Unit Operations to Transport Phenomena

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Engineering as a profession was first identified with weaponry and military works. The demand by the civilian populace for structures primarily designed for commerce and trade led only in the last 250 years to "civil" engineering and the civil engineer, whose job was defined in 1828 in the charter of the Institute of Civil Engineers. Civil engineering was "the art of directing the great sources of power in nature for the use and convenience of man, as the means of production and of traffic in states, both for external and internal trade, as applied in the construction of roads, bridges, aqueducts, canals, river navigation and docks for internal intercourse and exchange, and in the construction of ports, harmors, moles, breakwaters and lighthouses, and in the art of navigation by artificial power for the purposes of commerce, and the construction and adaptation of machinery, and in the drainage of cities and towns " *(2)*. This early definition of engineering is primarily concerned with construction not design, and with art rather than science. It is because of this latter point, in addition to the very ambitious nature of the defininition, that it became necessary to divide the field of engineering. The mechanical engineer came to be identified with "the construction and adaptation of machinery," the naval engineer with the "art of navigation by artificial power," and the sanitary engineer with "the drainage of cities and towns." Once under way, the subdivision of engineering increased as the demands of industry became more specialized.

The chemical engineer did not appear until about 70 years ago. The construction and selection of equipment for chemical plants was once largely in the hands of mechanical engineers who knew some chemistry or chemists who knew some mechanical engineering. As the process industry grew, the problems became more complex and peculiar, until it finally appeared that there was a need for a distinct branch of engineering to which such problems might be assigned. "In response . . . we have the development of chemical engineering, not as a composite of chemistry and mechanical or civil engineering, but as a separate branch of engineering, the basis of which is those unit operations . . . which, in their proper sequence and coordination, constitute a chemical process as conducted on the industrial scale" *(2)*. The unit operations really became the defining concept for chemical engineering and allowed the chemical engineer to use a systematic approach to the solution of complex industrial problems. The distinction between industrial chemistry and chemical engineering, in fact, is that the former is concerned with individual processes as entities in themselves, whereas the latter focuses attention on the unit operations common to many processes and on the proper grouping of these unit operations to produce a desired product.

In 1915 Arthur D. Little formally defined the unit operations of chemical engineering, and in 1923 the text by Walker, Lewis and McAdams entitled "Principles of Chemical Engineering" appeared. During the period from 1923 until 1960, this work and its two revisions served as models for subsequent chemical engineering text books *(1-6)*.

In the mid 1950's, it became apparent to some chemical engineers that, because of the economic demands, there had to be a departure form the traditional approach of multiple scale-up in the design of chemical plants. Some chemical engineering teachers were finding that "too often the fundamental concepts and laws have been slighted in the haste to teach application. The result has frequently been that a practicing engineer or graduate student, faced with problems for which his empirical training has not prepared him, has first had to learn the fundamental principles of the transport processes before he could proceed" *(3)*. The transport porcesses underlie the unit operations of chemical engineering, for "the unit operations themselves, although carried out in a wide variety of equipment types that apparently have nothing in common are, from the point of view of the theory involved, applications of a very few fundamental laws. In fact, these laws are the fundamental laws of physical sciences that underlie practically all technology . . . [They] are: first, the conservation of matter and energy; second, the relations pertaining to the equilibria of physical and chemical processes; and third, the laws governing the rate of change in systems not in equilibrium" *(2)*. The recent innovation, then, is not in recognizing that the unit operations are based on a few fundamental laws but in teaching these laws (particularly those that describe process rates) in a separate course which "should rank along with thermodynamics, mechanics, and electromagnetism as one of the key engineering sciences" (4).

What Is Meant by Transport Phenomena?

Courses in transport phenomena consist of the study of the transfer of momentum, energy, and mass. In order to transfer any of these quantities, a non-equibibrium situation must exist. For example, if internal energy is to be transferred, there must be a temperature difference. The temperature difference is the driving force and the quantity which is moved by this temperature difference is called the heat flux. From the observational point of view, a linear relation is postulated between the flux and the driving force in which the coefficient of proportionality is a property of the substance in which the energy transfer is occuring. In the case of heat transfer, the coefficient of proportionality is the thermal conductivity, k.

The observational or phenomenological approach is not concerned with the mechanism for the transfer of this energy. For the mechanism, the kinetic theory of molecular motion must be considered. From the simplified theory, the kinetic energy of a spherical molecule is directly related to the temperature

$$\frac{1}{2}mu^2 = \frac{3}{2}\mathbf{K}T \tag{1}$$

The tendency toward equilibrium of temperature then is a result of the transport of molecules with high kinetic energy to regions where the molecules have low kinetic energies and vice-versa. But while a molecule, by its change of location, is transferring kinetic energy, it must at the same time transfer mass, m, and momentum, mu. On a microscopic level, the mechanism for the transport of mass, momentum, and energy is fundamentally molecular diffusion.

