Modern Lab Experiments for Chemical Engineering

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Abstract

We describe new experiments developed, and installed, to bring our chemical engineering laboratory into the 21st century. These additions are:

1. Compact disc write and re-write systems
2. Fluidized bed polymer coating
3. Hydrogen fuel cell and hydrogen storage
4. Photocatalytic water purification
5. Rapid prototyping via ink jet printer
6. Silicon wafer oxidation

These new experiments collectively allow introduction of topics which are modern, yet not routinely covered in traditional chemical engineering laboratories. The experiments described are relevant to energy storage and utilization, polymer coating of consumer and microelectronics products, water purification, laser-driven material transformations for information storage, semiconductor circuit fabrication, and computer-aided solid prototype synthesis.

Introduction

In changing times, the keepers of engineering curricula must look to the most responsive academic elements to address new needs. We believe that the future of chemical engineering lies not only in biotechnology, but also in many other arenas, including electronic and photonic materials and devices. As the time needed to create a new lab experiment is mere months, whereas creation of new a text takes years, it follows that in times of change, our laboratories should be leading, rather than following, curricular changes. We report here the installation of six experiments which, taken together, substantially enlarge the range of experiments in our undergraduate ‘unit operations’ and “transport phenomena” laboratories.

The chemical engineering undergraduate laboratory has traditionally existed to satisfy either or both of the following objectives:

1. Illustrate individual unit operations (e.g., extraction, mixing, chromatography, adsorption, electrochemical deposition, fluidization)
(2) illustrate measurement of rate constants for physical processes (e.g., mass transfer, heat transfer, diffusion) and chemical reactions.

(3) illustrate measurement of physical properties (e.g., specific heat, vapor-liquid equilibria, viscosity).

Combined with report writing and subsequent oral presentation, these activities contribute both “hands-on” experience and team communication opportunities, routinely cited as preparation for the “real world”.

Of the recent hot topics in federal research, namely biotechnology, nanotechnology, and information technology, only biochemical engineering appears to have made inroads in chemical engineering lab instruction, as illustrated by papers CEE papers on fermentation and bioseparations.

Gradual reform of undergraduate laboratories have occurred through alteration of emphasis to include product design, device troubleshooting, safety, EC2000 criteria, process design, environmental awareness, commercial relevance, experimental design, industrial practice, and process dynamics and control.

Computers are more available leading to a “virtual unit operations laboratory” as a pre-lab resource.

However, materials and microelectronics are hardly visible, as we find singular mention of polymer processing and microelectronics, despite heavy emphasis in research in these areas. Photonic materials are notable by their absence.

**Expanding the universe of the undergraduate laboratory**

The present experiments were introduced in the last several years in order to bring a greater sense of modernity, and relevance to the only hands-on engineering experience in our 128 credit hour undergraduate curriculum.

The range of experiments also provide the following desirable features:

(1) The topics are non-traditional, and modern: fuel cells are in fashion, but not usually found in reaction engineering texts; silicon wafer oxidation describes reaction of a solid (vs gas, or liquid) for microelectronics fabrication; polymer coating of small metal objects occurs in a fluidized bed, photocatalysis involves light-activated semiconductors for water treatment, and compact disc writing involves use of laser to carryout physical transformations (change reflectance) and thereby information coding (record bits, bytes). Rapid prototyping involves use of lasers or ink jets, both modern, yet rarely covered topics in standard texts. Collectively, incorporation of these experiments into our lab provides an immediate exposure to topics which are modern, and important, but which have been slow to find entry into our “classical texts’ of chemical engineering.

(2) New topics in chemical engineering may be introduced more rapidly through lab experiments than via new textbook creation. These experiments are either inexpensive to build or buy (fuel cell, compact disc (re)write system, fluidized bed coating, photocatalytic water purification), or use equipment found commonly in the research and instructional labs of engineering schools: rapid prototyping (device) or silicon oxidation (ellipsometry).
Collectively, these devices provide hands-on experience, and explanations, of modern technologies which are pertinent to the future of chemical engineering, in domains including the “big three” of federal research: biotechnology, nano-materials, and information science.

We now describe the experiments briefly, including the principles illustrated, their relation to chemical engineering in the classical sense, and our initial results and evaluations. Whether a topic is “properly” a part of chemical engineering is up to the reader: here, we provide illustrations of modern, commercially important technologies and key principles, and seek therein thermodynamic and kinetic aspects suitable for quantitative exploration within the usual thought modes of chemical engineering. The ability to inform, and explain, how these technologies work in chemical engineering terms also demonstrates to the student that chemical engineering has multiple “modern aspects”, though many undergraduate labs are yet bereft of them.

**Experiment 1: HYDROGEN FUEL CELL AND HYDROGEN STORAGE**

This new, off-the-shelf apparatus from The Fuel Cell Store provides equipment to demonstrate three systems:

1. Hydrogen fuel cell consisting of Pt-loaded carbon electrodes separated by a Nafion (proton conducting polymer) electrolyte membrane,
2. a twin reservoir batch system for demonstrating the thermodynamics of hydrogen (fuel) storage as a metal hydride, and
3. a solar or artificial light photovoltaic cell providing light-driven generation of pure H₂ and O₂ by water electrolysis

The recommended experiments all worked well: namely the generation of polarization curves to demonstrate various kinetic regimes of fuel cell operation, calculation of fuel cell efficiency and power output curves, and the measurement of a decomposition enthalpy, and calculation of the corresponding free energy and entropy changes for hydride conversion to gaseous hydrogen.

**Fuel cell characterization**

A general equation for a fuel cell polarization curve gives the cell voltage, \( V \) (volts), as a function of current density, \( i \):

\[
V = E - iR
\]

where \( E \) is the cell potential, \( R \) is the cell resistance, and \( i \) is the current density.
\[ V(i) = V_{eq} - b \ln \left( \frac{i}{i_o} \right) - R i - d \ln \left( 1 - \frac{i}{i_{lim}} \right) \]

where \( V_{eq} \) = open circuit voltage

\( b \ln \left( \frac{i}{i_o} \right) \) = Tafel activation voltage at electrode surface

\( R i \) = ohmic potential drop across membrane, and

\( d \ln \left( 1 - \frac{i}{i_{lim}} \right) \) = external mass transfer limit

In operation, the Tafel and ohmic loss regions are clearly accessible with the present apparatus. Little or no indication of mass transfer influence of oxygen supply through air was evident, even at the highest achievable currents for our single or dual cells (in series).

