Mass Transfer from Large Oscillating Drops

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A mass transfer model for vigorously oscillating single liquid drops moving in a liquid field has been developed with the concepts of interfacial stretch and internal droplet mixing. The model takes into account both amplitude and frequency of drop oscillations. Experimental values of fraction extracted were predicted with an average deviation of 15%. Oscillations break up internal circulation streamlines and a type of turbulent internal mixing is achieved.

The contact of large drops of a dispersed liquid phase with a continuous liquid phase proceeds in four distinct stages if a spray or perforated plate tower is used to effect the extraction operation. These four major zones for mass transfer in the lifetime of such large drops are: formation of the discrete drops while they are still resident on the drop-forming device, an acceleration period immediately after the drops leave the nozzle or orifice, during the free rise (or fall) of the drops at a steady state slip velocity, and in a zone of flocculation and coalescence at the end of their vertical travel through the equipment (or stage) under consideration.

We are concerned here only with drops in the freely falling zone and of such a size that they will exhibit a cyclic, oscillatory motion as they move through the continuous phase.

The literature dealing with mass and heat transfer between fluid particles and their fluid surroundings is very extensive (*9*, *15*, *18*, *19*). Most studies have tried to isolate the resistances to such transfer into an internal and an external one, relative to the phase interface. The resistance to transfer, whether internal or external to the droplet surface, depends upon the motion of the fluid particle. Widely ranging magnitudes of resistance have been reported for drops which behave as rigid spheres, those performing like nonoscillating fluid (circulating) bodies, and those exhibiting a fully oscillating regime. Oscillating drops show a far greater rate of transfer than any other type. Summaries of the published work on the continuous (external) phase resistance are readily available (*4*, *13*, *17*, *18*). Garner and Tayeban (*3*) studied the effect that droplet oscillation had on the continuous phase resistance.

The dispersed phase resistance has been analyzed on the basis of three mathematical models. One of these, developed by Newman (*14*), is based upon a rigid sphere with no internal motion and leads to the expression

$$E = \frac{C_o - C_f}{C_o - C^*} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left[- n^2 \pi^2 \frac{D_D t}{a^2} \right] \quad (1)$$

When resistance to transfer in the continuous phase is zero and laminar circulation patterns which can be described by the Hadamard (*5*) streamlines are present, the result of Kronig and Brink (*10*) can be applied:

$$E = 1 - \frac{3}{8} \sum_{n=1}^{\infty} A_n^2 \exp\left[- \lambda_n \frac{16 D_D t}{a^2} \right] \quad (2)$$

Handlos and Baron (*6*) superimposed a turbulence due to random radial motion upon a circulatory pattern; this model yields, for zero resistance in the continuous phase

$$E = 1 - 2 \sum_{n=1}^{\infty} A_n^2 \exp\left\{ - \frac{\lambda_n U t}{128\left(1 + \frac{\mu_D}{\mu_c}\right) d} \right\} \quad (3)$$

The numerical values of A_n and λ_n in Equations (2) and (3) are not identical.

Previous workers (*1*, *3*, *8*, *12*, *19*) have used these three theoretical models, combined with one of the various empirical equations for the continuous phase resistance, to correlate droplet mass transfer data.

Stagnant droplet data show good agreement with the Newman relationship. Fully circulating droplets agree quite well with the Kronig and Brink expression, although specific instances of substantial deviation have been reported (*8*).

Oscillating drops deviate significantly from the Handlos and Baron model and there is no completely satisfactory relationship available for the estimation of transfer from such fully oscillating drops. Effects of such variables as frequency and amplitude of oscillation have yet to be accounted for.

The present paper is an attempt to characterize more fully mass and heat transfer between liquid drops and a liquid continuous phase for fully oscillatiing drops.

DROP OSCILLATION AND CIRCULATION

A photographic study was made to determine the effect of oscillation on internal circulation. The only oscillations considered here are those described by Schroeder and Kintner (*16*); they are either axially symmetric or of the random wobble type (*9*) and are large in amplitude. They occur only above drop Reynolds numbers of 200 and are maintained by vortex discharge behind the moving drops. Circulation is Hadamard-like movement of liquid within the drop in a manner that is almost laminar. It occurs in nonoscillating drops at Reynolds numbers well below 200 as well as in larger drops between periods of random wobble oscillatory regimes.

