The object of this column is to enhance our readers' collection of interesting and novel problems in chemical engineering. Problems of the type that can be used to motivate the student by presenting a particular principle in class, or in a new light, or that can be assigned as a novel home problem, are requested, as well as those that are more traditional in nature and which elucidate difficult concepts. Please submit them to Professors James O. Wilkes and Mark A. Burns, Chemical Engineering Department, University of Michigan, Ann Arbor, MI 48109-2136.

DESIGNS TO DEMONSTRATE THE CRITICAL STATE

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Emphasis on design considerations has led to a critical state apparatus that is easier to fabricate and use than what has been offered in the literature. There, focus has been on CO_2 as the working fluid in capillary tubes.[1-3] When Halpern and Lin[1] followed the technique of Banna and Mathews,[2] their tubes "failed to demonstrate critical behavior." Halpern and Lin present an extensive experimental portion that convincingly conveys that their tubes work, but it is not clear whether this is due to usage technique or fabrication technique. The previous two papers, as well as one by Smith and Boyington,[3] all basically use a capillary-fill technique that involves introducing CO_2 gas and then condensing it with external liquid nitrogen cooling. Smith and Boyington also do a solid CO_2 load, but this is generally regarded as unsatisfactory due to difficulties of quantifying granular solid CO_2 volumes.

DESIGN ISSUES

The essence of design, compared to, say, analysis or synthesis, is the open-endedness of the question. It is recognized at the outset that multiple solutions to a design problem could work, and at least several should be initially considered. Contrast that philosophy to the uniformity in the scope of the three cited papers—their exclusive consideration of CO_2, for example, may be due to the oldest paper in the series[3] or to a physical chemistry laboratory text.[4] Perhaps the roots of influence go back even further. Moore[5] begins his discussion of the critical region by pointing out that the first gas to be studied in the critical region was carbon dioxide—work done by Thomas Andrews in 1869. Dodge[6] implies the industrial importance of CO_2 in the introduction to his chapter on refrigeration and reinforces that impression with an extensive section on solid carbon dioxide processes.

Design, on the other hand, should respect history and in this case might begin with the priority criterion to make critical phenomena visible, perhaps even to highlight the vanishing meniscus or "critical opalescence"[7] that occurs in transition through the critical state. Realizing that these effects could be expected in any critical state situation, one might find the question shifting: "What working fluids might have critical conditions most readily obtainable in the laboratory, and can they be made visible?"

Some working fluids with mild critical conditions are gaseous at ambient laboratory conditions and have a particular disadvantage in that special efforts are needed to handle them compared to solids or liquids. Thus, true to the genuine

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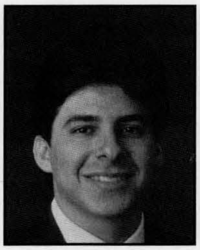

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design process, easing the difficulties in attaining a critical state for a system must be balanced against the difficulties of preparing the system. Ambient liquids, unlike ambient gases, could be injected into capillaries by syringe. Solids at ambient conditions have the quantification difficulties noted earlier. Ambient liquid and other working fluid candidates with critical temperatures well below the annealing point of Pyrex (about 823 °K) are represented in Table 1, along with some comments.

The foregoing comment on Pyrex annealing leads to the question of system-container materials of construction. Glass, quartz, or, at milder conditions, a synthetic could be considered. We proceeded with glass for reasons of performance and economy. Too often in the past our profession has suffered by its emphasis on performance and economy—safety must also be a factor.

SAFETY

Critical pressures are above atmospheric and so safety from explosion must be considered in addition to toxicological safety. Pressures that will be generated can be calculated from a thick wall formula involving an inside and outside radius as well as a simpler thin wall capillary tube formula[8]

$$S = \frac{R_o^2 + R_i^2}{R_o^2 - R_i^2} p_i ; \qquad S = \frac{p_i D}{2t} \tag{1}$$

where

S = maximum stress that may be experienced in the tube material
R_o = outside rube radius, 3.5mm
R_i = inside tube radius, 0.75mm
p_i = pressure inside the tube
D = tube diameter, equal to 2 R_o, 7.0mm
t = tube thickness, equal to R_o - R_i

For the 7-mm capillary tubes used and with the 33.7 bar critical pressure of n-pentane as an example, the two formulas in Eq. (1) yield (with 1.0133 bar/atm and 14.7 psi/atm) comparable results of 536 and 622 psi, respectively, for the experienced stress. Perry's *Chemical Engineering Handbook,* pages 23-60, gives the maximum stress (a yield stress or close relative, modulus of rupture) of 6,000 to 10,000 psi for borosilicate (Pyrex) glass. This represents a safety factor of about ten and is intended to secure occasional mild excursions above the critical pressure.

