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Volume 2

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Fundamentals of Biochemical Engineering

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Prof. Dr. H.-J. Rehm
Institut für Mikrobiologie
der Universität
Corrensstraße 3
D-4400 Münster
Federal Republic of Germany

Dr. G. Reed
Universal Foods Corp.
Technical Center
6143 N 60th Street
Milwaukee, WI 53218
USA

Prof. Dr.-Ing. H. Brauer
Institut für Chemieingenieurtechnik
Technische Universität Berlin
Straße des 17. Juni 135
D-1000 Berlin 12

Editorial Director: Dr. Hans F. Ebel
Copy Editors: Christa Maria Schultz and Theodor C. H. Cole
Production Manager: Peter J. Biel

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1 Fundamentals of Transport Phenomena

Chapter 1

Equations for Momentum, Heat and Mass Transport, and Mass Conversion

Heinz Brauer

Institut für Chemieingenieurtechnik
Technische Universität Berlin
Berlin (West), Germany

List of Symbols

A	m^2	area
a	m^2/s	molecular diffusivity of heat
c_A	$kmol/m^3$	partial mol density of component A
c_B	$kmol/m^3$	partial mol density of component B
c_p	kJ/(kg K)	specific heat capacity of fluid
D	m^2/s	diffusion coefficient
D_{AB}	m^2/s	diffusion coefficient of component A in a mixture with component B
D_{BA}	m^2/s	diffusion coefficient of component B in a mixture with component A
d	m	tube diameter
F	m^2	cross sectional area
K	$\tau_m/(-dw/dy)^n$	Ostwald factor
M_A	kg	mass of component A
$\dot{M}_A$	kg/s	mass flux of component A
$\dot{m}_{Am}$	$kg/(s\,m^2)$	molecular mass flux density of component A
$\dot{m}_{Bm}$	$kg/(s\,m^2)$	molecular mass flux density of component B
$\dot{m}_{At}$	$kg/(s\,m^2)$	turbulent mass flux density of component A
$\dot{m}_{Bt}$	$kg/(s\,m^2)$	turbulent mass flux density of component B
$\dot{n}_{Am}$	$kmol/(s\,m^2)$	molecular mol flux density of component A
$\dot{n}_{Bm}$	$kmol/(s\,m^2)$	molecular mol flux density of component B
$\dot{n}_{At}$	$kmol/(s\,m^2)$	turbulent mol flux density of component A
$\dot{n}_{Bt}$	$kmol/(s\,m^2)$	turbulent mol flux density of component B
p	N/m^2	total pressure
p_A	N/m^2	partial pressure of component A
p_B	N/m^2	partial pressure of component B
Q	kJ	heat
$\dot{Q}$	kJ/s	heat flux
$\dot{q}_m$	$kJ/(s\,m^2)$	molecular heat flux density
$\dot{q}_t$	$kJ/(s\,m^2)$	turbulent heat flux density
R	m	tube radius
R	kJ/(kmol K)	universal gas constant
$\dot{r}_A$	$kmol/(s\,m^2)$	reaction flux density, reaction rate
T	K	temperature
t	s	time
w	m/s	local velocity
$\bar{w}$	m/s	mean velocity over cross sectional area
w_s	m/s	mean velocity of Stefan flow
w'_x	m/s	fluctuation velocity in x-direction
w'_y	m/s	fluctuation velocity in y-direction
x	m	length coordinate
y	m	length coordinate
z	m	length coordinate
α_z	$kJ/(s\,m^2\,K)$	local coefficient of heat transfer
β_z	m/s	local coefficient of mass transfer
ε_m	m^2/s	turbulent diffusivity of mass
ε_q	m^2/s	turbulent diffusivity of heat
ε_τ	m^2/s	turbulent diffusivity of momentum
η	kg/(m s)	dynamic viscosity of fluid
λ	kJ/(m s K)	heat conductivity
μ_A	kmol/kg	mol mass of component A
μ_B	kmol/kg	mol mass of component B
ν	m^2/s	kinematic viscosity of fluid
ϱ	kg/m^3	density of fluid
ϱ_A	kg/m^3	partial density of component A
ϱ_B	kg/m^3	partial density of component B
τ_m	N/m^2	molecular shear stress
τ_t	N/m^2	turbulent shear stress
τ_0	N/m^2	yield stress of Bingham fluids

