

THE BASIC CONCEPTS IN TRANSPORT PHENOMENA

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The transport phenomena can be described at three scales: the molecular, the microscopic (continuum), and the macroscopic. At each scale the conservation laws for mass, momentum, angular momentum, and energy play a key role. Also, at each scale empiricisms have to be introduced to complete the description of the systems: an intermolecular potential expression at the molecular scale, the flux expressions (constitutive equations) at the microscopic scale, and the transfer coefficient correlations at the macroscopic scale. The three scales are intimately connected, with the results for each scale contributing to the understand-

ing of the next larger scale.

At the microscopic scale, some information about the constitutive equations can be obtained from the thermodynamics of irreversible processes. This approach is particularly important in understanding multicomponent diffusion and the "cross-effects" in energy and mass transport.

For the most part, the notation and sign conventions here will be those used in references 1, 2, 3, 4, and 5, hereinafter referred to as TrPh, DPL1, DPL2, STTP, and MTGL, respectively.

The Equations of Change

The basic equations of transport phenomena are the equations of change for the conserved quantities as shown in Table 1:

TABLE 1

The Equations of Change Based on Conservation Laws

$$(A) \frac{\partial}{\partial t} \rho_{\alpha} = -(\nabla \cdot \rho_{\alpha} \mathbf{v}) - (\nabla \cdot \mathbf{j}_{\alpha}) + r_{\alpha} \quad \alpha = 1, 2, 3, \dots$$

$$(B) \frac{\partial}{\partial t} \rho \mathbf{v} = -[\nabla \cdot \rho \mathbf{v} \mathbf{v}] - [\nabla \cdot \boldsymbol{\pi}] + \sum_{\alpha} \rho_{\alpha} \mathbf{g}_{\alpha}$$

$$(C) \frac{\partial}{\partial t} \rho([\mathbf{r} \times \mathbf{v}] + \hat{\mathbf{L}}) = -[\nabla \cdot \rho \mathbf{v}([\mathbf{r} \times \mathbf{v}] + \hat{\mathbf{L}})] - [\nabla \cdot \boldsymbol{\lambda}] - [\nabla \cdot \{\mathbf{r} \times \boldsymbol{\pi}^T\}^T] + \sum_{\alpha} [\mathbf{r} \times \rho_{\alpha} \mathbf{g}_{\alpha}] + \sum_{\alpha} \rho_{\alpha} \mathbf{t}_{\alpha}$$

$$(D) \frac{\partial}{\partial t} \rho\left(\frac{1}{2} v^2 + \hat{U}\right) = -(\nabla \cdot \rho \mathbf{v}[\frac{1}{2} v^2 + \hat{U}]) - (\nabla \cdot \mathbf{q}) - (\nabla \cdot [\boldsymbol{\pi} \cdot \mathbf{v}]) - \sum_{\alpha} ((\rho_{\alpha} \mathbf{v} + \mathbf{j}_{\alpha}) \cdot \mathbf{g}_{\alpha})$$

- ρ_{α} = mass concentration of species α
- ρ = density of fluid mixture
- \mathbf{v} = mass-average velocity
- \mathbf{j}_{α} = mass flux of α with respect to \mathbf{v}
- r_{α} = mass rate of production of α by chemical reaction
- $\boldsymbol{\pi}$ = (total) stress tensor
- \mathbf{g}_{α} = external force per unit mass acting on α
- \mathbf{r} = position vector
- $\hat{\mathbf{L}}$ = internal angular momentum per unit mass
- $\boldsymbol{\lambda}$ = couple stress tensor
- \mathbf{t}_{α} = external torque per unit mass acting on α
- \hat{U} = internal energy per unit mass
- \mathbf{q} = heat flux vector

(A) Conservation of mass for each species

TrPh Eq. 18.3-4; MTGL 11.1-1

(B) Conservation of momentum

TrPh Eq. 18.3-2; MTGL 11.1-3; DPL1, 1.1-8

(C) Conservation of angular momentum

MTGL, p. 831, Problem 6

(D) Conservation of energy

TrPh Eq. 18.3-6; MTGL 11.1-4; DPL1, 1.1-12

These equations can be obtained by writing conservation statements over

- (a) a region fixed in space through which the fluid is moving (DPL1, Chapter 1)
- (b) a material element of fluid (*i.e.*, a "dyed" blob of fluid) moving through space.^[6]

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The equations of change have been written in Table 1 in terms of the total stress tensor π which is conventionally split into two parts: $\pi = p\delta + \tau$ (where δ is the unit tensor); p is the "thermodynamic pressure"; and τ is the "(extra) stress tensor" which vanishes in the absence of velocity gradients. No assumption has been made here that the stress tensor be symmetric. Equations (A) through (D) have to be supplemented with the thermal equation of state $p = p(\rho, T, \omega_\alpha)$ and the caloric equation of state $\hat{U} = \hat{U}(\rho, T, \omega_\alpha)$, where ω_α stands for the mass fractions of all but one of the chemical species α in the mixture.

