

SUPERHEATED LIQUIDS A LABORATORY CURIOSITY AND, POSSIBLY, AN INDUSTRIAL CURSE

Part 2: Industrial Vapor Explosions

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VAPOR EXPLOSIONS—A REVIEW

IN PART 1, WE EMPHASIZED the concept of a superheated liquid and the fact that there is a superheat-limit temperature (SLT). Kinetic theory described, approximately, the rates and probabilities of vapor formation in superheated liquids—while thermodynamics placed an upper value on the SLT. We saw that experimental measurements of the superheat-limit temperature were in good agreement with predictions from kinetic theory and, correctly, less than limiting values estimated from thermodynamics.

Nevertheless, the experiments were carried out under laboratory conditions with great care taken to minimize heterogeneous nucleation. Only a very small fraction of all bubble-column tests are successful wherein a drop is indeed heated to the SLT. Most drops begin to vaporize before this limit is attained.

Can we, therefore, ever expect, in real world operations to superheat a liquid sufficiently high to induce true homogeneous nucleation where there is very rapid (even explosive) formation of vapor? We examine a number of case histories—drawn from research studies or plant accidents. In all instances, two liquids come into contact; one is significantly more volatile and at a lower initial temperature than the other. Modes of contact vary greatly and as will be suggested, the type of contact may be very important in determining the outcome.

MOLTEN TITANIUM-WATER VAPOR EXPLOSIONS

THROUGH THE KINDNESS of Dr. Robert A. Beall I have been allowed access to a number of

unpublished accident reports, several of which have recently been declassified. These deal with water-molten metal explosions in the cold-mold arc-melting and casting process. In this industrial operation, large ingots of titanium, zirconium, tantalum, columbium, molybdenum, tungsten, alloyed steels, etc., are prepared. To minimize contamination, crucibles are constructed of copper and kept cool by an external water jacket. The metal to be cast is prepared as a consumable electrode by compressing and welding "sponge" metal into a vertical cylinder. A high amperage-high voltage arc causes melting. (See Figure 12)

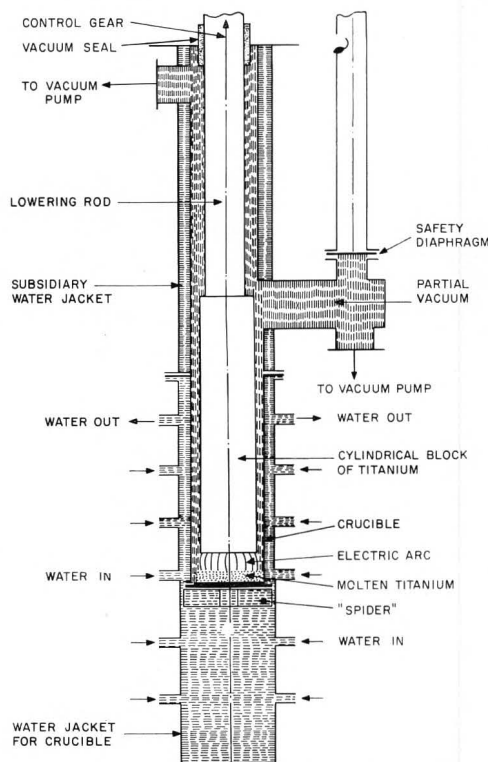


FIGURE 12 DIAGRAM OF TITANIUM MELTING FURNACE

A review of this process is available in a Bureau of Mines report (Beall et al., 1968).

In the past twenty-five years, a number of accidents have been reported. Essentially, all have resulted when, for various reasons, there was a failure of the copper mold with subsequent contact between molten metal and water. Fortunately, most led only to mild steam explosions, but a few were very different. These, in a Spockian sense were "most interesting," but in a humanoid view make for depressing reading.

