CHEMICAL ENGINEERING IN THE SPECTRUM OF KNOWLEDGE

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For at least two generations, chemical engineers have claimed the ability to "do anything." Because their education has been so broad, they had both the basic tools and the self-confidence needed to tackle nearly any problem. This versatility has remained even as chemical engineers have shifted their attention from commodity chemicals to biotechnology or materials processing. Unfortunately, undergraduate education has not yet sufficiently changed to meet the new challenges. The prevailing repertoire of homework problems and classroom examples does not adequately reflect the advent of new fields and,

FIGURE 1. *Woman Before a Mirror*, **Picasso (1930).**

perhaps more serious, has failed to show the growing interconnections between chemical engineering and societal concerns.

The dichotomy between current chemical engineering practice and what is commonly presented to undergraduates may be illustrated by analogy to Picasso's painting, *Woman Before a Mirror* (1930), shown in Figure 1. A woman gazing at herself in a mirror sees a distorted profile rather than an accurate representation of her face and figure. The painting symbolizes her inability or unwillingness to see herself as a complete, integrated whole; she can only see a part of herself. Similarly, by confining illustrative examples in undergraduate chemical engineering to traditional topics, we fail to reflect properly how "real," contemporary chemical engineering is practiced, and how intimately our branch of knowledge is related to issues of wider scope.

In practice, chemical engineering does not exist in a vacuum. As a field of knowledge, it is closely connected with many other disciplines. Therefore, modern chemical engineering education must transcend the compartmentalization of academic subjects. Students must be shown that what they learn in the classroom relates to the world outside. This relationship is best established through illustrative classroom examples and homework problems.

We present here three such problems, drawn from current societal concerns; these problems link chemical engineering with broad policy issues.

- **The depletion of the ozone layer**
- **A nuclear-winter scenario**
- **Air pollution by chemical solvents**

In these examples, we show the student how thermodynamics, fluid flow, and chemical kinetics can supply *partial* answers to significant social questions. At the same time, these problems serve to expose the student to issues which do not have a unique solution, where competing claims require consideration, and where chemical engineering skills must be integrated

with insights from other perspectives to arrive at a comprehensive solution.

We do not claim to give unique answers. Rather, the solutions presented should be viewed as best estimates. It is the procedure, rather than the numerical outcome, which we hope to stress.

DEPLETION OF THE OZONE LAYER

The first problem (suggested by Professor H. S. Johnston) analyzes alternative strategies for counteracting the depletion of the stratospheric ozone layer by chloro-fluorinated hydrocarbons (CFCs). The production of CFCs has increased markedly over the last decade, to about one billion kilograms per year [1]. CFCs are used as refrigerants, propellants, and as foaming agents in the production of polystyrene and polyurethane packing materials. Distinguished by their lack of toxicity and chemical stability at sea level, CFCs become photoactive and deplete ozone in the stratosphere at altitudes above fifteen kilometers. Ozone decomposition is dangerous because ozone shields the earth from harmful ultraviolet radiation. Even a ten percent reduction in stratospheric ozone concentration would lead to a significant increase in skin cancer and cause a drastic increase in the number of cataracts. As a result of recent activity by the United Nations, a landmark international treaty has been negotiated which would cut CFC emissions by fifty percent by the year 1999 [2].

Rising CFCs enter the stratosphere at an altitude

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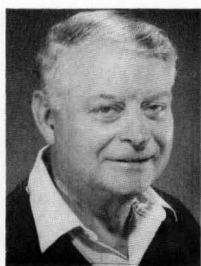
of approximately eleven kilometers. Below this layer, air temperature drops linearly with height, with a gradient close to the adiabatic limit (9.9°C per km) [3]. An inverted temperature gradient occurs in the stratosphere, however, caused by the absorption of incident solar radiation by oxygen and ozone, especially in the ultraviolet portion of the electromagnetic spectrum. It is this absorption which blocks harmful radiation from reaching the earth's surface.