Five organic-water systems were studied. The continuous phase was the aqueous one in all cases. The organic phases were nitrobenzene, a mixture of benzyl and butyl alcohols, ethyl acetoacetate, monochlorbenzene, and benzyl alcohol. The phases were mutually saturated in all cases. Degreased and levigated aluminum particles were dispersed in the drop phase. Drops were formed at a nozzle below the surface of the field phase and allowed to fall through the latter. Motion was recorded by a 16-mm. motion picture camera. Side lighting was employed with a dark background to emphasize the patterns.

Every droplet system which exhibited oscillation showed deformed or completely damped circulation. Any flow within such fully oscillating drops could only be described as some type of random mixing with, perhaps, a slight tendency to circulate. Such a slight circulatory tendency was of minor importance in the presence of the turbulent mixing due to large amplitude oscillation. It was also noted that the drop oscillations were from a spherical shape to an oblate one or from oblate to more oblate (*16*) rather the stylized oblate-prolate cycle. It was therefore concluded that oscillations damp out internal circulation but that if the oscillations be damped, a circulatory pattern may be restored.

THE MODEL

The basic equation for unidirectional mass transfer across a stagnant interface is (9):

$$\frac{dN_A}{dt} = DA\frac{\Delta C}{\Delta x} \tag{4}$$

If, by some mechanism, the thickness of the zone of transfer resistance Δx should be decreased and the area increased, the rate of mass transfer would increase to a very marked degree. Oscillatory motion, resulting in an alternate deviation from and a return to a spherical shape, causes such an interfacial area stretch and its accompanying variation in the term $(\Delta C/\Delta x)$. The resulting increase in the rate of mass transfer can be very large.

To describe mass transfer from an oscillating drop, the fluid spheroid was assumed to oscillate from a nearly spherical shape to an oblate ellipsoidal one and back to a spherical shape in one period of the oscillation. All resistance to transfer (in both continuous and dispersed phases) is assumed to lie in a thin zone near the interface. The core of the drop is assumed to be well mixed. This permits a single value to represent the drop internal concentration as shown in Figure 1.

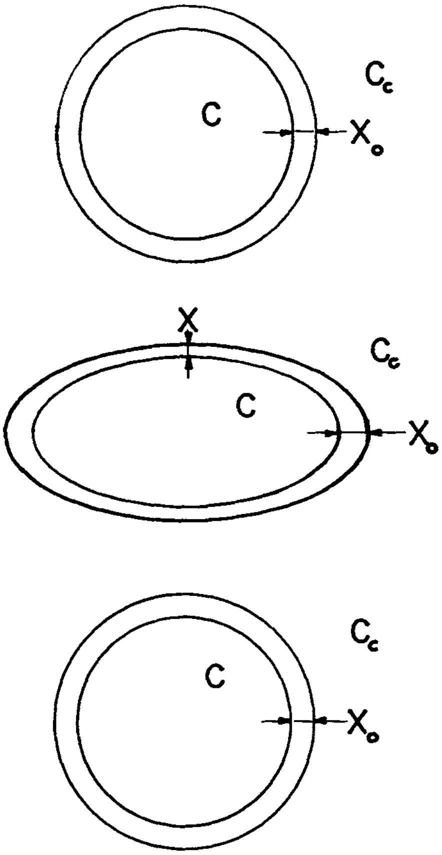

Fig. 1. One period of mass transfer model.

A material balance for the drop, based on the dispersed phase, is

$$-\frac{d(VC)}{dt} = \frac{D}{x}A(C - C^*) \tag{5}$$

Since the volume of the drop is constant, the mass balance across the zone is

$$-V\frac{dC}{dt} = \frac{D}{x}A(C - C^*) \tag{6}$$

The area of an oblate ellipsoid is given by

$$A = 2\pi a^2 + \frac{\pi b^2}{\left(\frac{a^2 - b^2}{a^2}\right)^{1/2}} \ln\left[\frac{1 + \left(\frac{a^2 - b^2}{a^2}\right)^{1/2}}{1 - \left(\frac{a^2 - b^2}{a^2}\right)^{1/2}}\right] \tag{7}$$

