Multicomponent Systems

MASS TRANSFER.

Mass transfer deals with situations in which there is more than one component present in a system; for instance, situations involving chemical reactions, dissolution, or mixing phenomena. A simple example of such a *multicomponent* system is a *binary* (two component) solution consisting of a solute in an excess of chemically different solvent.

1. Introduction and Basic Definitions. In a multicomponent system, the velocity of different components is in general different. For example, in Fig. 1 pure gas *A* is present on the left and pure gas *B* on the right. When the wall separating the two gases is removed and the gases begin to mix, *A* will flow from left to right and *B* from right to left – clearly the velocities of *A* and *B* will be different.

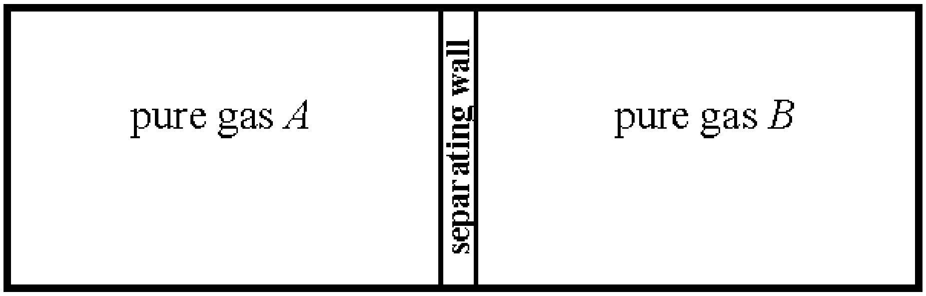

Fig. 1

The velocity of particles (molecules) of component *A* (relative to the laboratory frame of reference) will be denoted $\mathbf{v}_A$. Then, in this frame of reference, the **molar flux** $\mathbf{N}_A$ of species *A* (units: moles of *A*/(area time)) is

$$\mathbf{N}_A = c_A\, \mathbf{v}_A \tag{1}$$

where c_A is the **molar concentration** of *A* (moles of *A*/volume). For example, (1) could be used to calculate how many moles of *A* flow through an area A_C per unit time (Fig. 2). In Fig. 2, the flux is assumed to be normal to the area A_C. Then the amount of *A* carried across the area A_C per unit time is

$$\text{Amount of } A \text{ carried through } A_C \text{ per unit time} = N_A\, A_C = c_A\, v_A\, A_C \quad \text{(moles / time)}$$

Since the volume swept out by the flow of *A* per unit time equals $v_A\, A_C$ (see Fig. 2), the above expression is seen to equal this rate of volumetric "sweeping" times c_A, the amount of *A* per volume.

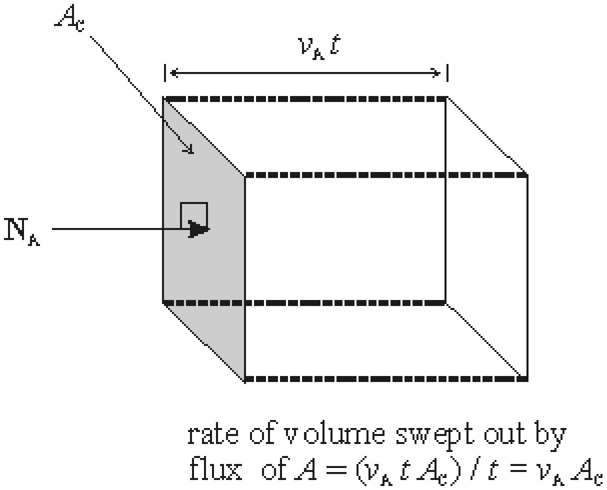

Fig. 2

More generally, for arbitrary direction of $\mathbf{N}_A$ and a differential area element dB, the rate of A transport through dB would be (Fig. 3),

$$\text{flux of } A \text{ through } dB = -c_A \mathbf{v}_A \cdot \mathbf{n}\, dB \qquad \text{(moles / time)} \qquad (2)$$

n is the outward unit normal vector to dB. One can understand equation (2) by realizing that $-\mathbf{v}_A \cdot \mathbf{n}\, dB$ is the volumetric flowrate of A species (volume/time) passing across dB from "outside" to "inside", where "outside" is pointed at by the unit normal vector **n**. Multiplying the volumetric flowrate $-\mathbf{v}_A \cdot \mathbf{n}\, dB$ by the number of moles of A per volume, c_A, equals the moles of A passing through dB per unit time.

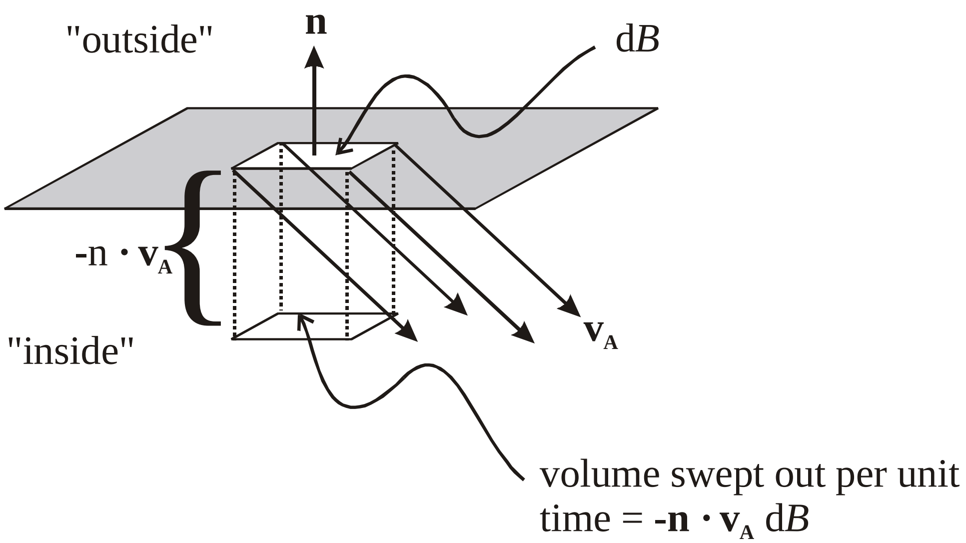

Fig. 3

c_A is related to the **total molar concentration** c (c is moles of particles, irrespective of particle type, per volume) via