As an example, quoting from a letter from Dr. Beall, "In one case, a hole was burned in the crucible, water intruded, and the arc was extinguished. Interlocks on this particular furnace called for the electrode to be drawn up (out of the water). However, the limit switches on the withdrawal mechanism

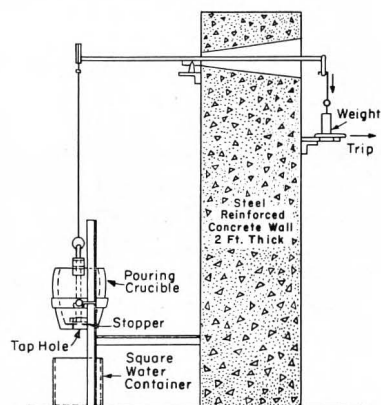


FIGURE 13 SKETCH OF DEVICE FOR INDUCING EXPLOSIONS WHEN DUMPING HOT ALUMINUM INTO WATER. FROM LONG, 1957.

We turn next to accidents which occur all too frequently in paper pulping operations. . . . Severe explosions have occurred in the step where the molten salt (smelt) from the furnace is dissolved in water.

ism failed to function, and when the electrode reached the top of the furnace, the cable broke, and the electrode fell, driving the water standing in the crucible into the molten pool of metal. A very severe explosion resulted, scattering furnace components like shrapnel."

With a good deal of insight, Dr. Beall concludes "Of important consideration is the fact that water leaks in arc furnaces of this type have occurred occasionally in the various melting establishments without any serious explosion resulting therefrom. In a few reported instances, steam buildups have been noted but not of serious consequence. It must be pointed out that the affair here reported required the coincidental occurrence of a water injection, intimate mixing with molten metal, and very possibly, tamping of the mixture by the falling electrode. Such a chain of circumstances can lead to a powerful explosion rather than the customary quiet extinguishing of the arc."

We cannot conclude with any certainty that explosions in cold-mold arc-melting furnaces are due to superheated liquid water. It does appear to us, however, that it is less than coincidental that two elements appear necessary to achieve an explosion: molten metal contacts water, and there is some impact event, i.e., the falling of a heavy electrode into the metal-water, the shock-wave due to

failure of a rupture disc, etc. It is easy to hypothesize—but more difficult to prove—that the impact event forced water and metal into intimate contact for a brief period to develop a highly superheated water layer that nucleated violently and efficiently mixed the metal-water together to enhance rapid steam (or hydrogen) production on a large scale.

MATTE-WATER EXPLOSIONS

A NEW DIMENSION was introduced to me by letter from Roland S. Young of Victoria, B. C. who told of several harrowing experiences when molten matte contacted water. In fact, he indicates that the problem is so serious that before transferring molten matte with cast iron ladles, the ladles must first be dried over an open fire to insure no moisture is present. He writes, "I recall a distressing incident in a large copper-cobalt smelter in Northern Rhodesia. Here too, careful attention was given to the drying of matte ladles, but on this occasion a small leak in the roof must have allowed water from a tropical downpour to fall unobserved into a ladle. The resulting explosion ejected matte 40 feet into the air, killing the craneman in his cab. Can you offer an explanation for the high activity of metallic sulphides, when molten, with water?"

Unfortunately, I have no firm answer for Mr. Young. Molten metallic sulfides appear to be par-

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ticularly sensitive when contacted with water.

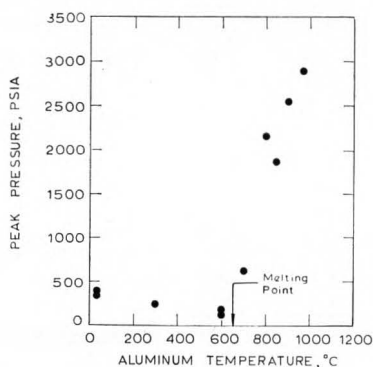
MOLTEN ALUMINUM-WATER EXPLOSIONS

EXPLOSIONS RESULTING from the contact between molten aluminum and water are often most impressive as documented by two research teams at Alcoa Research Laboratories (Long, 1957; Hess and Brondyke, 1969). Most tests consisted of tapping a molten aluminum crucible suspended above a small water tank (see Figure 13). Although the water containers were constructed of 3/16 to 1/4 inch welded steel plate (or were concrete), an explosion was readily detected since, as noted by Long, "all but the mildest . . . broke the steel water containers . . . and frequently hurled pieces several hundred feet."