By assuming that

$$a = a_o + a_p\,|\sin\omega' t| \tag{8}$$

then a varies from a_o to $(a_o + a_p)$ where a_p is the amplitude of oscillation. The value of b can be found from the fact that the drop is a constant volume. Hence

$$b = \frac{3V}{4\pi a^2} \tag{9}$$

The thickness of the interfacial resistance zone may be estimated by assuming that the zone volume is constant as the drop deforms from a sphere to an oblate ellipsoid. Motion pictures of oscillating drops showed that the greatest deformation occurred at the poles of the minor axis of the drop. It was assumed that the zone thickness was a minimum value at the minor axis poles and thickened to a larger value at the equator (major axis ends). It was further assumed that the zone thickness at the equator was the original thickness x_o and thinned to a minimum value x at the ends of the minor axis. Planar symmetry above and below the equatorial plane was also assumed. The value x at the minor axis is the value used in Equation (6), since it is believed that this value compensates for any additional thinning due to a possible thickening of the zone at the equator. The value of x used is thus a thickness compensated for additional unpredictable thinning.

As the drop oscillates, x varies from x_o to x as a function of time. The value of x at any time is given by

$$x = \frac{[a_o^2 b - (a - x_o)^2 (b_o - x_o)] - 2abx_o + bx_o^2}{a^2 - 2ax_o - x_o^2} = f_1(t) \tag{10}$$

To predict the initial zone thickness for a spherical drop with uniform internal concentration of solute, the two-film theory is used. The zones may then be properly designated as films and x becomes the thickness of the hypothetical fluid film. The outside film thickness is predicted by using the empirical correlation of Garner and Tayeban (*3*) for circulating droplets:

$$N_{Sh_c} = 0.6\, N_{Re}^{1/2}\, N_{Sc}^{1/2} \tag{11}$$

To predict the inside film thickness, the penetration theory (7) is used with the contact time equal to the time for one oscillation cycle. This contact time was chosen as a result of the photographic study of the patterns of movement inside a falling oscillating drop. During each time that the drop underwent a period of oscillation, the interior of the drop was violently mixed. It was therefore assumed that the interface would be renewed during each drop oscillation cycle. Hence

$$k_D = 0.450\,(D_D\omega)^{1/2} \tag{12}$$

With the two-film theory

$$\frac{1}{K_D} = \frac{1}{k_D} + \frac{m}{k_c} \qquad (13)$$

and

$$x_o = \frac{D_E}{K_D} \qquad (14)$$

where

$D_E =$ (fraction of resistance in dispersed phase) $\cdot D_D$
+ (fraction of resistance in continuous phase) $\cdot D_c$ (15)

The use of an effective diffusivity permits the individual ones to be proportioned between the two phases according to the relative resistance of each phase.

FREQUENCY OF OSCILLATION

The frequency of oscillation is predicted with the Schroeder and Kintner (*16*) modification of Lamb's (*11*) equation:

$$\omega^2 = \frac{\sigma b}{a^3} \frac{n(n+1)(n-1)(n+2)}{\{(n+1)\,\rho_D + n\rho_c\}} \qquad (16)$$

in which the empirical amplitude coefficient b is best estimated by

$$b = \frac{d_e^{0.225}}{1.242} \qquad (17)$$

The value of ω' used in Equation (8) is one half the value of ω in Equation (16), due to the use of the absolute value of the sine function.

AMPLITUDE OF OSCILLATION

Estimation of the amplitude of drop oscillations was made from motion pictures of falling drops. The lengths of the major and minor axes were measured from the films at maximum and minimum distortion of the drops. The films were examined frame-by-frame for fifteen systems of organic liquid vs. water at varied physical properties. Considerable scatter existed in the data and an average drop axis length at maximum and at minimum distortion was calculated. A plot was made (*15*) of $A_{\max}$ vs. d_e from which a_p could be found by the equation

$$a_p = \frac{A_{\max}}{2} - a_o \qquad (18)$$

SOLUTION OF THE DIFFERENTIAL EQUATION

Equation (5) is then solved along with the boundary conditions

$$C = C_o \quad \text{at} \quad t = t_o \qquad (19)$$
$$C = C_f \quad \text{at} \quad t = t_f$$