$$c_A = x_A c \tag{3}$$

where x_A is the **mole fraction** of A. Summing over the mole fractions of all species must produce unity (n equals the total number of different species present in solution),

$$\sum_{i=1}^{n} x_i = 1 \tag{4}$$

Similarly, we can also define a **mass flux** of A, $\mathbf{n}_A$ (units: mass of A/(area time)),

$$\mathbf{n}_A = \rho_A \mathbf{v}_A \tag{5}$$

Here, $\mathbf{v}_A$ is still the velocity of species A, exactly the same as in equation 1. ρ_A is the **mass concentration** of A (mass of A per volume of solution),

$$\rho_A = \omega_A \rho \tag{6}$$

where ρ is the **total density** (ρ is the summed mass of all particles, irrespective of particle type, per volume) of the solution and ω_A is called the **mass fraction** of A (i.e. $\omega_A = \rho_A/\rho$). Summing the mass fractions of all species must equal unity

$$\sum_{i=1}^{n} \omega_i = 1 \tag{7}$$

As previously stated, in general each chemical species "i" in a multicomponent mixture has a different velocity $\mathbf{v}_i$. However, it will nevertheless prove convenient to define an *average* velocity of the bulk fluid, a velocity that represents an average over all the $\mathbf{v}_i$'s. In general, three types of average velocities are employed: **mass average velocity v** (**v** is what is usually dealt with in Fluid Mechanics), **molar average velocity V**, and **volume average velocity** $\mathbf{v}^o$. We will only deal with the first two average velocities, defined as follows:

$$\mathbf{v} = \sum_{i=1}^{n} \omega_i \mathbf{v}_i \tag{8}$$

$$\mathbf{V} = \sum_{i=1}^{n} x_i \mathbf{v}_i \tag{9}$$

From its definition, **v** is a mass fraction based average of the individual species' velocities, while **V** is a mole fraction based average. It can be shown that if total density $\rho = \sum_{i=1}^{n} \rho_i$ is constant *irrespective of composition*, and if the total molar concentration $c = \sum_{i=1}^{n} c_i$ is constant *irrespective of composition*, then $\mathbf{v} = \mathbf{V}$. It can further be shown that if all particles have the same mass m, so that $m_i = m$ for all i where m_i is mass of i type particles, then $x_i = \omega_i$ and therefore $\mathbf{v} = \mathbf{V}$.

Why bother with two different average velocities? The mass average velocity is what is needed in equations such as the Navier Stokes equations, which deal with momentum, a property that depends on how much *mass* is in motion. Thus, the amount of momentum per unit volume of a flowing multicomponent mixture is $\rho\mathbf{v}$ ($\rho\mathbf{v} = m\mathbf{v}/Volume$, where m is the total mass traveling with velocity **v**; $m/Volume = \rho$); thus momentum must be calculated using the mass average velocity **v**. Similarly, the Equation of Continuity expresses conservation of mass, and is similarly written in terms of **v**. The physical laws expressed by these equations (conservation of momentum, conservation of mass) do not depend on the moles of particles involved, but they do depend on the *mass* of the particles.

On the other hand, when dealing with mass transfer, we will see that it is common to write some of the basic equations in terms of **V** as well as **v**. The reason for using **V**, in addition to **v**, is convenience. For instance, if in a particular problem there is no bulk flow of particles from one location to another so that, during the mass transfer process the number of particles at each point in space stays the same, then $\mathbf{V} = 0$. Setting **V** to zero simplifies the mathematics. Figure 1 at the beginning of this handout provides an example. Imagine that, in their separated state as drawn, A and B are both ideal gases at the same pressure p and temperature T. Then, from the ideal gas equation, the molar concentration of A and B is the same,

$$c_A = c_B = c = p/RT \qquad\qquad (R = \text{gas constant})$$

The equality of c_A and c_B to the total concentration c is appropriate because the gases are pure; thus in each compartment the concentration of the gas (A or B) must also equal the total concentration c. After the separating wall is removed, particles of A and B will mix until a uniform composition is achieved throughout the vessel. In the final state, assuming the gases remain ideal when mixed, the value of p and T will remain the same as in the unmixed state and therefore the total concentration c also remains the same, $c = p/RT$ (p is now the total pressure, a sum of the partial pressures of A and B). Thus, in the final mixed state, the number of particles per volume c (here a sum of particles of A and B types) is the same as the number of particles per volume in the initial unmixed state. Thus mixing produced no net transfer of particles from one side of the vessel to the other, it only mixed the different particle types together. Under these conditions, when there is not net transfer of particles from one part of a system to another, $\mathbf{V} = 0$.

In contrast, for the same mixing process, in general **v** will not be zero. For example, imagine that mass of A particles is twice as large as that of B particles. Then in the initial unmixed state the left hand side of the vessel (filled with A) contains more mass, and the density (mass/volume) of the gas A is higher than that of B even though its concentration (particles/volume) is the same. Once A and B mix, however, the density everywhere will become uniform. For this uniformity to be achieved mass must have been transferred from the *A* side to the *B* side; therefore, in contrast to the molar average velocity **V**, the mass average velocity **v** was not zero during the mixing process.

2. Integral and Differential Balances on Chemical Species. We will refer to the species under consideration as species *A*. Following a derivation that parallels that employed for the other conservation laws, the first step in the derivation of a conservation law on the amount of species *A* is to perform a balance for a closed control volume *V*'. *V*' is enclosed by a closed surface *B* (Fig. 4).

