Wave Inception in Falling Vertical Films

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In the recent communication by S. Portalski (*1*) on falling vertical films, there are two numerical errors. Equations (12) and (13) for wavy or pseudo-laminar flow should read

$$N_{Fr} = \frac{1}{2.4}\,\frac{Q}{\nu} \qquad (12)$$

and

$$N_{Re} = 9.6\,N_{Fr} \qquad (13)$$

the numbers 2.4 and 9.6 replacing the erroneous 4 and 16, respectively, of the original communication. The corresponding equation for laminar film flow remains as

$$N_{Re} = 12 N_{Fr} \qquad (9)$$

(Nomenclature and numbering of equations as in Portalski communication.) Conclusions drawn by the author are in no way affected by these changes.

It is interesting to note, consequently, that Jackson's (*2*) criterion for wave inception

$$N_{Fr}' = \sqrt{N_{Fr}} = 1 \qquad (1)$$

is equivalent to the statement that at the wave inception point $N_{Re} = 9.6 - 12$, according to Equations (13) and (9). Furthermore, his actual tabulation of experimental data showed values on N_{Fr}' for wave inception ranging from 0.70 to 1.44, which corresponds to $N_{Fr} = 0.490 - 2.074$. Again, according to Equations (13) and (9), the equivalent Reynolds range is 4.7 to 24.9. These results are in excellent agreement with the summary of experimental information for vertical falling films given by Bird et al. (*3*), according to which rippling starts in laminar flow at a Reynolds number somewhere between 4 and 25.

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3. Bird, R. B., W. E. Stewart, and E. N. Lightfoot, "Transport Phenomena," p. 41, Wiley, New York (1960).

Yield and Molecular Size Distributions in Batch and Continuous Linear Condensation Polymerizations

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Continuous polymerizations in perfectly mixed, stirred reaction vessels, under steady state conditions, involving propagation of active chains (x units in length) of the type

$$P_x + M_1 \xrightarrow{k'} P_{x+1}$$

were discussed by Denbigh (*1*) and others (*2, 3*). The first author concluded that, in the case of short mean lifetime of growing chains compared with mean residence time in the reactor, the molecular size distribution of the resulting polymer in continuous polymerization should be narrower than in batch polymerization; in the case of short mean residence time compared with mean chain lifetime, continuous polymerization should produce a broader distribution than batch.

(*Continued on page 371*)

TABLE 1. c_x-VALUES CALCULATED FROM (2)

x	c_x	x	c_x
1	$10{,}000{,}000 \times 10^{-7}$	11	$16{,}796{,}000 \times 10^{-3}$
2	$10{,}000{,}000 \times 10^{-7}$	20	$17{,}672{,}628 \times 10^{2}$
3	$20{,}000{,}000 \times 10^{-7}$	30	$10{,}022{,}411 \times 10^{8}$
4	$50{,}000{,}000 \times 10^{-7}$	40	$68{,}042{,}387 \times 10^{13}$
5	$14{,}000{,}000 \times 10^{-6}$	50	$50{,}955{,}055 \times 10^{19}$
6	$42{,}000{,}000 \times 10^{-6}$	60	$40{,}594{,}296 \times 10^{25}$
7	$13{,}200{,}000 \times 10^{-5}$	70	$33{,}748{,}317 \times 10^{31}$
8	$42{,}900{,}000 \times 10^{-5}$	80	$28{,}944{,}758 \times 10^{37}$
9	$14{,}300{,}000 \times 10^{-4}$	90	$25{,}422{,}145 \times 10^{43}$
10	$48{,}620{,}000 \times 10^{-4}$	100	$22{,}750{,}589 \times 10^{49}$

(*Continued from page 369*)

For condensation polymerizations involving propagation of bifunctional species (x or y units in length) of the type

$$M_x + M_y \xrightarrow{k'} M_{x+y}$$

the lifetime of each growing chain is as long as the duration of the polymerization; hence, the latter effect should prevail, regarding molecular size distribution.

Moreover, in batch polycondensation distributions, unlike addition polymerization, the maximum occurs at low degrees of polymerization even at high degrees of conversion. Hence, in the continuous stirred reactor, owing to the random manner in which molecules of all sizes leave in the exit stream, one might expect large fractions of unreacted monomer to appear in the distribution curve.