The potential (V) vs. current density, \( i \) (amps/cm\(^2\)), data obtained were conveniently analyzed to evaluate parameters as follows:

1. The straight line portion (ohmic loss dominance) of the V vs i polarization curve for one fuel cell yields \( R = 1.61 \) ohm-cm\(^2\), or a resistance of \( r = 0.161 \) ohm, given an electrode area of \( A = 10 \) cm\(^2\).

2. Extrapolation of the ohmic loss (only) line to \( i = 0 \) gives \( V(\text{open circuit}) = V_{eq} = 0.95 \) volts

3. In the apparent Tafel influence region of \( 0 < i < 0.5 \) amp/cm\(^2\), subtraction of \( V(\text{ohmic}) \) from \( V(\text{measured}) \) gives the Tafel or "activation" voltage loss, which plots nicely in a linear fashion vs \( \ln (i) \) as predicted. The slope of this second plot provides \( b = 0.0611 \) volts and the intercept yields the exchange current density: \( i_o = 4.3 \times 10^{-4} \) A/cm\(^2\).

The Tafel equation theory provides

\[ \ln \left( \frac{i}{i_o} \right) = \left( \frac{1}{b} \right) \left( V - V_{eq} \right) = (a \cdot n \cdot F / RT) \left( V - V_{eq} \right) \]

With \( n = 1 \), Faraday’s constant \( F \), gas constant \( R \), and \( T \) known, the electron exchange coefficient is calculated: \( a = 0.414 \) this parameter is normally in the range of 0.2 to 2.0)(Fuel CellStore).

**Efficiency of fuel utilization and power curve**

Defining a conversion **efficiency** as the ratio (electrical power output/higher heating value (HHV) of the gaseous fuel consumed), and the **power density** (W/cm\(^2\)) as the product \( V \cdot i \) allows calculation of both performance variables as a function of current density, \( i \). The former drops monotonically for both one cell, and two cells in series, and the latter exhibits a single maximum at 0.3 and 0.2 amps/cm\(^2\), respectively. The maximum power density of about \( 9 \times 10^{-3} \) W/cm\(^2\) occurred at an efficiency of about 27% for the two cells in series, and a similar result appeared to hold for a single fuel cell. This result nicely demonstrates the trade-off of operating at a low current density (maximum efficiency: conversion of fuel free energy to electrical power) vs the maximum power output (best condition for capital cost recovery).

**Hydrogen storage: metal hydride thermodynamics**
Fuel cells may be utilized in remote or mobile applications only if their fuel is easily stored and transported. Hydrogen storage as a solid hydride is far more compact and safe than as a compressed gas. This experiment demonstrates the easy reversibility of metal hydride formation, and asks students to determine the heat of decomposition of the hydride, a process just the reverse of hydride formation from the elemental metal and hydrogen. (Both processes are demonstrable with this simple apparatus)

Consider the hydride formation reaction:

\[ \text{H}_2(g) + \text{M}(s) \rightleftharpoons \text{MH}_2(s) \]

The enthalpy change from right to left (reverse step) is the enthalpy of desorption, \( H^d \), of hydrogen from the hydride. This is also the enthalpy of decomposition, to give back the elements hydrogen and metal, which in turn is the negative of the heat of formation, \( H^f \). The Clausius-Clapeyron equation for such a phase change is

\[ \frac{dP}{P} = (-H^d/RT^2) \, dT \]

Integration from a reference state \((P_o, T_o)\) to \((P, T)\) and rearrangement yields:

\[ \ln (P) = -H^f/RT + [ H^f/RT_o + \ln (P_o) ] \]

The standard free energy change \( G^o \) is, correspondingly,

\[ G^o = RT_o \ln (P/P_o) \]

The standard entropy change of desorption is

\[ S^o = ( G^o – H^o ) / T_o \]

Thus, given the vapor pressure \( P_o \) of the hydride at a reference temperature \( T_o \), the slope of \( \ln (P) \) vs \( 1/T \) provides \( H^d \). Following calculation of \( G^o \) at a given \( P \), the corresponding \( S^o \) is calculated.

Two small metal cylinders, one containing a high surface area, hydride-forming metal, and one without, are connected by \( \frac{1}{4} \)“ steel tubing, with a pressure gauge (0-600 psig) attached to the welded line as well. Students measure \( P(\text{H}_2) \) vs \( T \) for one reservoir (metal hydride) heated to progressively higher temperatures by a heating tape wrapping. The \( P \) vs \( T \) data are accumulated at each equilibrium point. A plot of \( \ln(P) \) vs \( 1/T \) is nicely linear, providing a slope of \(-2,542 \, (°K)^{-1}\). The desorption enthalpy is calculated from

\[ -H^d/R = \text{slope, hence } H^d = 21.14 \, \text{kJ/mol.} \]

The subsequent calculations of \( G^o \) and \( S^o \) yield:

\[ -H^d = +21.14 \, \text{kJ/mol} \]
\[ G^\circ = +6,565 \text{ J/mol} \]
\[ S^\circ = +48.9 \text{ kJ/mol.K} \]

The positive \( -H_d \) for hydride decomposition indicates endothermicity, hence the reverse reaction of hydride formation is exothermic (favorable, \( -H_f = 21.14 \text{ kJ/mol} \)) at ambient \( T_0 \). This fact is confirmed by the reformation of metal hydride when the heating tape is removed from the reservoir, and the batch system pressure falls dramatically as the reservoir cools. The positive \( S^\circ \) agrees with the notion that conversion of a solid into a vapor should provide an entropy increase. Finally, the easy reversibility of hydride decomposition and formation observed between 25 °C and about 60 °C (333 °K) reflects the good choice of metal (alloy) as a hydride storage medium.