The solution is

$$E = 1 - \exp\left[-\frac{2\pi D_E}{V} \int_{t_o}^{t_f} \frac{1}{f_1(t)} \left\{ \left(\frac{3V}{4\pi(a_o + a_p|\text{sine}\,\omega' t|)^2} \right)^2 \frac{1}{2\alpha} \ln\frac{1+\alpha}{1-\alpha} + (a_o + a_p|\text{sine}\,\omega' t|)^2 \right\} dt \right] \qquad (20)$$

in which

$$\alpha^2 = \frac{(a_o + a_p|\text{sine}\,\omega' t|)^2 - \left(\dfrac{3V}{4\pi(a_o + a_p|\text{sine}\,\omega' t|)^2} \right)^2}{(a_o + a_p|\text{sine}\,\omega' t|)^2} \qquad (21)$$

Since the integral of Equation (20) could not be analytically evaluated, a digital computer program was used to perform the operation numerically. Values of fractional extraction were then calculated and compared with experimental ones.

EXPERIMENTAL DATA

Experimental findings from several sources of mass and heat transfer data were used to test the validity of the model. The data used were for oscillating drops and represented a range of cases where the resistance was distributed to where the resistance was isolated in one phase only. The literature data used may be found in reference *15*.

DISCUSSION AND RESULTS

The literature data on mass and heat transfer from single oscillating drops are presented graphically in Figures 2 to 4. Values of E, calculated by Equation (20), are plotted as the abscissa with the experimental ones from various experimenters as the ordinate. The average deviation for all systems is approximately 15%. With some reservations the model appears to hold considerable promise.

The discrepancies may be due to

1. The drops may not have been fully and vigorously oscillating as the model requires.
2. The data used are for the free fall period. End effects caused by formation and coalescence, even though corrected for in the data, may influence the free fall period transfer.
3. The model predicted higher transfer rates than were observed at high values of E. These might be due to transient phenomena such as decay of oscillations.
4. The presence of impurities of a surface-active nature could cause lower experimental values and thus result in a calculated value higher than the observed ones.

The diffusivities used in Equation (15) were calculated by the Wilke-Chang (*20*) correlation. Values of the dis-

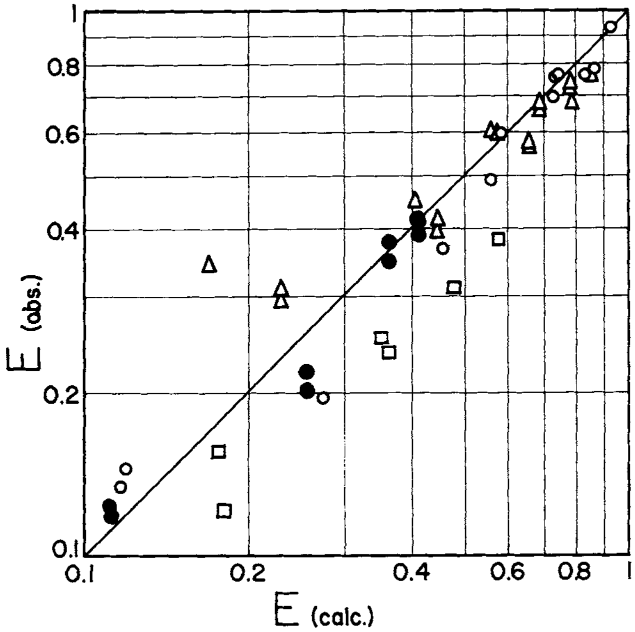

Fig. 2. Mass transfer in systems in which all or most of the resistance is in the drop phase. ○ = data of Skelland and Wellek (*19*) on water drops in ethyl acetate. △ = data of Johnson and Hamielec (*8*) on water drops in ethyl acetate. □ = data of Skelland and Wellek (*19*) on ethyl acetoacetate drops in water. ● = data of Garner and Skelland (*2*) on nitrobenzene drops in water-acetic acid.

