large voids between the octahedra occupied by the Ba^{++} ions. The TiO_6 octahedra are sufficiently distorted that the Ti^{4+} ions can "rattle around," which leads to very high polarizability (i.e., dipole moment), and hence to a large dielectric constant as well as to ferroelectricity.

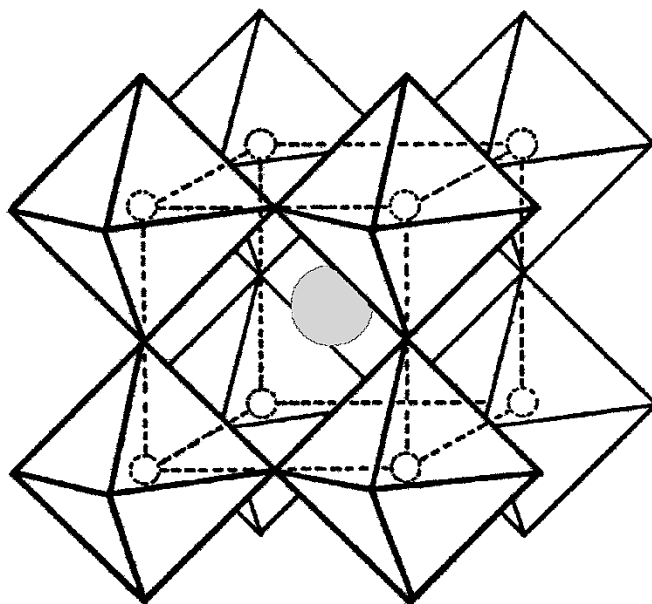


Figure 2.

Figure 2: Perovskite structure. An oxygen anion lies at each vertex shared between the octahedra. Small cations (e.g., Ti^{4+}), denoted by the small open circles, lie at the center of each octahedron. The large site between the octahedra is occupied by a large cation (e.g., Sr^{2+}). This site may be unoccupied, as in stoichiometric WO_3 (the so-called "ReO₃" structure). Generally the cubic symmetry of the ideal perovskite structure is distorted, especially if the large site is empty or only partly occupied.

More recently, a combination of very high surface area and very small charge separation has been achieved with so-called "double layer" capacitors. A "double layer" is formed at the interface between a charged surface and an electrolyte, because ions of opposite charge are attracted from the electrolyte to form a compensating layer (Figure 3). This acts like a capacitor in which the distance d (equation (E5)) is of the order of tenths of nanometers. On discharge of such a capacitor, electrical current flows between the electrodes while a compensating ionic current flows in the electrolyte. In conjunction with high-surface-area nanoporous electrodes, such as carbon aerogels (e.g., [Pekala et al., 1998](#)), this leads to extraordinarily high capacitances, on the order of farads per gram. Unfortunately, however, the voltage is limited by the breakdown voltage of the electrolyte (~1.2 V, in case of aqueous

solutions). Alternative electrolytes, especially solid electrolytes, promise to improve this value considerably. Experimental double-layer capacitors have been fabricated using a proton-conducting solid polymer electrolyte (Peled et al., 1998).

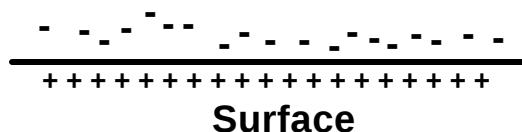


Figure 3.

Figure 3: Double layer. A charged surface, such as an electrode, in contact with an electrolyte attracts an "atmosphere" of compensating counter-ions from the solution, forming the so-called "double layer."

Finally, "supercapacitors" (Conway, 1991) or "ultracapacitors" (Liu & Anderson, 1997) are capacitors that store additional energy through surface redox reactions, a phenomenon termed "pseudocapacitance" (Huggins, 1996; Conway et al., 1997). Typically they are based on high-surface-area transition metal oxides. RuO₂ has had the best performance, but cheaper alternatives show much promise (e.g., Liu & Anderson, 1997; Lee & Goodenough, 1999ab). Specific capacitance 10-100 times higher than simple double-layer capacitors has been observed. They exhibit transitional behavior between capacitors and batteries, and so seem reminiscent of the "batacitor" postulated by science-fiction author Philip José Farmer (1971). Indeed, the electrodes in intercalation-based batteries also have some analogies (Conway, 1991).

Many issues arise in high-performance capacitors that could be addressed by better control of fabrication at the nanoscale. Carbon-based capacitors are plagued by high resistance due to the vagaries of the grain-grain contacts on which conduction relies. Individual capacitor elements can be "stacked" to yield high voltages (e.g., Bullard et al., 1989), but achieving this requires building a nanolayered structure with repeated "sandwiches" of electrode-electrolyte-electrode. Of course, if such capacitors are not to be restricted to niche markets, the nanofabrication must also be carried out *cheaply*.

2.2.4.1.c. Fuel cells. Alternatively, perhaps batteries and capacitors are a dead end except in niche markets. Maybe laptop computers and such will be better powered by small fuel cells, which potentially have much higher energy densities. One idea would be a metal hydride fuel pack that would exsolve hydrogen in a controlled manner. On its exhaustion, it would be swapped out, just like a conventional battery, and could then be recharged with H₂. If fuel cells that can use C-bearing fuels (e.g. methanol) can be perfected and miniaturized (section 2.2.1.1.), portable electronic devices may instead be simply fueled, rather as one today might fuel a cigarette lighter.

2.2.4.2. Electrosynthesis. The second, related but perhaps more important electricity-storage issue is the lack of a good way of storing large amounts of electricity, the immediate output of a great many energy-conversion systems. It turns out that a related issue is the long-term synthesis of liquid fuels. Because of their ease of handling, owing to their high density coupled with mobility, liquid fuels dominate transportation applications. At present, of course, they are largely obtained from petroleum.

In the future alternative fuels will be required, even though they will no longer be "primary" energy sources like petroleum but a merely a convenient form for storage and usage.

Electricity can be used to drive chemical reactions "uphill," as in the familiar example of electrolysis of H_2O into H_2 and O_2 . More complex transformations are termed *electrosynthesis*. *Electrocatalysis* is the term applied to catalysts activated by electric potential. Properly it should not be applied to reactions driven uphill, but this distinction does not seem to be made consistently.

A recent example is the ambient-pressure electrosynthesis of NH_3 directly from N_2 and H_2 (Marnellos & Stoukides, 1998). The current Haber process for synthesizing NH_3 is a paragon of the thermal paradigm, involving direct reaction of H_2 and N_2 at high pressure and red heat. Methanol electrosynthesis in acetonitrile has also been demonstrated (Pierre & Ziade, 1986). Perhaps reactions like those carried out currently thermally by catalysis of syngas (section 2.5.3.2.) could instead be carried out at low temperatures by electrosynthesis or electrocatalysis.

Solid electrolytes are again especially important, because they allow driving and controlling the reactions of ions to form new species. For example, in some cases reaction rates can be varied over orders of magnitude by varying the applied electrical field through the medium of a solid electrolyte (e.g., Lintz & Vayenas, 1989; Gur et al., 1991). Indeed, as electrosynthesis is formally just the reverse of electricity generation in a fuel cell, it has a broad synergy with fuel-cell research (e.g., Bebelis et al., 1993), both in catalysis and in solid electrolytes.

As discussed in section 2.2.2., the degree of selectivity of catalysts is of great economic importance in maximizing efficiency and minimizing byproducts. The nanoscale modification—"functionalization"—of electrode surface properties is also a focus of much recent work in electrochemistry (e.g., Rolison, 1990; Murray, 1992). One focus of such functionalization is to induce highly specific binding of reactive species to the electrode. This is an alternative approach to highly specific electrocatalytic reactions.

2.2.5. MNT, nanofabrication, and distributed fabrication.

Since the onset of the Industrial Revolution, the organization of matter has become progressively cheaper. A more recent trend is miniaturization: the dwindling cost of organizing matter at smaller and smaller scales. The progress from vacuum tube to transistor to ever more densely packed microchips is a familiar example.

MNT will continue both these trends, and in those cases it is evolutionary rather than revolutionary. The trends are important to energy applications nonetheless. How cheaply nanostructured materials can be fabricated will be crucial in exploiting diffuse energy resources, as emphasized in the discussions above and below. Conventional microtechnology, for example, is not nearly cheap enough for such bulk applications. A computer is relatively cheap only because the chip at its heart is so small. The present high cost of microfabrication is the major problem that besets photovoltaics, for example (section 2.5.11.).

A newer trend that MNT will also accelerate is "custom" rather than "mass" production. Not only is fabrication becoming cheaper, it is also becoming more flexible. This is due, of course, both to increased computer power and to computer-controlled design and manufacture.

In the long term, probably the most important effect of MNT is what might be termed "distributed fabrication": the local construction of artifacts out of local materials. The idea can be summed up by the slogan "Matter as software." Technologically this is a considerably more revolutionary advance, but it

merely replicates what biological systems do already. A plant, for example, is not assembled by sending off to the leaf factory, and the root factory, and the stem factory, and so on. These items are assembled from ambient sources according to a molecularly encoded digital instruction set: its DNA.

Distributed "fabrication" (or better, "distribution") is already happening with information products. Consider journal articles downloaded as .PDF files, rather than mailed as paper copies, or music distributed as .MP3s rather than as packaged CDs. Even this embryonic sort of distribution has the potential of significant savings in conventional resources through minimizing paper and plastic usage as well as transportation costs. Of course, further growth in such distribution will be as much a function of legal and institutional constraints as it is of technology.

Obviously such a capability will have a huge effect on the global transportation network. The enormous energy demand involved in simply moving around partly organized matter will largely vanish. Of course, undoubtedly there will be a transition period. For example, simple chemical feedstocks are likely to be locally fabricated before complex machinery, much less foodstuffs. But since the transportation of bulk commodities such as raw ores currently accounts for a significant part of global energy costs, even primitive distributed capabilities will have a non-negligible effect.

2.2.6. *Passive energy handling.*

Passive energy handling is not so glamorous as the exploitation of raw energy sources. Nonetheless, it could make a significant contribution to the energy mix. Consider the 0.44×10^{18} J (0.42×10^{15} BTU) expended on household air-conditioning in the US alone in 1997 ([US DOE-EIA, 2001](#)).

2.2.6.1. *Smart materials.* A major part of the climate-control costs in modern buildings simply stem from waste heat, mostly dumped by the lighting system. Conventional incandescent lights exemplify the inefficiencies of the thermal paradigm. They are *considerably* better heaters than illuminators. A filament at 2500 K, assuming blackbody radiation, radiates ~96% of its output in the infrared. Even conventional fluorescent lights dump a great deal of waste heat. Thus, simply converting electricity into visible light with greater efficiency would yield energy savings, both directly in minimizing illumination costs, and indirectly in minimizing the costs of dealing with waste heat. Light-emitting diodes (LEDs) that emit white light are attracting serious attention now as low-energy alternatives to conventional lamps (e.g., [Tamura, 2000](#)), and again the main issue in making such alternatives practical is cheap nanofabrication (cf. [Scheel, 2000](#)).

Unwanted solar heating is of course also important, at least in summer. Using *electrochromic* layers to darken windows has attracted a great deal of attention (e.g., [Baucke, 1985](#); [Oi, 1986](#); [Deb, 1992, 1995](#)). Electrochromic materials change color under an applied electric field. Much attention has been directed toward Li^+ intercalation into WO_3 (e.g., [Passerini, 1989](#); [Rauh & Cogan, 1993](#); [Cogan et al., 1997](#); [Forslund, 1997](#); [Zhang et al., 1997](#)), which has an open distorted perovskite structure. Electrochemical reduction of some of the framework atoms from W^{6+} to W^{5+} puts the additional electrons into the conduction band, where they become delocalized to yield typical metallic behavior. The material thus changes from transparent to reflective. Charge balance is maintained by intercalation of the Li^+ ions. Reversal of the applied potential reoxidizes the W to W^{6+} , with expulsion of the Li^+ ions and loss of reflectivity. Obviously, construction such a window, particularly of significant area, presents a nanofabrication challenge.

In "photochromic" systems, the color change is driven instead by photon absorption, a particularly attractive feature for a self-shading window, or "smart window." In the 1960s, swift self-darkening under the sudden intense illumination of a nuclear explosion was also of military interest for protective sunglasses (Bertelson, 1971a). One type of photochromic glass relies on reversible photodriven redox reactions of dispersed nanoparticles, typically a silver halide (Araujo, 1997). An elegant new approach, however (Kostecki & McLarnon, 2000), combines electrochromic WO_3/Li -electrolyte layers, described above, with a layer of photoactive semiconductor. The current generated by the illuminated semiconductor provides the electric potential to drive intercalation and darkening. To be practical, however, such a system obviously requires low-cost fabrication of large-area nanolayered structures.

2.2.6.2. High-temperature superconductors. At present electricity is commonly sent long distances from its place of generation to its place of use. In part this is unavoidable: sites for hydropower dams, for example, commonly lie far from electrical markets. In fact, when they were built in the 1930s Hoover and Grand Coulee dams lay in remote wilderness. In part, however, this is due to the clumsiness of present technology. Because of present "economies of scale," thermal power plants must be large, and due to the pollution they generate it is often politically convenient to site them far from the markets they serve. Many coal-fired generation plants, for example, lie hundreds of miles from their urban California markets (e.g., Valmy and Mojave, Nevada; Page, Arizona). Because of issues of safety and land costs, the ground receivers for solar power satellites (section 4.1.) are also likely to be located far from their ultimate markets.

In any case, the resulting long-distance transmission of electrical current entails significant losses (~20%) due to electrical resistance. When "high-temperature" superconductors (i.e., substances that become superconducting near liquid nitrogen temperatures (~77 K) rather than near liquid helium temperatures (~4 K)) were discovered in the late 1980s, it was immediately predicted they would revolutionize power transmission (e.g., Lemonick, 1987). This hasn't happened. In part the mechanisms of high-temperature superconductivity remain poorly understood. However, it is likely that even if they were fully understood, the routine and economical fabrication of high-temperature superconductors would require a great deal of control at the nanoscale (cf. Rao, 1999). Here again, the large-scale fabrication of nanostructured materials could make a major contribution to energy efficiency.

2.3. Information intensive resource extraction.

2.3.1. Ubiquitous sensing.

When extracting from a subsurface natural energy source such as an oil or geothermal reservoir, the details of the subsurface structure are obviously of paramount importance. Subsurface information, however, is also extraordinarily difficult to get, particularly in the detail required. Nanotechnology has obvious applications here.

The extraordinary decrease in the cost of computing over the last few decades has already had a significant effect: the cost of domestic production since 1984 has dropped from \$14 to \$4/bbl, largely through information technologies (Paul, 2001). Most of this involves the processing and manipulation of seismic data to picture subsurface structure, and this trend is another that will only accelerate as information manipulation continues to become cheaper.

Another embryonic trend is cheap distributed sensors based on microtechnology, such as downhole thermometry, from fiber-optic cables, and autonomous micro-flowmeters, which are "throwaways" that

can be disseminated in the subsurface (Paul, 2001). This trend will also accelerate as MNT comes on line.

2.3.2. Diffuse resources.

A great many energy sources (sunlight, geothermal power) are intrinsically diffuse, and so practical collectors must be cheap as well as efficient. This obviously has major implications for their fabrication: it must be as simple and automated as possible. Hence, another result of cheap nanofabrication will be to make collecting energy from diffuse sources much more practical, with enormous potential implications.

Distributed fabrication will most likely accelerate this trend. Biosystems already carry out distributed fabrication of energy-gathering systems; consider photosynthesis by green plants.

2.4 Specific Technological Approaches: MNT and Solid-State Energy Generation.

Technologies applicable to a range of energy conversion applications are described in this section. Technologies specific to a particular application (e.g., photovoltaics) are described in the appropriate part of section 2.5.

2.4.1. Heat engines: thermoelectric power.

After emphasizing that thermalizing energy is a really silly thing to do, it now seems ironic to talk about using nanotechnology to extract work from heat. Nonetheless, heat engines are not going to vanish entirely. In some cases (e.g., nuclear fission) a non-thermal approach is very difficult to envision. In other cases (e.g., OTEC, geothermal power), a thermal gradient exists naturally, and so one might as well exploit such a gradient as efficiently as possible. Science-fiction writers, for example, have long suggested personal devices powered by body heat (e.g., Heinlein, 1956).

The most efficient exploitation technologies will probably involve nanotechnology. Conventional heat engines use a "working fluid" (steam, combustion products) whose thermal expansion is used to convert heat into mechanical work. Although such technologies are highly mature (consider steam turbines and internal combustion engines), they are high-maintenance and prone to catastrophic failure because of the abundance of macroscopic moving parts. They also require a large temperature difference, and the range of that difference must include a phase transition or other large volume change, such as occurs in the reaction of gasoline vapor with air. Alternative working fluids—in particular, liquids with lower boiling points than water—are sometimes used to exploit lower temperatures as in geothermal fields, but the increase in complexity makes such approaches marginal at best.

Direct nanoscale conversion of a thermal difference into another form of energy is likely to be considerably more reliable as well as more efficient. Considerably smaller temperature differences are also likely to become usable. Such devices already exist in embryonic form: thermoelectric power generators, which generate an electrical potential at a junction between two dissimilar materials, typically a *p-n* junction between two highly doped semiconductors (e.g., DiSalvo, 1999). (If a current is applied in the reverse direction, such junctions act as refrigerators.) Like fuel cells and photovoltaics, these devices have been restricted to niche markets, in this case due to both high cost and low efficiency. The best current conversion factors are only about 10% of the Carnot limit. Even a domestic refrigerator manages ~30% efficiency.

A dimensionless figure of merit ZT , where T is absolute temperature, is quoted to characterize thermoelectric materials (e.g., [Mahan, 1998](#); [DiSalvo, 1999](#)). For many years the best values have been ~ 1 , but recently values of ~ 1.8 ([Fleurial et al., 1999](#)) and ~ 3 ([Hagelstein et al., 2002ab](#)) have been reported. A value of $ZT \geq \sim 4$ would lead to a huge number of new applications and might even revolutionize power generation.

Optimizing thermoelectric materials perhaps no better illustrates the promise of nanoscale manufacture, because of the daunting number of parameters that must be optimized, often in inconsistent ways. For example, electrical resistance *and* thermal conductivity must be minimized. For most materials this is an incompatible objective. Approaches taken include attempting to synthesize structures that minimize phonon transmission while leaving the electronic structure relatively unaffected. Nonetheless, even if a bulk substance can be found that meets these criteria, it probably will be difficult to synthesize via traditional "shake and bake" approaches, so that nanofabrication ability will be critical. [Mahan \(1998\)](#) and [Mahan et al. \(1997\)](#) discuss the issues in finding better thermoelectric materials. [Hagelstein et al. \(2002ab\)](#) describe a "thermal diode" approach, in which the thermoelectric current is enhanced by thermionic emission from an adjacent layer.