By adding the equations in Eq. (A) over all species, one gets the equation of continuity for the fluid mixture [TrPh, Eq. 3.1-4]. By forming the cross product of the position vector \mathbf{r} with the equation of motion, Eq. (B), one obtains Eq. (E); when the latter is subtracted from Eq. (C) (the equation of conservation of total angular momentum), the equation for internal angular momentum, Eq. (F), is obtained.^[7] Similarly, by forming the dot product of the fluid velocity \mathbf{v} with the equation of motion, Eq. (B), one obtains Eq. (G), the equation of change for the kinetic energy; when the latter is subtracted from Eq. (D), the equation of change for the internal energy, Eq. (H), is obtained. These various derived equations are tabulated in Table 2.

As pointed out in TrPh (page 314), the term $(\pi^T : \nabla \mathbf{v})$ appears in Eq. (G) with a plus sign and in Eq. (H) with a minus sign; it describes the interconversion of mechanical and thermal energy. Similarly, the term $[\epsilon : \pi^T]$ appears with a plus sign in Eq. (E) and with a minus sign in Eq. (F), thus

describing the interconversion of external and internal angular momentum. In fluid dynamics textbooks, it is usually assumed that the stress tensor is symmetric ($\pi = \pi^T$), so that the external and internal angular momentum are conserved separately, since $[\epsilon : \pi^T]$ is then identically equal to zero. The so-called "proofs" that the stress tensor is symmetric (such as in Problem 3.L in TrPh, pages 114-115) tacitly assume that there is no interconversion of external and internal angular momentum, and that the external angular momentum is conserved in the fluid. The kinetic theory of dilute monatomic gases yields a symmetric stress tensor, as does the kinetic theory for dilute solutions of flexible and rodlike polymers. So far there is no experimental evidence that a nonsymmetric stress tensor is needed.

When all species are subjected to the same external forces (so that all \mathbf{g}_α equal \mathbf{g}), and when it is assumed that the stress tensor is symmetric, Eqs. (B) and (D) simplify to Eqs. 3.2-8 and 10.1-9 in TrPh. If all species are subjected to the same external torques so that all \mathbf{t}_α are equal to \mathbf{t} , a similar simplification occurs in Eq. (C).

We emphasize that the equations in Table 1 are to be considered the fundamental equations at the microscopic scale, whereas those in Table 2 are derived from those in Table 1. As explained in TrPh, the equations of change may be put into many alternative forms; for example, they may equally well be written in terms of the "substantial" (or "material") derivative operator D/Dt (TrPh Eq. 3.0-2). The energy equation has always been a special problem because it can be written in so many different ways (see TrPh, pages 322-323, 582, for useful tabular summaries).

TABLE 2

Equations of Change for Nonconserved Quantities

$$\begin{aligned} \text{(E)} \quad \frac{\partial}{\partial t} \rho[\mathbf{r} \times \mathbf{v}] &= -[\nabla \cdot \rho \mathbf{v}[\mathbf{r} \times \mathbf{v}]] - \left[\nabla \cdot \{ \mathbf{r} \times \pi^T \}^T \right] \\ &\quad + \sum_{\alpha} [\mathbf{r} \times \rho_{\alpha} \mathbf{g}_{\alpha}] + [\epsilon : \pi^T] \\ \text{(F)} \quad \frac{\partial}{\partial t} \rho \hat{\mathbf{L}} &= -[\nabla \cdot \rho \mathbf{v} \hat{\mathbf{L}}] - [\nabla \cdot \boldsymbol{\lambda}] - \sum_{\alpha} \rho_{\alpha} \mathbf{t}_{\alpha} - [\epsilon : \pi^T] \\ \text{(G)} \quad \frac{\partial}{\partial t} \rho \left(\frac{1}{2} v^2 \right) &= -(\nabla \cdot \rho \mathbf{v} \left(\frac{1}{2} v^2 \right)) - (\nabla \cdot [\pi \cdot \mathbf{v}]) \\ &\quad + (\pi^T : \nabla \mathbf{v}) - \sum_{\alpha} (\mathbf{v} \cdot \rho_{\alpha} \mathbf{g}_{\alpha}) \\ \text{(H)} \quad \frac{\partial}{\partial t} \rho \hat{U} &= -(\nabla \cdot \rho \mathbf{v} \hat{U}) - (\nabla \cdot \mathbf{q}) - (\pi^T : \nabla \mathbf{v}) + \sum_{\alpha} (\mathbf{v} \cdot \rho_{\alpha} \mathbf{g}_{\alpha}) \end{aligned}$$

NOTE: On page 831 of MTGL, Eq. (E) is given for a symmetric stress tensor, but $[\mathbf{r} \times \mathbf{p}]$ should be replaced by $[\mathbf{r} \times \mathbf{p}]^T$.

