A LABORATORY FOR GASEOUS DIFFUSION THROUGH PERMEABLE SOLIDS

The Time Lag

Olivier Dufaud, Eric Favre, Louis Marie Vincent
Ecole Nationale Supérieure des Industries Chimiques • 54001 Nancy, France

Mass transfer, one of the core areas of classical chemical engineering curricula, is most often presented to students through laboratory tutorials dedicated to unit operations (*e.g.,* distillation, gas absorption, extraction, etc.). Laboratory tutorials aimed at a more fundamental approach can also be proposed, based for instance on the study of one of the methods leading to diffusion coefficient determination in fluid phases (liquid, gases, etc)[1] To our knowledge, however, the study of a strict diffusion process in a less conventional phase, such as a permeable solid (polymer, adsorbent, microporous material), is seldom attempted at an undergraduate level in chemical engineering departments. In this paper, we will describe an experimental setup that enables study of the transitory mass transfer of a permanent gas through a permeable solid; apart from the simplicity and rapidity arguments, this technique, currently referred to as the *time-lag method*, permits us to stress either the mass-transfer or the physical-chemistry aspect in the solution approach proposed to the student.

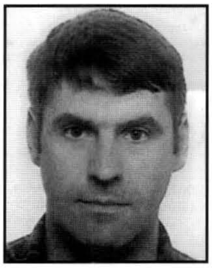
THEORY

The time-lag permeation technique was originally conceived in 1920 by Daynes in order to study the mass transfer through an elastomeric material.[2] The method was refined and widely used through the years by authors such as Barrer[3] and Crank,[2] and it has been applied successfully to numerous materials—from catalyst particles to metals and polymers—and to different sample geometries. Interest in the time-lag technique has been sustained over the past ten years, as shown by Vieth[4] in his work on permeation through polymer films.

A time-lag cell consists of an upper and lower chamber separated by an initially gas-free solid sample (see Figure 1). A permanent gas is introduced in the upstream part of the cell at time zero; while maintaining upstream pressure constant, the appearance of permeated gas is continuously monitored in the lower compartment using a pressure transducer. A significant pressure rise only occurs after a period called the *time lag*. This time lag, θ, indicates the onset of a quasi-steady-state diffusion process, which persists until the pressure in the entire cell equilibrates.

Two experimental configurations can be used to perform a time-lag experiment. The first one, called the "Wicke-

O. Dufaud *received his Master's Degree in Chemical Engineering at ENSIC Nancy (France) and is now a PhD student in the field of stereophotolithography.*



E. Favre *is a professor of chemical engineering at ENSIC Nancy (France). His major interests in research are mass transfer and membrane separations.*

L.M. Vincent *is a research engineer at LSGC-CNRS in data acquisition and electronic applications. (no photo available)*

Kallenbach" diffusion cell experiment, consists of two compartments initially containing the same inert gas at the same constant pressure and separated by the solid film to be tested. At time zero, another compound is introduced in the upper chamber and the response to this impulse is monitored in the downstream compartment.

As part of our study, we use another configuration termed the "traditional" time-lag experiment, which differs from the previous one in that a vacuum is initially applied in both compartments. Rutherford has discussed the advantages and drawbacks of each method.[5]

A theoretical computation of downstream-compartment pressure increase can be obtained starting from Fick's second law applied between the permeable sample boundaries[2]

$$D\left(\frac{\partial^2 c}{\partial x^2}\right)=\frac{\partial c}{\partial t} \qquad (1)$$

It should be stressed that Eq. (1) applies only for a constant diffusion coefficient, which is a special case; the didactic system selected for this study (oxygen/nitrogen/silicone rubber) is in agreement with this assumption. Frisch extensively discussed the more complex general situation of a concentration-dependent diffusion coefficient.[6] In this case, Eq. (1) has to be rewritten as

$$\frac{\partial}{\partial c}\left[D(c)\frac{\partial c}{\partial t}\right]=\frac{\partial c}{\partial t} \qquad (2)$$

For a flat sample, the following boundary conditions can be postulated: a film initially free from gas, the attainment of equilibrium at the inlet gas-polymer interface according to a Henry-type expression, and a near-zero concentration of gas at the downstream face:

$$c(x,0)=0 \qquad (3a)$$

$$c(0,t)=c_0=SP_0 \qquad (3b)$$

$$c(L,t)=c_L\cong 0 \qquad (3c)$$

where L is the sample thickness, P_0 the upstream pressure, and S (deriving from Henry's law expression) is usually called sorption coefficient. Again, Henry's law validity corresponds to a simple and special case; it is important to note that numerous systems, especially those involving glassy polymers (*e.g.,* polyethyleneterephthalate used in carbonated beverage packaging) show strong deviations from Henry's law. Nevertheless, the assumption of a constant sorption coefficient is correct for the system selected for this study.