Nanolayered structures are more promising theoretically, but their manufacturing is even more difficult. As [DiSalvo \(1999\)](#) notes, "The challenge in making modulated films is to make very thin, *atomically perfect* layers..." (emphasis added). And, it might be added once again, for macroscopic applications the even greater challenge is doing so *cheaply*.

2.4.2. Piezoelectric power.

Piezoelectric substances develop an electric potential along particular crystal axes when deformed; or alternatively, deform mechanically when an electric field is applied. Thus they potentially provide a way to transform mechanical work into electricity without macroscopic moving parts such as turbines.

Piezoelectric materials are widely used at present for oscillators and sensors, most notably for nanoscale science in scanning-probe microscopes (SPMs). However, although their potential for power generation has been discussed ([Galasso, 1969, p. 105-6](#); [Goldfarb & Jones, 1999](#)), it has not been practical as yet. One study has shown that the maximum efficiency of electricity production with conventional packages of PZT (lead zirconate titanate, $\text{Pb}(\text{Zr,Ti})\text{O}_3$, another perovskite), a commercially available piezoelectric material, is only $\sim 10\%$ ([Goldfarb & Jones, 1999](#)). According to this analysis, a great deal of energy is stored temporarily as strain without causing electrical generation. This energy is simply returned mechanically to the environment.

Quite apart from the potential of developing and fabricating new piezoelectric materials, nanofabrication would help make even the present low-efficiency materials more practical for power generation. Power generation would require nanostructuring on a large scale, not only for the sheer volume of material required, but because building up significant voltages requires nanolayered structures, in which thin layers of piezoelectric material are interlayered with electrodes of alternating polarity connected in series.

2.5 Energy sources.

Energy sources, both conventional and unconventional, will now be reviewed briefly, with notes as to the potential applications of MNT.

2.5.1. *Conventional fossil fuels.*

These still supply some 90% of total energy consumption in the industrialized world. In the US, the current mix is about 22% coal, 40% oil, and 28% natural gas (e.g., [Skinner et al., 1999, p. 431](#)). Proportions in other industrialized countries are similar, except that coal usage tends to be higher in the US because of the abundance of US coal reserves. Coal is *not* merely a relic of the 19th century; in 1999 coal generated some 39.8% (311,560 MW) of electricity in the US, the largest single share ([USDOE-EIA, 2000](#)). (One result of the 70s "oil shocks" is that petroleum was largely phased out in the US as a fuel for the routine generation of electricity.)

Fossil fuels are geologically processed reduced carbon compounds that originally came from biological material. They thus represent energy stored by ancient photosynthesis*. Hydrocarbons and carbon, because of their stability, are the ultimate product of processing organic material with heat and pressure under anoxic conditions.

Because of their tremendous importance, fossil fuels have an enormous literature on their formation, their characterization, the geologic settings in which they occur, and exploration for them. Oil in particular is the subject of libraries. Formation of oil occurs by thermal processing of buried organic matter in the so-called "oil window" of temperature and pressure. Too cool, and the organic matter remains embedded in the rock as a tangle of high molecular-weight, largely aliphatic polymers termed *kerogen*; too hot, and all the long-chain hydrocarbons break down into graphite and natural gas (mostly CH₄). Of even more importance, however, the rock "plumbing" must be such that the oil, once formed, can flow into porous "reservoirs" where it can be extracted conveniently.

Oil has been of particular value because of the convenience of storing and handling a high energy-density liquid. Because of this demand, therefore, it is not surprising that oil supplies are the most critical. Indeed, conventional oil production may peak this decade ([Duncan, 2001](#)). Moreover, the current US position in particular is precarious. For 1999, total US oil consumption was $\sim 5.9 \times 10^9$ bbl (1 bbl = 42 US gallons = 0.16 m³), of which some 3.5×10^9 bbl (60%) was imported (calculated from [Oil & Gas Journal Databook, 1999](#) and [Oil & Gas Journal, 2000](#)). Furthermore, the $\sim 2.4 \times 10^9$ bbl that was produced domestically amounts to the second-largest in the world, only Saudi Arabia producing more oil.

Supplies of other fossil fuels are larger, but they are considerably less convenient. Coal is environmentally damaging, not just in its mining but in its usage. Being nearly pure C, coal yields more CO₂ per joule on its complete combustion than any other fuel. Combustion of impurities such as pyrite (FeS₂) also contributes SO₂ to the exhaust gas. This is a source of acid rain through the atmospheric reactions:



Coal mining is also extremely dangerous for the miners.

Natural gas (CH₄) is much cleaner, but its domestic supply is also limited ([Duncan, 2001](#)).

* For various reasons the majority of the Earth-science community does not take seriously the notion of an abiogenic origin for the majority of hydrocarbon fuels. The issue is peripheral to the discussion here, but the interested reader can find entries to this controversy by consulting the papers and cited references in [Howell et al. \(1993\)](#).

Although considerably larger supplies remain available outside North America, it is also difficult to transport.

The basic problem is that conventional fossil fuels are highly limited although they still account for some 90% of energy usage in the industrialized world. Moreover, they are being depleted even while demand for energy grows worldwide, as people in developing nations aspire to a lifestyle like that in the wealthy, industrialized countries. One way or another, this trend will change sharply in the near future, probably within the next decade.

2.5.2. Unconventional fossil fuels.

As might be expected, conventional fossil fuels represent a tiny fraction of reduced organic matter, ultimately of biological origin, that is held in sedimentary rocks. By far the bulk of this material is much too dispersed to be realistically considered a fuel prospect*. Several types of relatively concentrated deposits, however, have excited interest as potential energy sources over the years.

2.5.2.1. *"Oil shale."* Oil shale is a sedimentary rock (not a shale, but a marl) that contains ~15% kerogen (Hinman, 1991). As noted, kerogen is "proto-petroleum"; heating kerogen causes depolymerization into shorter length hydrocarbon chains that can then flow more freely. Natural oil formation is thought to involve the thermal degradation of kerogen in the "oil window" of temperature and pressure.

Traditional attempts to process oil shale in essence carry out "artificial maturation": the rock is heated to "crack" (i.e., cleave) the kerogen into shorter aliphatic chains, which can then flow out. As might be expected, such processes are dirty and clumsy. The rock must be fractured extensively, which implies mining it, and "cooked" in bulk. This generates a great deal of waste. Additionally, of course, the concentration of kerogen must be great enough to make up for the energy expended in mining and heating.

2.5.2.2. *Tar sands.* These consist of a gummy mess of very high molecular-weight aliphatics dispersed in unconsolidated sand or in sandstone. They represent the "dregs" left behind when a conventional oil reservoir was breached by erosion so that all the low-molecular weight compounds escape. (This, by the way, is the ultimate geologic fate of all oil deposits. Most oil is <100 my old, which is quite young in a geologic sense. Oil deposits are ephemeral, geologically speaking.)

Tar sands in northern Alberta are currently being exploited. They are mined, heated to cause the thick oil to flow out, and then these long-chain aliphatics are cracked catalytically to yield lighter hydrocarbons typical of conventional oil. Although the degree of cracking is not so drastic as would be required for oil shale, the exploitation of tar sands involves similar environmental issues.

2.5.2.3. *Clathrates.* Also called gas hydrates, these consist of a form of water ice having a very open crystal structure that can accommodate small guest molecules such as methane (Kvenholden, 1993). Clathrate deposits are locally abundant beneath the sea floor in high latitudes, but they present

* The non-specialist tends not to realize that even so-called "dry holes" typically encounter hydrocarbons, just not in sufficient quantity to be economic. Indeed, hydrocarbons are ubiquitous in most sedimentary rocks. For example, for his dissertation the author had occasion to dissolve limestone samples, from rocks very similar to those in Figure 13, in formic acid to extract the other minerals present. Invariably there was a sheen of oil floating on the solution when dissolution was complete. What is unusual about oil deposits is not the mere formation of petroleum but its collection into exploitable deposits.

formidable problems for exploitation. Deep water drilling is difficult and expensive, and the degree of drilling needed to tap a deposit is uncertain. Conversely, on depressurization some such deposits may undergo catastrophic release, with potentially serious consequences. Naturally triggered catastrophic release has been speculated to have caused sudden warming events in the geologic past (e.g., [Nisbet, 1990](#); [Hesselbo et al., 2000](#)), as methane is an excellent greenhouse gas.

2.5.3. Applications of nanotechnology to fossil fuels.

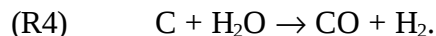
2.5.3.1. Extraction of fossil fuels. Probably the least glamorous but most important application of nanotechnology to fossil fuel recovery in the near term lies in "information intensive" extraction. This is particularly the case in "enhanced recovery," which involves techniques to mobilize the oil that would otherwise remain in the ground. (Conventional recovery typically leaves some two-thirds of the oil in the ground (e.g., [Montgomery, 1997, p. 305](#))). For example, one form of "tertiary recovery" involves injecting steam into the field to mobilize the oil. In one case ([Paul, 2001](#)), monitoring reservoir temperatures with downhole fiber-optic thermometers while tracking the flow of oil and steam with ultra-miniaturized flow sensors inserted into the stream led to substantial (~20%) savings. Less injected steam was required, and it could be targeted more effectively. This is an example of how nanotechnology will provide incremental improvements of techniques already carried out in embryonic form with microtechnology.

Bioprocessing may also be mentioned as an example of using natural molecular machinery to carry out distributed processing. Biotechnological approaches have been under investigation for tertiary oil recovery (e.g., [Yen, 1990](#)), and are likely to be both much cheaper and far less disruptive environmentally. Indeed, bacterial strains capable of metabolizing kerogen have recently been reported ([Petsch et al., 2001](#)). Such organisms, or the enzyme systems derived from them, may be able to carry out low-temperature cracking of kerogen or of the long-chain aliphatics in tar and asphalt. These could also provide considerably cleaner and less energy intensive approaches to processing of oil shale and tar sands.

2.5.3.2. Catalysis and syngas. Catalysis underlies most of the petrochemical industry at present. It involves far more than just cracking of long-chain aliphatics into the C₆-C₈ molecules that make up gasoline. Most simple feedstock organic chemicals (e.g., CH₃OH, CH₃COOH, HCOOH) are now made by catalytic processing using "synthesis gas" (syngas), a mixture of CO, CO₂ and H₂ (e.g., [Klier, 1982](#); [Sneeden, 1982ab](#)). CO and H₂ can be made by the steam cracking of methane (the usual route):

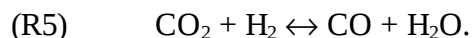


or by the water-gas reaction:



The latter is the basis of approaches to coal gasification. It was much used for fuel gas generation a century or so ago, but now has been largely supplanted by natural gas.

The CO/CO₂ ratio in the syngas is varied by the water-gas shift reaction:



Depending on the pressure-temperature conditions, the catalyst(s), and the ratio of molecular species, a wide variety of simple one- and two-carbon molecules can be synthesized. However, catalyst activity, selectivity and reproducibility would benefit greatly from greater synthetic control at the nanoscale (section 2.2.2.).

Similar processes provide a way to "fix" hydrogen that might be generated by other means, such as by artificial photosynthesis (section 2.5.10.2.). One possibility is the synthesis of methanol,



which has the further advantage of CO₂ fixation (Jessop et al., 1995). Methanol is not only usable in thermal engines; as a simple, storable, water-miscible fuel it is attracting attention for next-generation fuel cells (section 2.2.1.1.).

2.5.3.3. Usage of fossil fuels. The obvious improvement here is to release their energy in fuel cells rather than via combustion. As noted, however, fuel cells that can use hydrocarbons are in their infancy (section 2.2.1.1.), and are currently much too short-lived for practical applications. Near-term fuel cell applications in vehicles rely on "reforming" the hydrocarbons to extract only the hydrogen, which obviously increases complexity and decreases efficiency.

As with any fuel cell, a practical hydrocarbon cell will involve structuring at molecular scales, and its structure may even be more intricate to deal with the more complex fuel. Moreover, even when robust fuel cells are developed there remains the issue of fabricating them cheaply enough to be competitive.

2.5.3.4. Thermoelectrics. The use of thermoelectrics to extract electricity from waste process heat has been the subject of speculation (e.g., DiSalvo, 1999). As already noted (section 2.4.1.), such uses imply not only thermoelectrics with figures of merit considerably better than those available at present, but extraordinarily cheap, high-volume fabrication of them.

2.5.3.5. Superstrength materials. Superstrength materials will have many applications in conventional extraction. Besides the obvious improvements in efficiencies of transport, drilling will benefit particularly. The "drill string," the column of rotating pipe tipped by a diamond-studded bit for "making hole," could be considerably lighter, with consequent energy savings in its operations.

Additionally, much greater depths could become routinely accessible, although the destruction of permeability at great depth makes the value of this problematic. Of course, the fabrication of cheap, megascopic diamond, which is commonly envisioned as a result of MNT, is also going to make drill bits much cheaper.

In the far future, semi-autonomous burrowers, perhaps of microscale or even nanoscale dimensions, may be able to rove at depth in the crust seeking out valuable materials. This prospect, however, seems sufficiently remote that it does not now merit detailed discussion.

2.5.4. Nuclear fission.

Despite its air of "political incorrectness" and the very real problems of nuclear waste disposal, nuclear fission remains a major contributor to the energy mix worldwide, contributing some 26×10^{18} J of electrical energy in 2000 (USDOE-EIA, 2000). Its contribution, moreover, will almost certainly

increase in the next few years. The recent electricity shortages in California, for example, suggest that the political palatability of fission power is likely to increase substantially if the alternative is blackouts.

2.5.4.1. Uranium. All commercial power reactors use the isotope ^{235}U , which is fissionable by slow neutrons. As is well known, it constitutes only $\sim 0.7\%$ of natural uranium, so fuel must be enriched in the fissionable isotope, a cumbersome and capital-intensive procedure.

Most natural uranium consists of the isotope ^{238}U , which is not fissionable by slow neutrons. As is well known, however, ^{238}U will absorb a slow neutron to yield ^{239}Pu after a chain of short-lived β decays. Plutonium-239 is fissionable by slow neutrons. It has been extensively used in nuclear weapons but not for commercial power generation, both because of safety and nonproliferation concerns. Since Pu is an element, it can be separated from its environment by chemical means, and so making a concentration that would be usable in nuclear explosives is relatively simple. Enriching ^{235}U , on the other hand, requires isotopic separation, which is considerably more difficult and at least heretofore has required an enormous infrastructure. Pu-fueled power reactors, however, have been thought likely to be necessary some day. Indeed, "mixed oxide" fuels, containing up to 5% Pu obtained from reprocessed spent uranium fuel, are already used in a few countries (USDOE-EIA, 2000).

2.5.4.2. Thorium. A third nuclide of relevance for fission power is ^{232}Th , the only long-lived isotope ($t_{1/2} \sim 10^{10}$ y) of thorium. Like ^{238}U , it is not fissionable by slow neutrons, but it will absorb a neutron to form ^{233}Th , which β -decays over several days to fissionable ^{233}U . Although there has been interest in thorium as an energy source for decades—for many years the US Geological Survey had a "Branch of Uranium and Thorium Resources"— ^{233}U has not been employed on other than an experimental basis. Nonetheless it remains a "backstop" energy resource, particularly since the crustal abundance of Th (7.2 ppm) is about four times that of U (Mason & Moore, 1982, p. 47).

2.5.5. Applications of nanotechnology to fission energy.

Fission is obviously a thermal technology, and it's hard to see how it can be otherwise. The energies of nuclear reactions lie orders of magnitude above those of chemical bonds, so even molecularly structured assemblages seem unlikely to be able to control nuclear reactions at the atomic level. However, this does not mean MNT is irrelevant to fission. Most obviously, thermoelectric power generation may prove practical.

2.5.5.1. Mining and extraction. The big application of MNT toward fission fuels, however, probably lies in their extraction and separation. Fission fuels are "fossil," too, in a sense: they also are dug out of the Earth and their supply is ultimately finite. The considerations of concentration and grade (section 3.1) apply to uranium deposits just as they do to non-energy-related metals.

As described below, a major resource-related application of nanotechnology lies in the low-energy molecular separation of elements, most directly from aqueous solution (section 3.3.1.). As for other elemental commodities, therefore, nanotechnology could vastly increase the supply of U and Th. Leaching of low-grade U- or Th-bearing rocks, for hydrometallurgical extraction, has already been carried out (e.g., Sayed et al., 1997), and selective "uranophiles" (highly selective agents for complexing the uranyl ion, UO_2^{2+}) have been the focus of much research (Araki et al., 1993; Jacques & Desreux, 1996; Nagasaki & Shinkai, 1991; Shinkai et al., 1989; Xu & Raymond, 1999). Uranium also exists in natural brines; indeed, extraction of UO_2^{2+} from seawater has been investigated (Aihara et al., 1992; Kanno, 1981; Kelmers, 1981; Yamashita et al., 1981).

A potential "down side" relevant to nuclear proliferation should be mentioned. Protactinium-231 ($t_{1/2} \sim 3 \times 10^4$ y), which occurs naturally in small amounts in uranium-bearing materials from the decay of ^{235}U , could also be extracted. This isotope is the only naturally occurring one besides ^{235}U with possible utility in a nuclear device (Franka, 1994), and unlike ^{235}U it could be purified without the necessity of separating isotopes.

2.5.5.2. Reprocessing of nuclear fuel and separation of nuclear waste. The result of nuclear fission is a mishmash of fission products, the lighter nuclei formed by the fission of the U atoms, mixed together with a set of heavier U and actinide isotopes formed by absorption of stray neutrons. The fission products tend to be strongly β -active because they are neutron-rich. The actinides are α -active and typically long-lived on a human timescale (as with ^{239}Pu). A fair amount ($\sim 1\%$ ^{235}U , as well as $\sim 5\%$ Pu generated *in situ*; USDOE-EIA, 2000) of unreacted fuel also remains, but it is unusable because of competitive absorption of neutrons by the other nuclides.

Obviously, it would be attractive to separate the components of nuclear waste, for fuel recovery and also to recover potentially valuable radionuclides. However, separating—"reprocessing"—nuclear waste is both difficult and hazardous. Indeed, such complex mixtures are difficult to deal with even when not strongly radioactive. The procedures involve dissolution in strong acid and then separation via a long and complicated sequence of steps using precipitation, ion exchange, solvent extraction, and so on, with the additional difficulty that all reagents and materials used themselves become contaminated with radioactive material.

Separation from such solutions could alternatively be carried out molecularly, by systems like those described in section 3.3. Indeed, besides the "uranophiles" described above, effort has been directed toward finding actinide-specific binding agents, although the focus of these studies has been therapeutic applications (e.g., Raymond et al., 1984; Kappel et al., 1985). This is a more difficult problem, however, because of radiation damage to the nanomechanisms. They will have to be robust and ultimately probably self-repairing. If such systems can be developed, they will make the reprocessing of nuclear waste considerably more practical. Indeed, possibly each reactor installation could reprocess its own waste.