The Flux Expressions
(Also Called "Constitutive Equations")

In order to get solutions to the equations of change, we need to have expressions for the fluxes \mathbf{j}_α , τ , and \mathbf{q} . The standard expressions for these are the "linear laws," in which the fluxes are proportional to gradients, as shown in Table 3.

Equation (I) for the mass-flux vector is shown only for the binary system A-B, and the thermal diffusion, pressure diffusion, and forced diffusion terms have been omitted (see Eq. (Z) for the complete expression). Equation (K) shows the conductive and diffusive contributions to the heat-flux vector, but the diffusion-thermo (Dufour) effect has been omitted. In Eq. (J) we have included the two viscosity coefficients μ and κ , although the latter is omitted in most fluid dynamics texts since it is zero for mona-

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tomic gases (we know this from kinetic theory—see MTGL, Chapter 7) and since for liquids incompressibility is often assumed, so that $\text{div } \mathbf{v} = 0$ and the term containing κ is zero anyway.

The flux expressions do not have the exalted status accorded to the conservation laws in Table 1. They are empirical statements, proposed as the simplest possible linear forms; they also emerge from the kinetic theory of gases when one works to the lowest orders in the gradients of concentration, velocity, and temperature (see MTGL, Chapter 7). It is well known that Eq. (J) does not describe the mechanical responses of polymeric liquids (see DPL1, Chapter 2); various nonlinear expressions, and indeed time-dependent expressions, arise from the kinetic theory of polymeric liquids (see DPL2, Chapters 13-16, 19-20). Furthermore, for some complex materials it is found that the thermal conductivity and diffusivity are tensors rather than scalars, so that the fluxes and forces are not collinear. In order to use Eqs. (I,J,K), one needs numerical values for the diffusivity, viscosity, and thermal conductivity; these are preferably obtained from experiments, but in the absence of experimental values kinetic theory results can be used.

Once the flux expressions have been substituted into the equations of change, we then have a set of equations which, when solved, will give the concentration, velocity, and temperature distributions as functions of time. There are many ways in which these important equations can be used:

- Analytical solutions can be found (for simple, idealized problems, in which transport properties are assumed to be constant)^[8-10]
- Approximate solutions can be found with perturbation theories^[11]
- Numerical solutions can be found^[12-15]
- Boundary-layer solutions can be found^[16]
- Time smoothing can yield the turbulent transport equations^[17-19]
- Volume smoothing leads to the equations for porous media^[20]
- Flows with chemical reactions can be analyzed^[21]
- Approximate solutions can be used for lubrication flows^[11]
- Mixing and chaos can be studied^[22]
- Particulate motion, suspensions, and emulsions can be described^[12]
- Interfacial transport equations can be established^[23]
- Polymer fluid dynamics and transport phenomena can be studied^[DPL1]

This partial list of topics gives some idea as to the

breadth of the field of transport phenomena and the extremely great importance of the equations of change. All these topics are active research fields in which chemical engineers are obligated to play an important role.

The Macroscopic Balances

The statements of the laws of conservation of mass, momentum, angular momentum, and energy can be written down for a typical macroscopic engineering system, with one entry port ("1") and one exit port ("2"); heat can be added to the system at the rate Q , and the system can do work on the surroundings at a rate W_m by means of moving parts (such as pistons or rotatory devices). These conservation statements are given in Eqs. (L-O) in Table 4. It is assumed there that the fluid velocities at the inlet and outlet planes are parallel to the directions of flow \mathbf{n}_1 and \mathbf{n}_2 . It is also assumed that the extra stress tensor does not contribute to the work done on the system at the entry and exit planes. It is further assumed that there are no mass-transfer surfaces in the macroscopic system; such surfaces are considered in TrPh, Chapter 22, and in STTP, Chapter 1.