From the observational point of view, the following laws for the transfer of momentum, energy, and mass under the condition of constant density and heat capacity define the transport properties of viscosity, μ, thermal conductivity, k, and mass diffusivity, D_{AB}.

$$\tau_{yx} = -\left(\frac{\mu}{\rho}\right)\frac{d(\rho v_x)}{dy} \tag{2}$$

Newton's Law of Viscosity

$$q_y = -\left(\frac{k}{\rho C_p}\right)\frac{d(\rho C_p T)}{dy} \tag{3}$$

Fourier's Law of Heat Conduction

$$j_{A_y} = -D_{AB}\frac{d\rho A}{dy} \tag{4}$$

Fick's First Law of Diffusion

From the simplified kinetic theory, the expressions for transport properties are:

$$\mu = \frac{2}{3\pi^{3/2}}\frac{(m\mathbf{K}T)^{1/2}}{d^2} \tag{5}$$

$$k = \frac{1}{d^2}\left(\frac{\mathbf{K}^3 T}{\pi^3 m}\right)^{1/2} \tag{6}$$

$$D_{AB} = \frac{2}{3}\left(\frac{\mathbf{K}^3}{\pi^3 m_A}\right)^{1/2}\frac{T^{3/2}}{p d_A{}^2} \tag{7}$$

where d is the molecular diameter. Experiment agrees with the temperature and pressure dependence of the transport properties as shown in Equations 5-7 and therefore verifies the molecular transport mechanism. This is of engineering value in that for moderate ranges, the temperature and pressure dependence of the transport properties can be predicted.

What other information of engineering value can be obtained from these rate equations? The dimensions of $\mu/\alpha = \nu$, D_{AB}, and $k/\rho C_p = \alpha$ are (length) ^{2}/time.

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By analogy with the mass diffusivity, D_{AB}, ν is called the momentum diffusivity and α is called the thermal diffusivity. Since these three quantities have the same units, dimensionless numbers can be formed from the ratio of any two of them. For example, the Prandtl number is given as

$$\text{Prandtl number} = \frac{\mu C_p}{k} = \frac{\nu}{\alpha} = \frac{\text{momentum diffusivity}}{\text{thermal diffusivity}}$$

and can be interpreted as a measure of the capacity of a fluid to diffuse momentum as compared with its capacity to diffuse heat. The Prandtl numbers for air, water and mercury are approximately 1.0, 5.0 and 0.01, respectively.

The next question is how do the transport properties fit into the conservation statements for mass, momentum, and energy? The conservation statements must be applicable to all substances and, furthermore, they must be independent of any reference frame. The transport properties serve as parameters in the conservation statements and permit a distinction to be made when the same conservation statement is applied to two different substances. For the latter requirement the conservation statements must be expressed by a mathematics which is also independent of coordinate system. The calculus of vectors and tensors transforms the basic laws from reference frame to reference frame with no change in the fundamental law.

Consider now the application of the three conservation statements to a single one-dimensional, time-dependent system:

$$\frac{\delta}{\delta y}\left(\alpha \frac{\delta T}{\delta y}\right) = \frac{\delta T}{\delta t} \qquad (8)$$

Conservation of Energy

$$\frac{\delta}{\delta y}\left(\nu \frac{\delta(\rho v_x)}{\delta y}\right) = \frac{\delta(\rho v_x)}{\delta t} \qquad (9)$$

Conservation of Momentum

$$\frac{\delta}{\delta y}\left(D_{AB} \frac{\delta \rho_A}{\delta y}\right) = \frac{\delta \rho_A}{\delta t} \qquad (10)$$

Conservation of Chemical Species

These equations are all of the same form. Consequently, under certain conditions, there is an analogy among the conservation statements as well as an analogy among the mechanisms for transfer. This analogy can be very useful in the solution of certain engineering problems. For example, the transfer of momentum in a wire-coating operation where the coating is applied by pulling the wire through a die is exactly analogous to the flux of heat in the insulation on a steam pipe. Information about the first system can be inferred by a study of the second, since the systems are analogous.

Methodology of Transport Phenomena

In order to justify the statement made earlier that a course in the transport process should be ranked along with thermodynamics, let us compare the derivations of the Bernoulli equation.