Such technologies, however, will also have unfortunate political ramifications. They are likely to make it much easier for small groups to extract nuclear materials from radwaste such as that from conventional power reactors. Separation of elemental plutonium (or ^{233}U from irradiated thorium) should be relatively straightforward, even if the lifetimes of the nanomechanisms are limited due to radiation damage. These concerns become particularly cogent with the recent terrorist attacks against the US.

2.5.5.3. Isotope separation. Isotope separation is fundamental to nuclear materials. Unfortunately, separating isotopes is much more difficult than separating elements, and at least in the near term there seem to be few ways that MNT can yield major improvements, as described in section 3.4. If MNT approaches to isotope separation prove feasible, however, this is an obvious application. Unfortunately, if for example ^{235}U could be readily separated from ^{238}U it would lead to similar political ramifications as the cheap separation of Pu.

2.5.6. Geothermal energy.

The interior of the Earth is very hot, and so the thermal difference between the interior and the surface is potentially a vast energy resource. Unfortunately, it has been impractical in all but unusual

situations because the thermal gradient is generally so low. Prohibitive depths would need to be reached to obtain a thermal difference that could be exploited with conventional technology. The typical geothermal gradient in the crust is only $\sim 25^{\circ}\text{C}/\text{km}$, so that even reaching the boiling point of water (at STP) requires impractical depths. Moreover, conventional geothermal power generation relies on steam as a working fluid, and to get the volumes required the steam must have access to a large volume of rock. Thus the rock must be reasonably porous, with cracks if nothing else, but the deeper the level, the greater the degree to which any open space has been closed up by the confining pressure.

Therefore, for conventional geothermal power the geothermal gradient must be considerably elevated, so that temperatures of $100\text{--}200^{\circ}\text{C}$ can be attained within a kilometer or so of the surface. In addition, the rock must both be permeable and be thoroughly saturated either with steam, or with water sufficiently hot that a significant fraction will vaporize on exiting to atmospheric pressure. A further engineering difficulty ensues because hot water in contact with rock tends to be highly mineralized, so that scaling from the precipitation of solid compounds is a serious problem. The hot water is typically groundwater of ultimate meteoric origin, so the degree to which it is mineralized tends to reflect the average residence time of the water. The longer recharge takes, the more mineralized the water.

The requirement of a working fluid leads to further difficulties. First, water loss by extraction is often a serious issue. Hence many geothermal plants replenish the water by reinjecting the spent, cooled water back into the field. This has the added advantage of disposing of the water, which is commonly too mineralized or saline to release to conventional wastewater treatment without special pretreatment. Second, many areas of high geothermal gradient contain little groundwater: so-called "hot dry rocks." There have been ongoing experiments on drilling and fracturing such rocks, followed by injection of water to make steam. Los Alamos in particular has been conducting such studies since the late 1970s. However, the process is not yet practical. Finally, many geothermal fields are too cool to produce much steam. If conveniently located, these can be used as a source of low-grade heat for (e.g.) space heating or for such applications as drying food. Alternatively, in so-called "two-phase" generation systems, the hot water is used to boil a working fluid with a lower boiling point, which is used to drive a turbine. Obviously, however, this both increases complexity and decreases net power output.

2.5.7. Applications of nanotechnology to geothermal energy.

2.5.7.1. Information-intensive exploitation. As in so many cases involving the vagaries of natural systems, geothermal energy is both diffuse and additionally not very uniform. Conventionally a geothermal "field" is exploited somewhat similarly to an oil field. Wells are drilled for steam production, based on geologic and hydrologic models of the subsurface. Hence there is a great deal of practical similarity to oil production: because of incomplete information about subsurface structure, fracture connectivity, flow patterns, and so on, drilling "dry holes" (wells producing insufficient steam to be economic) occurs commonly and is a serious risk. Thus, many of the ideas for information intensive exploitation also apply to geothermal power. Extensive downhole monitoring of temperature, to monitor reservoir conditions, is an obvious first step, as are free-flowing microsensors for (say) determining the fate of reinjected water.

2.5.7.2. Automated fabrication. There is commonly significant variation in the temperature of steam even from different producing wells in the same field. Hence it would be most efficient to use the steam from each individual well to run its own optimized turbine. However, at present turbines are much too expensive to have one atop every well. Conventionally, therefore, the steam from all the wells

is combined in a manifold that feeds a single turbine. The additional expense of the plumbing, and the efficiency losses, are overwhelmed by turbine costs. Cheaper fabrication, probably also with superstrength materials, is likely to change this.

Finally, as described for oil (section 2.5.3.5.), superstrength materials are likely to have a pronounced effect on drilling technology in the near term. Strong materials are even more important for geothermal drilling because of the high temperatures encountered. In the far term, of course, developments such as automatic burrowers seem possible but do not warrant more than a mention now.

2.5.7.3. Thermoelectric materials. Turbines may not even be used with a mature nanotechnological approach to geothermal energy. Perhaps the most interesting application of thermoelectric materials lies in geothermal power. In few other cases are the difficulties of a working fluid so evident: temperature differences are often too modest, or span the wrong range, or else the fluid is absent completely, as in the case of hot dry rocks. The subsurface "plumbing," both natural and artificial, is also critical but difficult to ascertain, much less modify.

Unfortunately, a working fluid probably cannot be eliminated completely. In the case of a geothermal system, the function of the working fluid is not merely mechanical: it also gathers heat from a large volume, transferring it to a cooler environment so that a thermal gradient becomes available. However, better thermoelectric devices would allow replacing the mechanical turbines used in the current conversion approaches. Not only would such devices minimize the problems with fouling, corrosion, and mechanical mishap that plague conventional geothermal installations, they would allow direct use of lower geothermal gradients, because the phase change necessary to drive a turbine would no longer be required.

2.5.8. Solar energy, indirect sources.

Heating by the Sun drives the global systems of weather and ocean circulation. The fluid flows generated by this huge, albeit inefficient heat engine represent a source of energy that can be tapped. Some means of doing so (e.g., windmills, water wheels) go back centuries. To a much greater degree than other natural sources, however, they suffer from what might be termed "storm risk." The vagaries of weather demand that power-extracting infrastructure must be highly overdesigned to withstand the rare freak storms or floods. This obviously greatly increases the capital expenditure.

2.5.8.1. Hydropower. Electricity generation from large hydropower dams is certainly a mature technology, and it has a lot of advantages: no emissions, relatively low maintenance, and little start-up or shut-down delay. Indeed, hydraulic head in a reservoir is one of the few ways to "store" electricity at present. However, dams seriously disrupt river systems through profound and generally deleterious effects on riparian ecosystems, and through interruption of sediment transport. They also permanently flood farmland, and in any case reservoir lifetimes are finite, on the order of a few centuries at most, due to ongoing sedimentation. Finally, few sites remain for hydropower dams even if building them were not politically difficult.

Running water nonetheless still represents a large potential energy resource. In the US conventional hydropower accounts for <5% of energy consumption, but this reflects only ~20% of the total potentially available (Dowling, 1991). Of course, the remaining untapped hydropower is so dispersed that little could be tapped by conventional damming. Over the last few decades an alternative approach to hydropower generation has attracted attention: "low-head hydropower" or "microhydro." This ranges from turbines driven by low dams ("weirs") to "run of river" systems. Like wind power, the

latter use the natural currents to generate power, typically with small turbines or water wheels (Fraenkel, 1999).

2.5.8.2. Wind. Direct electrical generation from wind is a maturing technology, with a growing number of commercial installations. The issues are much as with distributed hydropower: the energy is diffuse, with large capital investments required, and with the added risk that not only the speed but the very direction of the current to be tapped is variable.

2.5.8.3. Wave energy. The surf raised by the wind contains a great deal of energy, and tapping it has intermittently excited interest over the years. It is another diffuse resource, however, and the "storm risk" factor is particularly severe.

2.5.8.4. Ocean-Thermal Energy Conversion (OTEC). In tropical areas there is a significant temperature difference between deep seawater ($\sim 4^\circ\text{C}$) and the surface ($\sim 25^\circ\text{C}$). This, of course, is maintained by solar energy. Deep ocean water is cold because it sinks at the poles and flows along the bottom toward lower latitudes, while the sun directly warms up the surface water. Although the temperature difference is small, it has attracted much interest because the reservoirs are both large and fluid. Thus the issue of dealing with cubic kilometers of unyielding rock, as in geothermal applications, does not arise.

2.5.9. Applications of nanotechnology to indirect solar energy sources.

2.5.9.1. Materials implications. Superstrength materials have many obvious applications. OTEC, for example, would profit from long cables that must hang under their own weight, to reach the sea floor, and yet still be strong enough to withstand the storm risk. Superstrength materials also have obvious applications in turbine and windmill blades.

Thermoelectric conversion also seems particularly relevant to OTEC, given the small temperature difference, but thermoelectrics capable of exploiting such small temperature differences do not yet exist.

Piezoelectric materials may also prove to be practical for power generation. A few studies have proposed piezoelectric-based arrays for generating power from surf (Taylor & Burns, 1983; Hausler & Stein, 1983). For example, the change in tension of a float-tethered cable could be exploited as waves raise the float as they cross it. Similar systems might be employed for low-head hydropower, to avoid such devices as turbines, paddlewheels, and others that use macroscopic rotation.

2.5.9.2. Automated nanofabrication and diffuse resources. Exploiting (say) the surge of surf with an array of piezoelectric cables obviously implies that the cables are made extremely cheaply, as would an array of micro-turbines in a "run-of-river" hydroelectric scheme. Once again the value of cheap fabrication at the nanoscale in exploiting diffuse resources becomes evident.

2.5.10. Solar energy, direct sources.

Solar energy has obvious advantages that have been recognized for nearly a century (Ciamician, 1912). It is free, ubiquitous, and overall amounts to an enormous energy input. Of course, its disadvantages are equally obvious: sunlight is intermittent, unreliable, and diffuse. Because of its diffuse nature, moreover, the area that must be devoted to energy collection also becomes an issue. Land is a high-value commodity in most of the places where energy is in high demand.

2.5.10.1. Photovoltaics. These are the most obvious and familiar solar-energy technology, devices that when illuminated generate an electrical current. Restricted to niche markets for decades,

costs have now dropped to the point that they now seem to be crossing the threshold into large-scale commercial applications.

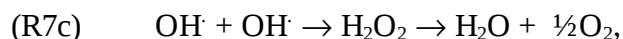
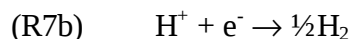
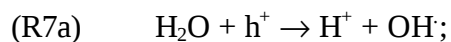
Photovoltaic devices are based on semiconductors, usually elemental Si. Absorption of a photon with energy greater than the semiconductor bandgap promote an electron across the bandgap into the conduction band, leaving behind a vacancy, or "hole" which acts like a unipositive charge in the valence band. If this electron-hole pair is formed in the vicinity of a space charge, such as at a p-n junction, charge separation takes place due to the electric field. With the proper provisions for collecting the opposite charges, this generates a potential that can drive an electric circuit.

Of course, this bald summary leaves a lot of practical details, and those details seem to be exactly where nanoscale fabrication can offer benefits, as discussed below (section 2.5.11.). The "storability" problem is also particularly urgent. As has been noted, the storage of electrical energy is already an issue even with power sources less fickle than sunlight. Transmission of electricity becomes another issue, because many of the places where sunlight is most attractive as an energy source, such as deserts, are remote from population centers.

2.5.10.2. Artificial Photosynthesis. This has a literature stretching back to the early 1970s (!). It's curious that "solar power" is so often thought of exclusively in terms of photovoltaics. Nature doesn't use solar energy that way, and there is no reason we have to. Via photosynthesis, green plants store energy of sunlight directly into chemical bonds. Indeed, as noted this is the ultimate source of most of the fuels we depend on today.

Using sunlight to make fuel solves immediately the storability and transport issues that arise with making electricity. Ironically, with such technology the desert countries of the Mideast also could continue to export fuel indefinitely.

Practical technological photosynthesis probably will be based on semiconductor-driven coupled redox reactions (photo-oxidation and photoreduction) (e.g., Nozik, 1978; Gerischer, 1979; Bard & Fox, 1995; Lewis, 1995). In such devices the electron-hole pairs formed by absorption of a photon, instead of being used to drive electric current, are used as chemically active agents to drive coupled redox reactions. The hole is a strong oxidizing agent, whereas the electron is a strong reducing agent, and they can bring about reactions that are energetically uphill. Ever since Fujishima and Honda's (1972) pioneering work, most effort has been directed toward decomposing water to H₂ and O₂, by reactions such as:



where h^+ and e^- are the photogenerated hole and electron, respectively (e.g., Tan et al., 1993). Other investigations have looked at the reduction of CO₂ or inorganic carbonate to simple organic molecules (e.g., Goren et al., 1990; Halmann et al., 1984; Heleg & Willner, 1994; Kuwabata et al., 1995; Raphael & Malati, 1989; Thampi et al., 1987; Yamashita et al., 1994), the reaction of N₂ with hydrogen-bearing molecules to yield ammonia (Schrauzer et al., 1983; Ileperuma et al., 1989), and so forth.

Parenthetically, because the electron and hole are capable of forming highly reactive species, such as the OH radicals in the equations above, or superoxide ion (O_2^-) from reduction of atmospheric O_2 , they can also drive "downhill" reactions that otherwise are kinetically inhibited. Such species react readily with many dissolved compounds, in particular organic pollutants such as halogenated hydrocarbons, aromatic hydrocarbons, cyanide ion, and so on. Such "photocatalysis" has spawned an extensive literature on using powdered oxide semiconductors, primarily TiO_2 , for pollutant destruction (e.g., [Matthews, 1988](#); [Wold, 1993](#); [Cunningham et al., 1994](#); [Linsebigler et al., 1995](#); [Riegel & Bolton, 1995](#); [Fujishima et al., 2000](#)).

Familiar semiconductors such as Si are not well suited for such applications, for a couple of reasons. One reason is bandgap energy: the band gap must be large enough, and its edges must be positioned properly, for the desired reactions to occur. For oxidation to occur, the energy of the top of the valence band must lie below that of the species to be oxidized. Similarly, a species to be reduced must have an energy below the bottom of the conduction band (Figure 4). Silicon is also too chemically reactive to tolerate aqueous solutions in the presence of air, much less in the case of direct water oxidation. It quickly develops a passivating layer of SiO_2 .

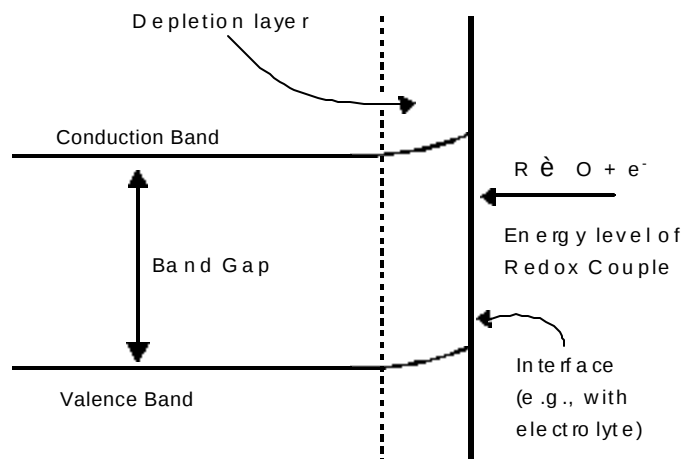


Figure 4.

Figure 4: Semiconductor band gap. Any semiconductor contains a "valence band" (V.B.) separated by an energy gap (the "band gap") from a higher-energy "conduction band." (C.B.) At absolute zero the valence band is completely filled with electrons, while the conduction band is completely empty. In the immediate vicinity of an interface with another substance, electrons will flow toward the substance with the lower Fermi level (highest filled energy level) until the increasing electrostatic charge makes such flow energetically unfavorable. This so-called depletion layer (space-charge region, Schottky barrier) then causes the energy levels of the bands to change, resulting in "band bending" near the interface.

Absorption of a photon with energy greater than the band gap promotes an electron to the C.B. while leaving a positive "hole" in the V.B. In the space-charge

region, the electric field there causes charge separation to occur. This is the basis both of photovoltaic devices and of semiconductor mediated photochemical reactions, as the hole is a powerful oxidizing agent while the promoted electron is a powerful reducing agent. A redox couple whose energy falls in the band gap can be oxidized by the hole ($R \rightarrow O + e^-$), or reduced by the electron ($O + e^- \rightarrow R$).

Although efforts have been made to passivate Si and other semiconductors with electroactive moieties so that they can be used in aqueous solution (Bocarsly et al, 1980; Bolts et al., 1979; Wrighton, 1978), most work has been carried out with wide-bandgap oxide semiconductors such as ZnO, SnO₂, and SrTiO₃. By far the majority of this work has employed TiO₂, which is cheap, nontoxic, and abundant, as well as stable indefinitely in contact with H₂O in the presence of O₂. In addition, one polymorph of TiO₂, anatase, generates an electron-hole pair energetic enough to completely decompose water. The bandgap of TiO₂ is 0.512 aJ (~3.2 eV), which corresponds to a wavelength of ~390 nm. This lies in the near ultraviolet (UV), which is why TiO₂ powder appears bright white.

Semiconductor-based photosynthesis is fundamentally different from natural photosynthesis, which relies on dye-based absorption in conjunction with a nanostructured molecular chain to carry out charge separation. The natural version is both more complicated and less efficient (~1%).

2.5.10.3. Solar thermal. The Sun, of course, also heats things up, and for completeness this aspect of solar power should be mentioned. Solar heat can be used not just for space heating, but also for low-grade process heating, some of whose applications (e.g., drying food) date back to antiquity. Even apart from the vagaries of weather, controlling incident solar radiation is difficult because of the changing position of the Sun in the sky. Either the changing incident angles must be lived with, or else complex mechanical arrangements of mirrors and lenses are required. An alternative method of control could be another application of photochromic or electrochromic glass, which could vary the reflectivity of panels as needed.

Finally, solar heat could be used to drive thermal engines directly, as in current experimental projects. Should such direct use of solar heat prove convenient, thermoelectric materials are likely to be more attractive than heat engines using working fluids.

2.5.11. Applications of nanotechnology to direct solar energy sources.

2.5.11.1. Nanofabrication. Present-day solar cells are expensive, and that expense results from their fabrication costs. The most efficient material is crystalline semiconductor-grade silicon, because electron-hole recombination is minimized, but this material is costly. The repeated cycles of purification through remelting and recrystallization required to make such material represent the thermal paradigm at an extreme. Moreover, the ultrapure silicon must be doped to yield a large-area *p-n* junction where the photons are absorbed, as the electrostatic field at this junction (Schottky barrier) causes the electron-hole separation. Alternative fabrication approaches could make a large difference in costs (Green, 1998), and nanofabrication techniques seem an obvious approach.