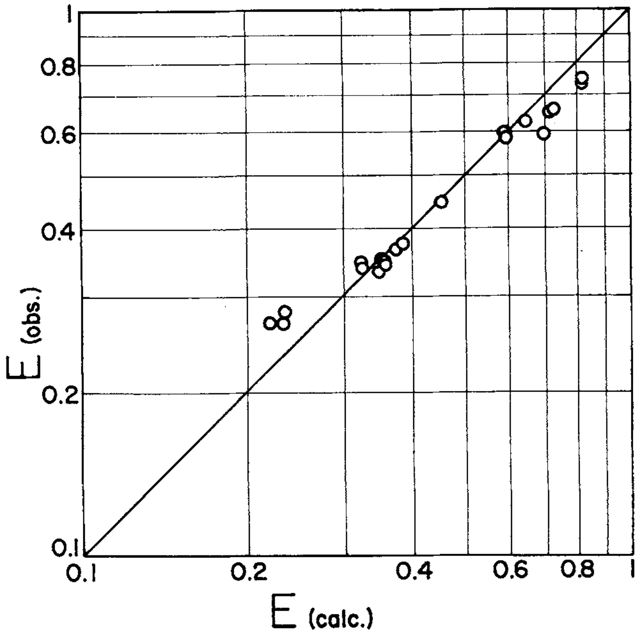

Fig. 3. Heat transfer from mercury drops to water [data of Calderbank and Korchinski (1)]. All resistance is in the continuous phase.

tribution coefficient, times of contact, etc., were taken from the original articles.

Values of the fractional extraction calculated by Equation (20) were, for some systems, higher than the observed values at high values of E and lower at low values of E. It is possible that the use of the pentration theory with a modified contact time assumes a rate of internal surface renewal which can only be achieved by vigorously oscillating drops. The data of Garner and Skelland (2) for vigorously oscillating nitrobenzene drops seem to indicate such a condition. The average deviation from their data was only 5%. The concept of interfacial stretch in the transfer zone (or film) due to oscillation of the drops results in good prediction of the data in clearly proper cases such as those of Calderbank and Korchinski (1) where all the resistance lay in the continuous phase. This model, which is based upon internal droplet mixing with periodic internal surface renewal and interfacial stretch, may well represent a closer approach to the actual phenomena present in an oscillating droplet.

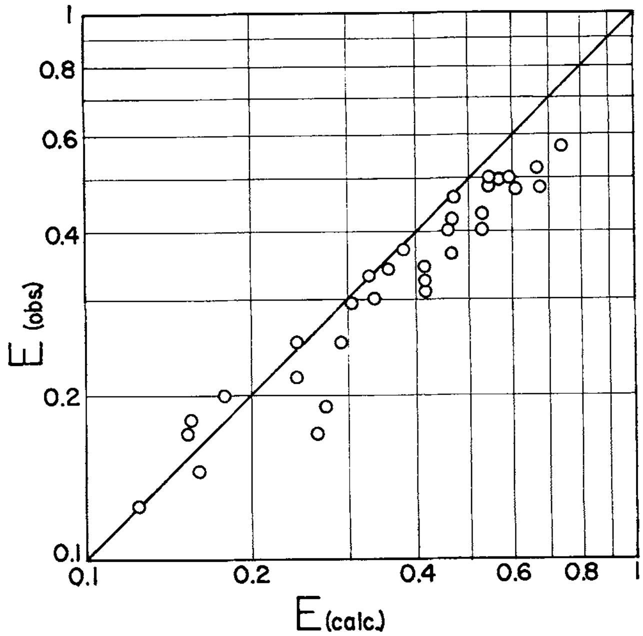

Fig. 4. Mass transfer between water drops and methyl isobutyl ketone; solute is acetic acid [data of Licht and Pansing (12)]. Resistance in both phases.

CONCLUSION

The very high rates of transfer from a truly oscillating drop to the surrounding continuous phase are calculated to a more satisfactory degree of accuracy by Equation (20) than was previously possible.

The concept of interfacial stretch due to oscillations from a nearly spherical shape to an oblate ellipsoidal one causes a higher interfacial area and a higher concentration gradient for the terms in Equation (4). While oscillations nearly eliminate circulatory patterns of the Hadamard type, there is a very high degree of turbulent mixing in fully oscillating drops. The combination of interfacial stretch and internal mixing results in a much more rapid transfer rate for such highly oscillating drops.