In the stratosphere, oxygen radicals react with an oxygen molecule forming ozone [1]

$$O_2 + h\nu(\lambda < 242\,nm) \rightarrow 2O\cdot \tag{1}$$

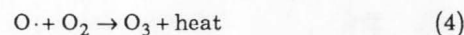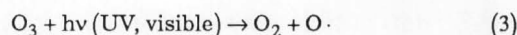$$O_2 + O\cdot \rightarrow O_3 \tag{2}$$
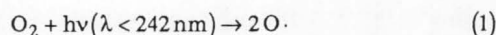
where
    h = Planck's constant
    ν = frequency
    λ = wavelength
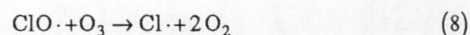
Ozone absorbs ultraviolet radiation and converts it into heat by

$$O_3 + h\nu\,(UV,\ visible) \rightarrow O_2 + O\cdot \tag{3}$$

$$O\cdot + O_2 \rightarrow O_3 + heat \tag{4}$$

The heat released warms the stratospheric air mass so that the temperature rises with height. This rise creates hydrodynamic conditions where free convection is almost completely suppressed, and a stagnant layer of air results. Thus, CFCs travel through this quiescent layer by molecular diffusion alone. At this height, they become photo-active and form chlorine radicals. For example, if the CFC is fluorotrichloromethane

$$CFCl_3 + h\nu\,(\lambda < 280\,nm) \rightarrow CFCl_2\cdot + Cl\cdot \tag{5}$$
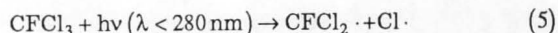
The chlorine radical reacts either directly with ozone or with an oxygen radical [1]. The chlorine radical acts as a reaction intermediate, continuously depleting the stratosphere of ozone:

$$Cl\cdot + O_3 \rightarrow O_2 + ClO\cdot \tag{6}$$

$$Cl\cdot + O\cdot \rightarrow ClO\cdot \tag{7}$$

$$ClO\cdot + O_3 \rightarrow Cl\cdot + 2O_2 \tag{8}$$

The result of this reaction chain is a perturbation of the steady-state ozone concentration. While simulation of the complex set of reactions lies beyond the scope of an undergraduate course, it is educationally

useful and relevant to inquire what can be done to return the stratospheric ozone concentration to the level prior to the introduction of man-made chemicals.

Students are told that under present conditions a ten-percent reduction in the steady-state ozone concentration may occur by the year 2000. To counteract this reduction, one alternative might be to augment the ozone production rate artificially to achieve the desired O_3 concentration, that is, to produce ozone on the earth and to send it to the stratosphere.

Students are given data on natural O_3 rates of production from the literature [4]. While these rates vary with height, latitude and season, an average rate of

$$1 \times 10^6 \frac{\text{molecules}}{\text{cm}^3 \text{ sec}}$$

may be used to estimate the energy required to replace the "lost" ozone. As a homework problem, students are asked to calculate the minimum amount of energy required to replenish the ozone layer and to compare that to annual U.S. energy production.

To establish a solution, students must first determine the volume of the stratosphere and then calculate a global production rate. The free energy of formation of ozone gives the approximate minimum energy required.

The calculated global production rate is 1.2×10^7 moles of ozone per second. Since the free energy of formation of ozone is positive

$$\Delta G_f = 39.06 \frac{\text{kcal}}{\text{gmol}} \qquad (9)$$

energy must be supplied for the reaction to proceed. The minimum energy needed to augment the O_3 production rate by ten percent would be

$$4.7 \times 10^{11} \frac{\text{cal}}{\text{sec}}$$

Converting this into more conventional units, and comparing it to the annual U.S. production of usable energy, we see that the energy required to increase the ozone production rate is prohibitive [5]. It would require a tripling of our annual energy production:

Energy to replace lost O_3:

$$5.77 \times 10^{16} \frac{\text{BTU}}{\text{yr}} \ (57.7 \, \text{Quads / yr})$$

1983 U.S. energy production:

$$2.71 \times 10^{16} \frac{\text{BTU}}{\text{yr}} \ (27.1 \, \text{Quads / yr})$$

This simple analysis shows that, if continued unchecked, the problem of ozone depletion could be beyond our direct control well before the year 2000.

To forestall serious and lasting damage to the environment, it is therefore necessary to address the issue of CFC emissions and to consider alternate chemical materials to replace CFCs in current chemical technology.