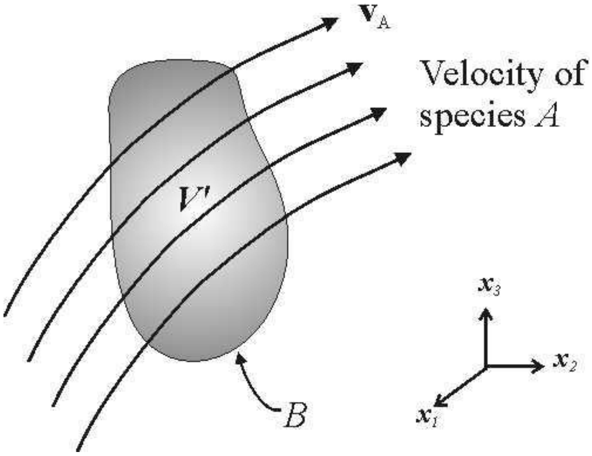

Fig.4

The amount of species *A* inside *V*' can change either due to **convection** through the boundary *B*, or by generation/consumption of *A* due to a chemical reaction. In words, the conservation for species *A* can stated as:

Accumulation of *A* in *V*' = convection of *A* into *V*' + generation of *A* by chemical reactions (10)

An **integral molar balance** on species *A*, performed over the control volume *V*', is written

$$\frac{\mathrm{d}}{\mathrm{d}t}\Big[\iiint_{V'} c_A \,\mathrm{d}V'\Big] = -\iint_{B} c_A \mathbf{v}_A \cdot \mathbf{n}\,\mathrm{d}B + \iiint_{V'} R_A \mathrm{d}V' \tag{11}$$

n is the outward unit normal vector to surface *B*, not to be confused with the mass flux $\mathbf{n}_i = \rho_i\, \mathbf{v}_i$ of species *i*. On the left side, c_A is concentration of *A* in moles per volume; thus $c_A \mathrm{d}V'$ is the number of moles of *A* in a differential volume d*V*'. Integrating (i.e. summing) this term over the entire control volume *V*' yields the total number of moles of *A* in *V*'; the time derivative of this integral is the rate of change of moles of *A* inside *V*' (units: moles/time). Thus, the left hand term is just the rate of accumulation of *A* in *V*', expressed in molar units.

The accumulation term equals the rate at which *A* is convected into *V*' (1st term on right) plus the rate at which *A* is generated inside *V*' by a **homogeneous** chemical reaction (2nd term on right). The convection term can be understood by referring to Fig. 5. $-\,\mathbf{v}_A \cdot \mathbf{n}$ is the component of the species velocity perpendicular to B, so that $-\mathbf{v}_A \cdot \mathbf{n}dB$ is the volumetric flowrate across the area element dB for particles traveling with a velocity $\mathbf{v}_A$. Multiplying this volumetric flowrate by the moles of A per volume results in $-c_A\mathbf{v}_A \cdot \mathbf{n}dB$, the molar flowrate of A through dB. Summing all the molar flowrates over the entire surface B then leads to the convection term (1st term on right) in equation (11).

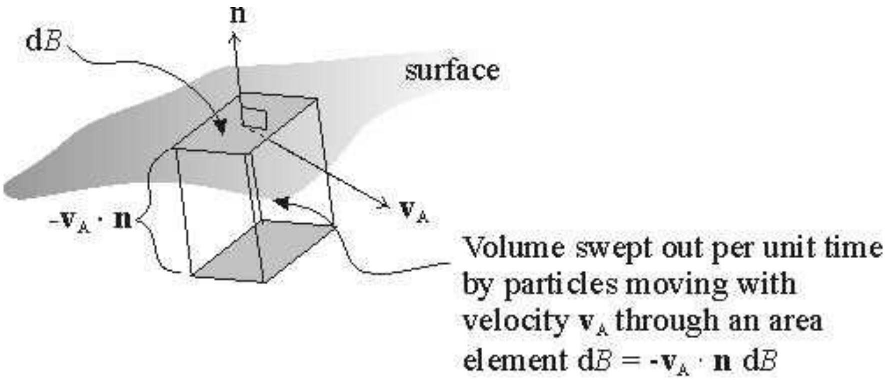

Fig. 5

The 2nd term on the right in equation (11) represents production of A by **homogeneous** reactions. A "homogeneous" reaction is one that occurs throughout the interior of V'. In contrast, a **heterogeneous** chemical reaction would be one that occurs only at an interface – for instance, between a solid and a liquid phase – and is not distributed throughout the entire volume. The **molar reaction rate** R_A has units of moles/(volume time) and represents the rate at which moles of A are produced or consumed by *all* homogeneous reactions. $R_A dV'$ is the number of moles of A produced inside a volume element dV' per unit time (units: moles/time). Summing this production over the entire control volume leads to the total molar rate of production of A, inside V', due to homogeneous chemical reactions.

Equation (11), by assumption, did not include any generation of A due to heterogeneous reactions. Clearly, if in V' there was a large interface at which a heterogeneous reaction leads to production of A, one would have to add that term to equation (11). The term would typically have the form of a rate of production of A per area (moles / (area time)) times the total area of the reacting surface. However, it may also be that a heterogeneous reaction is actually more conveniently modeled as homogeneous. For example, imagine that small catalyst particles (e.g. platinum powder) are suspended in a liquid inside V', and that a reaction that produces A occurs on the surface of these powder particles. Because the reaction occurs only at the interface between a particle and the liquid, it is heterogeneous. However, since the particles are dispersed throughout V', one could think of the reaction rate on a per volume basis (i.e. moles produced per volume of solution per time) as opposed to a per area basis (moles produced per surface area of particles per time).