**Solar Cell**

The commercial apparatus comes equipped with a solar cell which may conveniently be used to generate pure \( \text{H}_2 \) and \( \text{O}_2 \), which in turn are stored in separate reservoirs, then utilized in the reverse reaction (water formation) to demonstrate fuel cell operation. Due to time constraints, and variable weather conditions, we chose not to characterize the solar cell itself, although its \( V-i \) characteristics also show maximum power output at intermediate \( V \) and \( i \) values, as well known.

**Experiment #2: SILICON WAFER OXIDATION**

Oxidation of an ultrapure semiconductor silicon (Si) wafer produces an insulator silicon dioxide (\( \text{SiO}_2 \)) layer which may be incorporated into a microelectronics metal-oxide-semiconductor (MOS) device such as a field effect transistor (MOSFET). Other \( \text{SiO}_2 \) uses in microelectronics include impurity gettering, device isolation, masking against impurities, junction passivation, and insulating between metal layers.

The formation of a \( \text{SiO}_2 \) layer is accomplished by Si reaction with dioxygen (\( \text{O}_2 \)) in humidified or dry atmosphere. Our experiment measures oxidation kinetics in a dry atmosphere of pure oxygen. The students relate the observed rate to a kinetic model incorporating both oxygen diffusion through \( \text{SiO}_2 \) and subsequent chemical reaction at the Si-\( \text{SiO}_2 \) interface. (Deal-Grove, 1965)

The control of the \( \text{SiO}_2 \) layer thickness is crucial to MOSFET fabrication: the desired thickness has decreased over time (for smaller, faster electronic circuits), from several microns (early 1960s) to about 5 nm (2001), and less today. Accurate measure of the silicon dioxide layer thickness is crucial, and is accomplished here by use of ellipsometry.

**Theory of \( \text{SiO}_2 \) layer formation**

The gas-solid reaction leading to formation of an adherent, solid \( \text{SiO}_2 \) product layer involves the following transport and reaction steps in series:

(i) diffusion through an external gas film
(ii) dissolution of \( \text{O}_2 \)(gas) into the \( \text{SiO}_2 \) layer
(iii) diffusion of oxygen through the SiO$_2$ layer
(iv) reaction of oxygen at the Si-SiO$_2$ interface

The transport fluxes through film and oxide must, at “steady state”, each be equal to the reaction rate at the surface. Thus,

Oxygen flux (moles/cm$^2$-s) = $F_o$  

$= k_m (C_o - C_s )$ (external gas film)  

$= (D/d) ( C_s^* - C_i )$ (diffusion through oxide)  

- $k_R C_i$ (surface reaction; first order assumed)

where $k_m = \text{mass transfer coefficient}, D = \text{oxygen diffusivity in SiO}_2, d_o = \text{instantaneous oxide thickness}, \text{and } k_R = \text{reaction rate constant.}$

The gas phase concentration, $C_s$, just outside the SiO$_2$ layer is related by Henry’s law to $C_s^*$, the dissolved oxygen concentration just inside the outer surface:

$$C_s^* = H C_s$$

Eliminating the unmeasurable concentrations $C_s, C_s^*, \text{ and } C_i$ provides the oxygen flux in terms of the measurable gas phase concentration, $C_g$, hence the reaction rate ($k_R C_i = F_o$) is

$$\text{Rate} = F_o = C_o / [ 1/k_R H + d_o/D_c H + 1/k_m ] = k C_o$$

The apparent rate constant, $k$, is thus determined by the sum of the three resistances in series: mass transfer ($R_m = 1/k_m$), oxide diffusion ($R_{ox} = d_o/D_c H$), and chemical reaction ($R_R = 1/k_R H$). For our experiments in pure oxygen, no external mass transfer resistance exists: $R_m = 1/k_m = 0$, and this term is henceforth dropped.

The oxide thickness $d_o$(cm) changes with time, and is related to the flux $F_o$ (moles/cm$^2$-s) by $N_{O2}$, the number of moles of O$_2$ per unit volume SiO$_2$:

$$\frac{d(d_o)}{dt} = F_o / N_o$$

$$= \{ C_o/N_o \} / [ 1/k_R H + d_o / D_c H ]$$

which simplifies to

$$\frac{d(d_o)}{dt} = B / [ 2d_o + A ]$$

where $A = 2D_c/k_R$ and $B = 2D_o H C_o / N_o$.

Integration provides:
\[(d_o)^2 + A d_o - B (t + t_o) = 0\]

where \(t_o = [d_i^2 + A d_i] / B\) and \(d_i = \) initial (native) oxide thickness.

The general solution is the quadratic root:

\[d_o = A/2 \left[ (1 + 4B(t + t_o)/A^2) \right]^{1/2} - 1\]

We note two limiting circumstances:

For very small times, \(t + t_o < A^2/4B\), the first term in a Taylor series expansion for \(d_o\) gives:

\[d_o = \{B/A\} \left[t + t_o\right]\]

and \(B/A\) is denoted the “linear” law rate constant.

For large times, \(t + t_o > A^2/4B\), and

\[d_o^2 = B \left[t + t_o\right],\]

where \(B\) is the “parabolic” law rate constant.

Thus, early and long time rate data provide the two key kinetic rate constants, which govern the slow steps: \(k_R\) (reaction, early time) and \(d_o\) (diffusion, long time). As the two regimes are not easily distinguished with a limited range of data, the general quadratic is recommended:

\[d_o + A = -B (t + t_o) / d_o\]

where \(t_o = (d_i^2 + A d_o) / B\).

To evaluate \(A\) and \(B\) in this universal case, \(t_o\) is assumed, and data are regressed against this equation to find the optimal \(t_o\) value (best linear fit), from which \(A\) and \(B\) may be calculated. With \(A\) and \(B\) known, \(d_i\), the initial oxide thickness is calculated from the definition of \(t_o\).