Equation (1), subject to the experimental boundary conditions, Eq. (3), can be integrated by Laplace transform[2]

$$c=c_0\left(1-\frac{x}{L}\right)-\frac{2c_0}{\pi}\sum_{n=1}^{\infty}\left[\frac{1}{n}\sin\left(\frac{n\pi x}{L}\right)\exp\left(-\frac{Dn^2\pi^2 t}{L^2}\right)\right] \qquad (4)$$

where n is an integer.

The net gas flowrate can be computed from the concentration profile based on the integration of Fick's first law with respect to time. The resulting downstream pressure increase is

$$P_L=A\frac{RTDP_0}{VL}\left[St-\frac{SL^2}{6D}+\frac{2SL^2}{\pi^2 D}\sum_{n=1}^{\infty}\frac{(-1)^{n+1}}{n^2}\exp\left(\frac{-Dn^2\pi^2 t}{L^2}\right)\right] \qquad (5)$$

When a quasi-steady-state prevails, the transient summation terms are negligible and an asymptotic solution is reached for the downstream pressure P_L

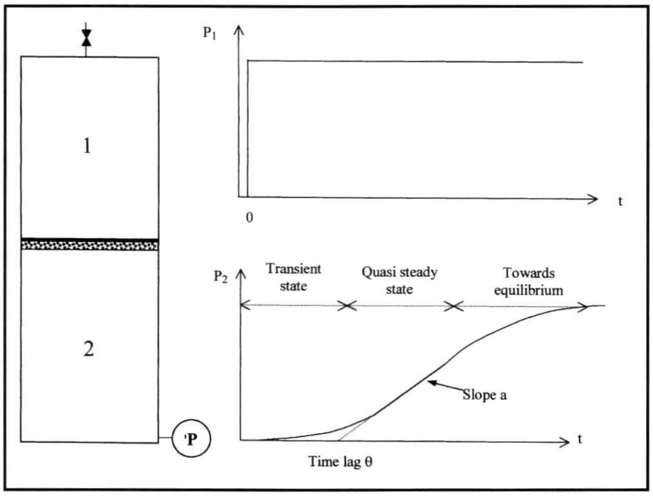


Figure 1. *Schematics of a time-lag apparatus and experiment.*

$$P_L(t)=A\frac{RTSD\,P_0}{VL}\left(t-\frac{L^2}{6D}\right) \qquad (6)$$

This equation reveals that the pressure-time plot shows a linear rise and allows determination of the following parameters (see Figure 1):

$$\theta=\frac{L^2}{6D} \quad \text{known from the intercept} \qquad (7)$$

$$a=A\frac{DRTS\,P_0}{VL} \quad \text{known from the asymptotic slope} \qquad (8)$$

In other words, the above analysis shows that an interpretation of the early events of a time-lag experiment allows simultaneous determination of the three main quantities characterizing mass transfer: the diffusion coefficient (D), the Henry law sorption coefficient of the gas in the solid (S), and the product of both, usually called permeability,

$$\wp = SD \qquad (9)$$

The objective of the laboratory tutorial described in this paper is to show and analyze the possibilities and limitations of a time-lag experiment performed according to the preceding data treatment.

MATERIAL AND METHODS

The experimental apparatus we set up consists of a stainless-steel permeation cell (see Figure 2), within which a circular polydimethylsiloxane film purchased from Dow Corning (Silastic™ sheeting, thickness 125 µm, diameter 8 cm, active surface area 30 cm^2) is inserted. The film is mechanically supported by a brass or Inox frit (Poral) sufficiently porous to assert that its mass-transfer resistance is far lower than the one of the analyzed material. A Viton™ seal ensures the airtightness of the cell and also reduces the film surface area exposed to the gas.