In most unit operations texts, the derivation is limited to a steady flow system consisting of a pump which takes an incompressible liquid at one elevation and raises it to a second elevation at mass flow rate w. A pound of liquid at the entrance has a potential energy gh_1, a kinetic energy $\langle v_1 \rangle^2/\beta$, where $\beta = 1$ for laminar flow and $\beta = 2$ for turbulent flow, and a pressure volume work, p_1/ρ, which the fluid needs to enter the system. The pump must raise the liquid and adds work W/w to the liquid. At the exit, the fluid has a potential energy gh_2, a kinetic energy $\langle v_2 \rangle^2/\beta$ and has a pressure volume work of p_2/ρ. The Bernoulli equation is simply written then as

$$gh_1 + \frac{\langle v_1 \rangle^2}{\beta} + \frac{p_1}{\rho} + \frac{W}{w} - E_v = gh_2 + \frac{\langle v_2 \rangle^2}{\beta} + \frac{p_2}{\rho} \qquad (11)$$

where E_v is a correction factor necessary for the equality.

In the study of transport phenomena, the starting point in the derivation is the local conservation statement for momentum or Newton's second law of motion for a fluid.

$$\rho \frac{D\underline{v}}{Dt} = \sum_i \underline{F}_i = -\nabla \cdot \underline{\underline{\tau}} - \nabla p + \rho g \qquad (12)$$

This statement says that on a unit volume basis, the mass times acceleration of a fluid particle is equal to the sum of the viscous forces, the pressure forces and the gravitational forces. Since mechanical energy is the product of a force and a displacement, this equation can be multiplied by the fluid velocity to obtain the local time rate of change of mechanical energy.

$$\rho \frac{D}{Dt}\left(\frac{1}{2}v^2\right) = -\left[\nabla \cdot p\underline{v} + \nabla \underline{\underline{\tau}} \cdot v + \rho\, v \cdot g\right] + p\nabla \cdot \underline{v} + \underline{\underline{\tau}} : \nabla \underline{v} \qquad (13)$$

The left hand term represents the accumulation of kinetic energy and the term in brackets on the right side represents products of forces and velocities and hence the rate of mechanical work done by pressure, viscous and gravity forces. In order to explain the last two terms, the equation of thermal energy must be examined.

$$\rho \frac{DU}{Dt} = -\nabla \cdot q - (p\nabla \cdot \underline{v} + \underline{\underline{\tau}} : \nabla \underline{v}) \qquad (14)$$

The term of the left represents the accumulation of internal energy and the first term on the right represents heat conduction. The last two terms in the internal energy equation also appear in the mechanical energy equation but with opposite signs. The term $p\,\nabla \cdot \underline{v}$ represents compressibility effects and may be either positive or negative. The term $(-\underline{\underline{\tau}} : \nabla \underline{v})$, for Newtonian fluids, is always positive which means that this term always causes a decrease in mechanical energy and an increase in thermal energy. This term then represents the irreversible degradation of mechanical energy into thermal energy.

In order to obtain the Bernoulli equation, the mechanical energy equation is integrated over an arbitrary volume consisting of three types of surfaces: inlet and exit surfaces, fixed surfaces and moving surfaces. The moving surfaces provide a means of adding or removing work from the system, the fixed surfaces represent the confines of the system and the inlet and exit surfaces allow mass to enter and leave the system. After integration, the result is dependent only upon the inlet and outlet conditions and for an unsteady state system is

$$\frac{d}{dt}(K_{tot} + \Phi_{tot} + A_{tot}) = -\Delta\left[\left(\frac{1}{2}\frac{\langle v^3\rangle}{v} + \frac{\Phi}{w} + G\right) w\right] + W - E_v \qquad (15)$$

where K_{tot}, Φ_{tot} and A_{tot}, are respectively, the total kinetic energy, potential energy and thermodynamic work content; W is the rate at which the surroundings perform mechanical work on the system; and E_v is the "friction loss." This term is given by

$$E_v = -\int_V (\underline{\underline{\tau}} : \nabla \underline{v})\, dV \qquad (16)$$

and represents the irreversible conversion of mechanical energy to thermal energy.