As done previously for the other balances, one can **(1)** use the Divergence Theorem to convert the surface integral of the convection term (1st term on right) into a volume integral, **(2)** move the d/dt derivative inside the accumulation integral since the integration limits are time independent (the limits do not depend on time because a *fixed* control volume is considered, whose shape and location do not change; this assumption can be relaxed at the expense of a somewhat more complicated mathematical expression), and **(3)** combine all terms under a common volume integral to obtain,

$$\iiint_{V'} \left(\frac{\partial c_A}{\partial t} + \nabla \cdot c_A \mathbf{v}_A - R_A \right) \mathrm{d}V' = 0 \tag{12}$$

The only way to ensure that equation (12) evaluates to zero for an arbitrary control volume V' is to require that

$$\frac{\partial c_A}{\partial t} + \nabla \cdot c_A \mathbf{v}_A - R_A = 0 \tag{13}$$

$$\frac{\partial c_A}{\partial t} = -\nabla \cdot c_A \mathbf{v}_A + R_A \tag{14}$$

Equation (14) is the **differential molar balance** on species A. It states that the rate of accumulation of moles of A at a point in space (left hand side) equals the rate at which moles of A are convected into that point (1st term on right), plus the rate at which moles of A are produced at that point by chemical reactions (2nd term on right). These physical interpretations can be verified by tracing the origin of the terms back to the corresponding terms in the integral balance, equation (11).

Multiplication of equation (11) by the molar mass M_A (mass / mole of A) of species A, and recognizing that ρ_A, the mass of A per volume, is given by

$$\rho_A = M_A c_A \tag{15}$$

leads to the **integral mass balance** on species A,

$$\frac{\mathrm{d}}{\mathrm{d}t}\left[\iiint_{V'} \rho_A \, \mathrm{d}V' \right] = -\iint_{B} \rho_A \mathbf{v}_A \cdot \mathbf{n} \, \mathrm{d}B + \iiint_{V'} r_A \, \mathrm{d}V' \tag{16}$$

In equation (16), the **mass reaction rate** r_A has units of mass/(volume time) and represents the production or consumption of *mass* of species A by *all* chemical reactions. r_A is given by

$$r_A = M_A R_A \tag{17}$$

Through manipulations analogous to those that led to (14), equation (16) can be converted to a **differential mass balance** on species A,

$$\frac{\partial \rho_A}{\partial t} = -\nabla \cdot \rho_A \mathbf{v}_A + r_A \tag{18}$$

Recalling that

$\mathbf{N}_A = c_A \mathbf{v}_A$ (molar flux) (1)

$\mathbf{n}_A = \rho_A \mathbf{v}_A$ (mass flux) (5) equations (14) and (18) can be written as

$$\frac{\partial c_A}{\partial t} = -\nabla \cdot \mathbf{N}_A + R_A \tag{19}$$

$$\frac{\partial \rho_A}{\partial t} = -\nabla \cdot \mathbf{n}_A + r_A \tag{20}$$

Note that, in deriving these equations, no assumptions were made as to which component of a solution (i.e. a solute, the solvent, etc.) is represented as species *A* – therefore, these equations apply to each solute species as well as the solvent. Thus, if one chooses to label the solvent as species *A*, then a solute species could be labeled as species *B*. The equations that would be used for the solute *B* are exactly as in (19) and (20) except that the subscript *A* would be replaced by the subscript *B*.

The differential species' balances were derived independent of any particular coordinate system. To apply them to solving a particular problem, one must first choose a coordinate system suited to describing the problem and then transcribe the equations into that coordinate system. For example, equation (18) becomes

$$\frac{\partial \rho_A}{\partial t} = -\frac{\partial(\rho_A v_{A1})}{\partial x_1} - \frac{\partial(\rho_A v_{A2})}{\partial x_2} - \frac{\partial(\rho_A v_{A3})}{\partial x_3} + r_A \quad \text{(Cartesian "CCS" coordinates)} \tag{21}$$

$$\frac{\partial \rho_A}{\partial t} = -\frac{1}{r}\frac{\partial(r\rho_A v_{Ar})}{\partial r} - \frac{1}{r}\frac{\partial(\rho_A v_{A\theta})}{\partial \theta} - \frac{\partial(\rho_A v_{AZ})}{\partial z} + r_A \quad \text{(cylindrical coordinates)} \tag{22}$$

$$\frac{\partial \rho_A}{\partial t} = -\frac{1}{r^2}\frac{\partial(r^2\rho_A v_{Ar})}{\partial r} - \frac{1}{r\sin\theta}\frac{\partial(\sin\theta\,\rho_A v_{A\theta})}{\partial \theta} - \frac{1}{r\sin\theta}\frac{\partial(\rho_A v_{A\varphi})}{\partial \varphi} + r_A \quad \text{(spherical coordinates)} \tag{23}$$

Compared to the CCS expression, the more complex form of the cylindrical and spherical coordinate expressions for the divergence term (the convection term) results from the curvilinear nature of these coordinates; i.e., the angular coordinate variables (such as θ and φ) change along curves, not lines (see later handout on curvilinear coordinate systems).