Another route to cost minimization is through minimizing the material used. Electron-hole formation is a near-surface process, so the bulk of the silicon goes unused. This has motivated much research into using thin film materials. Unfortunately, amorphous films, such as are commonly obtained from chemical vapor deposition, have very low efficiencies due to heightened electron-hole

recombination. Also, if the semiconductor layer is too thin, photon losses due to transmission become significant. Si is an "indirect" semiconductor in which promotion of an electron to the conduction band is formally forbidden (Tan et al., 1993). Such materials must be 10-100x thicker than a direct semiconductor to have an equivalent chance of absorbing a photon.

Optimizing the collection of the electrons and holes to driven the external circuit also is a nanofabrication issue. Ideally every electron and every hole would be collected before it has a chance to recombine, and approaching this ideal requires a dense network of fine wires (at present fabricated by conventional microtechnology techniques) on the semiconductor surface.

There also is an intrinsic loss in the very nature of photon-induced electron-hole pair formation in a semiconductor. The energy of photons with energy less than the band gap is completely lost because they are not absorbed, while the energy of those with energy greater than the bandgap is partly lost because the additional energy is thermalized, merely going into heating the semiconductor. Thus the bandgap value has a "leveling" effect, and the best bandgap value for a given wavelength distribution of the incoming radiation represents a tradeoff between these loss mechanisms.

In principle, the efficiency of semiconductor collection can be improved by using a stack of semiconductors with bandgaps of different energies, termed multijunction solar cells. Obviously, however, this efficiency is bought at the cost of a great increase in complexity, and moreover complexity at the nanoscale. Again we are confronted with the issue of fabricating nanolayers with near-atomic precision.

For semiconductor-based photosynthesis, some issues are the same as with semiconductor-based photovoltaics. Large surface area remains an issue, and opacity is also an issue because TiO_2 and other oxide semiconductors are also indirect semiconductors.

However, a number of issues are considerably simpler or even irrelevant. Junction fabrication is not required because a Schottky barrier is set up automatically at the semiconductor interface with the aqueous solution, due to the difference in Fermi levels between water and the semiconductor. Micro- or nanoscale wiring to collect the generated holes and electrons is also not an issue. However, it has been shown that dispersed surface deposits of a catalyst such as Pt greatly improve photoredox efficiency, probably through facilitating hole-electron separation as well as through direct electrocatalytic activity (e.g., Disdier et al., 1983; Hope & Bard, 1983; Kobayashi et al., 1983; Ohtani et al., 1997; Sakata et al., 1982). This obviously increases cost and complexity.

An even more critical issue, however, is the utilization of the incident energy. A wide-bandgap semiconductor such as TiO_2 absorbs <12% of the incident sunlight, because relatively few solar photons lie in the UV. One approach toward improving the energy efficiency is by means of surface attachment of some other strongly absorbing species, such as a dye. If the energy difference between the ground and excited states of the dye straddles the bottom of the conduction band, an electron from the excited state of the dye can be injected into the conduction band, where it becomes available for photoreduction reactions. Hence, more of the incident radiation becomes usable.

Such "sensitized" semiconductors have an additional problem in that the dye layer is too thin to have a large cross-section for photon absorption. Most photons, even of the proper energy, continue to be transmitted. One solution to this problem is to have a fractal surface, so that due to scattering a photon has a large chance of being absorbed ultimately (O'Regan & Graetzel, 1991).

Finally, there remains the issue of what fuel to produce. The disadvantages of H_2 storage and delivery remain, although being gaseous it tends to escape automatically once synthesized in an aqueous

solution and so diminishes separation problems. Direct, semiconductor-mediated synthesis of C-bearing fuels such as methanol has been demonstrated, and could use such attractive substrates as CO₂ or inorganic carbonate (section 2.5.10.2.), the latter abundant in rocks such as limestone (section 3.5.4.). However, water-miscible fuels such as alcohols are difficult to separate from the aqueous synthesis environment, and pure hydrocarbon fuels are much more difficult to synthesize because of the difficulty of sequestering oxygen-containing moieties derived from the original water and/or CO₂ molecules.

Although cheap nanofabrication also is likely to be necessary to make artificial photosynthesis practical, the issues seem less well-defined than they are for photovoltaics, a reflection of the lesser maturity of the field. Serious questions about the most advantageous technological approaches still remain. Nonetheless, in the author's opinion this seems a much more flexible and powerful way of harnessing solar energy, because of its automatic solution of three pressing problems: the fitfulness of solar irradiation, the storability of sunlight-derived power, and the imminent exhaustion of convenient chemical fuels. Of course, breakthroughs in the storage of electrical energy might change this assessment, particularly if large new sources of electricity (as with solar power satellites, section 4.1.) become available.

2.5.11.2. Dispersed collection. Sunlight is the *sine qua non* of a dispersed energy resource, so not only do we need nanoscale fabrication, we need *cheap* nanoscale fabrication. This is particularly pressing because power generation requires that substantial area be exposed to the sun. Land is a commodity in short supply in most of the industrialized world, particularly in urban areas where electricity demand is highest. In such areas, an obvious source of underutilized area is rooftops. Covering every roof with a solar array would obviously go a long way toward resolving issues of both land and power, although with photovoltaics the storage issues would remain. For this reason several countries have targeted rooftop installations, including Japan, Germany, and the US (Green, 1998). Roads are another potential source of area that is underutilized at present, although they are a considerably more demanding environment and would probably require self-cleaning materials, possibly through photocatalytic coatings.

Even solar arrays dispersed on roofs clearly imply considerably cheaper fabrication than exists at present. The form of the PV cells could also be considerably more convenient than the present rigid blocks. One "wishlist" item would be a PV material that could be dispersed off rolls like carpeting. Nanofabrication on such scales is particularly challenging in the case of even more complex systems, such as multijunction arrays, intended to exploit a larger percentage of the incident sunlight. Self-maintenance and repair are a desideratum, especially because urban roofs are not a very benign chemical or physical environment. At this point, however, we are moving beyond near-term nanotechnology into the realm of molecular machines.

Semiconductor-based artificial photosynthesis, by contrast, seems extremely promising for otherwise attractive solar-power sites, such as deserts, that are remote from demand centers. As mentioned, an irony is that such technologies would allow the traditional oil-exporting nations of the Mideast to continue exporting fuel indefinitely.

2.5.12. Tidal energy.

As the Earth spins on its axis, it rotates through the oceanic tidal bulge raised by the Moon. This leads to the well-known rise and fall of the tides, roughly at 12.5 hour intervals, along the seacoast.

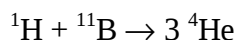
Although tidal currents have been used to generate electricity on a small scale, they represent another diffuse resource and thus their contribution has been negligible.

Although tidal energy is of course not derived from the Sun—the energy comes from the rotation of the Earth—the same sorts of issues arise as for surf power and low-head hydropower. These were discussed in sections 2.5.8. and 2.5.9.

2.5.13. Nuclear fusion.

Controlled nuclear fusion, of light isotopes such as D and ^7Li , has been the "holy grail" of energy research for over 50 years. Unfortunately, it still seems remote. Conventionally, fusion has been attempted by the "brute force" technique of magnetically squeezing a hot thermal plasma. An alternative using high-powered lasers to compress pellets has also been the subject of much interest. In all cases the result of fusion will be heat, which would power a heat engine.

A novel approach to "aprotonic" fusion using electrostatic accelerators to carry out reactions such as:



has been the subject of patents (Bussard, 1989). To add to its conceptual elegance, such fusion need not merely yield heat because the α -particles (^4He nuclei) could be braked electrostatically, and thus their energy be converted to electricity directly (Bussard & Jameson, 1995). Evidently, however, this approach has proved more difficult than expected. Certainly no commercial applications exist.

2.5.14. Applications of nanotechnology to fusion energy.

Whether nanotechnological fabrication would significantly help the fabrication of fusion reactors is unclear. Obviously, the same considerations of relative energy differences between the nuclear reactions vs. those of the chemical bonds in any confinement device apply just as strongly here as they do in the case of fission energy. Possibly, however, alternatives to the "brute-force" fusion by thermal plasmas, such as laser ignition or electrostatic confinement, will benefit from fabrication at nanoscale precision.

2.5.14.1. Separation of nuclear fuels. The obvious application of nanotechnology to fusion, as for fission, again lies in the cheap separation of nuclear materials. The nuclides proposed as most promising for fusion (e.g., ^7Li , ^{11}B) are all of rare elements. On a per-atom basis, B makes up 0.0019% of the crust; Li 0.0060% (calculated from Mason & Moore, 1982, p. 46-7). However, both have been enriched in certain natural brines, which would facilitate their separation by the techniques described in section 3.3.1. Indeed, natural brines are already a source of both elements even with current technology.

Also as with fission, nuclear reactions depend on the particular nuclide, not on the element. Hence isotope separation is again a critical issue (section 3.4.) The prospects of separating D from H seem best, because they have the largest relative mass difference of any two stable isotopes.

3. NANOTECHNOLOGY AND MINERAL RESOURCES

"If it can't be grown, it has to be mined"

- a common bumper sticker in northern Nevada

3.1 Minerals and Ores.

"Rich mineral deposits are a nation's most valuable but ephemeral material possession."

— T.S. Lovering, 1969

Fundamentally, all non-agricultural materials (save water and air) that humanity uses are obtained from geologically anomalous enhancements—"ores"—that occur locally on Earth. Ore is an economic term: it is a natural deposit "from which a desired material can be won *at a profit*." Thus what constitutes an ore is a function of demand and technology as well as of geology. Ores are commonly worked for particular elements, as with most metals (Fe, Ag, Au, Cu, Zn, etc.), but they include nonmetallic commodities as well. They need not even be elemental, but can be particular "pre-organized" materials, such as diamonds or other gems, mineral fibers such as asbestos (a valued "strategic material" until quite recently), or chemical compounds such as salts or limestone.

Ore deposits typically represent occurrences in which by happenstance some geologic process, or set of processes, has run to an extreme. There are three dominant considerations in whether a deposit is "ore":

- the *grade* (the concentration of the desired substance);
- the quantity ("tonnage") of the deposit;
- the access (which typically includes legal as well as physical constraints).

Of these, the grade is nearly always the most important. Aside from legal proscriptions, the only exceptions are high volume, low-value commodities such as sand and aggregate, for which local sources are required because transportation costs become dominant. With present separation techniques, letting Nature do as much of the separation as possible is so cost-effective that it is worth spending the effort—worldwide!—to seek out highly unusual deposits in which the concentration of a desired element is as enhanced as possible. Such orebodies are also difficult to find because they are highly localized, so that "exploration" for mineral deposits remains an important endeavor. "Prospecting" for ore is still carried out, and even though the techniques are substantially advanced beyond a burro, pick, and gold pan, the degree to which the principle remains unchanged is surprising. Sheer luck still plays a larger role than might be imagined*.

Even crustally common elements such as Al or Fe are obtained from their own ores, not from common rocks. Aluminum is the most common metal in the crust, and the third-most common element. Common rocks typically contain a few percent to a few tens of percent Al, but they are not commercial Al sources. As described in the Introduction, Al is currently extracted from a tropical soil (bauxite) in which Al oxyhydroxides have been concentrated due to millennia of leaching by rainwater. This ore is refined into metal in areas having cheap electricity, which commonly lie halfway around the world from where mining took place.

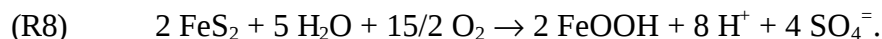
* Anyone who has worked around the minerals industry for any length of time has a collection of anecdotes about major deposits that were discovered accidentally by misinterpretation or misreading of sophisticated data sets.

Ore deposits are obviously limited, and the trend has been to exploiting lower and lower grade sources over time. For example, since the 1880s the average grade of US copper ores has dropped from ~3% to ~0.5% (Gordon et al., 1987, p. 42).

A further issue is looming here: even though the desired metal (Cu, say) makes up only 0.5% of the rock, in conventional ores it is nonetheless segregated in specific phases—so-called "ore minerals"—that can be separated from the host rock—the "gangue"[†]—by physical means. In the case of copper the typical ore minerals are sulfides, usually containing iron as well as copper, as for example chalcopyrite (CuFeS₂).

There is a fairly well-defined threshold concentration at which these separate phases do not form (e.g., Gordon et al., 1987, pp. 26-27). In that case the copper remains dispersed in the gangue minerals, into which it substitutes for more common elements such as Fe and Mg, a phenomenon termed "solid solution." This "background" concentration is the form in which most elements are present in the crust of the Earth, and it is a *considerably* more difficult form to deal with. No current technologies separate elements from their background values.

Conventional exploitation of an orebody also leads to serious environmental issues. First, as is obvious from the example of copper, most of an ore does not consist of the desired element, and the crushed piles of discarded gangue minerals are at best an eyesore that must be expensively reclaimed. At worst they become a significant source of pollution in their own right, through such phenomena as dust hazards or acid-mine drainage. The latter occurs when sulfide minerals newly exposed to air and water begin to oxidize. The usual culprit is pyrite (FeS₂), which is both abundant and usually discarded:



(Note the similarity of this reaction to that forming acid rain from sulfide impurities in coal combustion (reaction (R2)).) The mineral FeOOH is goethite, common rust. It is bright orange and accounts for the stains commonly seen along streams in mining areas. The sulfuric acid formed not only disrupts the pH of natural ground and surface waters, but also leaches metals into solution where they become a further source of pollution.

Even the processing of the extracted ore minerals is wasteful. As seen below (section 3.2.2.), Cu ores nearly always contain more Fe than Cu, but the iron is not recovered. It is merely discarded into the slag. Iron is extracted from its *own* ores, in which it is even more strongly concentrated.

Finally, it bears repeating that the US depends on foreign sources for much of its mineral commodities, as do most of the other industrialized nations.

3.2 Element Separation

Resources are but one aspect of a single, fundamental technological problem, that of separating out one type of atom or molecule from a huge (and arbitrary) background of other types. If we want what is extracted, then it is a resource. But viewed in another way, this is also the fundamental problem of pollution control, as well as of purification processes such as desalination. The difference is semantic: if we *don't* want what is extracted, it isn't resource extraction.

Because of the experience with conventional resource extraction, which requires enormously energy-intensive processes applied to deposits that are *already* anomalously enriched, element

[†] Pronounced "gang."

separation is widely believed to be a fundamentally energy-intensive process, and such beliefs are usually coupled with vague appeals to the Second Law. This misconception, moreover, is not confined merely to naïve popularizers, but is occasionally echoed by scientists, such as with Cloud's (1978, p. 321) assertion that the increase in extraction energy with lower ore grade "follows inexorably from the entropy law." These rather inchoate beliefs are further buttressed by the practical difficulties with pollution control and remediation, in which extraction of an intrinsically low-concentration component is especially difficult.

It's easy to show these perceptions are mistaken (Gillett, 1996b), as could have been anticipated by contemplating the capabilities of biosystems. The kidneys of higher animals extract certain solutes at high efficiency out of a background of many other solutes while working isothermally at near-ambient temperatures. Diatoms, algae that build intricate silica shells, extract the silica out of the ambient water at parts-per-million (ppm) levels (Figure 5). Plants extract atmospheric CO₂ (concentration ~300 ppm) to build their intricate organic structure, and their roots extract nutrient elements at low concentrations, some (e.g., Mo) at ppm levels. All this, moreover, is carried out using a diffuse and intermittent energy source—sunlight.

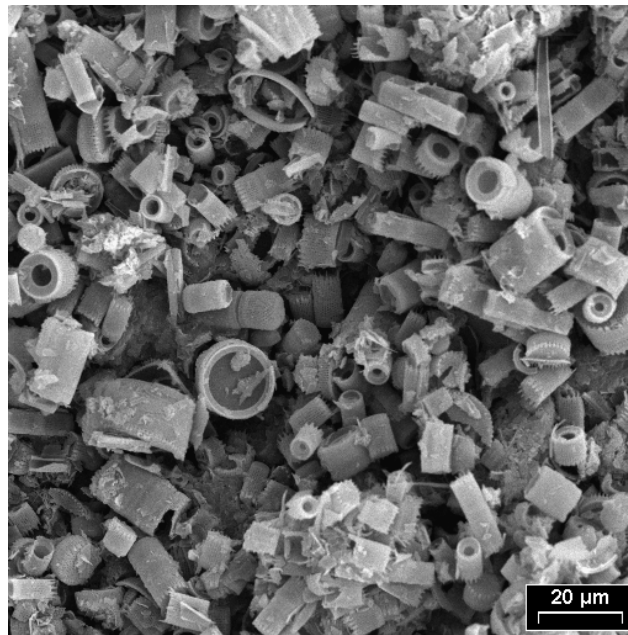


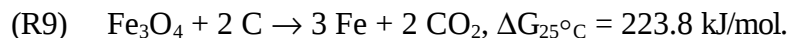
Figure 5.

Figure 5. Diatoms (*Melosira granulata*) from the Pliocene of western Nevada. This organism constructs a shell ("test") essentially made of a hydrous silica glass by extracting dissolved silica (as H₄SiO₄), which is present at levels of a few ppm in its aqueous environment. (Scanning electron microscope photo by the author with assistance of L.Grasseschi, UNR.)

To anticipate the conclusions below, biosystems are capable of such feats because they work at molecular scales.

3.2.1. Fundamental costs of element extraction.

But let us first examine the fundamental thermodynamic cost involved in separation. This cost is set by the free energy difference between the initial and final phases, e.g.:

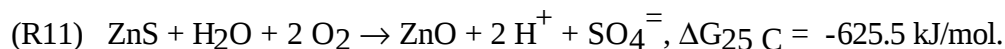


As [Kellogg \(1977\)](#) notes, if the initial phase (i.e., the ore mineral) is taken as the metal oxide, this true thermodynamic cost is typically a few percent of the actual energy costs; and this, moreover, is *only* the process cost for the chemical transformation. It ignores the crushing and beneficiation costs mentioned below.

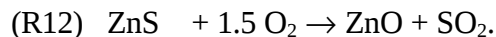
But in fact [Kellogg \(1977\)](#) drastically understates the inefficiencies in many cases, because many ore minerals are not oxides but sulfides. Metal sulfides react *exoergonically* with oxygen. In the case of zinc, for example:



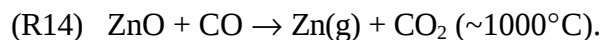
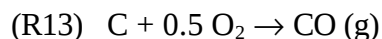
Thus, according to the laws of thermodynamics, we could use sulfide ores as fuels and get metal as a by-product! Here again, biosystems are way ahead of current technology. Chemolithotrophic bacteria nearly manage this, although they do not usually extract the free metal but oxidize it as well, e.g.:



Instead, current thermal technology begins by "roasting" the zinc sulfide to convert it to the oxide(!), thereby throwing its free energy away ([Rosenqvist, 1983, pp. 277-86](#)):



The oxide is then reduced to metal vapor (!!) by carbon monoxide at elevated temperature:



The zinc vapor is condensed to separate it from the CO_2 , while any silicate impurities form an immiscible liquid (a *slag*) that is left behind and discarded.