$Da \equiv \dfrac{\dot{r}_{A,max}/k}{D/R}$	Damköhler number
$Nu_z \equiv \dfrac{\alpha_z d}{\lambda}$	local Nusselt number
$Pr \equiv \dfrac{\eta c_p}{\lambda}$	"molecular" Prandtl number
$Pr_t \equiv \varepsilon_\tau/\varepsilon_q$	"turbulent" Prandtl number
$Re \equiv \dfrac{\bar{w} d}{\nu}$	Reynolds number for tube flow
$Re^+ \equiv \dfrac{\sqrt{\tau_w/\varrho}\, d}{\nu}$	shear Reynolds number
$r^* \equiv r/R$	radial coordinate

$Sc \equiv \nu/D$	"molecular" Schmidt number
$Sc_t \equiv \varepsilon_\tau/\varepsilon_m$	"turbulent" Schmidt number
$Sh_z \equiv \frac{\beta_z d}{D}$	local Sherwood number
$\psi_z \equiv \frac{dp/dz}{\varrho \bar{w}^2/2} d$	local friction coefficient

1.1 Introduction

Microbial technical processes are carried out in bioreactors. The bioreactor ist the containment for an almost unlimited number of microorganisms, each microorganism being a microreactor actually accomplishing the desired mass conversion. The contribution of an individual microorganism to the mass conversion is extremely small. Large-scale mass conversion technologies require a countless number of microorganisms, which must be contained within the smallest possible space.

Each one of the exceedingly large number of microorganisms has to be supplied with various nutrients, while at the same time conversion products have to be removed. Supply and removal are transport processes. For the prevailing conditions mass transport and mass conversion are closely linked with transport of heat and transport of momentum.

Transport of momentum, heat, and mass in bioreactors are processes with much greater consequences than in conventional chemical reactors. Insufficient transport of reactants results in substantially decreased production rates when non-microbial processes are considered. In the case of microbial processes the consequence of an inefficient mass transport process may be not only a reduced production rate but may result in an altogether different type of conversion process and conversion product. This kind of response of an organism to malfunctions or irregularities of transport processes is one of the most fascinating aspects of the "individuality" of microorganisms. Unfortunately we do not yet know enough about the processes involved.

The less we know about the individual response of a microorganism to transport deficiencies the more we have to make sure that such deficiencies are avoided. A thorough understanding of transport processes will be helpful in the design and operation of efficient bioreactors.

Transport of momentum, heat, and mass may be achieved by conductive and convective processes. Conductive processes are due to molecular and turbulent motions, while convective transport is related to fluid motion. The basic equations for momentum, heat, and mass transport are empirically derived. There are no strictly theoretical equations available. The same is true for mass conversion processes. All equations describing chemical or biochemical conversion processes are founded upon empirical data.

The equations which will be given for transport and conversion processes, represent physical or physico-chemical laws governing the behavior of solids and fluids; they include parameters specific for the considered processes and for the particular equipment, in which the processes are carried out. This chapter is therefore devoted to a discussion of the available empirical equations describing transport of momentum, heat, and mass and the conversion of mass.

1.2 Momentum Transport

Transport of momentum is due to molecular, turbulent, and convective motions. In this order the processes of momentum transport will be discussed. Molecular and turbulent momentum transport is the subject of this section. Convective transport will be discussed in a separate section. Momentum transport occurs only in fluids. These fluids consist of two large groups: Newtonian and non-Newtonian fluids.

1.2.1 Molecular Momentum Transport in Newtonian Fluids

The majority of the conventional fluids, especially inorganic gases and liquids as well as organic gases, but also a great number of organic liquids are so-called Newtonian fluids. In these fluids molecular momentum transport is described by an empirical equation presented by Newton:

$$\tau_m = -\eta \frac{dw}{dy}. \qquad (1.1)$$

This equation relates the molecular momentum flux density τ_m, which is also known as shear stress, with the velocity gradient dw/dy, which is also known as shear rate.