Of course, Eqs. (L-O) can also be obtained by integrating the equations of change in Eqs. (A,B,E,D) over the entire volume of the flow system; in doing this we must take into account the fact that the shape of the volume is changing with time because of the moving parts.^[24,25] The macroscopic mechanical energy balance (also called the engineering Bernoulli equation) cannot be written down directly since there is no conservation law for mechanical energy. It can be derived by integrating Eq. (G) over the macroscopic system as outlined in Table 5. For the sake of simplicity, we take the external forces g_α to be all the same ($g = -\hat{\phi}$, where $\hat{\phi}$ is the potential

TABLE 3
The Flux Equations (or "Constitutive Equations")

$$(I) \quad \mathbf{j}_A = -\rho \mathcal{D}_{AB} \nabla \omega_A \quad (\text{binary system of A and B})$$

$$(J) \quad \boldsymbol{\tau} = -\mu (\nabla \mathbf{v} + (\nabla \mathbf{v})^T) + \left(\frac{2}{3}\mu - \kappa\right) (\nabla \cdot \mathbf{v}) \boldsymbol{\delta}$$

$$(K) \quad \mathbf{q} = -k \nabla T + \sum_{\alpha} (\bar{H}_{\alpha} / M_{\alpha}) \mathbf{j}_{\alpha}$$

$$\mathcal{D}_{AB} = \text{binary diffusivity}$$

$$\omega_A = \rho_A / \rho = \text{mass fraction of } \alpha$$

$$\mu = \text{viscosity}$$

$$\kappa = \text{dilatational viscosity}$$

$$\boldsymbol{\delta} = \text{unit tensor (with components } \delta_{ij})$$

$$k = \text{thermal conductivity}$$

$$\bar{H}_{\alpha} = \text{partial molar enthalpy of } \alpha$$

TABLE 4
Macroscopic Balances

Assumptions:
no mass-transfer surfaces;
all species subject to same external forces and external torques;
 τ contributions neglected at "1" and "2"

(L) $\frac{d}{dt} m_{tot} = w_{\alpha 1} - w_{\alpha 2} + r_{\alpha, tot}$

(M) $\frac{d}{dt} \mathbf{P}_{tot} = \left(\frac{\langle v^2 \rangle_1}{\langle v \rangle_1} w_1 + p_1 S_1 \right) \mathbf{n}_1 - \left(\frac{\langle v^2 \rangle_2}{\langle v \rangle_2} w_2 + p_2 S_2 \right) \mathbf{n}_2 - \mathbf{F} + m_{tot} \mathbf{g}$

(N) $\frac{d}{dt} \mathbf{M}_{tot} = \left(\frac{\langle v^2 \rangle_1}{\langle v \rangle_1} w_1 + p_1 S_1 \right) [\mathbf{r}_1 \times \mathbf{n}_1] - \left(\frac{\langle v^2 \rangle_2}{\langle v \rangle_2} w_2 + p_2 S_2 \right) [\mathbf{r}_2 \times \mathbf{n}_2] - \mathbf{T} + [\mathbf{r}_c \times m_{tot} \mathbf{g}]$

(O) $\frac{d}{dt} (K_{tot} + \Phi_{tot} + U_{tot}) = \left(\frac{1}{2} \frac{\langle v^3 \rangle_1}{\langle v \rangle_1} + \hat{H}_1 + \hat{\Phi}_1 \right) w_1 - \left(\frac{1}{2} \frac{\langle v^3 \rangle_2}{\langle v \rangle_2} + \hat{H}_2 + \hat{\Phi}_2 \right) w_2 + Q - W_m$

(P) $\frac{d}{dt} (K_{tot} + \Phi_{tot}) = \left(\frac{1}{2} \frac{\langle v^3 \rangle_1}{\langle v \rangle_1} + \frac{p_1}{\rho_1} + \hat{\Phi}_1 \right) w_1 - \left(\frac{1}{2} \frac{\langle v^3 \rangle_2}{\langle v \rangle_2} + \frac{p_2}{\rho_2} + \hat{\Phi}_2 \right) w_2 - E_c - E_v - W_m$