The process is grossly energy intensive, but not because of the laws of thermodynamics.

3.2.1.1. Solution extraction. Let us consider another example of fundamental thermodynamic costs, this one of a dilute solution that is typical of "real world" cases that arise repeatedly in both resource extraction and pollution control. Assume we have a 1 part-per-million (ppm) aqueous solution of CuSO_4 , such as might arise from a sulfuric acid leach of ore rock or from acid-mine drainage, and calculate the true thermodynamic limiting cost at STP of separating out pure copper sulfate.

We assume that the solution species are fully dissociated into ions, which is reasonable for such a dilute solution. On converting to molarities:

$$1 \text{ ppm CuSO}_4 \sim 6.27 \text{ } \mu\text{M CuSO}_4 = 6.27 \text{ } \mu\text{M Cu}^{++} = 6.27 \text{ } \mu\text{M SO}_4^{--}.$$

The free energy is concentration dependent:

$$\Delta G = \Delta G_0 + RT \ln \{ \text{Cu}^{++} \} \{ \text{SO}_4^{--} \}$$

where ΔG_0 (= 16.8 kJ/mol, from [Robie et al., 1978](#)) is the free energy of formation of the aqueous ions in their standard state from solid CuSO_4 , R is the gas constant, T is absolute temperature, and the braces indicate the activities of the aqueous ions. Using the Debye-Hückel formula (e.g., [Stumm & Morgan, 1970, p. 83](#)) for aqueous activities, we find $\{ \text{Cu}^{++} \} = \{ \text{SO}_4^{--} \} = 6.13 \times 10^{-6}$, and hence $\Delta G \sim -42.7 \text{ kJ/mol CuSO}_4$. This is a trivial amount. For comparison, it is about the energy needed to evaporate 5 moles ($\sim 90 \text{ g}$) of water at STP; and along with 1 mole of pure CuSO_4 one has also gotten 999,999 moles of pure water.

3.2.1.2. Mixing entropy. In the limit of non-interacting particles—i.e., an ideal solution, the free energy of the solution reduces to the mixing entropy alone, multiplied by the absolute temperature:

$$\Delta G = -T\Delta S.$$

Molar mixing entropy is given by:

$$(E6) \quad S_m = -R \sum_{i=1}^N x_i \ln x_i,$$

where R is the gas constant, x_i the mole fraction of component i , and there are N components (e.g., [Moore, 1972, p. 239](#)). Note that it is independent of temperature.

For extraction of one component from a background of other components, we may treat the mixture as made of two components, with $x_1 = x$ = the mole fraction of the desired component and $x_2 = 1 - x_1 = 1 - x$ = "everything else." Equation (E6) then becomes:

$$(E7) \quad S_m = -R [x \ln x + (1-x) \ln (1-x)].$$

Eq. (E7) is entropy per mole of *mixture*. In the case of the desired component, we would like to determine its mixing entropy per mole of *component*, S_m' . To get this divide (E7) by its mole fraction x :

$$(E8) \quad S_m' = -R [\ln x + [(1-x)/x] \ln (1-x)].$$

As would be expected, this normalized entropy $\rightarrow \infty$ as $x \rightarrow 0$. As the solute concentration goes to zero, more and more solution must be processed to extract a mole. Even so, however, the absolute amounts remain surprisingly modest for quite low concentrations. Let us examine, for example, the 1 ppm CuSO_4 solution treated in the previous section. A concentration of $6.3 \text{ } \mu\text{M}$ corresponds to a mole fraction of $\sim 1.13 \times 10^{-7}$. Evaluating equation (E8) then yields $S_m' = 141.3 \text{ J/K mol}$, so that $-T\Delta S$

at 25°C is -42.1 kJ/mol. This value is within 1.5% of the value found by the more accurate calculation in section 3.2.1.1. The reason, of course, is that any solution approaches ideality as it becomes more dilute.

3.2.1.3. Macroscopic "entropy." Thus even for molecular mixtures the entropy cost is small. However, most things are *not* molecularly mixed, and in such cases the true thermodynamic entropy becomes utterly negligible. This will now be demonstrated.

Elementary textbooks (e.g., [Broecker & Oversby, 1971, p. 240](#)) assert that the entropy of a macroscopic mixture is "zero." The reason is simply combinatorial arithmetic: molecules and atoms are so much smaller than even "small" particles that the number of their possible arrangements swamps the number possible with the particles.

We can illustrate this with some crude examples. Consider a 1:1 mixture of 1 µm grains of salt (NaCl) and quartz (SiO₂). We can use (E6) to calculate the mixing entropy:

$$S_m = -2R(0.5 \ln(0.5)) = 5.76 \text{ J/mol K},$$

but this is per mole of *grains*. We now need to find the entropy per mole of compound. Each grain contains $(1 \text{ µm})^3 \rho_i / g_i$ moles of compound *i*, where ρ_i is the density and g_i the molecular weight. For salt $\rho_i = 2.165 \text{ g/cm}^3$ and $g_i = 58.44 \text{ g/mol}$, and so there are 3.70×10^{-14} moles/grain; for quartz ($\rho_i = 2.660 \text{ g/cm}^3$ and $g_i = 60.08 \text{ g/mol}$) there are 4.43×10^{-14} moles/grain. Hence there are $\sim 4 \times 10^{-14}$ moles/grain on average, so a mole of grains contains $\sim 6.02 \times 10^{23} \times 4 \times 10^{-14} \sim 2.4 \times 10^{10}$ moles of compound. The correct mixing entropy per mole of *compound* is then $\sim 5.76 / 2.4 \times 10^{10} \sim 2.4 \times 10^{-10} \text{ J/mol K}$, which is utterly negligible for all practical purposes.

For another illustrative example, consider an orebody containing 0.1% of an ore mineral that consists of randomly distributed 1 µm grains. These could be copper-bearing sulfides in a copper orebody. As described below, such grains need to be extracted for processing into Cu metal, so let us estimate the true entropy cost of doing so.

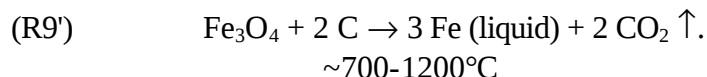
Using (12) with $x = 0.001$ yields $S_m' = 65.74 \text{ J/mol K}$, and again this is per mole of grains. If the grains are CuFeS₂ (chalcopyrite), there is $\sim 2.3 \times 10^{-14}$ mole/grain, and a mole of grains contains $6.02 \times 10^{23} \times 2.3 \times 10^{-14} = 1.4 \times 10^{10}$ moles. The resulting entropy is then $\sim 65.74 / 1.4 \times 10^{10} \sim 4.8 \times 10^{-9} \text{ J/mol K}$, which is again utterly negligible.

Extracting ore minerals from such orebodies is energetically intensive, but that energy consumption results from the technologies used, not from the laws of thermodynamics.

3.2.2. The Promethean paradigm, part II: Phase separation

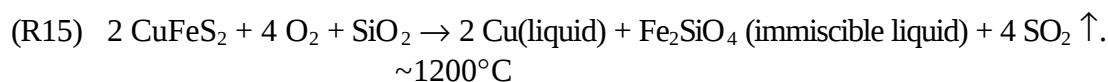
Thus element separation, despite conventional wisdom, is not intrinsically an energy-intensive process. The prodigious energy costs of conventional resource extraction are due to clumsy technology. In particular, they result from the application and extraction of vast amounts of heat. Thus the Promethean paradigm dominates extractive processes even more than it does energy-transformation processes. Most current extraction and purification technologies may be summarized as "heat and cool and wait for phase changes." Vast amounts of heat are input to cause melting and/or vaporization, and then extracted to cause condensation and/or crystallization. The spontaneous partitioning of different atoms between these coexisting phases is then exploited for separation.

This was already illustrated in the example of zinc pyrometallurgy (section 3.2.1.). For another example, to return to reaction(R9), conventional iron pyrometallurgy involves heating an Fe oxide with carbon (coke) to high temperature for an overall reaction ([Rosenqvist, 1983, p. 244-255](#)):



The CO₂ escapes while molten iron remains behind. Many impurities also separate into a slag, which is immiscible with the molten iron (much like oil and water) and so can be decanted and discarded separately.

Similarly, conventional copper ores, consisting of Fe-Cu sulfides, are melted to form a *matte* from which Fe is typically separated by oxidation and separation as a slag ([Rosenqvist, 1983, p. 324-41](#)):



Note that silica (SiO₂) must be added to separate the Fe into a slag. Again, nearly all Cu ores contain more Fe than Cu, but with current technology the Fe is not recovered but merely discarded into the slag(!). Previously the sulfur dioxide (SO₂) was also discarded, to become a significant source of pollution, but now it is generally recovered as a by-product for H₂SO₄ production.

Of course, not only do such pyrometallurgical processes consume vast amounts of heat, but by carrying out the processing at high temperatures the irreversible losses are greatly increased because the TΔS term is proportionately larger.

As can be seen in the example of Cu, reagents also are commonly added. These can cause new phases to become stable, or simply change the physical properties in useful ways, such as to make the slag fluid at lower temperatures (e.g., as with fluorite (CaF₂) in steelmaking). Although they save process energy by allowing processes to be carried out at lower temperatures, such reagents obviously add to costs, not least because they themselves are commonly extracted and purified by thermal means.

Even though thermal partitioning processes are simple—smelting hasn't fundamentally changed since antiquity—thermal separation is not only grossly inefficient but dirty, as the element partitioning is never perfect. Some of the desired element always goes into the waste phase, through the same "solid solution" phenomena that account for background concentrations of rare elements in ordinary rock-forming minerals.

Such losses are also greater the higher the temperature, because more thermal energy is available to overwhelm the difference in binding energies. (In other words, the higher the ambient temperature, the greater the degree to which solutions approach ideality.) This not only decreases recovery, but causes pollution due to the increased losses into the unwanted phase. In the case of copper, for example, some Cu goes into solid solution in the silicate phase and so is lost into the slag ([Rosenqvist, 1983, p. 331-2](#)). It also follows that concentrated sources are required for thermal partitioning techniques to work in the first place.

3.2.2.1 Beneficiation. As mentioned in section 3.1, orebodies typically consist of ore minerals dispersed in a much larger volume of gangue minerals. Thus, another major part of extraction costs is simply the crushing of rock before it can be beneficiated and smelted, as emphasized by [Kellogg](#)

(1977). "Beneficiation" is simply the set of processes by which the ore minerals are physically separated from the gangue so that they can be processed into metal, via the pyrometallurgical processes discussed above, and carrying out such separation requires that the host rock matrix be broken up. Although there is a fundamental energy cost in crushing, that of creating new surface energy, most (>90%) of the applied mechanical energy is simply thermalized (Kellogg, 1977).

Again, all the above are merely statements of current *engineering* limitations. They are *not* fundamental limits set by natural laws.

3.3. Molecular Separation.

"A pollutant is just a misplaced resource."

—Anonymous.

Biosystems are capable of their remarkable feats of separation because they do not rely on phase changes. Instead, molecular mechanisms literally carry out separations molecule by molecule. Such molecular separation is both far more efficient and capable of extraction from considerably lower concentrations. Diatoms (Figure 5), for example, bind individual molecules of H_4SiO_4 in the ambient water with specialized complexing agents, whence they are brought into the cell. (Organisms also are commonly effective in concentrating pollutants out of the environment.) Hence, nanotechnological emulation of such molecular mechanisms promises similar extraction capabilities.

3.3.1. Solution separation.

Among the most important separation problems is the extraction of solutes from aqueous solutions. This is basic to pollution control and purification, which are clearly not amenable to separation by thermally driven phase changes. Using fluid media also has the great advantage that the automatic diffusive transport of the atoms and molecules is exploited to separate them. Indeed, this advantage is probably critical to early applications of nanotechnology to element separation, as it is what allows the use of passive devices such as semipermeable membranes. Although nanomachines for mechanical disruption of solid materials could be envisioned, they are unlikely to reflect early applications of MNT!

Solution extraction also does not require the comminution of vast amounts of raw rock, which forms such a large and energy-intensive part of conventional resource extraction. Hence resource extraction based on solution chemistry (so-called *hydrometallurgy*) has been attracting increasing interest in recent years due to its potentially greater energy efficiency. Most simply, elements could be extracted from seawater, as is already the case for several elements such as Mg and Br. More concentrated natural solutions (e.g., saline lake or oil-field brines) are probably more practical, however, at least for certain elements. Elements such as Li and borates are already extracted from saline-lake brines in which they are unusually concentrated. Lithium, for example, is obtained from brines in Clayton Valley, near Tonopah, Nevada, currently the only domestic source of Li.

Selective dissolution—"leaching"—of ore rocks and processing of the solution is also already practical in certain cases. For over a century gold ores have been leached by dilute cyanide solution, which takes advantage of the near-quantitative formation of the very stable $\text{Au}(\text{CN})_2^-$ ion in aerated solutions. Cyanide leaching has now been developed to the point that ores can contain <1 ppm Au in favorable cases. Leaching of low-grade Cu ores with dilute H_2SO_4 has also become of commercial importance in the last few decades. Once again, too, biological systems have anticipated technology.

Digestion, after all, may be viewed as solubilizing food so that particular compounds can be extracted from it.

Whether the application is purification, pollution control, or hydrometallurgical extraction, *selective* extraction from solution is usually of paramount importance. Commonly a toxic (Pb^{++} , Cd^{++} , etc.), or valuable ($\text{Au}(\text{CN})_2^-$, Li^+ , etc.) solute is dispersed in a much more abundant background of innocuous solutes, and one wants to extract only the desired solute. In the case of Cu-bearing leachate solutions, for example, there is much more Fe than Cu in the solution. Hydrophobic organic ligands (e.g., hydroxyoxime, Figure 6) that are highly specific for Cu^{++} are dissolved in an organic solvent, usually kerosene, and this solvent is mixed with the aqueous Cu-bearing solution (e.g., [Kordosky et al., 1987](#)). The Cu is extracted essentially quantitatively into the organic phase while the Fe remains in the aqueous solution. Kerosene is, of course, immiscible with water, so the Cu-bearing organic phase can now be separated physically and the Cu extracted to regenerate the solution. The whole process, termed "solvent extraction," has become a routine approach to resource extraction.

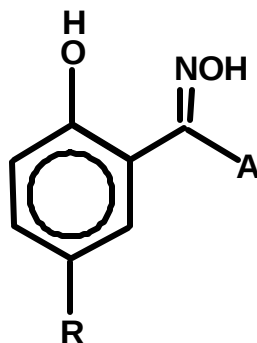


Figure 6.

Figure 6: Hydroxyoximes, the basis of the solvent extraction of Cu. These hydrophobic compounds are dissolved in a hydrocarbon phase, typically kerosene. They are highly specific complexing agents for Cu^{++} and extract it essentially quantitatively out of an adjacent aqueous phase. A is H, methyl, or ethyl; R is a longer alkyl sidechain, typically $\text{C}_9\text{-C}_{12}$.

Currently, however, the efficiencies of hydrometallurgical processes are still low. In part this is because most approaches still rely on isothermal phase changes, such as precipitation or the partitioning between immiscible liquids described above. Hence additional reagents, which probably *were* purified or synthesized thermally, are still required. The separation is also commonly not clean, a problem that plagues solvent extraction particularly: unmixing of the organic solvent from the aqueous solution is sufficiently incomplete that the aqueous phase becomes seriously contaminated and expensive reagents are also lost. Reaction rates also tend to be sluggish at low temperature, which biological systems overcome with highly specific catalysts (enzymes). Furthermore, less energy-intensive approaches, such as separation by membranes or ion exchangers, tend to be non-selective. Nonetheless, even with primitive present-day approaches, materials that are in part molecularly designed and structured are being applied to separation out of solution.

3.3.1.1. Semipermeable membranes. For example, semipermeable membranes, in which only certain dissolved species can cross the membrane barrier, are currently attracting enormous interest, especially in pollution control and purification (e.g., [Caetano et al., 1995](#)). In *electrodialysis* (e.g., [Korngold, 1984](#)) an electric potential is used to move ions differentially. A vessel containing the solution is partitioned by alternating membranes permeable to anions and cations, respectively. Application of a potential across the vessel causes cations and ions to migrate in opposite directions, such that the compartments walled by the membranes become alternately saltier and fresher (Figure 7). Electrodialysis has the advantage of ambient pressure operation, but the resistance of the solution becomes a serious source of efficiency loss for dilute solutions.

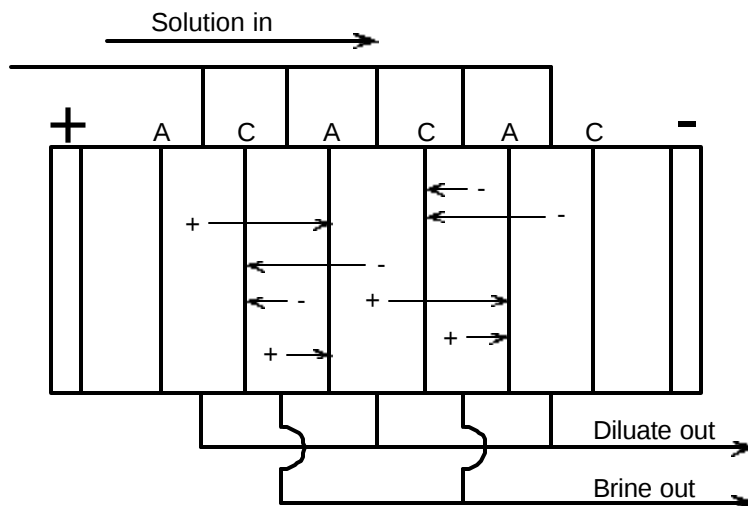


Figure 7.

Figure 7: Electrodialysis. Electrodialysis purifies water by means of the differential movement of ions, driven by an applied electric field, through permeable membranes. Alternating compartments, each bounded by an anion-permeable (A) and cation-permeable (C) membrane, thus become fresher and brinier.

In *reverse osmosis* dissolved ionic species are "strained" out of a solution by a pressure gradient. This is a reasonably mature technology for such applications as desalinating brackish water. Its big disadvantage is that it requires manipulation of pressures above ambient. Finally, *ultrafiltration* refers to the filtering out of macromolecules or colloids, so that it lies between reverse osmosis and conventional filtration.

Membrane processes tend to be non-selective. Conventional semipermeable membranes typically consist of aggregates of polymers, and as there is little control on the aggregation, the pore sizes in the membranes are non-uniform. In the case of membranes permeable to cations or anions, specific side chains bind the solution species, typically with electrostatic interaction. Because of the absence of atomistic control, these sidechains are not necessarily exposed to the solution and so many are useless.