The differential equation of continuity (total mass balance) derived in fluid mechanics for single component systems also applies to multicomponent systems in which chemical reactions happen. To prove this is straightforward, and begins by summing equation (18) over all species present in solution,

$$\sum_{i=1}^{n}\frac{\partial \rho_i}{\partial t} = -\nabla \cdot \sum_{i=1}^{n}\rho_i \mathbf{v}_i + \sum_{i=1}^{n} r_i \tag{24}$$

Interchanging the summation and $\partial/\partial t$ operations on the left hand side and making use of the relation

$$\sum_{i=1}^{n} \rho_i = \rho \tag{25}$$

the left hand side of equation (24) becomes

$$\frac{\partial \sum_{i=1}^{n} \rho_i}{\partial t} = \frac{\partial \rho}{\partial t} \tag{26}$$

Furthermore, using the definition of the mass average velocity **v**,

$$\mathbf{v} = \sum_{i=1}^{n} \omega_i \mathbf{v}_i \tag{27}$$

and the fact that the mass fraction $\omega_i = \rho_i/\rho$,

$$\rho\mathbf{v} = \rho \sum_{i=1}^{n} \omega_i \mathbf{v}_i = \sum_{i=1}^{n} \rho_i \mathbf{v}_i \tag{28}$$

Using equation (28), the convection term $-\nabla \cdot \sum_{i=1}^{n} \rho_i \mathbf{v}_i$ in equation (24) becomes

$$-\nabla \cdot \sum_{i=1}^{n} \rho_i \mathbf{v}_i = -\nabla \cdot \rho\mathbf{v} \tag{29}$$

Finally, the chemical reaction term in equation (24) is required to evaluate to zero

$$\sum_{i=1}^{n} r_i = 0 \tag{30}$$

since mass is not produced or destroyed in chemical reactions (*nuclear* reactions can interconvert mass and energy, but this case is not being considered). Substituting equations (30), (29), and (26) into equation (24) leads to

$$\frac{\partial \rho}{\partial t} = - \nabla \cdot \rho \mathbf{v} \tag{31}$$

Equation (31) is the differential **equation of continuity** familiar from fluid mechanics. This equation states the law of mass conservation; even in multicomponent systems, even if chemical reactions are present, the total accumulation of mass at a point (left hand side) can only occur by convection of mass to that point (right hand side). For multicomponent systems whose density ρ is constant (i.e. ρ does not vary from point to point irrespective of variations that may be present in temperature, pressure, *or* composition), equation (31) again simplifies to the condition for incompressible systems,

$$\nabla \cdot \mathbf{v} = 0 \tag{32}$$

3. Diffusion Fluxes. The **diffusion flux** of species *A* is that portion of its total flux that is not attributed to bulk flow (as represented by the mass or molar average velocities). More precisely, $\mathbf{j}_A$, the **mass diffusive flux** of *A*, is defined as

$$\begin{aligned}\mathbf{j}_A &= \text{total mass flux of } A - \text{mass flux of } A \text{ due to bulk motion} \\ &= \mathbf{n}_A - \rho_A \mathbf{v} = \rho_A \mathbf{v}_A - \rho_A \mathbf{v} = \rho_A(\mathbf{v}_A - \mathbf{v})\end{aligned} \tag{33}$$

Similarly, $\mathbf{J}_A$, the **molar diffusive flux** of *A*, is defined by

$$\begin{aligned}\mathbf{J}_A &= \text{total molar flux of } A - \text{molar flux of } A \text{ due to bulk motion} \\ &= \mathbf{N}_A - c_A \mathbf{V} = c_A(\mathbf{v}_A - \mathbf{V})\end{aligned} \tag{34}$$

For instance, in equation (34), the molar diffusion flux $\mathbf{J}_A$ is seen to be the difference between the total molar flux of *A* ($\mathbf{N}_A$) and molar flux of *A* ($c_A\mathbf{V}$) attributable to a bulk flow of molar average velocity $\mathbf{V}$. The total fluxes, $\mathbf{n}_A$ and $\mathbf{N}_A$, are then the sums of the fluxes of *A* due to bulk motion and diffusion,

$$\mathbf{n}_A = \mathbf{j}_A + \rho_A \mathbf{v} \tag{35}$$

$$\mathbf{N}_A = \mathbf{J}_A + c_A \mathbf{V} \tag{36}$$

Note that the diffusive fluxes $\mathbf{j}_A$ and $\mathbf{J}_A$ have different units, mass/(area time) for $\mathbf{j}_A$ and moles/(area time) for $\mathbf{J}_A$. Also, $\mathbf{j}_A$ and $\mathbf{J}_A$ in general possess different numerical values.

4. Causes of Diffusion. Why would a species move with a flux that is different from bulk motion? One cause of diffusion is concentration differences. For example, using a slight variation on Fig. 1, imagine a constant density (ρ = constant; irrespective of composition) mixture of liquids *A* and *B*, enclosed in an apparatus that consists of a pair of vessels connected by a narrow neck (Fig. 6). Initially, the stopcock on the neck is closed, and the amount of *A* is greater in the left vessel than in the right. The vessels have equal volume and, since the density of the mixture does not vary with composition by assumption, are filled with equal mass of liquid. Then, at some point, the stopcock is opened and the mixture is allowed to achieve a new state of equilibrium. The amount of mass in each vessel is fixed since ρ is assumed not to depend on composition, so opening the stopcock to mix up *A* and *B* does not result in a net transfer of mass. If there is no net, bulk flow of mass in the system, then $\mathbf{v} = 0$. Nevertheless, from experiment it is known that opening of the stopcock does result in a net transfer of *A* and *B* such that, at equilibrium, there are no differences in composition between the two vessels. In other words, a net transport of *A* occurred from a region of greater concentration (left vessel) to one of lesser concentration (right vessel), while *B* flowed in the opposite direction (right to left – i.e. from high concentration of *B* to low concentration of *B*). This mass transport eliminated the concentration differences that were present initially, and took place *in absence of any bulk flow* ($\mathbf{v} = 0$); it occurred entirely due to diffusive fluxes. The diffusion occurred spontaneously because it was thermodynamically favored.