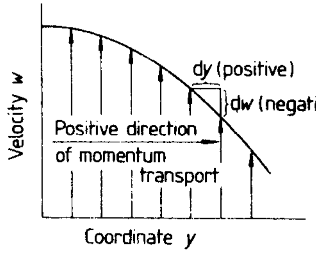

Figure 1.1. Explanation of molecular momentum transport in fluids.

The proportionality factor η is the molecular transport coefficient for momentum, better known as the dynamic viscosity of the fluid; η depends on pressure and temperature of the fluid. For all Newtonian fluids the viscosity is independent of shear stress τ_m or shear rate dw/dy. According to Eq. (1.1) even the smallest shear stress applied to Newtonian fluids will cause a fluid motion. In the absence of a gradient of the velocity ($dw/dy = 0$), there is no shear stress. Eq. (1.1) gives only one component of the stress tensor.

In Fig. 1.1 the local velocity w is plotted over the local coordinate y. According to Fig. 1.1 and Eq. (1.1) the momentum flux density τ_m is assumed to be positive in the direction of decreasing velocity.

The Newtonian equation for molecular momentum transport may also be written in the following way:

$$\tau_m = -\nu \frac{d(w\varrho)}{dy}. \qquad (1.2)$$

In this equation $\nu = \eta/\varrho$ denotes the kinematic viscosity of the fluid with ϱ as density, and $w\varrho$ the momentum per unit volume of the fluid. Eq. (1.2) presents the proportionality between momentum flux density τ_m and gradient of momentum per unit volume. In Table 1.1 values for the dynamic and kinematic viscosity are given for a few selected fluids.

Table 1.1. Kinematic and Dynamic Viscosity of Selected Fluids (pressure 1 bar; temperature 300 K)

	ν in m^2/s	η in kg/(m s)
Mercury	$0.0112 \cdot 10^{-5}$	$151.7 \cdot 10^{-5}$
Water	$0.0681 \cdot 10^{-5}$	$85.7 \cdot 10^{-5}$
Air	$1.58 \cdot 10^{-5}$	$1.86 \cdot 10^{-5}$
Hydrogen	$11.25 \cdot 10^{-5}$	$0.89 \cdot 10^{-5}$

There is no absolute proof for the validity of Newton's law. Applications of this law in calculations for velocity fields are, however, in excellent agreement with extrapolated experimental results.

1.2.2 Molecular Momentum Transport in Non-Newtonian Fluids

1.2.2.1 Classification of Non-Newtonian Fluids

All fluids which do not obey Newton's law for the shear stress τ_m, given by Eq. (1.1), will be classified as non-Newtonian fluids. For this group of fluids the viscosity depends not only on temperature and pressure but also on the shear stress τ_m, time, elasticity, and other parameters.

Typical non-Newtonian fluids are melts and solutions of, e.g., polymers, thick suspensions, paints, many fermentation fluids, i.e., primarily high molecular weight fluids. Rheology, the science of properties and behavior of flowing substances, has not yet been successful in presenting a shear stress relation for all important groups of non-Newtonian fluids. Only for certain groups of non-Newtonians, such relations have been developed [1.1] to [1.5]. From a scientific point of view such shear stress relations are based on physical insight into the flow behavior of these fluids. From an engineering point of view these equations are not yet very helpful in describing fluid flow in technical equipment. For this particular problem area engineers are still forced to refer to extremely simple empirical shear stress relations with a rather narrow range of application.

There are at least two large groups of non-Newtonian fluids:

1. viscous fluids,
2. elastic fluids.

For the group of viscous non-Newtonian fluids the viscosity depends only on the shear stress, but is independent of time:

$$\eta = f_1(\tau_m) \quad \text{or} \quad \eta = f_2(dw/dy). \tag{1.3}$$

For elastic non-Newtonian fluids the viscosity is a function of time t:

$$\eta = f_3(t). \tag{1.4}$$

This implies, that elastic fluids are sensitive to distortion from an experienced or preferred shape. These fluids remember for a certain stretch of time the shape they previously possessed. When the viscosity increases with time, the behavior of the fluids is rheopectic. Thixotropic behavior implies decreasing viscosity with time.