NUCLEAR WINTER

We now turn to another form of energy release: the detonation of nuclear weapons. Until recently, scientists believed that, however devastating, the effects of nuclear war on global climate due to blast, heat, and radio-activity would be slight. Recent research has brought this conclusion into question [6], noting that detonation of a nuclear arsenal would cause large-scale forest fires which would blow huge quantities of dust into the stratosphere. This dust prevents sunlight from reaching the earth, triggering nuclear winter. As proposed by Professor M. C. Williams, students are asked to estimate the settling time for the stratospheric dust.

The students are told to model the dust as spherical particles ten microns in diameter, forming a dilute dispersion in the stagnant stratospheric layer. They are asked to calculate the settling time from a height of fifty kilometers, and are given a hint that Stokes' law may apply.

In this context, the condition of diluteness implies that the particles have a nearest approach of 100 diameters, or one millimeter. Even as a dilute dispersion, this layer of dust would be quite opaque, since it would be twenty kilometers thick. The incident solar radiation would be completely blocked from reaching the earth's surface. The earth would be engulfed in darkness and there would be no light for photosynthesis.

To apply Stokes' law, we assume a stagnant layer of air; this is an optimistic assumption, since any winds or natural convection would tend to keep particles airborne longer. It may also be argued that large particles scavenge some small dust particles. However, once the large particles settled, it is plausible to assume that there would still be a dilute dispersion of small-diameter dust.

First, the student calculates the terminal velocity, V_t, from a force balance:

$$6 \pi \mu R V_t = \frac{4}{3} \pi R^3 (\rho_s - \rho_{air}) g \qquad (10)$$

where

g = gravitational constant
R = particle radius
V_t = terminal velocity
μ = viscosity of air
ρ_s = particle density
ρ_{air} = density of air

Assuming that $\rho_s \gg \rho_{air}$, and substituting known val-

ues, we obtain V_t for dust particles ten microns in diameter.

$$V_t \approx \frac{2}{9} \frac{\left(5 \times 10^{-4} \, cm\right)^2 \left(2.0 \, \frac{g}{cm^3}\right)\left(980 \, \frac{cm}{sec^2}\right)}{2.0 \times 10^{-4} \, \frac{g}{cm \, sec}} \quad (11)$$

$$V_t \approx 0.55 \, \frac{cm}{sec} \quad (12)$$

The settling time, τ, is the maximum height (50 kilometers) divided by the terminal velocity. For ten-micron spheres, $\tau = 9.09 \times 10^6$ sec., or about 105 days. This magnitude of τ is great enough to demonstrate the possibility of nuclear winter. If the initial dust content in the stratosphere were large enough to cool the earth to winter-like conditions, then at least one harvest, and perhaps two, would be destroyed. More serious, all summertime vegetation would perish, severely affecting wildlife dependent on such vegetation for food.

Settling time τ is inversely related to the square of particle diameter. Thus, τ becomes very large for very small particle diameters. For one-micron spheres, the settling time is 29 years!

This analysis does not consider the effects of nuclear explosions staggered in time. Staggering would delay the settling process considerably by re-injecting the stratosphere with dust. The consequences of nuclear war could cause climatic damage for a period of years.

Similar calculations may also be used to consider the effect on the atmosphere of a large meteorite impact or prolonged volcanic activity. It has been proposed that either of these mechanisms may have caused the extinction of dinosaurs at the Cretaceous-Tertiary boundary [7].

AIR POLLUTION BY CHEMICAL SOLVENTS

For our final example, we examine a common air-pollution problem: smog caused by the evaporation of solvents in lacquers and paints. This example differs from the previous two because it concerns a response to existing legislation rather than evaluating a need for political or social action.

Solvents vaporize and are subject to photochemical reaction with ozone, forming smog. In some geographic areas, local legislation has been enacted for controlling the emission of volatile materials. Los Angeles was the first major metropolitan area to enact such legislation, in conjunction with the Environmental Protection Agency. Los Angeles' Rule 66 limits both the type and amount of solvents which may be used in paint formulations. To meet Rule 66 limitations, typical paint and lacquer solvents have to be reformulated.