TABLE 1
Working Fluid Candidates

Fluid	*Critical Parameters* Temp./K	*Critical Parameters* Pres./bar	*Comments*
Carbon Dioxide	304.2	73.8	Solid (STP); hard to measure
Isobutane	408.1	36.5	Low T_c; gas (STP)
n-Pentane	469.6	33.7	Liquid (STP); low toxicity
Diethyl ether	466.7	36.4	Liquid (STP); low toxicity
111-Trichlorotrifluoroethane	422.2	20.4	Liquid (STP); low toxicity; not common*
Perfluoroethane	487.2	34.1	Liquid (STP); low toxicity; not common*

** From Refs. 10 and 11; other from Ref. 7.*

FABRICATION

The "Safety" section above explicitly mentions the capillary, and the earlier sections hinted that a capillary glass tube was used. Thermal transport questions include: Can the capillary volume be heated uniformly and can molecules exchange, on the microscopic scale, between liquid and gas states, sufficiently to ensure quasi-equilibrium? On both points a spherical cavity might be best. Thus, if a capillary is used, shortness would be desirable. However, sufficient length should be provided so that definition of a meniscus is promoted and meniscus activity is easily followed.

The cited papers[1-3] produced capillary tubes of approximate respective lengths 20, 35, and 20 cm. It is not clear why the long lengths were used (since shortness is desirable) unless the manifolding arrangements in some way required it.

Our end product was a 10-cm capillary, and fabrication began by sealing one end of the capillary with a gas/oxygen torch used for glass blowing. The small portion of the other end was drawn out in a tapered neck. This made the sealing step easier and may have helped in the purging process. Presence of the slight restriction due to the tapered neck may have promoted arrest of backflow. The length of the tube was measured and the required (quantitative information follows) height of the liquid meniscus noted. At that height (with pure saturated vapor above it) the contents in the constant volume capillary will have the critical specific volume when heated to the critical temperature.

The detailed technique is to inject more than the required amount of liquid with a syringe through the capillary neck. Low toxicity fluids like n-pentane or diethyl ether will, at ambient, partially vaporize and purge the capillaries of all gases except the pure vapor. This purge continues until the correct liquid amount is obtained. The tube is then quenched in a cold bath, and the tube neck is sealed with a blob of molten glass and annealed with a second or two of reducing flame. With some practice, the slightly drawn neck is easily reheated, quickly and specifically, without disturbing the rest of the container. The molten glass blob at the end of a glass rod is applied with a tamping acting that again thickens out the previously slightly drawn neck. Previous wall thicknesses (or greater) upon which the safety calculations were based, can be achieved. Again briefly, Figure 1 illustrates the situation within a second of sealing. The shape of the drawn neck is indicated. Filling with the syringe has been straightforwardly accomplished. The tube is in its cold bath with flame and partially melted glass rod ready. The shape after the closure, tamp, and anneal steps is also shown. With practice, one person of normal talent can perform the purge and seal step, but it is easier with two people.

USAGE

Since the working fluids have critical temperatures of about 200°C, tubes can be placed in a glycerol or silicone oil bath. (As an aside, another advantage of these working fluids over CO_2 is that special cooling, as with a fire extinguisher,[3] is not required to rapidly cool from supercritical down to temperatures at the upper edge of the critical state. The ambient air and higher critical temperature here provide sufficient gradient for cooling, the point being to save time in the set up, demonstration, cool off, and take down.) Slow heating with stirring of the bath causes the tubes to move slowly through the critical state. These shorter tubes evidently have none of the mass transport resistance to equilibrium (and the attendant need to be rotated) noted by Halpern and Lin. This in itself is a significant simplification of procedure.