Experimentally, in our oxidation in dry oxygen, student data (previous semester results) consistently indicated the presence of a measurable “native” oxide layer at \(t = 0\), as also noted by Deal/Grove in 1965 and since. Both the reaction limited (early time) and diffusion limited (late time) behaviors are clearly observable. The very modest transport rate through the growing oxide film makes the period of time under the parabolic law description the dominant portion of the reaction time.

**Experiment**

Wafer samples are oxidized at 900 °C in an oxygen flow-through tube furnace. Ellipsometry is used to measure film thickness ex situ after sample cooling. Given a SiO2
refractive index (1.462 at a wavelength of 632.8 nm) input to the ellipsometer, the measurement is read out as film thickness, \( d_o \), for each sample (time). Total experiment run time is 2-4 hours. Plots of \( d_o \) vs. time clearly revealed the two kinetic regimes discussed, and allowed evaluation of all rate parameters and initial oxide thickness.

**Experiment #3: COMPACT DISC (CD) WRITE & RE-WRITABLE SYSTEMS**

Compact disc technology is ubiquitous, found in computers, digital cameras, etc, as well as its descendents as mini-discs and as DVDs(digital video discs). The challenge for a lab experiment is to relate aspects of chemical engineering to the heart of CD technology, which is information storage and retrieval. The direction chosen here is to carry out transient energy balances on various aspects of CD recording, erasing, and reading, i.e., on the phase or dye transformations which are the basis for CD information recording, erasing and retrieval.

Through performing experiments with a CD “burner”, students learn that:

A CD is read with a focused laser light beam, wherein successive reflectance readings are read as digital ones (1s) or zeros(0), depending on whether sequential reflectances do change, or do not change, respectively.

When a CD is “written”, a strong laser beam carries out one of two types of transformations:

For a Write Once, read Many (WORM) or CD-R, a dye layer is photobleached during “writing”, and the resultant more transmissive layer allows a greater reflectance to be read (a gold mirror sits behind the dye layer) by the CD player.

For rewritable (RW) CDs (CD-RW), a mixed metal alloy layer undergoes phase transformation from crystallized (post-ERASE state) to amorphous (post-WRITE state), again resulting in change of layer transmissivity, and thus CD reflectance.

To the extent that chemical engineering labs involve characterization of rate processes, we provide exercises which allow kinetic calculation and characterization of this information storage/readout technology. We build student understanding through order of magnitude energy balance calculations in the microworld of READ, WRITE, and ERASE CDs. Table 1 summarizes the characterizations: calculated quantities are underlined at end of each line.

**Table 1**

**Energy balances on a CD “burner”**

A re-writable CD device utilizes a focused laser to carry out three separate functions: READ (low power), ERASE (medium power), and WRITE (high power).

The READ incident light level provides sufficient reflected light that the CD detector can read 1 or 0 codings.
The ERASE level profiles sufficient power to anneal an amorphous (written) alloy into a crystallized (erased) layer.

The WRITE level imparts sufficient heating to melt the alloy, which is then cooled very quickly to yield an amorphous (written) product.

During CD “burning” when new information is being written, the ERASE power in ON continuously in order to convert all prior amorphous (written) material into crystallized (erased) material. In addition, the WRITE power level is pulsed ON as needed for each write instruction. The WRITE laser heating time, and the cooling times are of different orders of magnitude, with the former so rapid that a simple adiabatic calculation suffices for estimation of maximum temperatures. The laser WRITE pulses are of typical duration 60 nanoseconds ($10^{-9}$ seconds), whereas a typical cooling time may be of the order of 10 milliseconds. The calculated temperature distribution at a CD spot during “writing” is in excess of 600 °C at the end of the 60 ns pulse.

To characterize the CD burner operation quantitatively, students are asked to complete the following calculations for a rewritable CD (CD-RW):

- $A = \text{written “pit” size} = 0.5 \, \mu\text{m (width)} \times 3 \, \mu\text{m (length)} = _1.5_ \, (\mu\text{m})^2 = _1.5 \times 10^{-8} \, (\text{cm})^2$.

- $P = \text{laser “WRITE” power} = 10 \, \text{mW} = _2.4 \times 10^{-3} \, (\text{cal/s}) = _2.4 \times 10^{-6} \, (\text{kcal/s})$

- $I = \text{Intensity during “pit” burning} = \frac{P}{A} = _1.6 \times 10^2 \, (\text{kcal/cm}^2\text{-s})$

- $t_p = \text{print time per pulse}: t_p = 60 \, \text{ns} = 60 \times 10^{-9} \, \text{s}$

- $E_p = \text{Power delivered per pulse} = I \times t_p = _9.6 \times 10^{-6} \, (\text{cal/cm}^2)$

Note: READ and ERASE powers are typically the order of 10% and 50% of the WRITE power. For this circumstance, calculate

- $P_R = P_{\text{READ}} = _2.4 \times 10^{-4} \, (\text{cal/s})$

- $P_E = P_{\text{ERASE}} = _1.2 \times 10^{-3} \, (\text{cal/s})$

The thermal response of the “active layer” (i. e., the writable mixed oxide) depends on its thermal inertia, $m_mC_p$, its absorbance of emitted power, and the combination of the rate of heating due to laser power input and the rate of cooling due to heat conduction away from the “burn” spot. Because these rates are very different, we can approximate the thermal time profile as a very short “burn” or heating period (adiabatic) of $t_p = 60 \, \text{ns}$, followed by a cooling period of characteristic length $t_c = 10 \, \text{microseconds} (10 \times 10^{-6} \, \text{s} = 10^{-5} \, \text{s}).$
Thus, for $0 < t < t_p$, we ignore cooling, and write for a transient energy balance on the “spot” to be heated:

$$m_M (\text{mols}) C_p (\text{kcal/mol} \cdot \text{o} \text{K}) \frac{dT}{dt} = P (\text{kcal/s})$$