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NOTATION

A = area, sq. cm.
$A_{\max}$ = maximum axis length, cm.
A_n = coefficient in a series
a = radius or half-axis length, cm.
a_o = initial radius or half-axis length, cm.
a_p = amplitude, cm.
C = concentration, g.-moles/cc.
C_c = continuous phase
C_f = final concentration
C_o = initial concentration
C^* = equilibrium concentration
D = diffusivity, sq. cm./sec.
D_c = continuous phase
D_D = dispersed phase
D_E = effective diffusivities
d = diameter, cm.
d_e = equivalent spherical diameter
E = fractional extraction = $(C_o - C_f)/(C_o - C^*)$
K_D = overall mass transfer coefficient, cm./sec.
k_c, k_D = continuous and dispersed phase film mass transfer coefficients, respectively, cm./sec.
N_A = number of moles of solute component
N_{Re} = Reynolds number, $dU\rho/\mu$
N_{Sc} = Schmidt number, $\mu/\rho D$
N_{Sh_c} = Sherwood number for the continuous phase, $k_c d/D$
n = mode of oscillation or index
t = time, sec.
U = velocity, cm./sec.
V = volume, cc.
x = film thickness, cm.
x_o = initial film thickness, cm.

Greek Letters

α = parameter in Equation (20), defined by Equation (21)
Δ = finite difference
λ_n = n^{th} eigenvalue
μ_c, μ_D = continuous and dispersed phase viscosity, respectively, g./(cm.)(sec.)
π = 3.1416
ρ_c, ρ_D = continuous and dispersed phase density, respectively, g./cc.
σ = interfacial tension, dynes/cm.

ω, ω' = frequency and modified frequency of oscillation, radians/sec.

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Effects of Product Recycle and Temperature on Autocatalytic Reactions

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The effect of product recycle and temperature on the maximum yield of product for several different autocatalytic reactions taking place in a tubular reactor is studied.

A generalized version of the maximum principle is used to determine the maximum conversion and optimal temperature profile for each of the reactions considered. The fraction of product recycled, which affects the concentration of autocatalytic agent entering the reactor, is investigated to determine its effect on the maximum conversion.

An autocatalytic reaction in which one or more of the products acts catalytically gives rise to a rather unusual problem in the design of a flow reactor, for its rate of reaction is influenced by the concentration of some of the products as well as that of some of the reactants (*1*). Examples of such reactions are found in the acid-catalyzed hydrolysis of various esters and similar compounds (*2, 3*) and in various biochemical processes such as the conversion of trypsiogen into trypsin with the trypsin catalyzing the reaction (*4*).

A kinetic model of the autocatalytic type is often used to represent the rate of growth of microorganisms in various biochemical processes in which several reactions are actually taking place in the system. In these systems the kinetic equation, which is used to represent the rate of growth, is often only an approximate model that one uses to mathematically represent the system. Such a model is usually valid over only a limited range of temperature and concentration. The biochemical oxidation of process waste water is a common example of such an autocatalytic system.

The rate of an autocatalytic reaction in a steady state tubular flow reactor with product recycle is often influenced by two important factors: the initial concentration of the autocatalytic agent and the temperature at which the reaction is carried out. The initial concentration of the autocatalytic agent may be controlled by varying the rate of product recycle from the exit to the entrance of the reactor, and the temperature may be controlled artificially. This paper deals with the interaction of product recycle and temperature in a flow reactor. The interaction is studied from the standpoint of how it affects the maximum yield of the product for several different reactions taking place in a tubular flow reactor of given size with a given volumetric flow rate of fresh feed fed to the system.

FORMULATION OF EQUATIONS

We shall consider an autocatalytic reaction of the type

$$A + R \underset{k_2}{\overset{k_1}{\rightleftarrows}} R + R \quad \text{or} \quad A \underset{k_2}{\overset{k_1}{\rightleftarrows}} R \qquad (1)$$

taking place in a tubular reactor where a portion of the product is recycled to the inlet of the reactor and mixed continuously with the stream of fresh feed as shown in Figure 1. In this figure v represents the volumetric flow rate of the reacting mixture and L denotes the length of the tubular reactor.

The steady state differential material balance for reactant A in a differential section $d\xi$ of the reacting section of the system is (a unit cross-sectional area is assumed):