A satisfactory mathematical description of the flow of non-Newtonian fluids in technical equipment is restricted to the groups of viscous fluids. For this group of fluids momentum transfer will be briefly discussed.

1.2.2.2 Momentum Transport in Viscous Non-Newtonian Fluids

According to the equations describing flow behavior there are three groups of viscous non-Newtonian fluids:

1. Pseudoplastic fluids,
2. dilatant fluids, and
3. Bingham fluids.

The discussion starts with the first two groups of fluids. Ostwald and de Waele presented the following equation for momentum transport, known as the power law [1.6], [1.7]:

$$\tau_m = K\left(-\frac{dw}{dy}\right)^n. \tag{1.5}$$

K is the Ostwald factor, and n is the fluid index. When $n = 1$ the Ostwald factor K is identical with the fluid viscosity η, so that Eq. (1.5) is reduced to Eq. (1.1), which has been presented for momentum transport in Newtonian fluids.

For $n > 1$ Eq. (1.5) describes the behavior of dilatant fluids, and for $n < 1$ of pseudoplastic fluids. In Fig. 1.2 the shear stress/shear rate relationship is given qualitatively for the three cases discussed. For Newtonian fluids with n = 1 a linear relationship exists, so that the viscosity is independent of shear stress or shear rate. For dilatant and pseudoplastic fluids a non-linear relationship exists. For dilatant fluids the viscosity is reduced with increasing shear stress, while for pseudoplastic fluids the viscosity increases with shear stress.

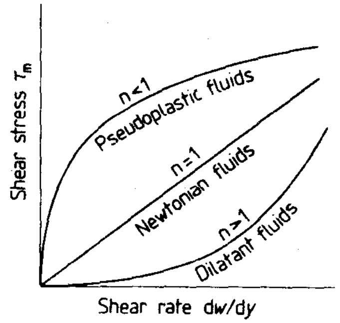

Figure 1.2. Relationship between shear stress and shear rate for Newtonian and non-Newtonian fluids.

According to Fig. 1.2 an infinitesimally small shear stress will set a dilatant fluid in motion, while for pseudoplastic fluids an infinitely large shear stress is required. This rather unrealistic behavior is expressed by the following relation:

$$\frac{d\tau_m}{d(dw/dy)} = nK\left(-\frac{dw}{dy}\right)^{n-1}. \qquad (1.6)$$

$n > 1$: $-dw/dy \to 0$ $\quad d\tau_m/d(dw/dy) \to 0$
$n < 1$: $-dw/dy \to 0$ $\quad d\tau_m/d(dw/dy) \to \infty$

In reality the flow behavior of viscous non-Newtonian fluids asymptotically approaches that of Newtonian fluids in low and high shear stress regions. This behavior is discussed in Fig. 1.3. Curve *a* gives the shear stress/shear rate relationship for a pseudoplastic fluid. When this curve approaches $\tau_m = 0$, it coincides at point 1 with curve *b*, which represents Newtonian flow behavior in the low shear stress region. Experimental data prove that in the high shear stress region non-Newtonian flow behavior will change into Newtonian behavior. Curve *a* therefore ends at point 2. For higher shear stress values the flow behavior follows curve *c*, approaching curve *d*, which represents Newtonian flow behavior in the high shear stress region.

Application of the power law is limited to the range between points 1 and 2 as given in Fig. 1.3. General expressions for these limits cannot be stated. Care should be taken in the use of Eq. (1.5).

From a physical point of view application of the power law is limited to linear flows. Bird [1.8] has proven that the power law, expressed by:

$$\tau_m = -K\left[\left(\frac{dw}{dy}\right)^2\right]^{\frac{n-1}{2}} \frac{dw}{dy}, \qquad (1.7)$$

is one component of the stress tensor for Ostwald fluids. Application of this power law on other than linear fluid flows requires extreme care.