(Q) $\frac{d}{dt} U_{tot} = \hat{U}_1 w_1 - \hat{U}_2 w_2 + Q + E_c + E_v$

m_{tot} = total mass in flow system	w_1, w_2 = mass rate of flow at entry and exit
\mathbf{P}_{tot} = total momentum in flow system	p_1, p_2 = thermodynamic pressure at entry and exit
\mathbf{M}_{tot} = total angular momentum in flow system	S_1, S_2 = cross-sectional areas of entry and exit conduits
K_{tot} = total kinetic energy in flow system	Q = heat added to system through container walls
Φ_{tot} = total potential energy in flow system	W_m = work done on surroundings
U_{tot} = total internal energy in flow system	E_c, E_v = quantities defined in Eq. (S)
$\langle \rangle$ = averages over tube cross section at entry and exit	$\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_c$ = location of the centers of the entry and exit planes and the center of mass of the fluid in the system
$\mathbf{n}_1, \mathbf{n}_2$ = unit vector in flow direction at entry and exit	
$w_{\alpha 1}, w_{\alpha 2}$ = mass rate of flow of α at entry and exit	

energy per unit mass, which is considered to be independent of time). In doing the integration, we need to use the Gauss divergence theorem (TrPh, A.5-1) and the 3-dimensional Leibniz formula (TrPh, A.5-5).

This leads to Eq. (R), in which S_1 and S_2 are the cross-sectional areas at "1" and "2", S_f stands for the fixed surfaces of the system, and S_m stands for the moving surfaces, by means of which work can be done on the surroundings. Since the velocity \mathbf{v} of the fluid equals the surface velocity \mathbf{v}_s on the fixed and moving surfaces, these surface integrals contribute nothing to the first term on the right side. Also, since the fluid velocity \mathbf{v} is zero on all fixed surfaces, the fixed-surface contribution to the second term on the right side is zero; the integral over the moving surfaces gives the work transmitted via these surfaces, W_m , (sometimes called the "shaft work"). The integrals of the extra

TABLE 5
Intermediate Steps in Deriving the Macroscopic Mechanical Energy Balance

(R) $\frac{d}{dt} \int_{V(t)} \left(\frac{1}{2} \rho v^2 + \rho \hat{\Phi} \right) dV = - \int_{S=S_1+S_2+S_f+S_m(t)} \left(\mathbf{n} \cdot \left(\frac{1}{2} \rho v^2 + \rho \hat{\Phi} \right) (\mathbf{v} - \mathbf{v}_s) \right) dS - \int_{S=S_1+S_2+S_f+S_m(t)} \left(\mathbf{n} \cdot [(\mathbf{p}\delta + \boldsymbol{\tau}) \cdot \mathbf{v}] \right) dS - E_c - E_v$

(S) in which $E_c = - \int_{V(t)} p(\nabla \cdot \mathbf{v}) dV$ and $E_v = - \int_{V(t)} (\boldsymbol{\tau} : \nabla \mathbf{v}) dV$

(T) $\frac{d}{dt} (K_{tot} + \Phi_{tot}) = \frac{1}{2} \rho_1 \langle v^3 \rangle_1 S_1 - \frac{1}{2} \rho_2 \langle v^3 \rangle_2 S_2 + \rho_1 \langle v \rangle_1 \hat{\Phi}_1 S_1 - \rho_2 \langle v \rangle_2 \hat{\Phi}_2 S_2 + p_1 \langle v \rangle_1 S_1 - p_2 \langle v \rangle_2 S_2 - E_c - E_v - W_m$

$V(t)$ = volume of engineering flow system	$\hat{\Phi}$ = potential energy per unit mass
S_f = fixed surfaces of flow system	\mathbf{n} = outwardly directed unit normal on surface S
S_m = moving surfaces of flow system	$\boldsymbol{\tau}$ = (extra) stress tensor
\mathbf{v}_s = velocity of surface (equals zero on S_1, S_2, S_f)	

stress tensor τ over S_1 and S_2 are presumed small and have been omitted here; they are identically zero for laminar, Newtonian flow when the fluid velocity vectors are parallel to the walls of the entry and exit tubes. The integrals labeled E_c and E_v are not evaluated; the latter gives the rate at which mechanical energy is degraded into thermal energy. From Eqs. (R) and (S) we get Eq. (T), which is easily rearranged to give the mechanical energy balance in Eq. (P); the latter includes the two special cases given in TrPh Eqs. 15.2-1 and 2. Equation (P) is particularly convenient for incompressible fluids for which E_c is exactly zero. Equations (L)-(P) are easily generalized to systems with multiple inlet and outlet ports.