For a steady-state liquid system, Equation 15 becomes

$$gh_1 + \frac{1}{2}\frac{\langle v_1^3\rangle}{\langle v_1\rangle} + \frac{p_1}{\rho} + \frac{W}{w} - \frac{E_v}{w} = gh_2 + \frac{1}{2}\frac{\langle v_2^3\rangle}{\langle v_2\rangle} + \frac{p_2}{\rho} \qquad (17)$$

A comparison of this equation with Equation 11 indicates that

$$\beta = \frac{2\langle v_1\rangle^3}{\langle v_1^3\rangle} \qquad (18)$$

This derivation proceeds from a fundamental law to a general equation of engineering utility by logical and reasonable steps. The scope of the equation, its relation to fundamentals, and the lack of balancing "fudge factors" illustrates to the student the scientific basis of engineering and gives him confidence in the application of this equation and others of similar origin.

ACKNOWLEDGEMENT

Permission of the McGraw-Hill Book Company to quote and paraphrase passages from the introduction and first chapter of Badger and McCabe's "Elements of Chemical Engineering" and from the preface of Bennett and Myers' "Momentum, Heat, and Mass Transfer"; and of John Wiley & Sons to quote a passage from the preface of Bird, Stewart, and Lightfoot's "Transport Phenomena" is gratefully acknowledged.

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NOMENCLATURE

Dimensions are given in terms of mass **(M)**, length **(L)**, time **t**, and temperature **(T.)** Vectors have a single underline and tensors have a double underline. Force is not considered a fundamental dimension, but is assigned instead the dimensions of mass-acceleration instead the dimensions of mass-acceleration product **(ML/t²)**. This "absolute" system of dimensions is commonly used by physicists, much less commonly by engineers.

- A = thermodynamic work function, $\mathbf{ML^2/t^2}$.
- C_p = heat capacity at constant pressure per unit mass, $\mathbf{L^2/t^2T}$.
- D_{AB} = binary diffusivity for system of species A-B, $\mathbf{L^2t}$.
- d = molecular diameter, **L**.
- E_v = total rate of viscous dissipation of mechanical energy, $\mathbf{ML^2/t^3}$.
- G = Gibbs free-energy per unit mass, $\mathbf{ML^2/t^2}$.
- g = gravitational acceleration, $\mathbf{L/t^2}$.
- h_1, h_2 = elevation, **L**.
- j_{A_y} = mass flux of species A in the y-direction, $\mathbf{M/tL^2}$.
- K = kinetic energy, $\mathbf{ML^2/t^2}$.
- $\mathbf{K}$ = Boltzmann constant, $\mathbf{ML^2/t^2T}$.
- k = thermal conductivity, $\mathbf{ML/t^3T}$.
- m = mass of molecule, **M**.
- p = fluid pressure, $\mathbf{M/Lt^2}$.
- q_y = y-component of the heat flux vector, $\mathbf{M/t^3}$.
- T = absolute temperature, **T**.
- t = time, **t**.
- u = mean molecular speed, **L/t**.
- $\underline{v}$ = mass average velocity, **L/t**.
- $\langle \underline{v} \rangle$ = space average value of velocity, **L/t**.
- W = rate of doing work on system, $\mathbf{ML^2/t^3}$.
- w = mass flow rate, **M/t**.
- α = thermal diffusivity, $\mathbf{L^2/t}$.
- β = velocity function (defined in Equation 18), dimensionless.
- μ = viscosity, **M/Lt**.
- ν = kinematic viscosity, $\mathbf{L^2/t}$.
- ρ = density, $\mathbf{M/L^3}$.
- $\underline{\underline{\tau}}$ = shear stress tensor, $\mathbf{M/t^2L}$.
- Φ = potential energy, $\mathbf{ML^2/t^2}$.

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averted the following spring. Jay's parents insisted that he bring his son home for a family inspection. Jay and Jayshee realized that a six-month old child from antiseptic America would have an extremely difficult time in India, possibly even dying of dysentery. They finally persuaded Jay's family to come to Wyoming instead.

Jay has moved steadily ahead with Sinclair. Shortly after his son was born, they asked him to move out to the company town of Sinclair so that he would be more readily available whenever technical difficulties arose. For $50 per month, he rents a two-bedroom, one-floor company-owned house. At his present salary rate of $700 per month, he has been able to live well and still help his family. Until his brother completed college last summer, he contributed $100 per month towards his expenses. Financial help to his family in India has been accomplished with the aid of a favorable exchange rate which converts one dollar into four rupees.

This true story points to one way that the continued shortage of U.S. chemical engineers is being met. Not an isolated example by any means, Jay Saraiya is only one of sixteen non-citizen chemical engineers graduated and placed in permanent positions in the U.S. by one educational institution, Montana State University, in the past six years. The employers of these men include some of the U.S.'s leading companies at some of their most attractive locations. Just as nature abhors a vacuum, so good jobs are going to be filled whether or not American boys want them.