An overview of the complete laboratory setup designed in our workshop is shown in Figure 3. For the sake of convenience, a simple, low-cost stainless-steel filter holder can be purchased (for instance, Millipore model 4404700) and works equally well in this application. The two compartments of the cell are connected to a vacuum pump (Alcatel Pascal 1015 SD), while the upper one can be fed by a permanent gas (nitrogen or oxygen) from a bottle by opening a needle valve (Nupro ABVT 1). The upstream compartment pressure is controlled by a Bourdon manometer. An active strain gauge (Edwards ASG NW16 2000 mbar) enables downstream compartment pressure to be monitored. The electric signal ranging from 0 to 10 volts is sent to a digital display (Edwards ADD). Afterwards, an analog-to-digital 24-bit converter (Sigma Delta) with an integrated oscillator (Linear Technology LTC2400) is used to allow a computerized acquisition at a maximum frequency of 20 Hz. A personal computer with the Test Point™ program carries out the analog data processing. It permits screen display of the downstream pressure rise in millibars versus time in seconds and the information backup in a data-extended file. This file is then imported into a spreadsheet program (such as Excel™) to determine the diffusion and sorption coefficient. Figure 4 shows an example of the complete pressure rise for illustrative purposes.

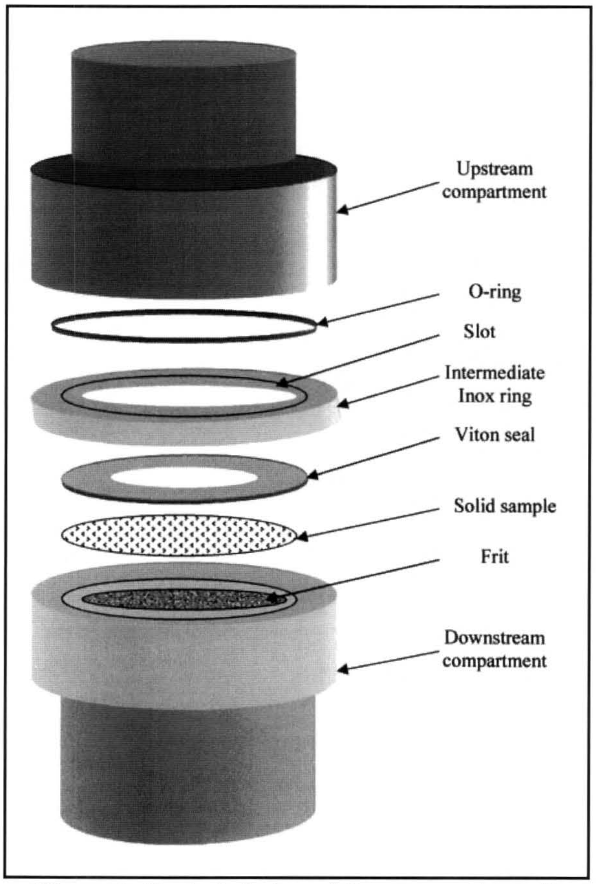


Figure 2. *Exploded view of the permeation cell.*

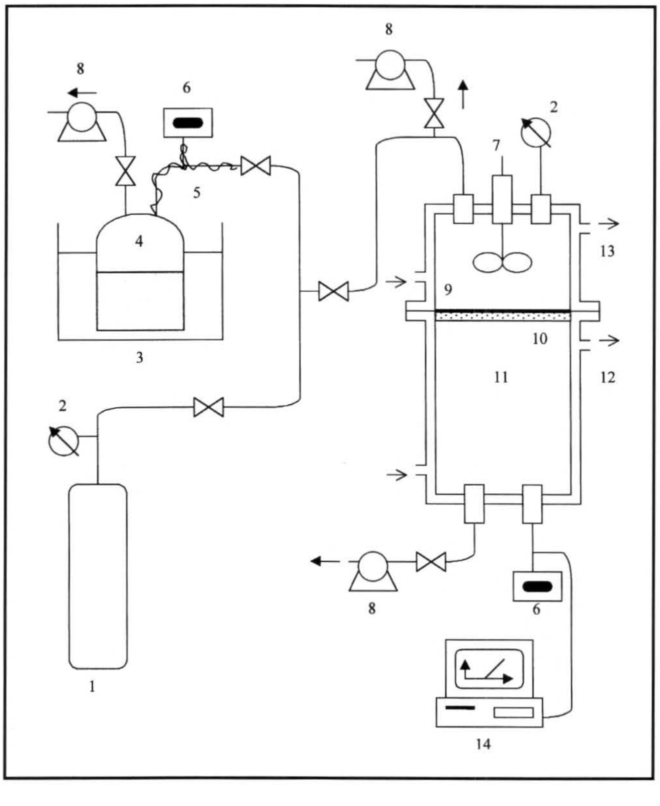


Figure 3.