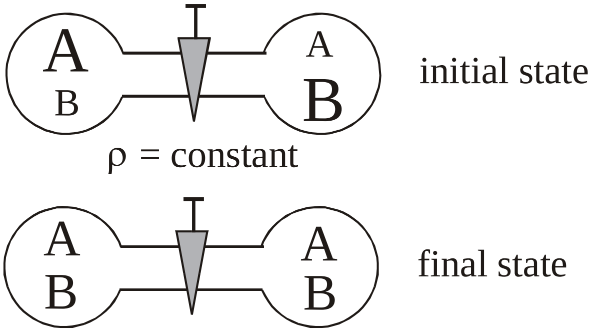

Fig. 6

Let's look a little closer at the thermodynamic origins of diffusion. The discussion will focus on binary mixtures, where the fluid of interest consists of two components, so that the number of species $n = 2$. One can imagine that such a mixture undergoes a process in which its extensive internal energy *U* plus extensive external potential energy *Y* are changed infinitesimally. Denoting the extensive entropy of the mixture by *S*, its volume by *V*, the chemical potential per *mass* of species *i* by μ_i, the external potential energy per mass of species *i* by y_i, and the total mass of species *i* by m_i, thermodynamics states that

$$d(U + Y) = TdS - pdV + \mu_A\, dm_A + y_A dm_A + \mu_B\, dm_B + y_B dm_B \tag{37}$$

Rewriting equation (37) for a unit mass of the solution yields

$$d(u + y) = Tds - pdv + \mu_A\, d\omega_A + y_A d\omega_A + \mu_B\, d\omega_B + y_B d\omega_B \tag{38}$$

where *s* is entropy per unit mass of the solution, *v* is volume occupied by unit mass of solution, *u* is internal energy per unit mass of solution, and *y* is external potential energy of a unit mass of solution. Now, ω_A and ω_B are subject to the constraint

$$\omega_A + \omega_B = 1 \tag{39}$$

From (39),

$$d\omega_B = - d\omega_A \tag{40}$$

Using (40) in (38) and slightly rearranging,

$$d(u + y) = T ds - p dv + \{(\mu_A + y_A) - (\mu_B + y_B)\} d\omega_A \tag{41}$$

The term in parentheses, $\{(\mu_A + y_A) - (\mu_B + y_B)\}$, is referred to as the "exchange potential" μ_T. Physically, $\mu_T d\omega_A$ represents a differential change in internal + potential energy of a unit mass of the solution when some species *B* is exchanged for species *A*, increasing the mass fraction of *A* by $d\omega_A$. Thus, (41) can be written

$$d(u + y) = T ds - p dv + \mu_T d\omega_A \tag{42}$$

$$\mu_T = (\mu_A + y_A) - (\mu_B + y_B) \tag{43}$$

Thermodynamics also states that, for a system with *n* components, *n* + 1 intensive variables are sufficient to fully specify the equilibrium state (this statement is subject to some restrictions, such as absence of materials whose internal state is dependent on their history, for instance past mechanical deformation). Since binary fluid mixtures are being considered, for which $n = 2$, three intensive variables are needed. It will be convenient to choose temperature *T*, pressure *p*, and μ_T. In the absence of equilibrium, one or more of these variables will vary with location in a way that non-equilibrium gradients in ∇T, ∇p, and $\nabla \mu_T$ exist. To move toward equilibrium, the system will transfer heat and masses of the different species around so as to eliminate these gradients. For instance, heat flux will occur from hot to cold to equalize the temperature, and mass fluxes of individual chemical species will occur so as to equalize each species' total $(\mu_i + y_i)$ potentials. Non-equilibrium pressure gradients can be normalized by bulk flow of material from high to low pressure regions.

One possible way the system can eliminate non-equilibrium gradients in ∇T, ∇p, and $\nabla \mu_T$ is by diffusion of the various chemical species; it is then logical to assume that the diffusive fluxes will be functions of these gradients, with steeper gradients producing greater fluxes. Let's consider the diffusive mass flux $\mathbf{j}_A$, assumed to be a function of the gradients such that $\mathbf{j}_A = \mathbf{j}_A(\nabla T, \nabla p, \nabla \mu_T)$. When the gradients ∇T, ∇p, and $\nabla \mu_T$ are not too large, one could perform a Taylor series expansion of $\mathbf{j}_A$ (around equilibrium) in the gradients and truncate it after the first order terms. Such an expansion would lead to the following mathematical relation for $\mathbf{j}_A$:

$$\mathbf{j}_A = - C_1 \nabla \mu_T - C_2 \nabla T - C_3 \nabla p \tag{44}$$

The proportionality factors C_i are functions of *T*, *p*, and μ_T, but not of the nonequilibrium gradients in these quantities (this is because, recalling Taylor Series expansions, these factors are to be evaluated at equilibrium, the "point" around which the expansion is being formed. However, at equilibrium, the non-equilibrium gradients are zero). Equation (44) must be constrained to obey requirements imposed by thermodynamics. In particular, using the second law of thermodynamics, it can be shown that C_3 must equal 0 (Landau & Lifshitz, *Fluid Mechanics*, Pergamon Press, pgs 187 and 222, 1959). Therefore, (44) simplifies to

$$\mathbf{j}_A = -C_1\nabla\mu_T - C_2\nabla T \qquad (45)$$

A species' chemical potential, at some point in the mixture, can be viewed as a function of the pressure, temperature, and composition at that point. For a binary mixture, this means that $\mu_A = \mu_A(T, p, \omega_A)$ and $\mu_B = \mu_B(T, p, \omega_A)$. [An implicit assumption is being made that thermodynamic relations such as $\mu_A = \mu_A(T, p, \omega_A)$, which are strictly applicable to systems at equilibrium, apply even though equilibrium does not exist throughout the system. Qualitatively, this assumption can be expected to hold over sufficiently short length scales over which only insignificant variations in temperature, pressure, and composition occur, so that the values of these quantities are well defined. Since thermodynamic quantities are only needed at a "point" (i.e. over very short lengths), from a practical perspective this consideration is not limiting. Also, note that ω_B is not an independent thermodynamic variable since, for a binary mixture, $\omega_B = 1 - \omega_A$.]

