

LANGMUIR AS CHEMICAL ENGINEER

...or, From Danckwerts to Bodenstein and Damköhler

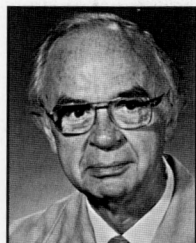
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The Danckwerts boundary conditions, derived during the course of a notable 1953 paper on residence time distribution, describe the inlet and outlet boundary conditions for a "closed-closed" flow reactor with axial dispersion.^[1] Footnotes in texts by Bischoff and Froment^[2] and by Aris^[3] mention that these conditions had also appeared in a 1908 paper by Langmuir.^[4] This is true, but the 1908 paper contains more: it is a harbinger of contemporary chemical engineering, written in the year that the AIChE was first organized.^[5]

LANGMUIR

Irving Langmuir (1881-1957) was a scientist of remarkable versatility. Chemical engineers recognize the Langmuir isotherm, basic for the kinetics of heterogeneous catalytic reactions; chemists know the Lewis-Langmuir theory of the chemical bond and the Langmuir trough for studying oil films on water; and the layman may remember his pioneering work on cloud-seeding. Not as widely known are his discovery of atomic hydrogen and his inventions of the modern gas-filled electric light bulb, the mercury condensation vacuum pump, the atomic hydrogen welding torch, and the Langmuir probe for characterizing plasmas. (Langmuir introduced the word "plasma" into the physics literature in 1923; in 1929 he and Tonks published their landmark theory explaining the existence of plasma oscillations.^[6] The char-



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acteristic plasma-electron frequency is known as the Langmuir frequency.)

Langmuir's undergraduate degree (from Columbia University, 1903) was in metallurgical engineering.^[7] His PhD research, however, was with the physical chemist Walther Nernst in Göttingen. The title of Langmuir's dissertation was "On the Partial Recombination of Dissociated Gases in the Process of Cooling" (rough translation from the German). Involved in the research was the use of a hot Pt wire to act both as a catalyst to dissociate gases and as a temperature probe by measurement of the electrical resistance; account had to be taken of heat transfer by conduction and convection from the hot surface. Langmuir's doctorate was awarded in 1906—the year in which Nernst proposed the Third Law of Thermodynamics.

THE 1908 PAPER

The title of Langmuir's 1908 paper^[4] was "The Velocity of Reactions in Gases Moving Through Heated Vessels and the Effect of Convection and Diffusion." Langmuir starts by noting that a 1908 paper of Bodenstein and Wolgast a) had already pointed out that the rate equations used for stationary gases (*e.g.*, a batch reactor) can be justified for flowing gases only if there is no mixing (*e.g.*, a plug flow reactor), and b) had developed formulas which hold if there is complete mixing (*e.g.*, a CSTR).^[9-12] The Bodenstein-Wolgast paper contains no quantitative treatment of a reactor with axial dispersion.

Langmuir proceeds to derive the differential equation describing a reactor with axial dispersion from a material balance (for a single reactant) over a differential reactor element. He guarantees a "closed-closed" pattern by postulating that the reactor section is bounded by thin porous plugs, as illustrated in Figure 1. The reactant gases move with such high velocity through the pores of the plugs that the quantity carried by diffusion is negligible compared with that carried

by mass movement of the gas. For an n -th order reaction, Langmuir arrives at the differential equation

$$D \frac{d^2C}{dy^2} - u \frac{dC}{dy} - kC^n = 0 \quad (1)$$

Although Langmuir calls D the "diffusion coefficient," it is clear that he intends D to mean the effective axial dispersion coefficient and not D , the molecular diffusion coefficient.

After pointing out that the equation "can only be integrated, as it stands, when $n = 1$," Langmuir suggests "let us be content, for the present, with approximate results." Then approximations are introduced, such as expansion of exponentials with cutting off after the first term, for n -th order kinetics. Two boundary conditions are still needed, and Langmuir arrives at the Danckwerts conditions with reasoning identical to that of Danckwerts. For n -th order reactions, Langmuir arrives at the approximate solution

$$nC_o - (n - 1)C = C \exp[-P] \left\{ \cosh M + [(N + P)/M] \sinh M \right\} \quad (2)$$

For the first-order reactions, Eq. (2) becomes

$$C_o = C \exp[-P] \left\{ \cosh M + [(N + P)/M] \sinh M \right\} \quad (3)$$

In these equations, the symbols are:

- C_o inlet concentration of feed to reactor
- C concentration of feed at outlet
- n reaction order
- P $uL/2D$
- N $nkC_o^{n-1}L/u$
- M $(P^2 + 2PN)^{1/2}$
- k reaction rate constant
- D axial dispersion coefficient
- u linear velocity of reacting gas through the reactor
- L reactor length

Langmuir next derives approximation formulas for the limiting cases of a) mixing almost complete and b) only slight mixing. Furthermore, he derives criteria, in terms of the dimensionless parameters P , N , and M , for deciding when the PFR and CSTR equations may be used and when the approximation formulas will give reasonably good answers.