The salient results show that below some minimum flow rate of metal, no explosions resulted. Also, a long fall through air reduced explosions as did deep water depth. Apparently, some molten metal had to reach the container bottom to obtain an explosion; any modification which fragmented the falling molten aluminum or allowed it to solidify before touching the bottom would reduce or eliminate explosions. Organic coatings or grease on the bottom of the water vessel were effective in eliminating explosions. The severity of the interaction was also reduced by dissolving oils or wetting agents in the water or by increasing the lateral dimensions (for the same quantity of aluminum poured—usually 22.6 kg).

On the other hand, the explosions became more violent if the water contained dissolved salt or if there were lime, rust, or gypsum coatings on the *bottom* (the condition of the sides was of little importance).

The negative effect of the hydrophobic coatings



Temperature Dependence of the Peak Pressure Resulting from Water Impact Upon Aluminum.
From Wright and Humberstone, 1966

FIGURE 14

certainly suggests that the initiating step occurs on the bottom of the water container between (still) molten aluminum and water. Superheating a thin water film could form the initiating steps, but recent experiments by Briggs (Board and Caldarola, 1977) have shown that when molten

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aluminum is poured into a tank of water, a coarse dispersion (~1 cm scale) is formed in the lower half of the tank. The vapor explosion seems to be initiated at the base of the tank and propagates at a velocity of about 200 m/s. Clearly, additional research is warranted.

As opposed to these studies, simply contacting the surface of a molten aluminum pool with water leads to little but film boiling. However, Wright and Humberstone (1966) impacted water on a 6 mm-deep molten pool of aluminum in a vacuum; the impact pressure was estimated as about 14 bar (200 psi). A violent disruption occurred and the highest observed pressure was about 200 bar (2900 psi). This pressure was achieved in about 40 μ s after contact and decayed in about 3 ms. Figure 14 shows low peak pressures were obtained when the aluminum was below the melting point but they increased with temperatures above 650°C. In another test, the impact of water on molten aluminum saturated the pressure transducer at 5800 psi.

SMELT-WATER EXPLOSIONS

WE TURN NEXT TO accidents which occur all too frequently in paper pulping operations. In the "Kraft" process, wood chips are "digested" with a cooking liquor consisting primarily of sodium sulfide, caustic soda and sodium carbonate. Hydrolysis of the lignins occurs. The spent cooking solution (black liquor) is concentrated in evaporators, salt cake (sodium sulfate) is added and the strong solution fed to a furnace. Organic compounds burn, much of the sodium sulfate is reduced to sodium sulfide and the molten salt residue is discharged and dissolved in water to form "green liquor".

Severe explosions have occurred in the step

where the molten salt (smelt) from the furnace is dissolved in water. At this stage, the principal salts are sodium carbonate and sodium sulfide with lesser amounts of other sodium (and potassium) salts; the furnace discharge temperature varies from about 870-1050°C. Other explosions have resulted when the water-tube wall of the furnace failed and leaks developed.

Studies over the past 10 years have attempted to clarify the mechanism of these smelt-water explosions. Although several theories are now available, there still remain a host of unanswered questions.

Let us review briefly some of the experimental research results which seem most relevant; these have been abstracted primarily from a report by Battelle—Columbus (Krause et al., 1973) and from development studies at Combustion Engineering (Nelson and Kennedy, 1951, 1956). In these studies, small quantities of water (or green liquor) were injected into a pool of smelt held in a cone and heated by an induction furnace.

The smelt composition was found to be critically important in establishing whether an explosion is probable. Pure molten Na_2CO_3 could never be made to explode when contacted with water. Addition of Na_2S (or NaCl , NaOH , etc.) sensitized the smelt and led to a higher likelihood of explosion (Sallack, 1955). Also, use of green liquor (water with dissolved Na_2CO_3 and Na_2S) led to more frequent (and more violent) explosions. Time lags after injection, before an explosion, were in the order of 2 ms. Higher injection velocities also increased the probability of an explosion and extended the temperature range of the smelt over which explosions occurred. This latter fact is quite interesting. For example, with a 70% Na_2CO_3 - 30% Na_2S smelt, the maximum temperature of the smelt leading to an explosion was about 850°C with a water injection pressure of 6.9 bar but increased to 925°C when the injection pressure was raised to 10.3 bar. One must conclude that the mode of contacting is also an important variable in these cases. Finally, very

hot water (>65°C) led to almost no explosions irrespective of smelt composition.