For non-Newtonian fluids a viscosity η_{n-N} can be defined as the ratio of shear stress and shear rate. From Eq. (1.7) one obtains:

$$\frac{\tau_m}{dw/dy} \equiv \eta_{n-N} = K\left[\left(\frac{dw}{dy}\right)^2\right]^{\frac{n-1}{2}}. \qquad (1.8)$$

This equation shows clearly that the viscosity of Ostwald fluids is a function of the

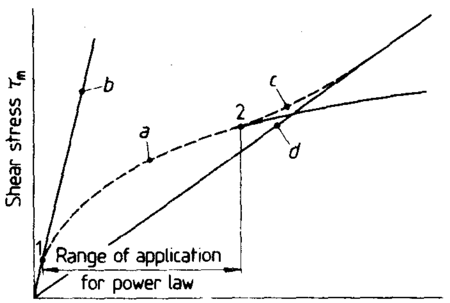

Figure 1.3. Shear stress/shear rate relationship for a pseudoplastic non-Newtonian fluid according to curve *a*; limiting Newtonian conditions given by curves *b* and *d* in the low and high shear stress region.

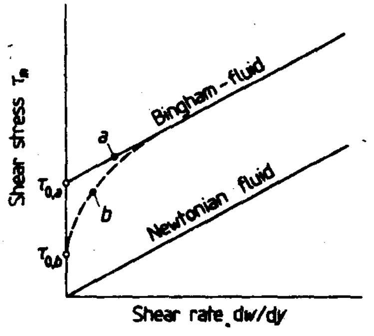

Figure 1.4. Flow behavior of a Bingham fluid.

velocity gradient. The Ostwald factor K is, however, independent of the velocity gradient.

The third group of viscous non-Newtonian fluids are called Bingham fluids [1.9]. The flow behavior of these fluids is qualitatively given by curve a in Fig. 1.4 and quantitatively by:

$$\tau_m = \tau_0 + \eta_B \left(- \frac{dw}{dy} \right). \tag{1.9}$$

The characteristic property of a Bingham fluid is the yield stress τ_0 at $dw/dy = 0$. The stress that sets a Bingham fluid into motion must exceed the yield stress. Bingham fluids do not always show a linear relationship between τ_m and dw/dy, while they do exert a non-linear behavior according to curve b in the low shear stress region.

1.2.3 Turbulent Momentum Transport

In turbulent flows molecular momentum transport is enhanced by "turbulent" momentum transport. This mode of transport is due to velocity fluctuations which are observed in the direction of the three coordinates. HINZE [1.10] therefore defines turbulence as follows: "Turbulent fluid motion is an irregular condition of flow in which the various quantities show a random variation with time and space coordinates, so that statistically distinct average values can be discerned." Turbulence can be generated by friction forces at solid walls (flow through conduits, flow past plates and bodies) or by the flow of layers of fluids with different velocities past or over one another, as stated by VON KÁRMÁN [1.11].

Turbulence will be explained here only in a very simple way. Velocity fluctuations are of statistical nature. Each component of a velocity vector has three fluctuation velocities: w_x', w_y', and w_z'. In Fig. 1.5 fluctuation velocity w_y' is given as a function of the time coordinate t. The time average of the fluctuation velocity is by definition zero. Fluctuation results in momentum transfer, which is explained in Fig. 1.6 as an example, between streamlines 1 and 2. The velocity of streamline 1 at a fixed point in space and time t is $w_x + w_x'$, with w_x as the time mean value of the velocity in x-direction

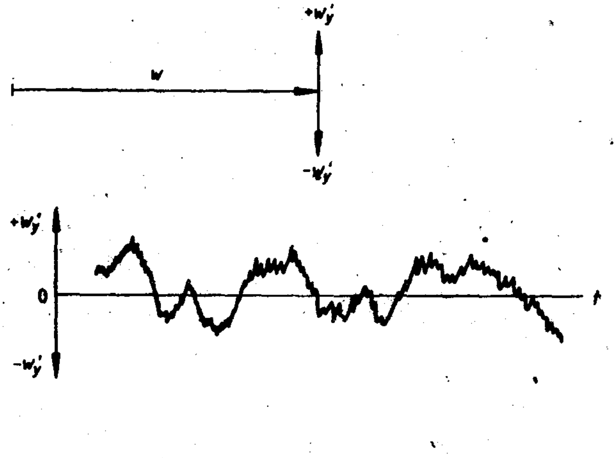

Figure 1.5. Explanation of random turbulent velocity fluctuations.