To illustrate the application of Eq. (3), a comparison is made here of the conversions predicted from the dispersion model for an example worked out in the text of Levenspiel.^[13] Levenspiel proposed nonideal flow in a reaction system with $D/uL = 0.12$, first-order kinetics with $k = 0.307 \text{ min}^{-1}$, and $L/u = \tau = 15 \text{ min}$. In an ideal PFR, the fraction of feed remaining would be $C/C_o = 0.01$.^[13: p. 270]

For the nonideal reactor, Levenspiel uses his Figure 22 and page 289 to arrive at $C/C_o =$ (approximately) 0.035. An approximation formula derived from the exact solution, Levenspiel's Eq. (43) gives $C/C_o = 0.127$. A second approximation formula, taken from the treatment by Pasquon and Dente^[15] of n -th order reactions gives (Levenspiel, Eq. 48) for this case $C/C_o = 0.0354$. Levenspiel's Eq. (46) for small deviations from plug flow also

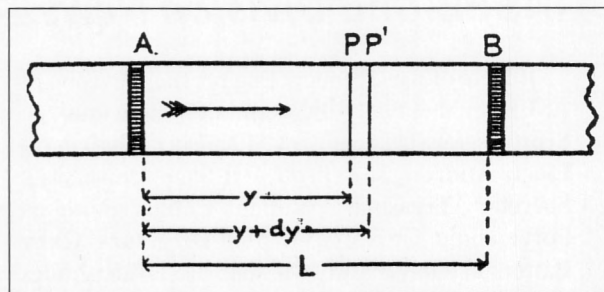


Figure 1

gives $C/C_o = 0.0354$. The above Eq. (3) of Langmuir gives $C/C_o = 0.0339$, as does the exact solution to Eq. (1) given by Danckwerts^[1] and by Wehner and Wilhelm.^[14]

DIMENSIONLESS GROUPS

What is the significance of Langmuir's dimensionless constants P , N , and M ? Since M is defined by Langmuir as a function solely of P and N , there are only two independent dimensionless groups, P and N . Let us first consider Langmuir's P .

Langmuir defines P as $P = 1/2 (uL/D)$. There is disagreement concerning the name which should be attached to the group (uL/D) . The 1966 summary of dimensionless groups by Catchpole and Fulford,^[16] a convenient but secondary source, offers the term "Bodenstein number" for the group uL/D , where D is the effective axial diffusivity.

The reference given by Catchpole and Fulford for the Bodenstein number is another secondary source—the 1963 compilation by Boucher and Alves.^[17] This started an instructive and cautionary chase through the literature: Boucher and Alves use a 1961 article by Hofmann as their source for "Bodenstein number";^[18] Hofmann simply quotes a 1958 article by van Krevelen;^[18] astonishingly, as his source van Krevelen refers back to the 1908 article by Bodenstein and Wolgast^[9] that started Langmuir on his theoretical treatment of nonideal reactors; and the Bodenstein-Wolgast article contains no mention of a group (uL/D) —or any other dimensionless group!

The use of "mass transfer analog of the Peclet number" (or its reciprocal) is quite common for this group in texts, notwithstanding the fact that in the definition of the Peclet number the molecular diffusion coefficient, D , appears, not the axial dispersion coefficient, D . Levenspiel, a major contributor to the modeling of nonideal reactors, is outspoken in his opposition to this use. In his 1979 text, *The Chemical Reactor Omnibook*,^[20] he has this to say about (D/uL) :

This is a new and different type of dimensionless group introduced by workers in chemical engineer-

ASEE-ChE Division News

Officers of the Chemical Engineering Division of ASEE for the 1994-1995 term are: **Chairman, F. Scott Fogler** (University of Michigan); **Chairman-Elect, Andrew J. Wilson** (Tri-State University); **Secretary-Treasurer, William Conger** (Virginia Polytechnic University); and **Directors Gary Patterson** (University of Missouri-Rolla) and **James E. Townsend** (Dow Chemical USA).

The 32nd Annual Division **Lectureship Award** winner was **G. V. Reklaitis**. His lecture "Computer Aided Design and Operation of Batch Processes," will be published in one of the 1995 issues of *CEE*.

The 1993 **Martin Award** for best presentation at the annual ASEE meeting went to **William K. Durphee** for "The MIT New Products Program."

The **Corcoran Award**, recognizing the best paper published in *CEE* in 1993, was given to a group of authors for their individual contributions to a series of papers on "Knowledge Structure in Chemical Engineering." Those authors and their contributions were: **Donald R. Woods** and **Rebecca J. Sawchuk** for "Fundamentals of Chemical Engineering"; **Stuart W. Churchill** for "Mathematics"; **Richard M. Felder**, for "Knowledge Structure of the Stoichiometry Course"; **John P. O'Connell** for "Thermodynamics"; **R. Byron Bird** for "The Basic Concepts in Transport Phenomena"; and **H. Scott Fogler** for "An Appetizing Structure of Chemical Reaction Engineering for Undergraduates."

ing. Unfortunately someone started calling the reciprocal of this group the Peclet number. This is wrong. It is neither the Peclet number nor its mass transfer analog, which is widely called the Bodenstein number in Europe. The difference rests in the use of D instead of D , hence these groups have completely different meanings.^[21] A name is needed for this group.