Taking the chemical potentials to be functions of T, p, and ω_A, using them in the definition for μ_T (equation (24)), and applying the chain rule of differentiation to obtain an expression for $\nabla\mu_T$ yields

$$\nabla\mu_T = \left(\frac{\partial(\mu_A-\mu_B)}{\partial T}\right)_{p,\omega_A}\nabla T \;+\; \left(\frac{\partial(\mu_A-\mu_B)}{\partial p}\right)_{T,\omega_A}\nabla p \;+\; \left(\frac{\partial(\mu_A-\mu_B)}{\partial \omega_A}\right)_{p,T}\nabla\omega_A$$

$$+\;\nabla y_A - \nabla y_B \qquad (46)$$

Inserting (46) into (45) results in

$$\mathbf{j}_A = -\left[C_1\left(\frac{\partial(\mu_A-\mu_B)}{\partial T}\right)_{p,\omega_A} + C_2\right]\nabla T \;-\; C_1\left(\frac{\partial(\mu_A-\mu_B)}{\partial p}\right)_{T,\omega_A}\nabla p$$

$$-\;C_1\left(\frac{\partial(\mu_A-\mu_B)}{\partial \omega_A}\right)_{T,p}\nabla\omega_A \;-\; C_1\left(\nabla y_A - \nabla y_B\right) \qquad (47)$$

The unwieldy prefactors in front of the various gradients are usually expressed more succinctly by defining three quantities D_{AB}, k_T, and k_P as follows,

$$\rho\, k_T D_{AB}/T = C_1\left(\frac{\partial(\mu_A-\mu_B)}{\partial T}\right)_{p,\omega_A} + C_2 \qquad (48)$$

$$\rho\, k_P\, D_{AB} / p = C_1 \left(\frac{\partial(\mu_A - \mu_B)}{\partial p} \right)_{T,\omega_A} \tag{49}$$

$$\rho\, D_{AB} = C_1 \left(\frac{\partial(\mu_A - \mu_B)}{\partial \omega_A} \right)_{T,p} \tag{50}$$

If the **diffusion coefficient** D_{AB} (equation (50)) and chemical potentials are known (i.e. from experimental measurement), C_1 can be evaluated from (50) and substituted into (48) and (49). With equations (48) through (50), (47) becomes

$$\mathbf{j}_A = -\ (\rho D_{AB}\, k_T / T)\, \nabla T\ -\ (\rho D_{AB}\, k_P / p) \nabla p\ -\ \rho D_{AB}\, \nabla \omega_A\ -\ C_1 \left(\nabla y_A - \nabla y_B \right) \tag{51}$$

The product $D_{AB}\, k_T$ is called the **thermal diffusion coefficient**, k_T the thermal diffusion ratio, and $D_{AB}\, k_P$ may be called the **barodiffusion coefficient**. Equation (51) shows that diffusive flux of mass of species *A*, in a binary solution of *A* and *B*, can arise from four different contributions.

(i). **Ordinary Diffusion**. Ordinary diffusion arises from variation in composition, and is represented by the third term on the right of equation (51). This term involves $\nabla \omega_A$, and would be zero if the mass fraction of *A* was uniform (constant). Ordinary diffusion is the most common cause of diffusion. When diffusion arises only from variations in composition, equation (51) simplifies to

$$\mathbf{j}_A = -\ \rho D_{AB}\, \nabla \omega_A \tag{52}$$

Equation (52) is known as **Fick's Law**, a central equation in mass transport that states that the diffusive mass flux is equal to a material parameter (ρD_{AB}) times a gradient in composition. As written in equation (52), diffusion occurs from higher to lower mass fractions; in other words, down a composition gradient. The "-" sign ensures that the diffusive flux $\mathbf{j}_A$ points in the opposite direction of the gradient $\nabla \omega_A$; $\mathbf{j}_A$ points in the direction of steepest decrease of ω_A.

While often D_{AB} is assumed constant, in general it varies with *T*, *p*, and ω_A. A constant D_{AB} is usually a good assumption if the solution is sufficiently dilute; that is, one species (the solute) is present at much lower concentrations than the other species (the solvent). Under dilute conditions, the solute molecules are far apart and "do not see" each other and therefore their diffusion is not influenced by changes in their concentration as long as dilute conditions persist. The units of D_{AB} are length^2/time (eg. cm^2/sec).

It is useful to briefly comment on the molecular basis of ordinary diffusion. Imagine having 1000 blue molecules and 1000 red molecules. You then explore all the ways of arranging these molecules in a pattern on a surface. You would discover that many more arrangements exist in which blue and red molecules are well mixed on the surface than ones in which significant separation of red and blue molecules is present. In other words, the probability of finding a well mixed state, in which red molecules are interspersed with blue ones, is much higher than that of a poorly mixed one in which the two colors are well separated. In thermodynamic terminology, the entropy of a well mixed state is greater. Therefore, a system prepared in a less probable state, one that includes significant separation of red and blue particles (i.e. concentration gradients) will spontaneously evolve to a more probable, well-mixed state.

(ii). **Forced Diffusion**. Forced diffusion arises due to variation in the external potential of species *A* and *B*, and is represented by the fourth term on the right of equation (51). One common example of forced diffusion occurs with charged species in an electric field. For example, if a solution with Na^+ cations and Cl^- anions is placed in an external electric field, the cations will migrate in the direction of the electric field while the anions will migrate opposite to it. This is one possible manifestation of forced diffusion. Fluids containing charged particles are dealt with extensively in electrochemistry.