If all properties are approximated as constant, i.e., independent of temperature, then integration provides:

$$m_M (\text{mols}) C_p (\text{kcal/mol} \cdot \text{o} \text{K}) (T_{\text{max}} - T_o) = P t_p$$

Given:
Spot dimensions = .5 µm x 3. µm
Active layer thickness = 50 nm
Active layer density = 8.9 g/cm²
Active layer mol wt. = 63 g/mol
Active layer $C_p = 0.024 \text{ kJ/mol} \cdot \text{o} \text{K}$
$P(\text{WRITE}) = 2.39 \times 10^{-6} \text{ kcal/s}$
Fraction of incident power absorbed by alloy layer: 7%

Calculate $T_{\text{max}}$ (maximum possible temperature) achieved in each of three modes:

**WRITE:**
$P = P_w \Rightarrow T_{\text{max}} = \ldots 650 \^\circ \text{C}$

**ERASE**
$P = P_E \Rightarrow T_{\text{max}} = \ldots 350 \^\circ \text{C}$

**READ**
$P = P_R \Rightarrow T_{\text{max}} = \ldots 90 \^\circ \text{C}$

The minimum temperatures to achieve writing (melt mode) or recrystallization (erase mode) are shown below. Indicate where the three calculated temperature MUST lie in order for this device to properly operate:

Locate (approximately): $T_{\text{max}}(\text{WRITE})$ and $T_{\text{max}}(\text{ERASE})$ for Ge$_2$Sb$_2$Te$_4$

$T_{\text{melt}}$ (614 $^\circ \text{C}$)

$T_{\text{recryst'}n}$ (131 $^\circ \text{C}$)

$T_{\text{ambient}}$ (25 $^\circ \text{C}$)

**Cooling**

The re-writable CD-RW structure includes an active “writable” alloy layer, separated from a highly reflective, excellent thermal conducting gold mirror by a poor thermal conductor layer of ZnS-SiO2. The gold layer is not heated appreciably, and may act as a perfect heat sink at $T_o$ to remove heat from the metal alloy. A simplified temperature profile which assumes good
thermal conductivity in the active, alloy and in the gold layer, and a poor thermal conductivity in the intervening ZnS-SiO2 (glass-like) layer is thus:

<table>
<thead>
<tr>
<th>Layer</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gold (50 nm)</td>
<td>Temperature (T₀ = 25 °C)</td>
</tr>
<tr>
<td>ZnS-SiO2 (12 nm)</td>
<td>(all of T gradient here)</td>
</tr>
<tr>
<td>Ge-Sb-Te alloy (30nm)</td>
<td>Temperature (T)</td>
</tr>
</tbody>
</table>

Next, students estimate a cooling rate by a one dimensional calculation (neglecting lateral heat conduction). If the gold layer temperature is assumed constant (high thermal conductivity), the transient energy balance for post-laser cooling is:

\[
m_M (\text{mols}) C_p (\text{kcal/mol}^{-\circ} \text{K}) \frac{dT}{dt} = -k A \frac{dT}{dx}
\]

Given: \( k = k (\text{SiO}_2(\text{glass})) = 0.0017 \text{ cal/s-cm}^{-\circ} \text{K} \) and \( A = \text{area of laser spot} = 1.5 \times 10^{-8} \text{ cm}^2 \)

Writing the transient energy balance, we have

\[
m_M C_p \frac{dT}{dt} = -k A (T - T_{\text{gold}})/z \quad \text{where } z = \text{ZnO-SiO2 layer thickness}
\]

Integrating,

\[
\ln \left[ \frac{(T_{\text{max}} - T_{\text{gold}})/(T - T_{\text{gold}})}{(T_{\text{max}} - T_{\text{gold}})/z} \right] = k A t / (m_M C_p z)
\]

or

\[
(T - T_{\text{gold}}) / (T_{\text{max}} - T_{\text{gold}}) = \exp(-k A t / m_M C_p z) = \exp -t/t_c
\]

where \( t_c \) is a typical cooling time.

Calculate \( t_c = \frac{m_M C_p z}{k A} = \_0.54 \text{ ms} \_ \)

The extensive calculations above offset somewhat the limited manipulations available with our current CD burners. The lab manipulations were the following simple exercises:
- identify (by observation) the following unmarked CD samples: new vs burned vs fully erased.; dye(WORM) vs metal oxide (RW)
- burn music tracks of various lengths and calculate the typical information densities stored on CD surfaces.
- write with ballpoint pens on the top and bottom CD surfaces to establish which are scratch resistant, and which damage the CD signal
- play CDs after progressively thicker portions of black insulating tape have been attached radially (this exercise demonstrates that a pre-recorded CD has an interleaved recording sequence, enabling recorded signal recovery by interpolation for small tape thickness!).
Experiment #4: FLUIDIZED POLYMER BED COATING

This experiment was constructed by two undergraduates in one month, using the description found in “Fluidized Bed Polymer Coating Experiment” authored by Hesketh, Slater, Farrell, and Carney (see reference at section end) As these authors note, “The main uses of fluidized bed coating techniques are in the pharmaceutical industry for controlled-release coatings on drugs and for microencapsulating drug components, protective coatings for glass containers and other components, coating of particles as small as 50 µm, fluidized-bed electrostatic coating, chemical vapor deposition in a fluidized bed for metal-coated microspheres for inertial confinement fusion targets, and fluidized bed coating of aluminum.” (These authors note a recent literature search revealing over 800 references).

Our apparatus was basically the same as theirs, modified to allow for six different fluidization tubes. The “polymer” used is a wax (Polyarmor Powder-PFS Thermoplastic Powder Coatings,) of density .934 g/cm$^3$, and melting point about 105 °C (21 °F). We, like they, coated metal washers, first warmed by a forced air heater gun to various initial temperatures, then immersed in the fluidized bed for different periods of time. In the time interval while the outer surface is appreciably above the wax melting point, wax particle collisions with the immersed, heated surface result in the continuing accumulation of wax deposition. Ultimately, the incoming cold air reduces the temperature of the immersed object sufficiently that further wax deposition halts.