Overall set up:

1. *Gas bottle (pure oxygen or nitrogen)*
2. *Bourdon manometer*
3. *Thermoregulated bath*
4. *Solvent reservoir*
5. *Heating resistance*
6. *Pressure gauge and digital display*
7. *Magnetic stirret*
8. *Pump*
9. *Solid sample*
10. *Porous support*
11. *Downstream volume*
12. *Thermoregulated water flow*
13. *Thermoregulated water flow*
14. *Computerized data acquisition.*

LABORATORY TUTORIAL

After a short review of the principles and the theoretical development underlying the technique (see the section on "Theory"), we ask the students to familiarize themselves with the equipment and then operate it according to the following instructions:

① Start thermostated bath and apply a primary vacuum in both compartments. Attention should be paid at this stage to the fact that the downstream side only has to be degassed in a first step, before treating the upstream part. If not, film disruption will occur as soon as a reverse pressure differential takes place (the sample is not supported on the upstream side).

② Evaluate the cell's leakage rate by closing all connections around the module (vacuum pump, gas bottles, etc.). This is of crucial importance since any background in downstream pressure increase will affect data treatment. An average value of about 0.1 millibar per hour should be achievable; if not, cell screws should be tightened, as well as the O-ring and sample positioning checked. The above value should be kept in mind if error calculation on D or S are needed. Nevertheless, it is negligible in regard to PDMS permeability and experiment duration in the present case.

③ A typical time-lag experiment can then be undertaken for a given pressure and temperature. Depending on the duration of the tutorial, 2 to 4 different pressure and/or temperature values (typically ranging between 20 and 80°C and 0.5 to 5 bar) can be explored with pure nitrogen and oxygen. The student is asked to assess D and S values and check the consistency with literature data.[7-9] The key importance of downstream compartment volume V can be discussed at this stage (see Eq. 8); in our case, direct as well as indirect measurements credit this chamber with a 585 cm^3 volume, which fits the needs regarding gauge sensitivity, air losses, and material permeability.

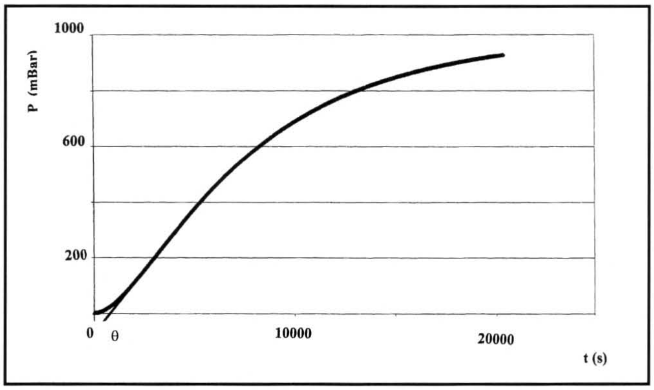


Figure 4. *Example of an experimental result obtained by the setup described in this work (downstream pressure vs. time), including the determination of time-lag intercept (θ). Oxygen permeation through a 125-µm thick Silastic™ film; upstream pressure 4 bar, temperature 50°C, acquisition frequency 5 Hz.*

④ An error calculation can be optionally performed, based on an analysis already discussed by Paul and DiBenedetto[10] and later by Siegel and Coughlin,[11] showing that the technique can lead to small errors in permeability but far greater errors in the diffusion coefficient. For instance, the relative error on θ is about five times larger than that on the slope for data collected at $t \cong 4\theta$:

$$\left|\frac{\Delta\theta}{\theta}\right| \cong 5\left|\frac{\Delta a}{a}\right| \tag{10}$$

Thus, a 2% error on the slope means a 10% error on the diffusion coefficient—which are commonly assumed values for a single measurement. Therefore, the duration of the time-lag experiment should be carefully considered. While data taken at times greater than 10θ will lead to sizeable errors in diffusivity, the attainment of steady state requires duration times around 4θ.