In cases where the critical composition is not obtained during fabrication, the meniscus slowly rises or falls until it disappears, which indicates a saturated liquid or saturated vapor condition, respectively, the temperature of which can be noted. Thus the saturation boundary ("steam dome") can be constructed directly on a temperature versus specific volume plot. Figure 2 shows this with our data. We have estimated the uncertainty involved in reading, simultaneously, the slowly rising temperature and the slowly moving meniscus. Specific volume, v, is found from room temperature liquid and vapor specific volumes v_l and v_g, along with meniscus height, h, and the tube length, L, from the relation

$$v = xv_g + (1-x)v_l; \qquad x = \frac{1}{1+\dfrac{hv_g}{(L-h)v_l}} \tag{2}$$

There is no need to introduce the new parameter[1]

$$\alpha = 1 - x$$

because it is trivially related to x, the "quality" parameter as defined and widely used in many engineering thermodynamics texts as mass of vapor over total mass for a pure component in a control volume. A plot of saturated liquid and vapor specific volume vs. temperature may offer better economy of data than plotting either alpha or x in the saturation region vs. temperature. The first is a line while the second two would yield areas, and as such have a manifold increase in data-base size. From another point of view, however, the extra data may be reassuring and even helpful if one is uncertain what the plot is turning out to be in a continuous sense as the discrete, necessarily discontinuous, experimental points are plotted. Essentially the same information is displayed in either plot.

When a tube of critical composition is carefully heated or cooled, the meniscus of Figure 3 gently vanishes, as shown. Then the so-called "critical opalescence" is reached,[7] varying from a smoky to a twinkly appearance. Notice also, that the curvature of the liquid surface relaxes as the critical state is reached.

With practice, the tube can be mounted on a stand with a test-tube clamp and a hand-held propane torch can be used to heat it, circumventing the need for a temperature bath. Hand movement compensates for uneven cooling sufficiently to demonstrate the critical opalescence. A stand-up transparent reach-around shield should be used; ours is approximately 1/4-inch thick Lexan or similar material that is standard issue in many laboratory supply catalogs.

This apparatus makes a short (five- to ten-minute) demonstration that can be offered as a vital lecture stimulus to a small number of students in a classroom setting, although it is ideally suited to the laboratory.

Several ideas have been mentioned for expanding this to a mini-exercise for the Class and Home Problem section of this journal, such as calculating the liquid height, h, to give a critical specific volume. A starting point might be the quality,[7] identified here as

$$x = \frac{M_g}{M} = \frac{(L-h)A\rho_g}{(L-h)A\rho_g + hA\rho_l}$$

(Dividing the right side by the numerator yields Eq. 2. The letter v, for specific volume, is just the reciprocal of the density; the gas and liquid densities are indicated, again, by the g and l subscripts, respectively.) Note that M_g and M are the gas and total mass, respectively, and that h and L refer to liquid height and total height in the closed capillary. Capillary cross-section is A. Some rearrangement of Eq. (2) yields the L over h ratio

$$\frac{1}{x} = 1 + \frac{h\rho_l}{(L-h)\rho_g}$$

$$\frac{L}{h} = 1 + \left(\frac{x}{1-x}\right)\frac{\rho_l}{\rho_g} \tag{3}$$

The densities and quality must still be found. Quality can

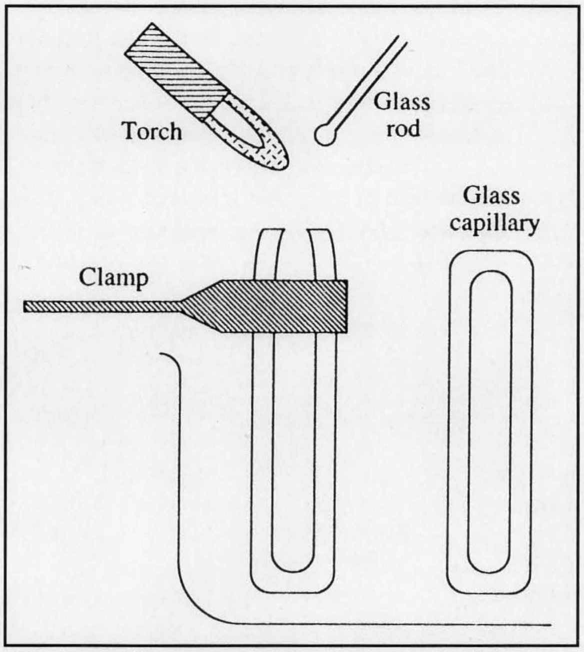

Figure 1. *Illustration of the drawn neck, flame, and molten glass rod at the moment of quench and seal.*

be obtained from Eq. (2)

$$v_c = x\,v_g + (1-x)\,v_l \tag{4}$$

The quantity 304 x 10^{-6}m^3/mol[7] can be combined with the 72 molecular weight to yield the critical specific volume, v_c. The *Handbook of Physics and Chemistry* (HPC)[10] value for the liquid density, about 0.63 g/cc, agrees well with the Rackett equation[7]

$$v_l = v_c Z_c^{(1-T_r)^{0.2857}}$$

of 0.66 g/cc; where

T_r = 298/466.7
Z_c = 0.262
v_c = 304/72 cc/g

Iterative approaches such as the Redlich/Kwong approach could have also been used.