3.3.1.2. Ion Exchangers. *Ion exchangers* may be solids such as zeolites, or polymers ("resins") with ionic side chains that have varying affinities for specific ions. In both cases dissolved ions

having greater affinities with the binding sites replace the species already there. (Obviously this in turn implies that the ions must have access to those sites.)

Some issues are much as with membranes, and indeed often the same polymers are used. For one thing, ion exchange is often not very selective. Ion exchangers are widely used domestically, for example, for softening water. Hard water contains sufficient divalent cations (Ca and/or Mg) to interfere with cleaning by soap, because these ions form insoluble salts with stearate and other fatty-acid anions used in soaps, so they cannot act as surfactants. In a domestic water softener, Ca^{++} or Mg^{++} is exchanged for Na^+ , which has no effect on soap action. The basis of the exchange is simply the greater electrostatic attraction of the dications for the binding sites.

What might be termed "dynamic" selectivity exists through subtle difference in dissociation constants between the active sites and the solution species, so that on repeated exchanges over time a significant separation builds up. If a batch of mixed solution is inserted in the top of an ion-exchange column and allowed to flow through, for example, the solution that eventually exits will have varying composition depending on the time it exits. The solution that first exits will be enriched in the ion with the least affinity for the binding sites, and so forth. The same principle underlies the various kinds of chromatography, which are widely used on a laboratory scale for separation. This can be used for quantitative separation if the ion-exchange column is sufficiently long. Such a scheme is practical for separating solutes such as rare earth elements, whose separation is otherwise extremely difficult, but it is not otherwise economic as it is a time-consuming batch process.

Another disadvantage of exchange is that it doesn't change the total number of solutes. As the name implies, it just exchanges one for another, so that the overall salinity of the solution does not change. Hence it is a separation technique but not a purification technique.

Ion exchangers also suffer from what might be called the "elution problem." Once the exchanger has been fully loaded with the ion to be extracted, the exchanger must be "regenerated": the extracted ions must be removed from the exchanger so that it can be used again. Typically this involves "overwhelming" the ion exchange sites with a high concentration of the replacement ion. In this way an ion with less affinity for the binding sites can displace an ion with a greater affinity simply through LeChatier's Principle. For example, once completely charged with Ca^{++} , water softeners are regenerated by flushing a concentrated NaCl brine through them. The concentration of Na^+ is so much greater than Ca^{++} that the Ca^{++} is displaced quantitatively. The result is an ion exchanger whose active sites are again occupied by Na^+ ions, so that it is again ready to exchange Ca^{++} from dilute solution. This has been achieved, however, at the cost of generating a huge volume of secondary waste brine. Thus, not only do ion exchangers not change the total solute content, but in practice they worsen overall pollution problems.

3.3.1.3. Complexing agents and molecular recognition. A great deal of work has been done on "molecular recognition," the selective binding of particular molecular species through fitting to molecular substrates in a "lock and key" manner (e.g., [Lehn, 1994](#); [Gellman, 1997](#); [Mallouk & Gavin, 1998](#); [Rebek, 1998](#)). In this way individual solutes (molecules or ions) could be extracted extremely selectively. The approach is used by biological systems, in which various species (e.g., nutrient molecules) are extracted and transported by means of selective binding to sites on specific proteins.

Several research groups have designed highly selective molecules for the extraction of ions from solution. Macrocyclic polyethers and substituted polyethers (so-called "crown ethers") are highly effective complexing agents for many metal ions (e.g., [Bradshaw & Izatt, 1997](#), and refs. therein). They

can also be strongly selective, in part due to the differing fits of ions into the ring ("crown"), and the selectivity can be varied by changing the crown size, by substituting other atoms into the crown (Figure 8), and so forth (e.g., [Fenton, 1993](#); [Bradshaw & Izatt, 1997](#)).

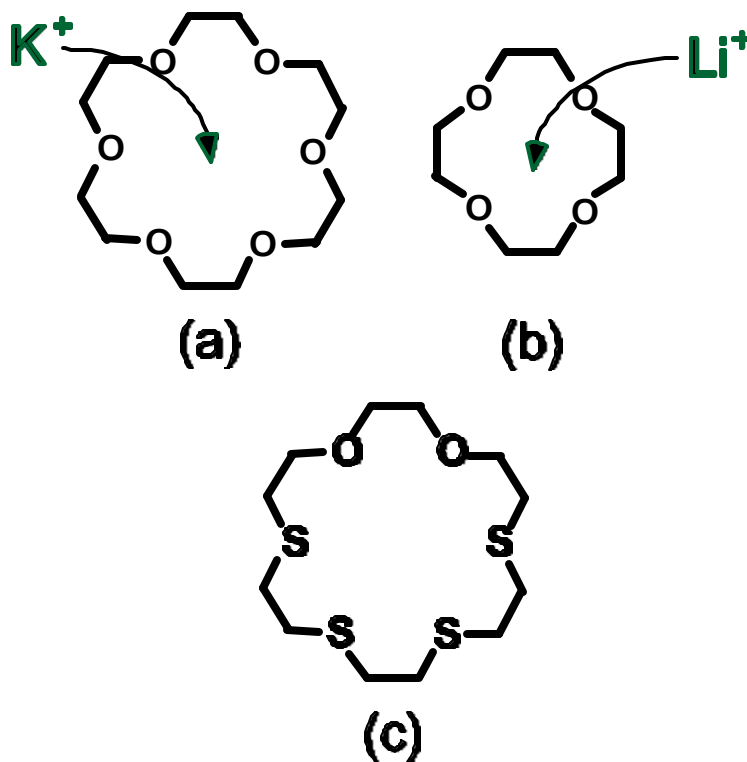


Figure 8.

Figure 8: Crown ethers, one type of macrocyclic ligand. Selectivity depends on the fit of the ion inside the ring. (a) 18-crown-6 is highly selective for K^+ . (b) 12-crown-4 is highly selective for the small Li^+ ion. (c) Substituted crown ether, 1,4,7,10-tetrathia-18-crown-6. Because of the replacement of O by S, this macrocycle has a selectivity for Ag^+ over Na^+ of $>10^{10}$ ([Bruening et al., 1991](#)).

Although similar complexing agents have attracted attention for therapeutic treatment of toxic metal poisoning (e.g., [Abu-Dari et al., 1990, 1993](#); [Kappel et al., 1985](#); [Raymond et al., 1984](#)), merely complexing an ion is generally of limited value because the complexed ion remains in solution. To effect separation, such molecules have been "tethered" (covalently bound) to a silica surface ([Izatt et al., 1995, 1996](#)) to make a "functionalized" substrate, in essence a highly specific adsorbing surface for particular metals. Such surfaces have been used for recovering Pt and Pd selectively from catalytic converter scrap ([Anonymous, 1997](#)). Due to the expenses of the syntheses, however, this approach at present makes sense only in high-value applications. Other such applications include nuclear waste separation ([Izatt et al., 1996](#)), and analysis, for which little material is required.

In effect such a surface is an extremely selective, molecularly designed ion-exchanger. Unfortunately, this makes the elution problem even worse: in general the more selective and quantitative the binding of a solute to a substrate, the more difficult it is to *unbind*. Typically, therefore, extracting the solute (and regenerating the substrate) require extreme chemical conditions such as elution with strong acids or bases. Obviously, this seriously compromises the value of this separation approach because the eluted solutions themselves become a major separation and disposal problem.

3.3.1.4. Switchable binding. Biological molecules that bind solutes avoid the elution problem by being "switchable": under one set of conditions they bind strongly, but under different conditions the binding is weak or nonexistent. An example is hemoglobin, whose affinity for O₂ depends on its molecular configuration. Switchable binding would obviously be of great interest for technological applications as well and seems a particularly obvious area to apply molecular design and construction. Some of the so-far embryonic research in this area is briefly sketched below. [Shinkai \(1996\)](#) gives a more detailed review.

3.3.1.4.a. Redox-switchable binding. One obvious approach is redox switching, in which the affinity of the substrate for the solute depends on whether it is reduced or oxidized. A few of these systems will be briefly described below. [Kaifer & Mendoza's \(1996\)](#) review has more detail.

Various redox-active species have been functionalized to give switchable binding. [Devonport et al. \(1997\)](#) and [Le Derf et al. \(1999\)](#) have incorporated a tetrathiafulvalene moiety into a macrocycle. Several groups (e.g., [Raban et al., 1983](#); [Shinkai et al., 1985ab](#); [Ramesha & Chandrasekaran, 1994](#)) have based redox-switching on the reversible formation and cleavage of a sulfur-sulfur link in a macrocycle. Crown ethers with redox-active sidechains ("lariat ethers") have also been investigated ([Gustowski et al., 1984](#); [Kaifer et al., 1985](#); [Delgado et al., 1986](#); [Miller et al., 1988](#)).

Quinones, a well-known redox system in organic chemistry, have been functionalized with cation-binding moieties (e.g., [Sugihara et al., 1981](#); [Gustowski et al., 1986](#); [Delgado et al., 1988, 1992](#); [Echegoyen et al., 1989, 1994](#); [Gomez-Kaifer et al., 1994](#)). Quinones readily and reversibly undergo reduction to the "hydroquinone" form (Figure 9), and in fact are the basis of many biological electron-transfer reactions. The stoichiometry is:



quinone (oxidized)

hydroquinone (reduced)

Incorporation of a quinone moiety into a macrocycle causes the macrocycle's affinity for a cation to depend on the oxidation state of the quinone. Typically the reduced form shows higher affinity, as in effect the hydrogen of the hydroquinone is displaced by the cation.

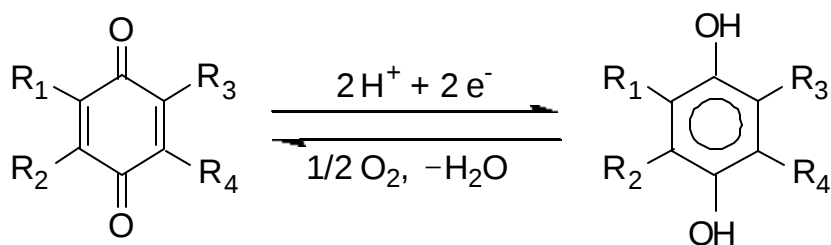


Figure 9.

Figure 9: Quinone $\rightleftharpoons$ hydroquinone. Quinones (left) are readily reduced to the hydroquinone form (right), and this redox switching is already extensively employed by biological electron-transfer mechanisms. Incorporation of a (hydro)quinone moiety into a macrocycle can greatly alter its affinity for incorporated ions, depending on its oxidation state.

Much of this research has been directed toward modeling of biological membrane transport. Transport across cell membranes, which are lipophilic, typically involves complexation of the solute to be transported with a hydrophobic, switchable "carrier," which releases the complexed solute on crossing the membrane. If such a system can be emulated technologically sufficiently cheaply, it would have obvious applications in separation involving solvent extraction or in so-called "liquid membranes," in which the membrane is an immiscible liquid phase separating two aqueous phases.

A great deal of research has also been focused on solution-based systems involving redox-activated binding to functionalized ferrocenes. The "iron sandwich" compound ferrocene (Fc; Figure 10) is a very stable moiety that has been incorporated into a vast number of compounds. It undergoes a highly reversible oxidation to the "ferricenium" cation:

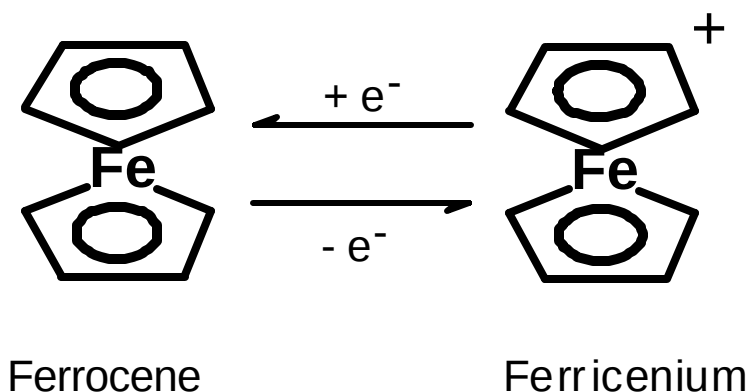


Figure 10.

Figure 10: Ferrocene. The "iron sandwich" compound ferrocene (dicyclopentadienyliron(II), abbreviated Fc) undergoes ready and reversible oxidation to the ferricenium cation, Fc^+ .

Many groups have functionalized ferrocenes for redox-switchable binding to cations by linking complexing moieties such as crown ethers or cryptands to the ferrocene group (e.g., Allgeier et al., 1997; Beer & Smith, 1998; Beer & Wild, 1996; Beer et al., 1993ab, 1994, 1995; Chen et al., 1995; De Santis et al., 1992; Hall et al., 1993, 1997; Lloris et al., 1998; Plenio & Aberle, 1997; Plenio & Diodone, 1995; Plenio et al., 1997; Su et al., 1999; Tendero et al., 1996). In general, oxidation of the ferrocene group to ferricenium causes the bound cation to be expelled through electrostatic repulsion. Because the binding to the ferrocene also causes a measurable change in its potential, such modified ferrocenes have been used as sensors for particular solutes. Modified ferrocenes attached to electrode surfaces are now routinely used for analysis, particularly for biological applications where very low concentrations are involved (e.g., Albagli et al., 1993; Anicet et al., 1998; Audebert et al., 1996; Bashkin & Kinlen, 1990; Blonder et al., 1996; Bruening et al., 1997; Bu et al., 1995; Chao et al., 1983; Chen et al., 1994; Ching et al., 1994, 1995; Di Gleria & Hill, 1992; Hale et al., 1991; Moutet et al., 1996; Schuhmann et al., 1991; Wang & Mulchandani, 1995).

A few groups have demonstrated prototype systems using functionalized ferrocenes for separation. Saji & Kinoshita (1986) demonstrated that a functionalized ferrocene could be a carrier in switchable liquid membrane transport. Another example is the redox-switched binding and release of pertechnetate ion (TcO_4^-) by modified ferrocenes (Clark et al., 1996, 1999; Strauss, 1999; Chambliss et al., 1998; Dorhout & Strauss, 1999). Ferrocene is already a hydrophobic molecule, but these researchers rendered it even more hydrophobic by attaching branched hydrocarbon chains at two points on each cyclopentadienyl ring. This molecule could also be adsorbed to a silica gel surface (Chambliss et al., 1998). In the ferricenium form, this modified ferrocene forms ion pairs with large, low-charge, relatively hydrophobic anions such as TcO_4^- , so such anions are preferentially adsorbed to this functionalized surface. On reduction of the ferricenium, however, the ion pairs break up so that the anion can be extracted and concentrated. Re-oxidation of the ferrocene to ferricenium then regenerates the adsorbing surface.

Technetium ($Z = 43$), of course, has no stable isotopes. The isotope ^{99}Tc , however, is a long-lived ($t_{1/2} \sim 2 \times 10^5$ y) fission product that is a source of serious environmental concern. In aerated water it readily oxidizes to the soluble and mobile TcO_4^- ion, so methods of extracting low concentration of TcO_4^- from aqueous solutions are obviously of great interest.

A different approach to redox-switched binding is through electrochemically switched intercalation and release of ions into an open crystal structure. Kanoh et al. (1993a), for example, demonstrated switchable lithium intercalation into $\lambda\text{-MnO}_2$. In this case, the $\lambda\text{-MnO}_2$ forms the surface of an electrode and the redox switching is driven by the application of a potential, not by redox reactions. This compound has a defect spinel structure (Hunter, 1981) in which 1/3 of the tetrahedral sites are not occupied. Electrochemical reduction of 1/3rd of the Mn^{4+} to Mn^{3+} causes the small Li^+ ion to be drawn into those sites to maintain charge balance. Reoxidation of the Mn^{3+} by reversing the potential expels the Li^+ again. Other unipositive metal ions such as Na^+ are too large to be intercalated in this way. As Na^+ is much more common than Li^+ , the intercalation also provides an elegant way of

separating Li^+ . This system is the subject of a patent for selective removal of Li^+ from dilute brines (Kano et al., 1993b).

A similar system was demonstrated by Lilga et al. (1997), involving reversible Cs^+ intercalation into an electrode covered with cesium nickel hexacyanoferrate ($\text{CsNiFe}(\text{CN})_6$). Nickel hexacyanoferrate has the open perovskite structure with cyanide ions replacing oxygen ions (Figure 2). Thus six cyanide ions surround each Fe atom at the vertices of an octahedron and the vertices of the octahedra are all shared. On reduction of some of the Fe^{3+} to Fe^{2+} , the large Cs^+ ion is preferentially intercalated into the large voids that remain between the octahedra to preserve charge balance. This intercalation is surprisingly selective even in the presence of other unipositive cations like Na^+ , typically an abundant background ion. Reoxidizing the Fe^{2+} in the electrode expels the intercalated cations. As ^{137}Cs is of great concern in fission waste, the reason for interest in selective Cs^+ removal at low concentrations is obvious. Ikeshoji (1986) proposed a similar reversible intercalation system for alkali metal cations using Prussian blue (potassium iron hexacyanoferrate, $\text{KFe}_2(\text{CN})_6$). To illustrate the difficulties with a practical system, though, Doštal et al. (1996) found irreversible behavior on Rb^+ and Tl^+ intercalation, which these workers attributed to changes in channel sizes in the hexacyanoferrate structure on intercalation.

Ion intercalation was already mentioned in the context of batteries (section 2.2.4.1.a.). Indeed, $\lambda\text{-MnO}_2$ has also been proposed as an electrode for Li-batteries. Crystal structures capable of intercalating ions are also obviously closely akin to solid electrolytes (section 2.2.1.1.b.), so developmental synergies with these other applications should exist.

3.3.1.4.b. Electrosorption. Electrosorption has seemed a promising technique for water purification since the 1960s (Johnson & Newman, 1971), but only recently have improvements in electrode materials made it appear practical (e.g., Farmer et al., 1996). The technique is elegantly simple in conception: charged electrodes attract dissolved ions out of water to establish a double layer. When the electrodes are filled to capacity, they can then be regenerated merely by switching their polarity.

To extract a significant amount of material a high-surface-area electrode is obviously required. A kinship to double-layer capacitors (section 2.2.4.1.b.) is also obvious. Indeed, some of the same high-surface-area materials, such as carbon aerogels, are used for electrosorption electrodes. Also, because the completely filled electrode is essentially a charged capacitor, the energy stored therein can be recycled at least partly when the electrode polarity is reversed.

3.3.1.4.c. Light-driven switching. An attractive "reagent" for switching the binding state of a solute is light, and a number of systems involving photoswitchable binding of a solute species have been described. Most utilize photoactive organic molecules of various sorts. Typically a chelating moiety such as a crown ether is linked to the active molecule so that the degree of binding depends on the state of the photoactive molecule (e.g., Al'fimov et al., 1991; Barrett et al., 1995; Kimura et al., 1997; Martin et al., 1996; Stauffer et al., 1997; Tucker et al., 1997).