Nevertheless, the error in steady-state slope can be greatly minimized by simply re-evacuating the downstream chamber with the feed pressure still applied to the top face of the membrane. Reclosing the receiver valve ahead of the vacuum pump (item 8 in Figure 3) allows measuring the steady-state slope without bend-over problems up to a downstream pressure below 1% of the feed pressure. This repeated evacuation and retesting of the slope gives students an easy way to evaluate measurement reproducibility.

⑤ Based on the D and S values, permeability ℘ can then be calculated from Eq. (9). The student is asked to express the results in Barrers, the most common permeability unit:

$$\wp\left(\text{Barrer}\,10^{10}\right)=\frac{273}{T(K)}\,\frac{V\left(cm^3\right)}{P_0(cmHg)}\,\frac{L(cm)}{A\left(cm^2\right)}\,a\left(cmHg\,s^{-1}\right)\frac{1}{76} \tag{11}$$

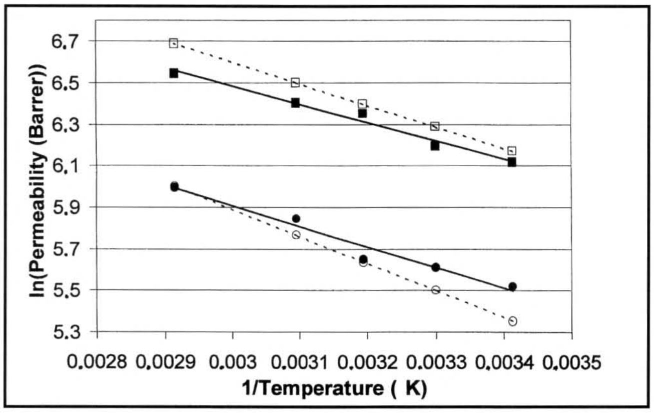


Figure 5. *Example of Arrhenius plots for oxygen and nitrogen permeability variation with temperature through Silastic™ film (upstream pressure 2 bar). Comparison between experimental (solid line) and literature (dashed line) values.*

Typical oxygen permeability values in PDMS obtained by the setup can be seen in Figure 5 where the good reproducibility of measurement is illustrated.

⑥ For a more physicochemical insight, undertaking the study of the influence of temperature on sorption, diffusion, and permeability can be worth the time. A simple expression is often shown to describe correctly the results for all three parameters:

$$X = X^0 \exp\left(-\frac{E_X}{RT}\right) \qquad X = D, S, \text{or } \wp \qquad (12)$$

While the analogy to Arrhenius expression is correct for rate parameters (leading to the often-used vocable activation energy of diffusion and activation energy of permeability), it should be explained to students that the same is incorrect for sorption, which is not an activated process (E_S corresponds to the heat of sorption ΔH_S, as classically obtained by a van't Hoff plot). The following relationship, linking the two activation energies E_P and E_D with ΔH_S can be derived by using Eqs. (9) and (12)

$$E_P = \Delta H_S + E_D \qquad (13)$$

Figure 5 illustrates the good accordance between the experimental and the literature values for oxygen and nitrogen permeabilities[7,12,13]

$$E_P^{O2} = 7.4 \text{ kJ/mol} \qquad E_P^{N2} = 8.2 \text{ kJ/mol}$$

$$\wp_{O2}^0 = 9180 \text{ Barrer} \qquad \wp_{N2}^0 = 7150 \text{ Barrer}$$

These results are satisfactory in that the oxygen permeability is greater than the one of nitrogen and conversely for the energies of activation. At this stage, students can be asked to explore potential separation applications based on this peculiarity, such as gas-separation membrane processes.

Typical experimental results are summarized in Table 1. The already-discussed inaccuracies on the intercept lead to significant errors on D values; however, D_{O2}^0 remains always greater than D_{N2}^0, which agrees with the theory because nitrogen's kinetic diameter is larger than oxygen's.

⑦ The influence of upstream pressure can also be optionally investigated, similar to the work already addressed by Koros and Jordan with a silicone-nitrogen system.[14]

CONCLUSION

The objective of this work was to point out an easy-to-carry-out experiment of didactical importance for the understanding of gas mass transfer in different solid media. The time-lag permeation method is a flexible and powerful technique that can give both equilibrium (sorption coefficient S) and transport properties (diffusivity D and permeability $\wp$) in a single experiment; based on the setup described in this work, we have shown that reliable and accurate data with regard to the permeabilities of permanent gases can be obtained, while estimation of D and S is achievable. We focused first on simplicity, especially regarding the data-treatment aspects. We want to stress, however, that more sophisticated approaches (such as those proposed in advanced mass-transfer topics) can be equally well-proposed based on the same setup. A few examples, listed below, show how to open various didactical extensions.