The distribution for the second type of propagation has been predicted for batch conditions by Flory (*4*) using statistical arguments; Dostal and Raff (*5*) attempted to calculate the distribution kinetically.

The following treatment represents a complete analytical analysis of the batch and continuous cases with the usual assumptions:

1. The principle of equal reactivity is valid; that is k' is independent of chain length, x.
2. Density changes may be neglected.
3. Isothermal conditions prevail.
4. Mixing is perfect.
5. Continuous polymerization proceeds under steady state conditions.

BATCH POLYMERIZATION

The equations are, for $x = 1$

$$\frac{dM_1}{dt} = -K' M_1 \sum_{i=1}^{\infty} M_i$$

or

$$\frac{dm_1}{dt} = -2K m_1 \phi$$

and for $x > 1$

$$\frac{dm_x}{dt} = -2K m_x \phi + K \sum_{i=1}^{x-1} m_i m_{x-i}$$

with

$$\frac{d\phi}{dt} = -K\phi^2$$

and initial conditions

$$m_x = \begin{cases} 1 \text{ if } x = 1 \\ 0 \text{ if } x > 1 \text{ at } t = 0 \end{cases}$$

The time required for a given degree of conversion (P) may be computed at once from the last equation as

$$t = \frac{1-\phi}{K\phi} = \frac{P}{K(1-P)}$$

Books

(*Continued from page 194*)

drag, and turbulence. The wall temperature distribution and fluid temperature distribution for a tube having a sine flux distribution(such as occurs in nuclear reactors) are derived. Separate chapters are devoted to high velocity flow and rarified gas flow.

The presentation of conduction consists of a selection of the traditional topics. No mention is made of Carslaw and Jaeger, but familiarity with their work is evident. The equations and graphs for fins are mostly those of Harper and Brown and of E. Schmidt, but without credit. The Graetz treatment of laminar flow in a tube is given, but again without credit. In fact, very little credit is given to non-Soviet authors, although their many works were obviously used. The failure to indicate credit is very common among Soviet science writers, therefore, Kutateladze is by no means peculiar.

Today no one man can be expert in all branches of heat transfer. Kutateladze's one page of filmwise condensation is scarcely more than a short introduction. Radiation is treated concisely; however, the omission of Hottel's charts for the view factor detracts from the practical value of this chapter. A chapter on combined heat and mass transfer is given. It is aimed primarily at presenting the three-way analogy among heat, mass, and momentum transfer. The information is insufficient to permit calculations of a condenser for mixed vapors or a vapor in the presence of a non-condensable gas.

The practicing engineer will have modest interest in the book. Research workers will find it very interesting, primarily for the inclusion of some Soviet work not readily available otherwise.

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Engineering Design, Joseph H. Faupel, Wiley, New York, 960 pages, $19.75.

The subtitle of this book describes the contents, "a synthesis of stress analysis and materials engineering." Experimental results from the literature of the mechanical properties of materials are interspersed with analyses ranging from elementary mechanics of materials to the results of analyses by the theories of elasticity and plasticity. Design is here taken to be the calculation of stresses in load-carrying members or the dimensioning of loaded elements of structures, machines, pressure vessels, and composites for static, repeated, or rapidly applied loads. Essentially, this book is a handbook of mechanics of materials.

In its 960 pages, the book covers all topics to be found in the subject of mechanics of materials, from elementary riveted connections in tanks to stress wave propagation. Starting with a chapter on mechanical properties of materials, the book proceeds with analyses of tension, torsion and bending, and combined stresses. Theories of failure and their application are included in the latter chapter. The analysis of composite, honeycomb, and reinforced materials includes stress-strain relations (elastic) for orthotropic materials as well as the two-material problems and filament-reinforced structures. A considerable discussion of creep properties is included in the chapter on designing with plastics. Inelastic behavior in structures and machine parts, energy methods, and a chapter on buckling present analyses in the named areas. A long chapter on "Shock, Impact, Inertia and Fatigue" reviews the literature on high-loading-rate materials tests and fatigue tests, together with stress wave and vibration analyses and an analytical treatment of stresses in rotating members.