Commonly the change in binding ability relies on a change in molecular shape due to photoisomerization. For example, several groups (e.g., Blank et al., 1981; Shinkai et al., 1982, 1983, 1987; Akabori et al., 1995; Fürstner et al., 1996) have incorporated an azobenzene moiety in the macrocyclic ring (Figure 11). Photoisomerization around the $\text{N}=\text{N}$ double bond in the azobenzene then drastically changes the shape of the ring and hence its ability to incorporate cations. Similarly,

photoisomerization around a C=C double bond has also been exploited (e.g., [Irie & Kato, 1985](#); [Marquis et al., 1998](#)).

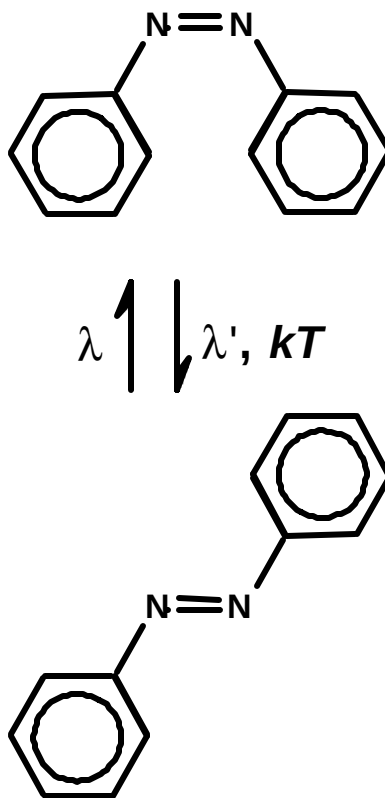
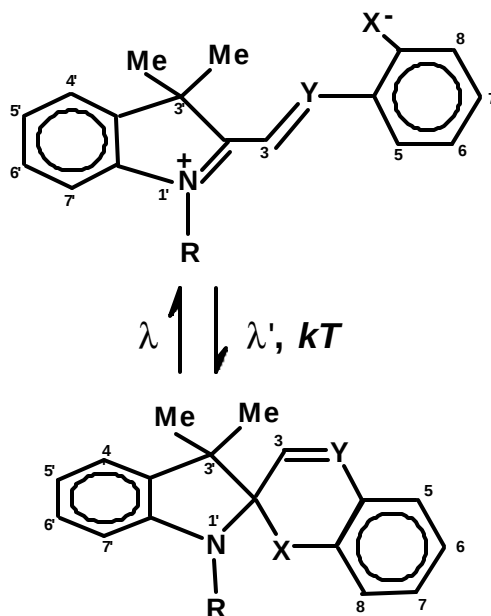


Figure 11.

Figure 11: Azobenzene. UV illumination causes rotation around the double bond to the sterically hindered (*cis*-) form. Long-wavelength illumination, or exposure to ambient temperatures, cause reversion to the open (*trans*-) form.

Several research groups (e.g., [Atabekyan & Chibisov, 1986, 1997](#); [Gorner & Chibisov, 1998](#); [Inouye et al., 1997](#); [Kimura et al., 1994](#); [Sasaki et al., 1986](#)) have investigated light-driven cation binding based on spiropyrans and spiroxazines, a class of photoactive organic compounds that has attracted particular attention (e.g., [Bertelson, 1971b](#); [Guglielmetti, 1986](#); [Chu, 1986](#); [Berkovic et al., 2000](#)). These molecules are photochromic. On UV illumination they change their shape completely (Figure 12): cleavage of the C-X bond at the "spiro" (tetrahedrally coordinated) carbon between carbons 1' and 3 causes free rotation around the 1'-3 axis to yield a structure with a double-bonded linkage like a merocyanine dye. This utterly rearranges the electronic structure of the molecule so that its absorption spectrum changes drastically, and in turn this causes the color change on illumination. Typically they return to the *spiro*- form in the dark, but also commonly under longer-wavelength illumination. Depending on the sidegroups (R', R," etc. in Figure 12) and other molecular details (e.g., whether X = O, S, etc.), one isomer can be a much better complexing agent for a particular species than the other.

**MEROCYANINE (OPEN-~~trans~~-
zwitterionic) FORM**



SPIRO- FORM

Figure 12.

Figure 12: Spiropyrans/spiroxazines. Spiropyran/spiroxazine photoisomerization and photochromism. (Spiropyran: Y = CH; spiroxazine, Y = N). X is O, S, or Se; R is H or an alkyl group. Depending on X and with appropriate chelating side groups at the numbered positions, reversible light-driven ion binding can occur (e.g., [Alward, 1998](#)).

The reversible photochromism of these compounds has attracted much interest for possible applications in information storage (e.g., [Irie, 2000](#)), in analysis, and as biological signaling models ([Inouye, 1996](#)), but light-mediated switching of binding specifically for solute extraction has been a particular focus of one study ([Alward, 1998](#)). Stability of these compounds is a pressing issue, however, because many tend to degrade ("fatigue") due to side reactions so that the switching ability is soon lost. Spiroxazines have been attracting particular attention recently because of their greater fatigue resistance.

Several other groups have reported photoswitching systems based instead on oxide semiconductors. In these cases redox reactions induced by the electron-hole pair spontaneously reverse when illumination is discontinued, typically by re-oxidation from atmospheric O₂. [Foster et al. \(1993, 1994, 1995\)](#) demonstrated that illumination of TiO₂ in deaerated solutions, in the presence of certain organic compounds, causes precipitation of an ill-defined purple Cu⁺ complex from

photoreduction of Cu^{++} in solution. On exposure to air oxidation by O_2 re-oxidizes Cu^+ to Cu^{++} , which goes back into solution. They have proposed this system for Cu extraction and recovery.

Similarly, [Muraoka et al. \(2001ab\)](#) demonstrated reversible photoreduction of ferricenium to ferrocene from acidic solution onto TiO_2 . On standing in the dark for several hours, the ferrocene would spontaneously reoxidize to ferricenium through reaction with atmospheric O_2 . The TiO_2 had been functionalized by a covalently bound surface hydrocarbon layer, and so on photoreduction the hydrophobic Fc molecules would dissolve into this layer. This hindered the re-oxidation sufficiently that the ferricenium could be removed from the solution essentially quantitatively as long as illumination was maintained.

Finally, many researchers have demonstrated the photoreduction of metal ions out of solution by illuminated semiconductors, usually oxides (e.g., [Brown et al., 1985](#); [Chenthamarakshan et al., 1999](#); [Curran et al., 1985](#); [Eliet & Bidoglio, 1998](#); [Jacobs et al., 1989](#); [Serpone et al., 1987](#); [Tanaka et al., 1986](#)), and this has even been suggested as a recovery method for precious metals (e.g., [Borgarello et al., 1985, 1986](#); [Herrmann et al., 1988](#)). None of these processes has as yet proven practical, however, and they underscore the value of switchability. Eluting the photoreduced metals to regenerate the semiconductor surface has so far proven to be prohibitively expensive.

3.3.1.5. MNT and molecular separation. A general nanofabrication ability, for nanoscale control of passive structures, would obviously be valuable in making better membranes and resins. Such issues are much as discussed previously for nanostructures such as nanolayered materials and large-area interfaces.

However, in the case of molecular separation technologies some issues go beyond the nanoscale fabrication of passive structures to what might be termed "specific synthesis." At present compounds such as crown ethers and substituted spiropyrans involve elaborate, inefficient, and expensive syntheses, and this has been a major obstacle to their wider use. Of course, organisms carry out the routine and specific synthesis of complicated compounds by molecular machinery, so the availability of a full-scale molecular machine capability should yield considerably cheaper and more specific syntheses. This seems unnecessarily complicated, however, and if efficient syntheses have to await the arrival of full MNT they hardly are near-term. A nearer-term route to improved syntheses might be through molecularly designed and nanofabricated catalysts (section 2.2.2.), and this might provide another economic incentive for catalyst development.

3.3.1.6. Microbial-based extraction. Microbial-based approaches to molecular extraction, both for resource extraction and pollution control, are receiving a great deal of attention (e.g., [Smith & Misra, 1993](#); [Silver, 1994, 1997, 1998](#)). Microbes, of course, have the advantage of being molecular machines that already are capable of self-replication. They have some serious disadvantages, though: they are commonly delicate, requiring an ongoing source of nutrients and (in the case of aerobic organisms) oxygen, and they are generally not optimized to carry out the element extractions of technological interest. Nonetheless, they are likely to remain the focus of intense research, particularly as genetic engineering becomes more commonplace. The mechanisms for binding particular metal ions are of particular interest (e.g., [Silver, 1992](#); [Silver & Ji, 1994](#)), and incorporation of the genetic encoding for them into bacteria that might be more robust seems an obvious extension of such research.

3.3.1.7. Implications of biomimetic extraction. There is little doubt that low-temperature "biomimetic" approaches, capable of switchable binding of solutes (section 3.3.1.4.), will make

aqueous-based extraction processes both considerably more efficient and—like biosystems—capable of dealing effectively with considerably lower concentrations.

Another result of such extraction technologies will be to blur the distinction between a "pollutant" and a "resource": the distinction becomes a matter of context. Already, for example, economic recovery of Mn from waste streams by ion-exchange resins (Lotz et al., 1987) has been demonstrated. In fact pollution control, more than resource extraction, is driving the development of these technologies right now. In retrospect, the worst assumption in *Limits to Growth* was that even with unlimited energy supplies, rising pollution would eventually cause global collapse.

The author suspects that the ~5000 year era of digging up and "cooking" anomalous geologic deposits for their metal content is coming to its end irrespective of whether such deposits will still exist to be exploited. Conventional pyrometallurgy is not only dirty, it is wasteful on a vast scale, and economic considerations are likely to figure in its obsolescence. When (say) zinc can be recovered cheaply from wastewater streams at parts-per-million concentrations, there will be little incentive to process virgin ore.

Finally, of course, plants use molecular machinery to build intricate molecular structures from materials extracted at low concentrations from the ambient environment, using only the diffuse and fitful energy of sunlight. Application of nanotechnology to extraction of material resources is thus also likely to blur the distinction between "growing" and "mining."

3.4. Isotope Separation

Isotope separation is crucial for nuclear materials because the nuclear properties are what's relevant. This has already been commented on in the case of nuclear fuels, waste reprocessing, and the potential separation of radionuclides for research or medical use (sections 2.5.5.1. and 2.5.14.1.).

The utility of isotopes ranges well beyond nuclear materials, however. Stable isotopes are widely used as tracers in biological, geochemical, and environmental systems. They are preferred for biological tracing at present because of their ease of handling due to the absence of radiological safety issues. Geochemical and environmental studies already exploit the fractionation of isotopes by natural processes. If isotopically enhanced material could be obtained cheaply enough, however, tracking processes such as pollutant pathways by stable isotopic tracing would also become of great interest. Isotopically enhanced sulfur, for example, has been proposed as a method of definitively tracing the source of the sulfate in acid rain (Mills, 1990). This in turn would imply having cheap isotopically enhanced material available in ton-scale lots.

In no place, however, does a dichotomy between the trivial thermodynamic costs and the enormous practical costs of separation loom so large as in the separation of isotopes. Because isotopes have essentially identical chemical properties, their mixtures are well-described by the mixing entropy alone. For deuterium in hydrogen (mole fraction $x = 0.00015$), for example, the normalized mixing entropy (eq. (E8)) is:

$$S_m' = -R (\ln x + ((1-x)/x) \ln (1-x)) = 81.5 \text{ J/K mol.}$$

At 25°C (298 K), this corresponds to a limiting energy cost $T\Delta S$ of 24.3 kJ/mol

Vastly more energy than this is spent in purifying deuterium. As is well known, practical techniques for isotope separation mostly rely on the repetition of physical processes such as diffusion or phase

changes, so that small effects due to the mass difference slowly accumulate. Such separation also relies on having a molecular species with the appropriate physical properties (e.g., a vapor phase or phase change at a convenient temperature). Electromagnetic separators ("calutrons"), essentially industrial-scale mass spectrometers, are more generally applicable but even more energy-intensive.

The exact energy levels of the vibrational spectrum of a molecular species depend on the isotopes involved. Thus, illumination of a mixture of isotopic species by radiation of sufficiently precise wavelength could excite only one isotopic species and cause its separation. Lasers are capable of radiating light with sufficient precision, and a number of groups have investigated such "spectroscopic separation" of isotopes (e.g., [Balling and Wright, 1976](#); [Arisawa et al., 1993](#); [Kojima et al., 1983ab](#); [Okada et al., 1990](#); [van der Veer and Uylings, 1993](#); [Pino et al., 1996](#)). The molecular species proves to be very important, since most molecules have too many vibrational modes for clean separation, the number of modes depending on both the molecular symmetry and the number of different isotopic species of each element.

For example, SF₆ has been the subject of many studies. The molecule has octahedral symmetry, so all six F atoms are equivalent. Since ¹⁹F is the only stable fluorine isotope, the vibrational modes thus depend only on the mass of the sulfur atom. Isotope separation of SF₆ by laser excitation has been demonstrated (e.g., [Lin et al., 1978](#); [Lyman et al., 1977](#); [Del Bello, 1987](#); [D'Ambrosio et al., 1988](#)); unfortunately, SF₆ is such a stable molecule that incorporating the isotopically enriched S into more useful chemical forms proves to be a significant expense (e.g., [Caudill, 1990](#)).

More speculatively, perhaps the quantum-mechanical phenomenon of vibronic mixing could be exploited for isotopic separation. A vibrational mode whose energy overlaps with that of an electronic transition yields a so-called "mixed state," the degree of mixing depending on the energy difference. Such a state will absorb radiation of the correct energy much more strongly, and so heighten any separation effect. The practicality of this phenomenon will depend even more on molecular details than conventional spectroscopic separation, however. Not only must vibrational modes be minimized, an unusually low-energy electronic transition is required. Most electronic transitions lie in the UV or visible, whereas most vibrational transitions lie in the IR.

Overall, it seems that MNT has little to offer directly to isotope separation except in the general sense of cheap nanofabrication. Fabricating conventional isotope separators, such as diffusion membranes, at the nanoscale may yield improvements in both cost and speed.

3.5 Change of Materials Mix

"Some ... argue that supplies of all resources are linked together. The weakest links ... in the chain have never been tested, but they are clearly metals"

[Gordon et al., 1987, p. 1](#)

Biomimetic extraction technologies (section 3.3.) are likely to defer indefinitely any shortages of metals. In ironic contrast to the sentiment expressed above, then, metals may be becoming superabundant just as demand for them plummets. The reason is that as nanotechnology matures, the desired materials mix will change considerably.

3.5.1. *The obsolescence of structural metals.*

Structural materials at present are dominated by metals because of their resistance to so-called "Griffith failure." Before the First World War, workers such as Inglis and Kolosoff had shown that a crack, once formed, concentrates stress at its tip and thus tends to propagate (discussion in [Kelly & MacMillan, 1986, pp. 57 ff.](#)). Then, in a classic set of papers in the 1920s, Griffith derived a set of criteria for material failure by the propagation of cracks. In particular, he showed that cracks will propagate more readily in brittle materials because of their inability to relieve the stress at the crack tip by plastic flow. Moreover, conventional materials are riddled with micro- and nanoflaws (grain boundaries, crystal defects, etc.) at which cracks will tend to nucleate. Hence, in a brittle material macroscopic failure occurs due to the catastrophic propagation of a vast number of cracks. A shattering water glass dropped on the floor is a familiar example.

Metals, however, are capable of plastic flow when sufficiently stressed, and thus crack tips tend to "heal" rather than propagate. Hence, metals retain usable strength even when riddled with microflaws, and also tend to fail "gracefully." As current fabrication techniques are unable to make materials not containing vast numbers of flaws, this robustness has been the overwhelming engineering consideration.

Nonetheless, metals are intrinsically weak. Even in a strong metal, plastic deformation still occurs. It merely requires a large energy input (e.g., [Carlsson & Thomson, 1998](#)). Indeed, the metallic bond is nondirectional and so is *fundamentally* weak. Even if the *tensile* strength is high; i.e., there is great resistance to pulling adjacent atoms apart, there is little energy barrier to relative shear between them, and hence little barrier to the propagation of dislocations. Approaches to fabricating strong metals thus must involve a tradeoff: they must make the propagation of dislocations energetically expensive, but not so much so as to completely prevent plastic flow and so embrittle the material. Thus the role of alloying elements can largely be viewed as agents to inhibit the movement of dislocations.

Brittle materials are potentially far stronger than metals, but are subject to catastrophic failure due to crack propagation unless essentially defect-free at the molecular level. MNT makes fabrication of such defect-free materials conceivable, though admittedly routine fabrication of such materials still lies some years away.

Composite materials, however, can yield great strength improvements with considerably less perfection in fabrication, and so extreme-strength composites are likely to be available in the nearer term. Composites typically consist of a mat or felt of high-tensile-strength fibers embedded in a matrix. The fibers even may be oriented, to yield preferred tensile strength in one direction. Often, however, they are randomly oriented to yield an isotropic material.

As is shown by biological materials, the improvements in strength can be extraordinary. Abalone shell, for example, consists of an improbable composite of aragonite plates (orthorhombic CaCO_3 , a brittle ionic solid) and protein strands, but the composite has orders of magnitude greater strength than aragonite alone. Furthermore, the fact that the strong elements are fibers helps limit crack propagation. Even if one fiber breaks, the break is not automatically propagated. Finally, fabricating arbitrarily long but essentially defect-free *fibers* is likely to be a considerably easier engineering problem than fabricating two- or three-dimensional objects. In conventional composites such as fiberglass the fiber length is limited, and of course such fibers are hardly defect-free.

In any case, the phrase "structural metal" may well strike future engineers as oxymoronic.

3.5.2. Carbon: "*Diamondoid*" and otherwise.

Given a molecular fabrication capability, carbon becomes the most desirable structural material. This is due to three factors:

- The relatively low mass of the carbon atom. Four out of the atom's six electrons contribute to chemical bonding, which means that the nucleus is contributing relatively little dead weight. In most applications, and especially those in space, the figure of merit is not strength per se but *specific* strength, the strength per unit mass, and so small atomic mass is critical.
- The great strength and directionality of the C-C bond. The C-C bond is covalent and is thus strongly directed, its position being constrained by the quantum-mechanical orbitals in which the valence electrons are localized. Such bonds, unlike metallic bonds, offer strong resistance to a shear stress between the atoms. The C-C bond in diamond, for example, has a tensile strength of 10.6 nN/bond but a shear strength nearly as great, of 6.7 nN/bond (quoted in [Drexler, 1992, pp. 142-143](#)).
- The carbon atom's ability to bond in three dimensions, which means that C can build three-dimensional frameworks. Indeed, tetrahedrally polymerized (sp^3) "diamondoid" frameworks, based on the crystalline structure of diamond, are commonly proposed.