This example concerns the cost of choosing a permissible solvent mixture for cellulose nitrate, which is widely used as a lacquer for textiles and furniture. Cellulose nitrate has been used for such applications for over a century, due to its low cost and the durability of nitrocellulose films. For use as a coating material, cellulose nitrate is dissolved in a mixture of solvents. The active (and relatively expensive) solvent is a polar liquid having functional groups containing oxygen: aliphatic esters of acetic acid, ketones, and glycol ethers are the most common solvents. Co-solvents and diluents may also be used to reduce cost. However, these diluents tend to be smog-forming aromatic hydrocarbons. Rule 66 limits both the aggregate volume fraction in the paint mixture of these diluents, as well as individual volume fractions of certain types of diluents. Olefins are limited to five percent by volume, eight-carbon aromatics are limited to eight percent, while toluene, trichlorethane, and branched ketones are also subject to the aggregate limit of twenty volume percent.

The students are introduced to a method of designing solvent blends based on a 2-dimensional map of Gardon's fractional polarity versus solubility parameter, shown in Figure 2. Fractional cohesion paramet-
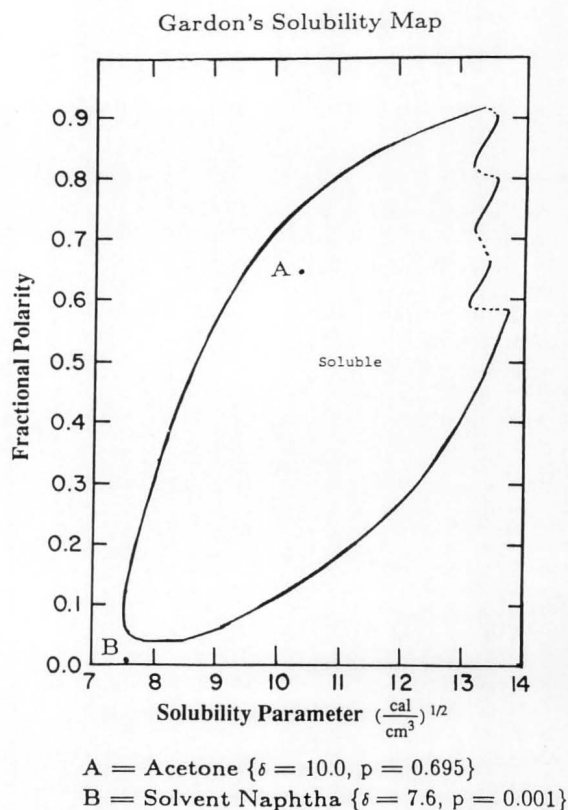

Gardon's Solubility Map

A = Acetone $\{\delta = 10.0, \, p = 0.695\}$
B = Solvent Naphtha $\{\delta = 7.6, \, p = 0.001\}$

FIGURE 2. A solubility map for cellulose nitrate.

ers are used to represent the solubility behavior of polymer-solvent systems. Gardon has shown that a good solvent matches both the solubility parameter and the fractional polarity of the solute [8, 9].

Students are given solubility data and current prices for various categories of solvents, as listed in Table 1. They are asked to compare the cost of the cheapest acceptable solvent mixture to that of the least expensive mixture which also satisfies Rule 66. Several additional constraints must also be met to achieve an acceptable solvent for cellulose nitrate:

- **The volume fraction of the active solvent should be three times that of the co-solvent (this insures solubility).**

- **High-boiling solvents should not exceed ten percent of the total solvent volume. (Required for proper drying characteristics.)**

- **The volume fraction of the diluent must not exceed three times that of the slow-evaporating, high-boiling component. (Required for even flow and uniform coating.)**

- **Proper flow and blush resistance requires that low-boiling active solvents do not exceed twenty percent of the total volume. (Nitrocellulose lacquers tend to precipitate resins if the temperature is lowered by rapidly evaporating solvents.)**

Table 2 shows both the original inexpensive solvent mixture and the mixture which satisfies Rule 66.

The cost of the original solvent mixture is $1.48/gallon, while that of the environmentally benign, redesigned mixture is fifty percent higher, $2.21/gallon.

This example shows students that chemical engineers have a role in establishing a cost-effective response which adheres to legislated concerns.