Most studies have discounted any significant effects of chemical reaction in the explosion mechanism. It seems clear that some physical initiating step is required to cause intense fragmentation of the water (and smelt?) to produce very large volumes of steam in a short time scale. Superheating of thin films of water with subsequent homogeneous nucleation has been proposed by Nelson (1972) and not rejected by Krause et al. (1973). In some manner, there is assumed to be local liquid-liquid contact between the smelt and water for a brief period of time. A thin film of water superheats (theoretical limit $\sim 300^\circ\text{C}$)

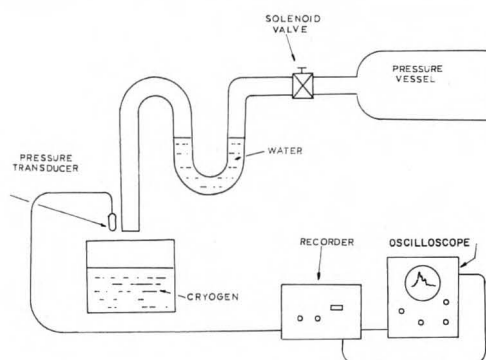


FIGURE 15 IMPACT APPARATUS

and nucleates. This generates local, but very strong, pressure and shock waves. These both fragment the water and smelt in the near vicinity, but may also cause collapse of other vapor films separating water and smelt to produce secondary superheat explosions, and these, in turn, etc.

Does this mechanism agree with the experimental facts? In most instances, yes, but there remain critical experiments to be done.

Molten sodium carbonate will not explode with water; presumably there is CO_2 generated at the boundary and this inhibits liquid-liquid contact. Sodium sulfide sensitizes the smelt. Why should this molten salt enhance liquid-liquid contact? There is a definite time lag, after injection, before

Continued on page 127.

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REID: Award Lecture

Continued from page 111.

an explosion; is this the time to superheat water or does it represent an interval of time to place water below the smelt surface so that the later injection force can collapse the vapor film? Higher injection velocities enhanced explosion probabilities—for the same reason? Hot water explodes with difficulty: is the steam vapor film now too thick to be collapsed? Why should “green liquor” lead to more violent explosions?

Studies are critically needed to determine *if* there is a minimum force or shock necessary to establish initial liquid-liquid contact—and, if so, what is the effect of the independent system variables on this force.

CRYOGEN-WATER EXPLOSIONS

IN ALL CASES DESCRIBED earlier, water was contacted with a hot liquid. But vapor explosions can also occur when cryogenic liquids contact water. The system R-12 or R-22/water has been studied in several laboratories (Holt and Muenker, 1972; Rausch and Levine, 1973; Henry et al., 1974; Anderson and Armstrong, 1977).

We have been interested in vapor explosions involving light hydrocarbons. The impetus for this study began in 1970 when the U. S. Bureau of Mines reported that, in two instances, vapor explosions resulted when liquefied natural gas (LNG) spilled upon a water surface (Burgess et al., 1970). The explosions did not lead to ignition, but they were sufficiently severe to cause concern to the burgeoning LNG industry.

Extensive research programs were initiated by the Shell Pipe Line Corp. (Enger and Hart-

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man, 1972) and in our own laboratories (Nakanishi and Reid, 1971; Porteous and Reid, 1976). (See also, Katz and Sliepcevic, 1971; Katz, 1972; Burgess et al., 1972.)

Light hydrocarbon-water vapor explosions almost certainly result when a portion of the liquid hydrocarbon is heated to a temperature where it may undergo homogeneous nucleation. Usually, in simple spills, only a thin film is involved and the

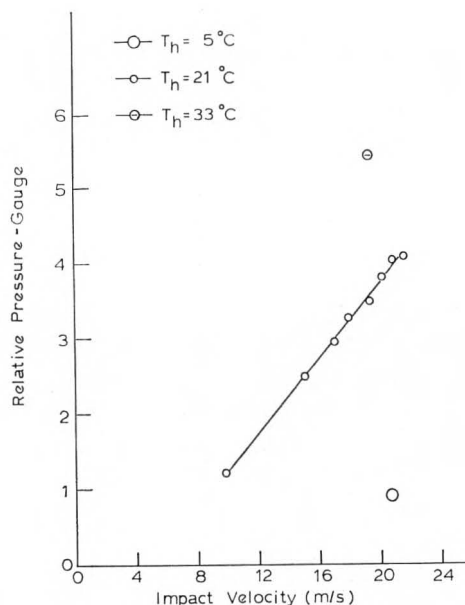


FIGURE 16 EFFECT OF IMPACT VELOCITY AND WATER TEMPERATURE ON PEAK PRESSURE, ETHANE AND WATER

resulting explosion, while impressive, is not particularly energetic nor damaging.