For macroscopic structures, however, nanotubes ("buckytubes"), consisting of a single graphene (sp^2) layer fused into tube of molecular diameter, may be even more valuable. First, these seem to have ultimate tensile strengths comparable to diamond (~100 GPa; e.g., [Yakobson & Smalley, 1997](#)). However, as their bulk density will presumably be similar to graphite's (~2.2 g/cm³), over a third less than diamond's (3.5 g/cm³), their specific strength will be substantially (>35%) larger. Furthermore, diamond has well-defined cleavage along the (111) crystal plane, which indicates that large diamond-based objects can fail preferentially in certain orientations. Finally, as noted above one-dimensional objects such as fibers are likely to be considerably easier to fabricate than three-dimensional molecular frameworks.

In macroscopic lengths, such fibers have obvious applications in tethers and cables. Fiber-composite materials, moreover, would combine great strength with a very large resistance to crack propagation.

3.5.3. Terrestrial carbon resources, I. The obsolescence of petroleum.

Some 10% of oil production is used as a feedstock for the petrochemical industry, and it's been widely thought that petroleum is much too valuable as a source of chemically reduced carbon compounds to waste as fuel (e.g., [Committee on Resources and Man, 1969, p. 7, 15](#)). Ironically, however, once oil has been supplanted as an energy source it may well become *obsolete* before it runs out.

For one thing, green plants make reduced carbon compounds routinely, using a diffuse source of carbon (the CO₂ in the atmosphere) and sunlight. Hence if the natural nanosystems in plants can manage to make reduced carbon compounds from CO₂, surely synthetic nanosystems can too (section 2.5.10.2.).

A much more obvious alternative near-term source of reduced carbon, however, is biological waste. Such materials include a whole host of noxious waste products whose disposal is currently both expensive and inadequate, such as sewage, agricultural waste, timber slash, fermentation dregs, feedlot manure, and so forth. In fact, the petrochemical industry is fully aware that the days of abundant oil as a chemical feedstock are numbered, and they are already investigating biowaste as an alternative (Spitz, 1988; R. Phair, pers. comm., 1997.)

Indeed, petroleum's value as a chemical feedstock results merely from historical accident. It derives ultimately from 19th century efforts to use coal tar, a noxious waste (!) from making coke from coal. The efforts were spectacularly successful—they laid the foundation for the modern chemical industry—and they were later readily adapted to oil.

The reason that oil may become obsolete lies in the expense of extraction. As sketched in section 2.5.1., at present we have a *very* expensive infrastructure, paid for by the value of oil as fuel, for finding and extracting petroleum from kilometers deep in the Earth. That infrastructure is likely to become considerably less cost-effective if the oil is merely to be used as a source of reduced carbon.

A further irony is that this infrastructure coexists with other very expensive infrastructures to destroy reduced carbon compounds as fast as possible: the sewage collection and disposal systems throughout the industrialized world. Aside from its infection hazard, the main deleterious effect of sewage dumped back into streams is its "biological oxygen demand." Because it is chemically reduced, micro-organisms can oxidize sewage to derive energy, and that consumes the oxygen in surrounding water. Hence sewage treatment focuses on oxidizing such material before its discharge into the environment.

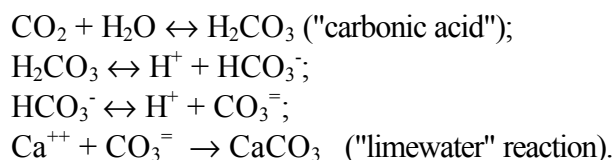
3.5.4. Terrestrial carbon resources, II: The significance of carbonates.

There seems to be a widespread misperception in the MNT community that near-surface C reservoirs on Earth are very limited. This is untrue. What is true is that only a tiny percentage of Earth's carbon resides in the atmosphere. Reduced carbon in the crust constitutes a much larger percentage (Table 1), this carbon representing biological material that was buried in sedimentary rocks over geologic time. Fossil fuels (coal, oil, and natural gas) constitute in turn a tiny percentage of this material (section 2.5.1.). It is all ultimately derived from CO₂ via photosynthesis.

Reservoir	Amount
Atmosphere	0.025
Ocean	1.4
Crust:	
reduced C	700
carbonates	2600
Total:	3300
Upper mantle:	6600
Grand Total	9900

Table 1. Terrestrial Carbon Reservoirs. Total carbon as CO₂, in units of 10¹⁷ kilograms ("geograms"; Garrels & Mackenzie, 1971). All carbon is expressed as CO₂ equivalent regardless of actual chemical state. Sources of data as follows: CO₂ abundances for Earth from Walker (1977, pp. 200, 233), except that subdivision of crustal carbon is from Hunt (1972); his crustal total agrees with Walker's.

By far the largest percentage of Earth's carbon, however, resides in carbonate rocks (Table 1), nearly all consisting of limestone (composed of calcite, rhombohedral CaCO₃) and dolostone (composed of dolomite, CaMg(CO₃)₂.) Indeed, carbonate rock can be regarded as "petrified" CO₂, being formed by the reaction of CO₂ with water and dissolved metal ions, via reactions like the following:



Hence carbonate rocks, which comprise the "backstop" terrestrial C reservoir, can ultimately be expected to become considerably more valuable than traditional metal ores (Figure 13). This is not a scenario typically envisioned in conventional speculations on the future of nonrenewable resources and economic geology.



Figure 13.

Figure 13: Limestone outcrop. Limestone cliffs of Late Paleozoic age in Lee Canyon, Spring Mountains, Nevada. Such rocks are composed of >90% calcium carbonate (calcite, rhombohedral CaCO_3) and represent the bulk of the carbon inventory in Earth's crust. Photograph by the author.

Parenthetically, another unexpected implication is that the CO_2 atmosphere of Venus becomes of staggering long-term value as the largest off-Earth store of carbon in the inner Solar System.

3.5.5. Silicate MNT and resources.

The most abundant elements in a rocky planet are Si and O (Table 2). In turn, silicon and oxygen are the fundamental building blocks of silicates, and so silicate minerals are the most abundant compounds in any rocky planet. Indeed, ordinary rocks are largely composed of such minerals. Silicates, however, are not traditionally viewed as resources, except perhaps for high-volume, low-value applications such as fill, aggregate, and riprap. They are also brittle. Silicate glass, of course, is the everyday epitome of brittleness.

Element	Mole Percentage
O	60.4
Si	20.5
Al	6.3
H	2.9
Na	2.6
Ca	1.9
Fe	1.9
Mg	1.8
K	1.4
Rest	0.5

Table 2. Composition of the Earth's crust. Calculated from [Mason, 1982](#).

However, silicates may prove extremely useful as an alternative basis for MNT ([Gillett, 1998ab](#)). At ambient pressures, silicates are based on an SiO_4 tetrahedron, with the Si atom fitting into the tetrahedral hole inside the four oxygen anions. The Si-O bond also has about 50% covalent character, so it is not only strong but directional. Furthermore, these tetrahedra can share one through four vertices to form an enormous variety of silicate polyanions and three-dimensional networks. Indeed, a fully polymerized silicate network, in which all four vertices of one tetrahedron are shared with an adjacent one, is simply silica (SiO_2). The various polymorphs of silica (quartz, coesite, cristobalite, and so on) merely reflect different ways in which the tetrahedra can be linked. Finally, although considerably weaker than carbon, the strength of silica (~16 GPa; [Kelly & MacMillan, 1986, p. 6, 8, 371](#); review in [Gillett, 1998a](#)) compares well with other ultrastrong materials.

The overwhelming abundance of silicate minerals, on Earth and other rocky bodies, may seem to make discussion of silicate "resources" somewhat superfluous. When ordinary dirt becomes more valuable than metals, so that things like (say) dry lake sediments become extraordinarily valuable feedstocks, the immense exploration infrastructure of present-day mining is hardly required. It is noteworthy, however, that the *waste* from conventional mining operations is largely silicate debris. Due

to the great strength of the Si-O bond, silicates are seldom attractive as ore minerals. Instead, they constitute the bulk of the gangue (section 3.1). Thus beneficiation yields a fine-grained, dominantly silicate waste material ("tailings") that, as noted, is commonly a source of environmental problems. However, such comminuted debris would make an excellent feedstock for a silicate-based MNT.

As an aside, silicate-based MNT is likely to prove critical on rocky bodies on which carbon is essentially absent, such as the Moon. Lunar regolith, the surface layer of rock comminuted by eons of meteorite impact, would be an ideal feedstock for a silicate MNT.

3.6. MNT and Rare Elements.

Even though demand for such familiar elements as iron and aluminum is likely to dwindle, at least in their traditional uses, the rest of the Periodic Table is unlikely to become irrelevant. Indeed, MNT-related applications will probably increase the demand for certain rare elements. Even though molecular scale element separation (section 3.3.) makes it less likely that shortages of such elements will exist, they merit mention.

3.6.1. Thermoelectric materials.

Theoretical analyses of the factors that lead to good thermoelectric materials imply that they will be based on heavy ($Z > \sim 40$) elements. Elements such as lead ($Z = 82$), tellurium ($Z = 52$), and bismuth ($Z = 83$), for example, figure prominently in currently known thermoelectric materials.

Such elements are intrinsically rare in the crust. The peak of nucleon binding energy lies in the vicinity of ^{56}Fe ($Z = 26$), so elements heavier than this cost energy to make, and this is reflected in vastly lower abundance of elements with $Z > \sim 28$. Hence selective binding agents for these elements may merit attention. Because of its toxicity, selective complexing agents for Pb have already been investigated ([Abu-Dari et al., 1990, 1993](#)).

3.6.2. Redox-active framework formers.

A number of elements besides Si are also capable of forming highly polymeric oxide frameworks, in particular certain transition metals such as Ti, V, Mn, Nb, Mo, Ta and especially W. For nanotechnology the potential advantage of such transition-metal oxide frameworks is that their bulk electronic and optical properties can be varied drastically by minor reduction or oxidation of some of the framework atoms, due to the multiple stable oxidation states of a transition element. The same basic framework can thus range from an insulator through a semiconductor to a metal.

Such frameworks have interesting potential nanotechnological applications ([Gillett, 2001](#)), in particular for solid electrolytes and similar intercalation substrates. As already described, these include such energy-related applications as electrochromic and self-darkening windows (section 2.2.6.), intercalation-based batteries (section 2.2.4.1.a.) and supercapacitors (section 2.2.4.1.b.), and substrates for reversible, selective intercalation of solutes (section 3.3.1.4.a.).

Many of these framework-forming elements are rare. Tungsten ($Z = 74$) is one of the best but only comprises 0.000017% of the crust on a per-mole basis (calculated from [Mason & Moore, 1982, p. 46-7](#)). It has already been a subject of intense search as a strategic material because of its refractory and alloying properties. Tungsten has been concentrated into ores by geochemical processes, most particularly in the "contact zones" around certain igneous bodies. However, a non-traditional source that has been the subject of research but so far has proved uneconomic is in certain brines, e.g., at

Searles Lake, California (Altringer et al., 1981). Tungstate anions make up a very small (equivalent to ~49 ppm W or ~0.265 mM) percentage of such brines, and they are obvious candidates for selective solution-based molecular separation.

3.6.3. Nuclear fuels.

As has already been indicated (sections 2.5.5.1. and 2.5.14.1.), most nuclear fuels are isotopes of rare elements, deuterium being the only exception. Indeed, as might be expected, Th and U are among the rarer elements in the crust, amounting to only 0.000064% and 0.000016%, respectively. Even so, of course, the absolute crustal quantities are enormous, although extraction is problematic. Hydrometallurgical processes involving leaching of low-grade ore have been suggested for U extraction (section 2.5.5.1.). In the very long term, though, fission is also not sustainable because its fuels are limited.

4. SPACE RESOURCES AND NANOTECHNOLOGY

Off-earth resources of both energy and materials have come under increasingly serious scrutiny over the last few decades (e.g., Gillett, 1984; Lewis & Lewis, 1987; Lewis et al., 1993). They have many potential advantages, including minimal environmental impact and vast potential abundance. Their overwhelming disadvantage, of course, has been the high cost of access to space, and this factor has dominated the economics. (Returning material from space is *not* expensive, however. Hence the economics are dominated by the "payback" possible for a given payload mass.)

Nanotechnology promises to decrease greatly this access cost. First, the favorable economics of high materials strengths on transportation costs are nowhere more pronounced than in the case of space. Even with conventional chemical fuels, the payload increase is highly significant due to the diminished vehicle mass (McKendree, 1995). Indeed, single-stage to orbit (SSTO) becomes practical. Second, the payload mass itself will decrease drastically. Both these factors will have a dramatic effect on the economics of space operations.

In fact, rockets may be supplanted as the routine means for getting off Earth. The enormous potential strength of "buckytube" cables has motivated serious looks at a "space elevator" or "skystalk" (Cowen, 2002). These have been a staple of science fiction for a generation (Clarke, 1979; Sheffield, 1979), but known materials had been far too weak to merit serious study until now. An extremely strong cable would connect a point on Earth's surface with a satellite in geosynchronous orbit, effectively making a suspension bridge to space. Because the cable would extend to a counterweight beyond geosynchronous orbit, at which point the cable is traveling faster than orbital velocity at that height, material could be flung off into space with no expenditure of reaction mass at all. Such a system would have a more profound effect on space access than did the transcontinental railroad for access to the US west in the late 19th century.

4.1. Solar Power Satellites (SPS).

A trivial calculation shows that the entire Earth intercepts only $\sim 5 \times 10^{-10}$ th of the $\sim 4 \times 10^{26}$ watts radiated by the Sun. This "missed" solar energy represents an enormous potential energy resource. Indeed, many years ago Dyson (1960) speculated that an extremely advanced civilization might trap all its star's outgoing energy by surrounding it completely with a shell.

This is obviously not of near-term relevance for humanity. Nonetheless, sunlight passing by Earth seems accessible to near-term technology. So-called "solar power satellites" were first discussed seriously over 30 years ago (Glaser, 1968) and have been (and continue to be; Glaser 1998) the subject of studies worldwide. Such satellites would intercept sunlight in near-Earth orbit and beam it down to receivers on Earth, probably via collimated microwaves.

Space holds many advantages as a location for solar energy collection. First, the incident sunlight is at least 30% stronger, not having been partly reflected or absorbed by the atmosphere. Obviously there is no weather, which decreases maintenance costs as well. Depending on the orbit details, the satellites are also not subjected to a day-night cycle, but only short and intermittent eclipses. Against these must be set the high costs of access and construction, as well as potential public fears of beamed power.

The economics of such satellites are analogous to those of large hydropower dams: an enormous up-front capital expenditure is required before any payback is received. Once the expenditure is made, however, the ongoing costs are minimal. Hence the costs are dominated by the amortization of the investment.

4.1.1. Nanotechnology and SPS.

The same economies of fabrication that will make ground-based PVs considerably more attractive also make SPS more feasible. The economies of mass would be particularly valuable because of the necessity to decrease costs to orbit. Thus the economics of space- vs. ground-based solar power seem poised particularly finely between the economics of production, the tradeoffs of competing technologies (e.g., photovoltaics vs. photosynthesis), and space access costs.

4.2 Lunar Helium-3.

The isotope ^3He , nearly absent on the Earth, is present at low levels in lunar regolith due to solar-wind implantation. It offers theoretical advantages for controlled fusion, and the lunar surface therefore has been suggested as a source (Kulcinski & Schmitt, 2000).

4.3 Near-Earth Materials.

Near-earth sources of *materials* are more problematic. So-called near-earth asteroids, a population of small objects with orbits crossing the inner planets', have excited interest as resources (Kuck, 1979). These objects are widely thought to constitute the parent material for most of the present meteorite flux on the terrestrial planets. For terrestrial resource purposes, objects with compositions typical of nickel-iron meteorites have been particularly favored (Drexler, 1983; Lewis & Nozette, 1983). Such objects also contain platinum-group metals (PGMs) and precious metals at concentrations comparable to or greater than the best terrestrial ores. Indeed, mining such objects has become a staple of much serious futurism as well as of science fiction.

An ironic consequence of maturing nanotechnology, however, is that asteroidal nickel-iron becomes of merely historical interest, at least for terrestrial use. Not only are molecular separation technologies likely to make asteroid retrieval for Ni-Fe considerably less attractive, but availability of superstrong materials, probably C-based, will make Ni-Fe alloy unimportant.

The relative abundance of PGMs, however, may yet prove an economic motivator if they maintain their present importance in catalysts, even with the availability of molecular separation for extracting

PGMs from terrestrial materials. It seems problematic, however, whether they will remain so valuable once molecular-scale understanding and fabrication of catalysts is achieved.

5. CONCLUSION: A VIEW FROM THE PALEOTECHNICAL ERA

Conventional technology is depleting its resource base at an accelerating rate and creating an increasingly unlivable mess in doing so, even as rising expectations around the world heighten demand still further. We simply cannot maintain the standard of living in the industrialized world much longer with conventional technology, much less raise the rest of the world's.

Nonetheless, it is critical to recognize that the dwindling resource base is not set by the laws of nature, despite occasional assertions to the contrary. Typically such assertions are based on misconceptions about the laws of thermodynamics, and—unsurprisingly—are unbuttressed with any calculations of limiting thermodynamic costs.

In fact, present technology is grossly inefficient and gratuitously dirty, and this results from an overwhelming reliance on heat—the "Promethean paradigm." The present might well be termed the "Paleotechnical Era." Molecular nanotechnology will allow us to supplant the Promethean paradigm and move beyond the Paleotechnical. Assuming of course that the terrestrial population does not rise indefinitely, the prospects of using MNT to preserve the standard of living in the industrialized nations while raising those of the rest of the world appear good. However, the sweeping changes implied by MNT indicate that the transition is nonetheless likely to be painful. The looming obsolescence of much of the present transportation and fabrication infrastructure is merely a beginning.

We can also conclude that if industrial civilization is to survive, the following are true:

- The phase-out of fossil fuels will be well advanced in another decade, and nanotechnology will play a great role in that phase-out;
- The five-millennium era of locating anomalous deposits to "dig up and cook" for metals extraction is coming to its close, probably over the next few decades and certainly within the next century.

Furthermore, over the long term as the "distributed fabrication" promised by MNT becomes realized, global energy consumption for transportation will also drop massively. If almost any artifact can be fabricated locally, no longer will it be necessary to ship raw materials and finished goods halfway around the world, with the enormous energy consumption this entails.

The real question becomes how traumatic the transition will be.

5.1 Toward a New Stone Age?

Finally, we think of technological history as a series of Ages of Metals; but with a mature nanotechnology metals become obsolete. The earliest materials used by humanity were wood (a carbon-based composite) and stone (silicates). Ironically, therefore, the technology of materials seems to be coming full circle. Metal, as well as fire, may prove to be a stigma of the Paleotechnical Era.

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