The chapter on prestressing for strength includes methods of determining residual stresses and development of stresses in such processes as shrink fits. Methods of experimental stress analysis and diagrams for geometric stress concentration factors are given for many kinds of members. Thermal stress, creep, and stress rupture are covered in the final chapter. Large numbers of references are given throughout the book.

The treatment throughout the book is somewhere between a handbook and a text book. In some cases complete derivations are given, whereas in others the formulas resulting from more complex analysis are presented without derivation. In this sense, the book is more complete in giving background than is a handbook. On the other hand, the absence of illustrative examples or problems would make it difficult for one not familiar with the subject to teach himself from this book. In attaining a breadth of subject matter coverage, there is a sacrifice of depth of development in nearly all subjects, when compared with the reference text books available to the student of mechanics.

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INFORMATION RETRIEVAL*

Study of nitrogen and neon pool boiling on a short vertical pipe, Lapin, Abraham, L. A. Wenzel, and H. C. Totten, **A.I.Ch.E. Journal, 11,** No. 2. p. 197 (March, 1965).

Key Words: Nitrogen-2, Neon-2, Boiling-8, Heat Transfer-8, Submergence-6, Temperature Difference-6, Surface Roughness-6, Heat Flux-7, Copper-10, Nickel-10, Cadmium-10, Pool-5, Cryogenic Fluids-5, Nucleate Boiling-8, Vertical Cylinder-10, Condenser-Heater-10, Empirical Equations-10.

Abstract: An experimental study in the behavior of nitrogen and neon pool boiling was performed. The test section consisted of a vertical pipe 3 in. O.D. x 7½ in. long. The variables studied were heat input, submergence, and surface finish. Several copper heaters were tested, in addition to nickel and cadmium plated heaters. The results were correlated for nitrogen by an equation which gave an average deviation of ± 16% for all the heaters except the cadmium plated heater. The paper describes the experimental equipment and technique, summarizes the data, and compares them to literature values and equations.

Generalized thermodynamic properties of real gases: Part I. Generalized PVT behavior of real gases, Viswanath, D. S., and Gouq-Jen Su, **A.I.Ch.E. Journal, 11,** No. 2, p. 202 (March, 1965).

Key Words: Thermodynamic-8, 9, Properties-8, 9, Gases-8, 9, Temperature-6, Pressure-6, Volume-6, Density-6, Compressibility-7, 9, Critical-4, Correlation-2.

Abstract: The object of this paper, first in the series dealing with the generalized thermodynamic properties of real gases, is to present generalized compressibility charts in the reduced temperature range of 1.0 to 15.0 and a reduced pressure range of 0 to 40.0, up to twice the critical density. A detailed summary of deviations of the present charts with PVT values of different gases is presented. A summary of the comparison of the present charts with the existing charts is also given.

Generalized thermodynamic properties of real gases: Part II. Generalized Benedict-Webb-Rubin equation of state for real gases, Su, Gouq-Jen, and D. S. Viswanath, **A.I.Ch.E. Journal, 11,** No. 2, p. 205 (March, 1965).

Key Words: Thermodynamics-8, 9, Least-Squares-10, Equation of State-8, Gases-8, 9, Pressure-6, Temperature-6, Density-6, Critical-4, Constants-2.

Abstract: With a least-squares technique used, a set of parameters for the generalized Benedict-Webb-Rubin equation is determined. The generalization of the Benedict-Webb-Rubin equation is based on the modified theorem of corresponding states. The generalized equation shows a grand average absolute deviation of 1.6% in predicting the observed values of reduced pressure. The set of constants has been determined for densities up to twice the critical density in the reduced pressure range of 0 to 40.0 and a reduced temperature range of 1.0 to 15.0. The recommended generalized constants are
$A'_0 = 0.24180980$, $a' = 0.04407059$, $a'\alpha' = 0.11369478 \times 10^{-3}$, $B'_0 = 0.07643101$, $b' = 0.03715171$, $C'_0 = 0.31317005$, $c' = 0.06448001$, and $\gamma' = 0.06$.