In addition to having a remarkably complete tabulation of quantitative thermodynamic property data, Smith and Van Ness[7] also has a wealth of such information in the problems. On page 319, for example, Antoine's equation is given for n-pentane. It predicts to many places the saturation pressure, temperature pairs given on page 2378 of HPC. (That data would make a wonderful basis for constructing an Antoine-type equation. That is not our purpose here, but it could be included—students need to go through such an effort at least once in their career to appreciate correlations and other sources for such information.) The saturation pressure at, say, 25C, could be used with the ideal gas law to find v_g = 503 cc/g, but we cannot expect this to be very accurate. It could be used as a starting value for an iterative scheme[7] for a more accurate value. It is on the order of the 3-to-4 g/l that one might expect from Section 3-72 of Perry's *Chemical Engineering Handbook*,[9] where ethane and butane are 1.4 and 2.6 g/l, respectively. n-Pentane is not listed there, but let us assume the 4 g/l value, or v_g = 250 cc/g. This could also be used in an iterative scheme (3 cycles with Redlich/Kwong yields 318 cc/g). With v_l = 1/0.63 cc/g and v_c having the only value before calculated, 304/72 cc/g, Eq. (4) will yield x = 1.1% with v_g = 250 cc/g or x = 0.83% with v_g = 318 cc/g. In either case, Eq. (3) then will lead to h = 0.37 L when rounded to two significant digits.

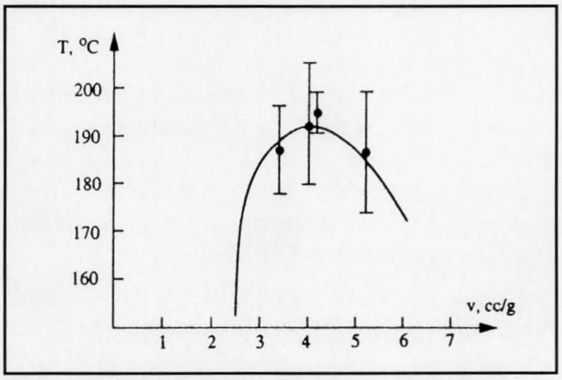

***Figure 2.** The temperature vs. specific volume plot by the described techniques.*

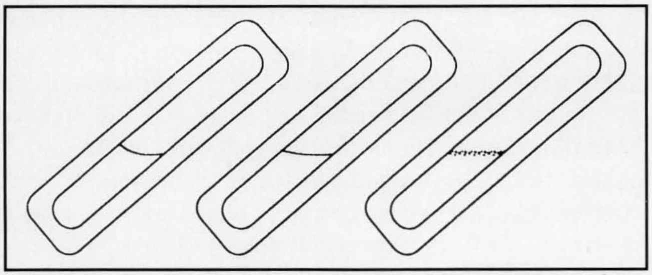

***Figure 3.** Progressive meniscus relaxation as it vanishes at critical conditions and "critical opalescence" appears.*

Other issues could be pursued. We could start with Eq. (3) and form

$$\frac{L}{h} = 1 + \frac{x}{1-x}\left(\frac{1}{\frac{\rho_g}{\rho_l} - 1 + 1}\right) = 1 + \frac{x}{1-x}\left(\frac{1}{1-y}\right) \tag{5}$$

We might like to ignore the gas-to-liquid density ratio here by considering the parameter y as unity minus the density ratio. Dropping the density ratio is introducing error into y. Propagation of error (y approaching 1) in standard fashion

$$\delta\left(\frac{L}{h}\right) = \frac{\partial\left(\frac{L}{h}\right)}{\partial y}\,\delta y$$

produces a singular form, as would direct comparisons of exact and approximate expressions. The singularity can be cast in terms of densities, and l'Hopital's rule will close. Probing density uncertainties, however, might be more meaningful, with the characteristic form

$$\frac{\delta(L/h)}{(L/h-1)} = \left(\frac{\delta\rho_l}{\rho_l} + \frac{\delta\rho_g}{\rho_g}\right)$$

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