Our initial results were similar to those of Hesketh et al (2002), which indicate nicely that a given coating thickness can be achieved through different (initial temperature) – (immersion time) coating conditions. An early polymer coating process cited by Kunii and Levenspiel indicates a large scale apparatus of similar configuration for batch coating. An early analysis of Gaynor predicts a decaying exponential approach to a final coating mass or thickness vs time.

The simplest analysis would consider the heated object (metal) and the adherent wax film to be virtually isothermal thanks to the relatively poor thermal conductivity of air. Elementary analysis predicts that:

\[ m_M C_p \frac{dT}{dt} = -h A_M (T - T_o). \]

which is the same form of equation as the earlier description for CD ‘burner operation.

Integrating gives

\[ \ln \left( \frac{T - T_o}{T_{max} - T_o} \right) = \frac{h A t}{m_M C_p} \]

or

\[ \frac{T - T_o}{T_{max} - T_o} = \exp \left( -h A_M t / m_M C_p \right) = \exp( -t/t_c ) \]

where \( t_c \) is a typical cooling time.
Accordingly, we use the heat capacity of the metal washer to estimate the initial relaxation time for air cooling:

Given (student calculates or estimates):

\[ A (\text{washer}) = 14.5 \text{ cm}^2 \]
\[ m_M = 17.8 \text{ g} \]
\[ C_p = 0.91 \times 10^{-4} \text{ kcal/g} \cdot ^\circ\text{C} \]
\[ H(\text{unkown: use 30x gas-only value (B.S.L.) of 40} \rightarrow 1200 \text{ kcal/m}^2 \cdot \text{h} \cdot ^\circ\text{C} \]

Calculate \( t_c = \frac{m_M C_p}{h A_M} = 48.3 \text{ s} \)

Students take weight vs time data during the coating experiment, from which average coating thickness vs. time is calculated. In principle, any predicted rate of wax particle deposition could be fitted to our data or the data of Hesketh et al if the particle sticking probability is known as a function of temperature. Empirically, students can plot their results as coating thickness vs time for various metal washer initial temperatures. The results characteristically showed conclusions demonstrated earlier by Hesketh et al:

1. Coating occurs for all initial temperatures substantially above the wax particle melting point. Coating halts when the washer has cooled to near the melting point.
2. The same coating thickness may be achieved with a short contact time and high initial temperature, or a longer time at somewhat lower initial temperature.
3. The coating process is complicated: individual particles are found to “stick” progressively less strongly with time as the washer/wax object cools, and the last particles adhering before the immersed object’s temperature falls below the melting point of the wax are easily removed with a light brushing, whereas the first particles deposited melt well, and are not removable by brushing. A post-deposition thermal treatment in an oven will smooth the rough wax coating.

The results of this coating experiment relate well to the student’s experience, as such coated surfaces are widely encountered in everyday life. Common examples include polymer coated small tools (screwdrivers, pliers, wire cutters,), insulated wires, key chain components, steering wheels, etc.

Given use of air, rather than liquid fluidization, and use of fine particles, the typical fluidization regime encountered here is a bubbly type, experiencing periodic strong release of powder at the air-fluidized bed top as large air bubbles break through the fine polymer ‘emulsion” fluidized phase. Student suggestions include lengthening this vertical tube, and adding a wider, disengagement section, to minimize powder carryover.

This experiment may be assembled for the order of $2,500. The fluid bed in our case was fabricated from common PVC pipe and fittings (elbows, expander/contractors, valves) available at any hardware store, and is mounted on lab table, supported with a 3’ x 6’ plywood backing.
Experiment #5: PHOTOCATALYTIC WATER PURIFICATION

In the past fifteen years, a new set of water treatment processes have appeared, based upon hydroxyl radical (OH) chemistry. These technologies include UV/ozone, UV/peroxide, UV/photocatalysis, and ozone/peroxide systems. The major advantages of these systems vs prior oxidants such as ozone, peroxide, or photolysis (UV) only, are two:

(i) The hydroxyl radical are sufficiently oxidative to allow complete mineralization of water pollutants, whereas the previous, common oxidants achieve only partial oxidation, and

(ii) The hydroxyl radical in particular can attack synthetic organic pollutants which are otherwise resistant to oxidative attack, either chemically or biologically.

Heterogeneous photocatalysis involves indirect photochemistry, in which an intermediary (photocatalyst) is activated the light, and the activated catalyst then converts reactant, and deactivates. Continuous reaction is required to maintain reaction. Absorption of bandgap energy (near-UV or shorter wavelengths) photons by the semiconductor catalyst will photoexcite an electron from the valence band into the conduction band. The resultant pair of excited species, the photoproduced conduction band electron (e-) and residual hole (h+) in the valence band, can migrate to the surface of the small catalyst particle (primary crystallites of order 20-30 nm), and be trapped (stabilized). From this surface, these energetic species may then participate in half cell reactions with (adsorbed) solutes reactions to generate oxidants, including hydroxyl radicals:

\[(h^+) + OH^- \rightarrow OH^- \text{ (radical)}\]

\[(e^-) + O_2 \rightarrow O_2^-\]
\[O_2^- + H^+ \rightarrow HO_2(\text{radical})\]

The stronger oxidant (OH) and the weaker (HO2) may both participate to attack and mineralize recalcitrant pollutants, e.g. chlorinated hydrocarbons trichloroethylene (TCE) and chloroform (trichloromethane) (Pruden and Ollis, 1983 a,b).

The present experiment utilizes ambient conditions of pressure and temperature, with the white paint pigment, titanium dioxide (anatase/rutile mixture), in aqueous suspension, to decolorize aqueous dye solutions via illumination with near-UV (300-400 nm) light.