(*Continued on page 374*)

By solving the above equations consecutively one obtains

$$\frac{dm_x}{d\phi} - \frac{2}{\phi} m_x = (1 - x)\phi^2 (1 - \phi)^{x-2} \text{ for } x \geqq 1$$

which may be solved without difficulty to yield Flory's most probable distribution

$$m_x = \phi^2 (1 - \phi)^{x-1} = (1 - P)^2 P^{x-1}$$

Hence

$$W_x = x P^{x-1} (1 - P)^2 \text{ for } x \geqq 1 \quad (1)$$

CONTINUOUS POLYMERIZATION

The equations become, for $x = 1$

$$\frac{m_1 - 1}{\theta} = -2 K m_1 \phi$$

and for $x > 1$

$$\frac{m_x}{\theta} = -2 K m_x \phi + K \sum_{i=1}^{x-1} m_i m_{x-i}$$

with

$$\frac{\phi - 1}{\theta} = -K\phi^2$$

The mean residence time required for a given degree of conversion is greater than for the corresponding batch case:

$$\theta = \frac{1 - \phi}{K\phi^2} = \frac{P}{K(1 - P)^2}$$

By solving the above equations consecutively, one obtains

$$m_x = \frac{c_x \phi (1 - \phi)^{x-1}}{(2 - \phi)^{2x-1}} \text{ for } x \geqq 1$$

where

$$c_x = \sum_{i=1}^{x-1} c_i c_{x-i} \quad (2)$$

and may be generated by starting with $c_1 = 1$.
Hence

$$W_x = \frac{x c_x P^{x-1} (1 - P)}{(1 + P)^{2x-1}} \text{ for } x \geqq 1 \quad (3)$$

The values of c_x in Table 1 have been generated from Equation (2) with an IBM-1620 computer.

Examination of Figure 1 shows that the distribution curve is considerably broader in the continuous case and that no maximum occurs, indicating that a large fraction of unreacted monomer prevails.

The solution of Equation (2) in terms of x, which does not involve previous values of c_x, was found to be

$$c_x = \frac{2^{x-1} \prod_{i=1}^{x-1} (2i - 1)}{x!} \text{ for } x \geqq 1$$

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* For details on the use of these Key Words and the A.I.Ch.E. Information Retrieval Program, see **Chem. Eng. Progr.,** Vol. 60, No. 8, p. 88 (August, 1964). A free copy of this article may be obtained by sending a post card, with the words "Key Word Article" and your name and address (please print) to Publications Department, A.I.Ch.E., 345 East 47 St., N.Y. N.Y., 10017. Price quotations for volume quantities on request.

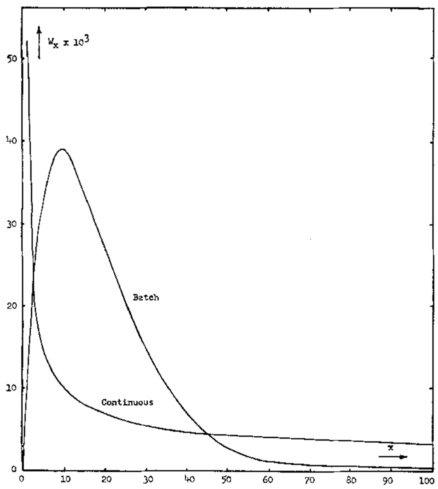

Fig. 1. Molecular size distributions for P = 0.90.

As x becomes large

$$c_x \approx \frac{2^{2x-1}}{(2x-1)\sqrt{\pi x}}$$

When one uses the last equation to compute c_{10}, the error was found to be less than 1.5%.

NOTATION

k' = kinetic rate constant for propagation, liter/mole sec.
k = $(k'M_1^\circ)/2$, sec.$^{-1}$
M_1° = initial or inlet monomer concentration, mole/liter
M_x = concentration of polymer chains having x units, mole/liter
P_x = concentration of active chains having x units, moles/liter
m_x = M_x/M_1°
ϕ = $\sum_{i=1}^{\infty} m_i$ = fraction of functional groups of one kind which remains unreacted
P = $1 - \phi$ = fraction of functional groups of one kind which have reacted
W_x = weight fraction of total polymer which contains x units
t = time in batch reactor, sec.
θ = mean residence time in continuous reactor, sec.

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