Based on the proposed theory, there then exists a clear definition of interactions which cannot produce vapor explosions. If T_w is the bulk water temperature and T_{SL} the homogeneous nucleation temperature of the light hydrocarbon (pure or mixture), then, for a true vapor explosion, $T_w \geq T_{SL}$. In literally hundreds of different experiments with various water temperatures and cryogenes, this criterion is rarely violated.* There now is general agreement that one can predict if a vapor explosion is possible knowing only the initial water temperature and the value of T_{SL} for the hydrocarbon. (It is important to note that if $T_{SL} > T_w$, and the two liquids are rapidly mixed, rather violent boiling may still ensue, but no shock waves characteristic of an explosion are noted.)

For simple spills of hydrocarbons into water (or vice versa), the probability of an explosion is the highest when T_w only slightly exceeds T_{SL} . That is,

$$T_w/T_{SL} \geq 1, \text{ criterion for a vapor explosion}$$

$$T_w/T_{SL} = 1.04 - 1.06, \text{ criterion for maximum probability for a vapor explosion in simple spills of light hydrocarbons on water.}$$

*Porteous and Reid (1976) show data which indicate a vapor explosion resulted in the propene-water system when $T_w/T_{SL} \sim 0.97$ to 1.06 and for n-butane-water at $T_w/T_{SL} = 0.98$. In all other cases $T_w/T_{SL} \geq 1$.

These criteria are in excellent agreement with experimental data; the first is general and independent of the fluids, the second must be modified if the hot liquid has thermal properties different from water. For example, if methanol is used, the T_w/T_{SL} range for maximum probability increases to about 1.14 - 1.20.

Such a variation of the limiting T_{hot}/T_{SL} criteria follows the hypothesis of Henry et al. (1974) that one should employ the interface temperature rather than the bulk hot liquid temperature to develop a criterion for vapor explosions. That is, the interface temperature upon contact of the two liquids must be greater than the homogeneous nucleation temperature of the volatile one before a large-scale vapor explosion can occur. To estimate this interface temperature, a simple one-dimensional heat transfer model is proposed wherein the two liquids are contacted at time zero. Assuming constant thermal properties and no phase changes, the interfacial temperature, T_i , is invariant with time and depends only on the original temperatures of the hot liquid (T_h) and cold liquid (T_c) and their thermal properties, i.e.,

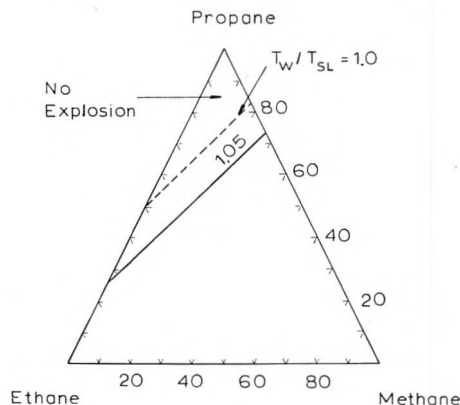
$$\frac{T_i - T_c}{T_h - T_i} = \left(\frac{k_h \rho_h C_h}{k_c \rho_c C_c} \right)^{1/2} \quad (11)$$

The symbols k , ρ , and C refer to the thermal conductivity, the density, and the heat capacity with subscripts h and c denoting the hot and cold liquids.

Of considerable current interest is the development of an explosion criteria for large values of T_w/T_{SL} . For example, pure liquefied methane on 300 K water has a ratio of $T_w/T_{SL} \sim 1.77$. To date no one has been able to obtain a vapor explosion by contacting liquid methane ($T_b = 111.7$ K) and

water at any temperature. The argument usually presented is not dissimilar to those invoked earlier for water-molten metal, water-smelt, etc., i.e., for large temperature differences, stable film boiling occurs and liquid-liquid contact is not possible. Yet as we have seen several times, explosions may become possible *if* there is some sufficiently severe impact event to drive the liquids into contact.