NOTE: In some textbooks it is stated that the mechanical energy balance (Eq. P) is an "alternative form" of the total energy balance (Eq. O). Such a comment seems inappropriate since Eq. (P) comes from the equation of conservation of momentum, whereas Eq. (O) has its origins in the equation of conservation of energy. In other textbooks some thermodynamic "incantations" are offered to get from Eq. (O) to Eq. (P). The arguments must essentially involve Eq. (Q), obtained by subtracting Eq. (P) from Eq. (O); of course, Eq. (Q) can also be obtained from integrating Eq. (H)—which is a consequence of the equations of energy and motion—over the macroscopic flow system. Certainly Eq. (Q) cannot be written down directly, since there is no conservation law for the internal energy in an open system with dissipative processes. Furthermore, the thermodynamic arguments cannot yield the expressions in Eq. (S), showing how E_c and E_v are related to the velocities and stresses in the system. Comments from textbook authors (and others) on this point would be welcome; before commenting, however, it would be advisable to read Whitaker's historical essay.^[6, pp.90-93]

The Transfer Coefficients

Although the macroscopic balances can be used, as shown in Table 4, it is often useful to estimate some of the terms in them by using dimensionless correlations:

- F** can be estimated by using friction factor correlations
- E_v** can be estimated by using friction loss factor correlations
- Q** can be estimated by using heat-transfer

coefficient correlations

$w_\alpha^{(m)}$ can be estimated by using mass-transfer coefficient correlations

These quantities are given in the form of dimensionless correlations based on large amounts of experimental data; they contain the transport properties and the density and the heat capacity, as well as quantities describing the characteristic length, velocity, temperature, etc.

For steady-state systems, the macroscopic balances form a set of algebraic relations; for unsteady-systems they become a set of differential equations, with time as the independent variable. The macroscopic balances are the starting point for calculations involving heat exchangers, separations equipment, chemical reactors, and fluids-handling systems.

The Three Levels of Transport Phenomena

For many engineering applications, one starts with the macroscopic balances in order to understand the overall behavior of the system. One can often estimate some of the quantities in the balances by using transfer coefficient correlations, photographic or other visualization methods, direct pressure, temperature, and density measurements on the system, etc. Other quantities may be assigned by crude methods.

In other problems, one needs to know more about the details of the pressure, velocity, temperature, and concentration distributions within the system. This calls for "moving down" one level (see Table 6) and solving the equations of change. Many analytical solutions are available, but there are also modern computing techniques if numerical solutions are needed (usually the case if pressure, temperature,

TABLE 6
The Three "Levels" of Transport Phenomena

	Basic Equations	+ Empirical Expressions	Results
Macroscopic Level	Macroscopic balances over engineering system	Dimensionless correlations $f, h, k_x,$ and e_v	Solve to get relations among inlet, outlet, and transfer quantities
	↑ ∫	↑ dimensional analysis	
Microscopic Level	Equations of change for conserved quantities	Flux expressions for j_α, τ, q	Solve to get concentration, pressure, velocity, and temperature
	↑ ∫	↑	
Molecular Level	Equation for time evolution of phase-space distribution function	Intermolecular force expression	Solve to get $D_{AB}, \mu, \kappa,$ and k_T in the flux expressions

and concentration dependence of the physical properties have to be taken into account). Dimensional analysis of the equations of change suggests the form that the transport-coefficient correlations should take, these being needed for the macroscopic balances.

It should be recognized that there is still one scale smaller than the *macroscopic* and *microscopic* scales, namely the *molecular* scale. Although this part of the subject normally lies in the domain of the theoretical physicist or the theoretical chemist, engineers occasionally need some familiarity with the molecular aspects of transport phenomena. The basic equation at the molecular level is an equation for the time evolution of a phase-space distribution function. One example of this is the Boltzmann equation for dilute gases (MTGL, Chapter 7), and additional examples may be found for dilute polymer solutions and polymer melts in DPL2, Chapters 17-19.

From the differential equation for the phase-space distribution function, one can obtain a "general equation of change," special cases of which are the usual equations of change in Table 1; in developing these equations, one makes use of the fundamental con-

servation laws as applied to molecular collisions. As a by-product of this derivation, formal expressions are obtained for the fluxes in terms of the distribution function. In this way expressions are obtained for the transport properties in terms of molecular models.

Recently there has been an interesting development in connection with the kinetic theory of dilute gases and the Boltzmann equation. This famous equation, although over one hundred years old, has been found to be in error in that it cannot be obtained by starting with the quantum Boltzmann equation and letting Planck's constant vanish.^[26] The new "Boltzmann-Curtiss equation" does not suffer from this defect since it accounts properly for the contributions associated with bound pairs of molecules; the added terms in the equation are apparently important at low temperatures; as a result the table in TrPh, page 746, will have to be modified.

It is seen in Table 5 that at each of the three scales, use is made of the basic conservation laws. Also, at each scale some kind of empiricism is introduced. Each scale can be better understood by going to the next smaller scale in order better to appreciate the origins of the equations and their limitations.