CONCLUSION

The examples presented here have been drawn from environmental issues. While forming a coherent set, they illustrate an important point: chemical engineering science offers useful contributions toward a better understanding of broad topics. Just as we combine kinetics, thermodynamics, and fluid mechanics into an engineering curriculum, so must we integrate chemical engineering with knowledge and concerns from other academic areas. Educational experience is enriched when its relevance is clearly demonstrated to the student.

We plead for integrating chemical engineering education with the world around us. The goal of such integration can be illustrated by looking at another Picasso portrait, *Dora Maar* (1937), in Figure 3. In contrast to the first painting, we now have an integrated portrait of the woman, that is, a representation which shows the subject in many dimensions. The artist combines both full-face and profile images to give

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TABLE 1
Suggested Solvents and Prices (Sept. 1986)

ACTIVE SOLVENTS	PRICE
Low boiling solvents:	
acetone	$ 0.27/lb
methyl ethyl ketone	$ 0.235/lb
Medium boiling solvents:	
methyl isobutyl ketone	$ 0.38/lb
n-butyl acetate	$ 0.52/lb
iso-butyl acetate	$ 0.45/lb
High boiling solvents:	
methyl methoxy pentanone	$ 0.50/lb
methyl amyl acetate	$ 0.52/lb
LATENT SOLVENTS	
iso-propyl alcohol	$ 1.31/gal
n-butyl alcohol	$ 0.34/lb
ethyl alcohol	$ 1.81/gal
HYDROCARBONS	
toluene	$ 0.73/gal
xylene	$ 0.80/gal
benzene	$ 0.85/gal
solvent naphtha	$ 1.30/gal

TABLE 2
Cost Comparison Between Solvent Mixtures

Standard Solvent (pre-Rule 66)

Active Solvents	
methyl ethyl ketone	$ 0.235/lb
methyl isobutyl ketone	$ 0.38/lb
methyl methoxy pentanone	$ 0.50/lb
Latent Solvent	
isopropyl alcohol	$ 1.31/gal
Hydrocarbons	
toluene	$ 0.73/gal
Total Cost Per Gallon	**$ 1.48**

Environmentally Benign Solvent

Active Solvents	
acetone	$ 0.275/lb
n-butyl acetate	$ 0.52/lb
methyl amyl acetate	$ 0.52/lb
Latent Solvent	
ethyl alcohol	$ 1.81/gal
Hydrocarbons	
includes solvent naphtha	$ 1.30/gal
Total Cost Per Gallon	**$ 2.21**

FIGURE 3. *Dora Maar*, *Picasso (1937)*

us a more complete description of his subject. By analogy, showing students how to link their technical skills with contemporary problems gives them a more complete image of what chemical engineering is and what it can do. Versatility means to establish connections, to practice a form of "networking" by building bridges between a variety of intellectual domains. By helping our students to become more versatile, they will see chemical engineering as a component in the spectrum of knowledge.

APPENDIX:
Viscosities at High Altitudes

The calculations presented in the preceding problems are meant to be estimates rather than exact values. They incorporate enough precision to allow the examination of possible environmental scenarios. It has been suggested, for example, that the estimates presented in the nuclear winter problem are sensitive to the value of viscosity used in the model. While vis-

cosities are only a function of temperature at low pressures, it may be instructive to analyze the variation of calculated viscosities as a function of height. According to the kinetic theory of gases, as modified by Chapman and Enskog (1906), the viscosity of air depends only on the square root of temperature. Thus, the viscosity varies as the particle falls through warmer regions of air. The range of values is relatively small, however. At the extreme of 200K, the viscosity is 1.30 cp, only 35% lower than the quantity used in the present work.

A second objection concerns the inapplicability of using bulk-viscosity values in regions of very low pressure. A simple calculation shows that the mean free path of a dust particle is less than one diameter up to heights of 20 - 25 kilometers. Even at 30 kilometers, the particle experiences over 2000 collisions per second. It would seem appropriate, given the statistically large number of collisions, to use ordinary viscosities to predict the particle's terminal velocity. The model is here applied to a particle falling from a height of 50 kilometers; if 30 kilometers were substituted for 50, there would be no change in the qualitative conclusion that injection of sufficient dust into the upper stratosphere may portend grave environmental damage.

ACKNOWLEDGEMENTS

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