We have been investigating this possibility in our laboratory in the past year, and initial results

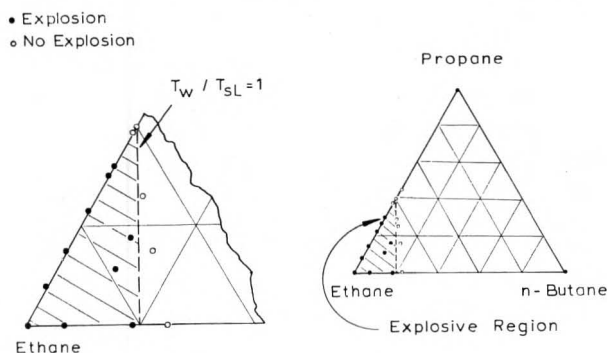


Explosive Envelope for Simple Spills of Methane-Ethane-Propane on 298 K Water

FIGURE 18

strongly confirm this hypothesis. As an illustration, pure ethane has always been somewhat of an enigma. The homogeneous nucleation temperature, T_{SL} , is 269 K yet we have never obtained a vapor explosion by spilling ethane on water at any temperature. Rapid boiling does occur with concomitant ice formation—but nothing more. Recent experiments by Jazayeri (1977) have nevertheless been quite successful in obtaining ethane-water explosions by impacting the two liquids. The experimental equipment is shown in Figure 15 and the ethane-water data in Figure 16. A high frequency quartz transducer mounted about 10 cm above the surface of the polyethylene cryogen vessel was used to measure the combined interaction pressure and the impaction pressure of the ejected mass of liquid. Usually, 350 cm³ of water was impacted on about 200 cm³ of liquid ethane. High speed motion pictures were also taken.

Rather large peak pressures were measured but the rise time was below 1 ms and it decayed very rapidly. The force was, however, usually sufficient to fragment the polyethylene vessel holding the ethane. (In one recent test, the explosion was sufficiently violent to break a Lexan shield and shatter the protective glass in a safety hood!)



EXPLOSIVE CORNER ENLARGED

Explosive Envelope for Ethane-Propane-n-Butane Mixtures with 298 K Water. Impact Velocity = 21.5 m/s

FIGURE 17

Clearly, higher water temperatures seem to lead to a more forceful explosion, and we plan to study this effect in more detail. Finally, extrapolation of the line for a water temperature of 21°C to a peak pressure of zero gauge pressure indicates that a minimum velocity of about 5 m/s is required to be successful in attaining vapor explosions. Higher inception velocities would be expected as the water temperature increases. These values are, however, not general and are certainly related to the specific geometry and impacting technique employed.

Our "map" showing explosive regions (including impact experiments) for the ethane-propane-n-butane ternary is shown in Figure 17 for 298 K water. A similar plot, showing the theoretical limits for the methane-ethane-propane system is shown in Figure 18.

In Part 3, we discuss other types of vapor explosions and summarize theories (other than superheated liquids) that have been proposed to explain their occurrence. □

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ChE letters

BOOK AUTHOR RESPONDS TO REVIEWER'S CRITICISMS

Sir:

I very much appreciated the detailed review of my book "Biomedical Engineering Principles" by Professor E. F. Leonard in the Spring 1978 issue. I would like to point out, however, that I was every bit as disturbed as Professor Leonard that the reproduction was by photo-offset means and that the list price was set so high (\$36.50). About the style of reproduction there was really no choice—it was a simple matter of being published in that form or not being published at all. Regarding the price, I am happy to report that my own displeasure encouraged the publisher to reduce the "classroom adoption price" (5 or more copies) to \$19.75.

Finally, I agree with Professor Leonard that the biomedical engineering field seems to lack a clear direction and sense of purpose. It is thus not surprising that the book reflects this to some degree. I struggled internally while writing the book to define a clear direction, and still continue to do so as I teach in the biomedical area. Unfortunately, in the continued absence of any significant job market in biomedical engineering, I (and I would guess most everyone else) remain at least a little unsure as to what the proper pedagogical approach should be.

David O. Cooney
Clarkson School of Tech.