Thermodynamics of Irreversible Processes

If into Eq. (H), the equation of change for the internal energy, we insert the thermodynamic relation Eq. (U) (see Table 7) for a binary mixture, we get (after using the equation of continuity) the result in Eq. (V)—an equation of change for the entropy. In this equation we can identify an entropy flux *s* as the sum of two contributions, one associated with heat conduction and one with diffusion; we can also identify a rate of entropy production σ , which is given as a sum of terms, each of which is the product of a flux and a force.

Then, according to the thermodynamics of irreversible processes, every flux will depend linearly on each of the

TABLE 7

Thermodynamics of Irreversible Processes (Binary Systems)

(U) $d\hat{U} = Td\hat{S} - pd(1/\rho) + \hat{\mu}d\omega_A$

(V) $\frac{\partial}{\partial t} \rho\hat{S} = -(\nabla \cdot \rho\mathbf{s}) - (\nabla \cdot \mathbf{s}) + \sigma$

in which $\mathbf{s} = \frac{1}{T}(\mathbf{q} - \hat{\mu}\mathbf{j}_A)$

$$\sigma = -\left((\mathbf{q} - \hat{\mu}\mathbf{j}_A) \cdot \frac{1}{T^2} \nabla T \right) - \left(\mathbf{j}_A \cdot \frac{1}{T} (\nabla \hat{\mu} + (\mathbf{g}_B - \mathbf{g}_A)) \right) - \frac{1}{T} r_A \hat{\mu} - \left(\tau : \frac{1}{T} \nabla \mathbf{v} \right)$$

(W) $\mathbf{j}_A = -\alpha_{11} \frac{1}{T} (\nabla \hat{\mu} + (\mathbf{g}_B - \mathbf{g}_A)) - \alpha_{12} \frac{1}{T^2} \nabla T$

(X) $\mathbf{q} - \hat{\mu}\mathbf{j}_A = -\alpha_{21} \frac{1}{T} (\nabla \hat{\mu} + (\mathbf{g}_B - \mathbf{g}_A)) - \alpha_{22} \frac{1}{T^2} \nabla T$

(Y) $\mathbf{q} = \left(\hat{\mu} + \frac{\alpha_{12}}{\alpha_{11}} \right) \mathbf{j}_A - \left(\alpha_{22} - \frac{\alpha_{12}^2}{\alpha_{11}} \right) \frac{1}{T^2} \nabla T = \left(\frac{\bar{H}_A}{M_A} - \frac{\bar{H}_B}{M_B} \right) \mathbf{j}_A + \mathbf{q}^{(x)} - k \nabla T$

(Z) $\mathbf{j}_A = -\rho \mathcal{D}_{AB} (\nabla \omega_A + k_T \nabla \ln T + k_p \nabla \ln p) + k_F (\mathbf{g}_B - \mathbf{g}_A)$

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- \hat{S} = entropy per unit mass
 - $\hat{\mu}$ = $(\bar{G}_A / M_A) - (\bar{G}_B / M_B)$
 - \mathbf{s} = entropy flux
 - σ = rate of entropy production
 - α_{ij} = phenomenological coefficients
 - $\mathbf{q}^{(x)}$ = Dufour effect contribution to heat flux
 - k_T = thermal diffusion coefficient
 - k_p = pressure diffusion coefficient
 - k_F = forced diffusion coefficient

forces, with the restriction that fluxes must depend on forces of the same tensorial order, or with order differing by 2 (Curie's law). There is also the restriction that the matrix of coefficients in the flux-force relations be symmetric (Onsager-Casimir reciprocal relations). This leads us to Eqs. (W) and (X), in which $\alpha_{12} = \alpha_{21}$. Then combination of Eqs. (W) and (X) gives Eq. (Y) for the heat flux vector. In this equation, the coefficient of $-\nabla T$ can be identified as the thermal conductivity for the mixture. The other term in Eq. (Y) leads to the second term on the right side of Eq. (K), the diffusion term, plus one additional very small term associated with the Dufour effect.

The term involving $\nabla \hat{\mu}$ in Eq. (W) can be expanded by using the chain rule of partial differentiation

$$\nabla \hat{\mu} = (\partial \hat{\mu} / \partial \omega_A) \nabla \omega_A + (\partial \hat{\mu} / \partial T) \nabla T + (\partial \hat{\mu} / \partial p) \nabla p$$

The term in ∇T combines with the other ∇T term in Eq. (W), and the final result is Eq. (Z); in this equation the coefficients k_p and k_F are completely determined from the thermodynamic properties of the mixture, whereas the diffusivity \mathcal{D}_{AB} and k_T are two phenomenological coefficients that have to be determined experimentally for each gas pair or estimated by kinetic theory. As a result of the Onsager relations, the four phenomenological coefficients in Eqs. (W) and (X) have been reduced to the three transport properties: diffusivity, thermal diffusion ratio, and thermal conductivity.