The author suggests that "Langmuir group I" (La_1) may be an appropriate name for Langmuir's P .

What about Langmuir's N , defined as $nkC^{n-1}L/u$? In his unifying treatment of mass and heat transfer effects in flow reactors, Damköhler defined four dimensionless groups.^[22] The first of these, Da_1 , is defined as UL/uC , where U is the chemical reaction rate and C is reactant concentration. For an n -th order reaction, this become kC^nL/uC or $kC^{n-1}L/u$. This is Langmuir's N except for the factor n . Damköhler does not mention Langmuir's 1908 paper. It serves no purpose to change an established term (Da_1) at this late stage, but considering the priorities (1908 vs. 1936), it would have been appropriate to call Langmuir's term N the "Langmuir

group II" (La_{II}). As a matter of interest, for first-order reactions, this group reduces simply to κ .

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2. Bischoff, K.B., and G. Froment, *Chemical Reactor Analysis*, John Wiley and Sons, New York, NY; p. 624 (1979)
3. Aris, R., *The Mathematical Theory of Diffusion and Reaction in Permeable Catalysts*, Vol. 1, Clarendon Press, Oxford, England; p. 38 (1975)
4. Langmuir, I., *J. Amer. Chem. Soc.*, **30**, 1742 (1908)
5. In 1907 a "Committee of Six" circularized some 300 prominent chemists about possible creation of a society. From the responses a "Committee of Fifty" was selected and invited to meet (January 1908); after the meeting a mail ballot was sent to all members of the Committee of Fifty. Forty responses were received, with the following distribution of vote: 22 affirmative; 7 negative, 7 neutral, 2 "had not had time to consider," 1 member abroad, and 1 death. The "Committee of Six" considered this vote as a mandate to organize the American Institute of Chemical Engineers. Also of possible interest: the first five volumes of *Trans. A.I.Ch.E.* (1908-1913) contain no papers which can be described as mathematical modeling, in the sense that Langmuir's 1908 paper is mathematical modeling of reactor behavior.
6. Tonks, L., and I. Langmuir, *Phys. Rev.*, **33**, 195, 990 (1929)
7. Langmuir explained his choice of undergraduate major by noting: "The course was strong in chemistry. It had more physics than the chemical course, and more mathematics than the course in physics—and I wanted all three."
8. Langmuir, disillusioned with his teaching situation, was successfully wooed by GE in 1909; he spent the remaining decades of his professional life at GE. He was awarded the Nobel Prize in Chemistry in 1932.
9. Bodenstein, M., and K. Wolgast, *Z. Phys. Chem.*, **61**, 422 (1908)
10. Bodenstein, a noted kineticist, had earlier published (1906) with his student Lind the classic study of H_2 - Br_2 reaction kinetics. It was Bodenstein who introduced in 1913 the "stationary-state approximation" that is commonly used for the analysis of complex reaction mechanisms.
11. The paper of Bodenstein and Wolgast was published in 1908. Langmuir submitted his paper in September, 1908, and it was published in 1908. Publication times like this must be the envy of authors and editors nowadays.
12. The pioneering paper of K.G. Denbigh on the CSTR ("Velocity and Yield in Continuous Reaction Systems," *Trans. Far. Soc.*, **40**, 352 [1944]) contains the statement "There appears to be no treatment in the literature of the distinctive features of the continuous process."
13. Levenspiel, O., *Chemical Reaction Engineering*, 2nd ed., Wiley, New York, NY (1972)
14. Wehner, J.F., and R.H. Wilhelm, *Chem. Eng. Sci.*, **6**, 89 (1956)
15. Pasquon, I., and M. Dente, *J. Catalysis*, **1**, 508 (1962)
16. Catchpole, J.P., and G. Fulford, *Ind. Eng. Chem.*, **58**, 46 (1966)
17. Boucher, D.F., and G.D. Alves, *Chem. Eng. Prof.*, **59**(8), 75 (1963)
18. Hofmann, H., *Chem. Eng. Sci.*, **14**, 193 (1961)
19. van Krevelen, D.W., *Chem. -Ing. -Tech.*, **30**, 523 (1958)
20. Levenspiel, O., *The Chemical Reactor Omnibook*, Oregon State University, Corvallis, OR; 100.6 (1979)
21. Levenspiel uses D for molecular diffusivity and D for longitudinal dispersion. He refers to (D/uL) as a "vessel dispersion coefficient."
22. Damköhler, G., *Z. Elektrochem.*, **42**, 846 (1936) □