TABLE 1

Experimental (exp) and Literature Values ([7]) for Oxygen Sorption, Diffusion, and Permeability through PDMS for 1 Bar Upstream Pressure

T(°C)	$\wp$ exp (Barrer)	$\wp$ literature (Barrer)	D exp (m^2s^{-1})	D literature (m^2s^{-1})	S exp (Pa^{-1})	S literature (Pa^{-1})
20	454	479	1.0E-09	1.6E-09	0.34	0.31
30	492	539	7.1E-10	1.8E-09	0.53	0.31
40	574	601	1.1E-09	2.0E-09	0.41	0.30
50	605	667	1.6E-09	2.2E-09	0.29	0.30
70	696	806	2.1E-09	2.7E-09	0.25	0.30

- ► *A first possibility consists in replacing the silicone rubber membrane with a glassy polymer. For instance, polyethyleneterephthalate (PET), which is readily available since most overhead transparency materials used in projectors are composed of PET; a more permeable Lexan™ film, produced by General Electric, can also be used. If carbon dioxide is used in place of oxygen or nitrogen, experiment duration would remain compatible with a laboratory tutorial providing that a thin enough film (25μm or less) is available. Investigating the more-complex case of gas permeation through glassy polymers is of value for the students in order to point out polymer barrier properties.*
- ► *In place of permanent gases, organic-vapors transport could be equally well investigated, based on the vapor generator system connected to the module (see Figure 3); in that case, complications arising from the non-constancy of the diffusion coefficient with concentration can lead to complex, but interesting, transport behavior (and thus, data treatment). The incidence of a variable D on the experimental time lag has been explored by Frisch.[6] Attention should be paid, however, to explosion hazards or O-ring damage when manipulating organic vapors.*

- *In this work, the solid sample is considered as the single mass-transfer resistance; nevertheless, boundary-layer resistance can arise, particularly when binary mixtures are transported through a very permeable media; in that event, the influence of hydrodynamic conditions on overall transfer (concentration polarization phenomenon) is a good indication that can be best achieved by a magnetic Rushton turbine already existing on the setup.*
- *The independent temperature jackets for the two compartments also offer an opportunity to experiment with the incidence of non-isothermal conditions, already shown to strongly affect the observed transfer rate of a pure organic vapor.*[15]

ACKNOWLEDGMENTS

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NOMENCLATURE

A	sample surface area
a	asymptote slope
c	concentration
c_0	upstream concentration
c_L	downstream concentration
D	diffusion coefficient
$E_{D,P}$	energy of activation for diffusion (D) and permeability (P)
L	sample thickness
P	pressure
$\wp$	permeability
R	perfect gas constant
S	sorption coefficient
t	time
T	temperature
V	downstream volume
Greek Symbols	
θ	time lag
ΔH_s	heat of sorption

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Letter to the Editor

Continued from page 167.

three undergraduates.

Used in this way, a lecture course provides a highly effective way not only for the dissemination of information but also for capturing the interest of students. The formal lectures does *not* provide a good format for developing problem-solving skills, for dealing with engineering design, or even for presenting and discussing solutions to pre-assigned problems.

Unfortunately, in many (if not most) universities the lecture format has been widely misused since it has become the universal workhorse. This may be a more serious issue in engineering education where "design" and "problem solving" constitute a major portion of the curriculum. Nevertheless, within the chemical engineering curriculum, there are many subject areas that are well-suited to the lecture approach and, in the hands of a skilled practitioner and especially if supported by appropriate tutorial sessions, this approach can be very effective. Essentially this same point is made by Wankat and Oreovicz in *Teaching Engineering.* This is one of the references cited in the present article as showing the superiority of alternative approaches! Such a conclusion is hardly surprising since, in any attempt at a quantitative assessment, it would be very difficult, if not impossible, to establish whether the apparent disadvantages of a lecture course are really intrinsic to the format or stem from an inappropriate application of this format. There seems to be a clear danger that, in the current enthusiasm for "new" instructional methods, the very real advantages (and equally real limitations) of the lecture format will be overlooked.

Douglas M. Ruthven
University of Maine