and w_x' the fluctuation velocity in the same direction. For streamline 2 the velocity is assumed to be w_x, so that $w_x'=0$. For this condition turbulent momentum transfer is

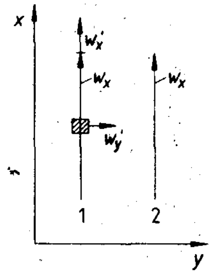

Figure 1.6. Turbulent momentum transport from streamline 1 to streamline 2.

achieved by the motion of a small fluid element from streamline 1 to streamline 2. The size of the turbulence element depends on the local conditions of turbulence. The mass transported per unit of time and area is given by $\varrho w_y'$, and the turbulent momentum per time unit transported from streamline 1 to 2 is given by:

$$\tau_{xy}' = -\varrho w_y' w_x' . \tag{1.10}$$

The average time value for the turbulent shear stress is defined as follows:

$$\tau_{xy} = -\varrho \overline{w_y' w_x'} . \tag{1.11}$$

To describe turbulent momentum transport BOUSSINESQ [1.12] introduced the simple equation:

$$\tau_t = -\varrho \varepsilon_\tau \frac{dw}{dy} , \tag{1.12}$$

which is from a mathematical point of view an analogous equation to that for molecular momentum transport as given by Eq. (1.1). The product $\varrho \varepsilon_\tau$ is the coefficient of turbulent momentum transfer, the analogous coefficient to η, which is the coefficient for molecular momentum transport. The coefficient ε_τ has the same dimension as ν, that is m^2/s.

In turbulent flow fields momentum transport is due to molecular and turbulent motion. The equation for momentum transport is therefore given by:

$$\tau = \tau_m + \tau_t = -\eta (1 + \varepsilon_\tau/\nu) \frac{dw}{dy} . \tag{1.13}$$

The ratio ε_τ/ν is a dimensionless quantity. It is a function of the properties of the turbulent flow field and local coordinates.

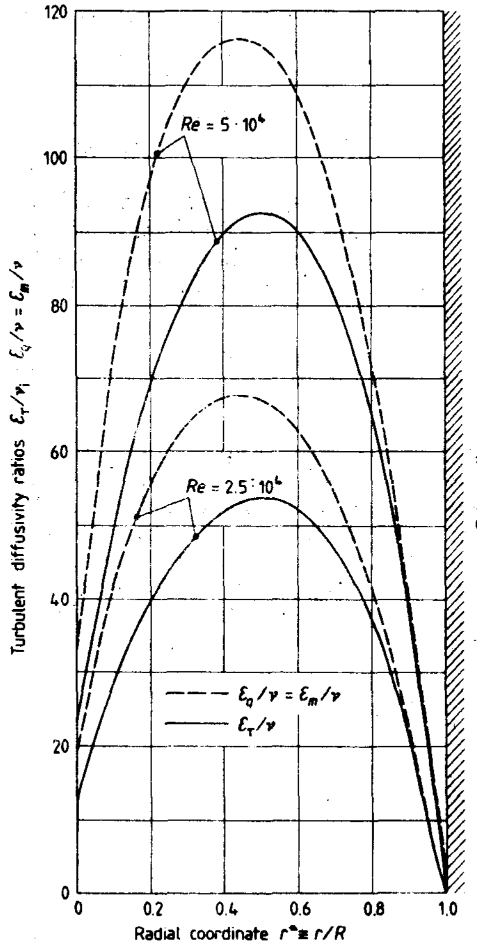

Figure 1.7. Ratio ε_τ/ν of turbulent to molecular momentum transport coefficients; ε_q/ν and τ_m/ν are presented as well as for turbulent pipe flow over the local radius r^* for two values of the Reynolds number *Re*.