Equation (Z) shows clearly that a mass flux of species "A" can result from a concentration gradient (ordinary diffusion), a temperature gradient (thermal diffusion), a pressure gradient (pressure diffusion), and a difference of external forces (forced diffusion) (TrPh, Chapter 18 and MTGL, Chapter 11). A concise introduction to the thermodynamics of irreversible processes has been given by Landau and Lifshitz;^[27] a more thorough discussion can be found in the classic text by de Groot and Mazur.^[28] The thermodynamics of irreversible processes has been found to be particularly useful in the systematization of the flux expressions for multicomponent diffusion as well as in linear viscoelasticity.^[29] Although this topic is not essential for undergraduate students, perhaps graduate students can benefit from the extra insight provided by the thermodynamic approach.

CONCLUDING COMMENTS

It is essential that students of transport phenomena recognize the central position occupied by the conservation statements. The conservation laws for

mass, momentum, and energy applied to a large engineering system through which a fluid is flowing lead to the macroscopic balances; the two additional balances for angular momentum and mechanical energy can be obtained from the integration of moments of the equation of motion. The utility of the balances is enhanced by the use of empirical correlations for the transfer coefficients. The five macroscopic balances are the starting point for many analyses of unit operations and chemical reactors. They are invaluable for making order-of-magnitude estimates for engineering systems.

The conservation laws, when applied to a small region of space through which a fluid is flowing, lead to the equations of continuity, motion, and energy; the assumption of the symmetry of the stress tensor is usually made, and this assumption makes it unnecessary to deal with the interconversion of external and internal angular momentum. The flux expressions usually used in the equations of change are the simplest possible relations that are linear in the gradients. The vast literature dealing with solutions of the equations of change should be familiar to engineers, even though these solutions are for idealized systems; they are, however, very useful for making order-of-magnitude estimates and for checking the computer programs used for obtaining numerical solutions.

The conservation laws applied at the molecular scale are used in kinetic theory developments. Kinetic theory provides expressions for the transport properties in terms of intermolecular forces; these expressions are highly developed for dilute monatomic gases. In the last several decades the kinetic theory of polymers has developed rapidly, so that much more is now known about the transport properties of polymeric liquids.^[30]

The subject of transport phenomena can be useful in many fields, including micrometeorology, zoology, analytical chemistry, nuclear engineering, tribology, metallurgy, biomedical engineering, pharmacology, and space science. Chemical engineering departments are in a good position to provide general service courses in transport phenomena for other department on campus.

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ChE book review

NATURAL GAS ENGINEERING: PRODUCTION AND STORAGE

by Donald L. Katz, Robert L. Lee
 McGraw Hill, New York, NY 10020; 760 pages, \$54.95 (1989)

Reviewed by
R. A. Greenkorn
 Purdue University

This book covers most aspects of natural gas engineering. It is a survey suitable for a short course to introduce practicing engineers to the topic. The book is descriptive and as such is much too broad to be used as a textbook. The later half of the book is essentially a monograph recording the senior author's extensive experience in this area. Chapters 1-7 describe the material properties of the system, chapters 8-13 contain the core of the material concerned with the production and storage of natural gas, chapters 14-15 mainly discuss operations, and chapters 16-17 contain miscellaneous topics.

Chapter 1 • *Natural Gas Technology and Earth*
 Spring 1993

Sciences. This chapter is a concise review of natural gas engineering production and underground storage of natural gas. Several subjects are covered, e.g., the branches of petroleum industry, sources of information for natural gas engineering, a brief discussion of geology and earth sciences, and earth temperatures and pressures.

Chapter 2 • *Properties of Rocks*. This chapter contains some descriptions of the properties of rocks or porous media, including a description of how these properties are measured. The discussion is understandable and relatively clear—but very terse.

Chapter 3 • *Thermodynamics: Flow Equation, Fluid Properties, Combustion*. This chapter is basically descriptive. It is terse, explaining how the equations are derived and giving some limited information on how to calculate combustion of natural gas.

Chapter 4 • *Physical Behavior of Natural Gas Systems: Physical and Thermal Properties, Phase Behavior, Analyses*. The initial part of this chapter is a review of pressure, volume, and temperature relationships of pure fluids. The phase rule and the behavior of complex mixtures are briefly discussed.

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