**Experiment**

Suspensions of 0.1 wt% TiO2 with variable initial dye concentrations are prepared. Photocatalytic bleaching for color removal is carried our by exposure to near-UV blue-black light for various time. The liquid phase reaction progress is followed by spectroscopy to monitor parent compound disappearance. Data are tested against various assumed rate forms: first order, zero order, Langmuir-Hinshelwood (non-linear), and power law:

First order: \[\text{rate} = -k_1C\]
Zero order: \[ \text{rate} = -k_o \]

Langmuir-Hinshelwood: \[ \text{rate} = -kKC / (1 + KC) \]

Power law: \[ \text{rate} = -k_n C^n \]

**Differential and integral methods of rate analysis for parameter evaluations.**

As traditional, differential evaluation of data produces substantial scatter and uncertainty, making choice among rate laws difficult.

In contrast, integral analysis smooths out scatter, and produces graphs which render fitting of integral rate forms more convincing:

First order: \[ C(t) = C(0) \exp(-k_1 t) \]

Zero order: \[ C(t) = C(0) - k_o t \]

Langmuir-Hinshelwood: \[ 1 + 1/K \ln \left( \frac{C}{C_0} \right)/(C - C_0) = -k \frac{t}{C - C_0} \]

Power law: \[ \frac{1/C^{n-1} - 1/C_0^{n-1}}{(1-n)} = -k t \]

This inexpensive photoreactor requires only small glass Petri dishes, a multi-sample stirring platform for the suspension loaded dishes, a bank of 4-6 near UV actinic lamp (low P mercury lamp with near UV emitting phosphor on inside lamp surface) Samples are taken periodically, centrifuged to remove particular catalyst suspension, and analyzed spectroscopically. The total experimental reactor (lamps, ballasts, plywood enclosure) is several hundred dollars maximum. A centrifuge suitable for removal of 0.1 µm particles is needed, along with a simple UN-vis spectrometer and multi-sample stir platform.

A second set of experiments invites students to examine the influence of light. When the volume of the catalyst and reactant solution/suspension is doubled in the same Petri dishes, the apparent rate constant declines, often by about 50%. This behavior, contrary to conventional homogeneous solution chemistry, reminds the students that the reaction is light driven, and thus only regions of the suspension which can absorb light are active. Since the original suspension has an optical density near 2 (opaque), doubling of the reaction volume by doubling its depth in the same Petri dish has a negligible or small influence on the absolute reaction rate, and thus the rate per unit liquid suspension volume is cut in half. An improved experiment would invite constant liquid volume runs in Petri dishes of different surface areas.

A more enterprising groups was well enough organized to obtain data for two different dyes, Methylene Blue and Congo Red. The first conversion was nearly zero order, the second apparently first order in the range of concentrations explored.

The relevance of this experiment to student experience is high:
-the experiment involves dye bleaching, thus the reaction progress can be followed visually, as well as spectroscopically.
-NCSU has a large College of Textiles (a number of our majors also double major in Textile disciplines), where disposal of textile wastewaters is a recognized problem.

**Experiment #6: RAPID PROTOTYPING**

The use of computers in process control and monitoring is long established in chemical engineering. Similarly, use of computation for plant design and optimization is now traditional. Computer-Aided Design (CAD) is a more recent activity, whose maturation has led to integration of CAAD with prototyping.

“Rapid prototyping is the name given to a host of related technologies that are used to fabricate physical objects directly from CAD data sources. These methods are generally similar to each other in that they add and bond materials in layerwise-fashion to form objects. This is the opposite of what classical methods such as milling or turning do: objects are formed in these latter processes by mechanical removal of material. Rapid prototyping is also known by the names of freeform fabrication (FFF), layered manufacturing, automated fabrication and other variants”.

Rapid prototyping machines operate on one of three principle methods of layer-by-layer synthesis: stereolithography, selective laser sintering, and ink jet printing, with further variations within these categories. In all cases, the three dimensional model held within the CAD system is sectioned computationally into individual horizontal layers, which are then fed sequentially to a scanning system (laser, ink jet) which creates the new layer materially through a scanning or printing pass over the accumulating object.

**Sterolithography** A liquid layer of photosensitive monomer is selectively exposed from above to a scanning laser to create a solid, photopolymerized layer. Subsequent to a scan, the monomer liquid level is raised incrementally (or the object is lowered) and the next laser scan “builds” the next layer by selective photopolymerization of the new “top” layer of liquid. The “finished” object is often subjected to post-synthesis photo- or thermal-cure to further strengthen the object prior to use.

**Selective laser sintering** A bed of thermoplastic powder is held just below its melting point. A CO2 laser scans the top surface, locally heating and melting the powder to sinter the particles together. This method has now been applied to organic, ceramic and metal powders.

**Ink jet technologies** The more expensive laser scanning systems described above may be replaced by cheaper layer-by-layer systems based upon ink jet printing. The following variants are commercial:

**Thermal phase change**: a heated, melted or liquid, state material is passed through the ink jet which selectively ”prints” the desired layer. The melt or liquid droplets ejected from the ink jet solidify upon contact with the prior “build” surface of the growing, solid object. Between ink jet scans, a mechanical milling layers the most recently deposited layer to a desired uniformity. The melt or liquid material may be a solution or a suspension.

**Photopolymer layer cure.** The expensive single beam scanning laser is replaced by an inexpensive ink jet printing of a photo-monomer layer, followed by a non-selective UV light
flood exposure for curing. Thus, the slow laser scan is replaced by a fast ink jet printing and rapid photocure process for the construction of each layer.

**Three dimensional printing** An ink jet deposits an adhering, liquid compound (or solution) on top of a powder bed. The local uptake of liquid bonds the particles into a nascent solid form. Following each scan, a new layer of dry powder is applied, and receives the next selective printing scan.

In virtually all cases above, the initial object is relatively unstable or “green”, and is further stabilized by a subsequent curing process involving either wicking of a stabilizer (e.g., melted wax), into the sintered or adherent powder structure, or using a post-synthesis UV or thermal cure.

These systems are expensive, ranging from $35,000 (ink jet) -$300,000(laser scan). However, many campuses will have such instruments already on hand for research purposes. Thee are easily adaptable as chemical engineering lab experiments, because: (1) they are relatively simple to operate and require little supervision, and (2) the simple CAD models may be written by the students and fed into the rapid prototype machine PC to “custom” synthesize any given geometry, thus nicely demonstrating the “rapid prototyping” principles.

At NCSU, the following campus machines were “discovered” and considered for utilization: three Z Corp machines (ink jet three dimensional printing of “glue” on to powder), a 3D systems stereolithography apparatus, and a singular electron beam scanning systems for fully melting metal powders to produce a fully dense prototype (Swedish). Professor Denis Cormier of NCSU’s Industrial Engineering department advises that the most frequently found locations in academia for such machines are in manufacturing disciplines (mechanical and industrial engineering), technology education component of colleges of education, and the industrial design studio within schools of design and architecture. At NCSU, a Z Corp machine (powder adhering) is found in each of three colleges: engineering, education, and architecture.

Our machine was the 3D Systems inkjet printer located in Industrial Engineering. The first experiments for student lab groups was to used a “canned’ program for a reasonably simple, but cute shape: a 1” cube containing a large, centered spherical hole, with circular holes cut into each face through to the hollow inner spherical hole. In the central spherical “hole” is a second cube, large enough so that it cannot pass out of the cylindrical holes in the large cube faces. On four of the surfaces of the inner cube appear the raised letters “N, C, S, and U”. As a simple exercise, we asked one lab group to estimate the manufacturing cost, and projected selling price, for 10,000 such cubes as souvenirs for students and alumni !

In our initial lab exercises, the student group synthesized simultaneously sixteen (4 x 4 array) of the 1” cubes in a 2 hour scanning period. The machine “build” time is fully automated, so the total student lab time was for set-up and initiation, later removal after synthesis, air cleaning to remove adherent powder, and stabilization by liquid wax infiltration into the cooled cubes. The original instructions for the industrial engineering demo included subsequent measurement on “green” and wax infiltrated cubes to determine the statistical distribution of dimensions on the finished product, and to demonstrate that the height was slightly less than the width, due to a small sag in the green version while it sat and matured.
A student in our second lab group had an acquaintance in the Veterinary Medicine college with a database for a brainscan profile. This data base his group loaded into the Z Corp machine PC, and a 3D model of the full brain was “printed” and wax infiltrated.

A yet more enterprising lab group wrote a brief introduction to the SolidWorks software utilized by the Z Corp. machine. In their demonstration chapter, instructions are presented for CAD construction of a chemical reactor vessel: a tank with axial symmetry, thus allowing easy entry of the outline for a vessel with a cylindrical, vertical wall, a conical base, and a hemispheric top, plus fitting of top and bottom for material entry and withdrawal. The group entered the data, and prototyped the vessel, all within a reasonable time period. Clearly, a strong creative element is available with the Rapid Prototype process, and advance planning of an experiment could produce individualized products which would be a most welcome change of pace vs. conventional “cookbook” approaches to chemical engineering lab experiments.

Student evaluations: ROUND #1

Table 2
Evaluation Summary
Per Cent of Responses

<table>
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<tr>
<th></th>
<th>Agree strongly</th>
<th>Agree</th>
<th>(Agree strongly + Agree)</th>
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<tbody>
<tr>
<td>DEVICE</td>
<td></td>
<td></td>
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<tr>
<td>Fully operational</td>
<td>27</td>
<td>45</td>
<td>72</td>
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<tr>
<td>Illustrated principles</td>
<td>36</td>
<td>64</td>
<td>100</td>
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<tr>
<td>WRITTEN CHAPTER</td>
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<tr>
<td>Is clearly written</td>
<td>9</td>
<td>72</td>
<td>81</td>
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<tr>
<td>Sufficient lab exercises</td>
<td>0</td>
<td>63</td>
<td>63</td>
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<tr>
<td>VS ORIGINAL EXPTS:</td>
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<tr>
<td>More interesting</td>
<td>55</td>
<td>45</td>
<td>100</td>
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<tr>
<td>Learned more</td>
<td>27</td>
<td>45</td>
<td>72</td>
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<tr>
<td>RECOMMENDATIONS</td>
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<td>Add</td>
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<tr>
<td>Fuel cell: Pure O2 feed in place of air; better pressure gauge</td>
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<tr>
<td>Rapid prototype: material science application</td>
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<tr>
<td>CD burner: chemical properties of phase changes; microscope to view “pits” and tracks</td>
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<tr>
<td>Fluidized bed coating: longer tube; better T measurement; hot sample holding device; heat transfer calculations</td>
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<td>Delete</td>
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<tr>
<td>Fuel cell: single cell measurements; solar cell write-up</td>
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<tr>
<td>Rapid Prototype: less theory on other systems</td>
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</table>
In fall 2003, five of the six experiments were evaluated: rapid prototyping, CD burner, water purification, fuel cell, and fluidized bed polymer coating. The sixth (silicon oxidation) was unavailable and was not evaluated. Students were given the questionnaire below, which indicated that new experiments were being introduced to the undergraduate laboratory, and that evaluation and suggestions were sought. Eleven student lab groups, comprised of 35 students, carried out group evaluations of their experiment. Students responded to six evaluation statements, and also were invited to make recommendations as to what to add, or delete in each experiment. Other comments were also invited. For each of the six statements, students could elect AGREE STRONGLY, AGREE, NEUTRAL, OR DISAGREE.

In the fall 2003 semester, each student group first performed three of the OLDER experiments, then one of the NEW experiments. The questionnaire also asked students to compare the OLDER with NEW experiments in terms of subject interest, and of learning achieved.

A evaluation summary appears in the table above. The results indicate that devices and chapters were viewed favorably, and that the NEW experiments were more interesting, and provided more learning, than the OLDER experiment. For future improvements, all chapter writing can be improved, and more specific lab exercises (manipulations, calculations) may be added.

Acknowledgement

We are pleased to thank the Camille and Henry Dreyfus Foundation for funding the development of lab experiments in CD “burning”, fuel cell operation, water purification, rapid prototyping, and polymer coating.

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