An interesting observation is that gravitational potential does not lead to *mass* diffusion. Rather, this term evaluates to zero. This can be understood as follows. Imagine a particle of *A* with gravitational potential energy $m_A gz$, where z is height in the gravitational field, m_A is the mass of the particle, and g is the gravitational constant. Then y_A, the gravitational potential per unit mass of *A*, is

$$y_A = m_A gz / m_A = gz$$

Therefore,

$$\nabla y_A = \mathbf{g}$$

Similarly, for a particle *B* with a different mass m_B,

$$y_B = m_B gz / m_B = gz$$

and

$$\nabla y_B = \mathbf{g}.$$

Since $\nabla y_A = \nabla y_B = \mathbf{g}$, $\nabla y_A - \nabla y_B = \mathbf{g} - \mathbf{g} = 0$. For gravitational potential, therefore, the forced diffusion term in equation (28) evaluates to zero. The reason for the null result is that gravitational potential of a particle, when normalized by the particle's mass, is always simply gz, independent of whether it is an *A* particle, *B* particle, etc. Thus, on a *per unit mass* basis, different density materials do not possess different gravitational potentials and no forced diffusion results.

Having said this, one may be wondering why do denser particles settle in a gravitational field – does that not represent mass transfer due to an external field? For diffusive *mass* fluxes such as $\mathbf{j}_A$, this effect is accounted for by the second term (pressure diffusion) in equation (51) (see below).

(iii). **Thermal Diffusion (Soret effect)**. Thermal diffusion arises due to spatial variation in temperature. Thermal diffusion is represented by the first term on the right of equation (51). In most problems of practical interest, this cause of mass diffusion is quite small. Referring back to equation (47), the prefactor in front of the thermal diffusion term has two contributions: (1) variation of chemical potentials with temperature and (2) directly from the presence of a temperature gradient (the "C_2"

contribution). By inspection, the chemical potential contribution, $-C_1\left(\frac{\partial(\mu_A-\mu_B)}{\partial T}\right)_{p,\omega_A}$ ∇T, will produce a flux of species A in the direction of increasing temperature if $\left(\frac{\partial(\mu_A-\mu_B)}{\partial T}\right)_{p,\omega_A}$ is negative (note: C_1 can be shown to be positive). Usually, the derivative of a chemical potential with respect to temperature is negative. Then *A* will concentrate in (diffuse to) hotter regions if its chemical potential decreases with temperature faster than the chemical potential of *B*. The effect of such thermal diffusion is to take advantage of existing variations in temperature so as to decrease the chemical potentials of the various species as much as possible, leading to the lowest possible total free energy of the solution.

The underlying physical causes of thermal diffusion originating directly from the presence of a thermal gradient, $-C_2\nabla T$, depend on the particular situation considered and are difficult to explain in general. One cause has to do with the fact that, at a given temperature, the mass flux associated with a heavier molecule (the mass flux is proportional to the mass of the molecule times its velocity) is larger than for a light molecule. This dependence of mass flux on molecular mass, when combined with a gradient in temperature can lead to different rates of thermal mass diffusion due to differences in molecular masses.

(iv). **Pressure Diffusion**. Pressure diffusion arises from variations in pressure, and is represented by the second term on the right in equation (51). By inspection (see equation (47)), pressure diffusion of *A* to a region of higher pressure will result if $\left(\frac{\partial(\mu_A-\mu_B)}{\partial p}\right)_{T,\omega_A}$ is negative (under this condition $\mathbf{j}_A$ points in the same direction as ∇p). Thermodynamics tells us that the derivative

$$\left(\frac{\partial\mu_A}{\partial p}\right)_{T,\omega_A} = \hat{V}_A$$

where $\hat{V}_A$ is the volume occupied by a unit mass of *A* in solution, referred to as the **partial mass volume** of *A*. Thus $\left(\frac{\partial(\mu_A-\mu_B)}{\partial p}\right)_{T,\omega_A} = \hat{V}_A - \hat{V}_B$, and will be negative if a unit mass of *A* occupies a smaller volume in solution that a unit mass of *B*. In other words, this term will be negative if *A* is denser than *B*, under which condition *A* will preferentially diffuse to regions of higher pressure. From a thermodynamic perspective, pressure diffusion occurs because denser fluids have lower pressure-volume energy per unit mass (i.e. it costs less work to insert a unit mass of a denser fluid into a region of high pressure because the denser fluid occupies less volume), and by increasing the mass concentration of denser fluids in high pressure regions the total free energy of the system is minimized. Since gravity induces pressure variations inside a liquid, it can lead to pressure diffusion. In devices such as centrifuges in which pressure differences corresponding to thousands of *g*'s can be attained, pressure driven mass diffusion is used to separate different solution components based on minute differences in their densities.

5. Fick's Law. Having briefly outlined the four causes of mass diffusion – spatial variations in composition, external potential, temperature, and pressure – it is useful to highlight the most common scenario in which only ordinary diffusion is of importance. The discussion will be specialized to binary solutions that obey **Fick's Law**, equation (52). The restriction to binary solutions is not as limiting as it may seem. Indeed, even when more than two components are present, as long as the solutions are sufficiently dilute the diffusion of solute species can be modeled as for a binary system. This is because when one of the species (the solvent) is present in vast excess, with all the rest (the solutes) in trace amounts, the diffusion of each solute species can be treated as if it was in pure solvent alone. Under these dilute conditions a solute particle will not "see" any of the other solute particles, and so its diffusion will not be affected by their presence but only by the solvent. Such a situation is effectively a two component problem, the solute of interest plus the solvent.

Fick's Law can be written in several common forms:

Mass diffusion flux; reference bulk average velocity **v** (equation 52 above):

$$\mathbf{j}_A = \rho_A(\mathbf{v}_A - \mathbf{v}) = -\rho D_{AB}\,\nabla\omega_A \qquad (52)$$

If the total mass density ρ = constant throughout the solution, irrespective of composition, then ρ can be moved inside the gradient operator:

$$\mathbf{j}_A = -D_{AB}\,\nabla\rho_A \qquad (\rho = \text{constant}) \qquad (53)$$

Molar diffusion flux; reference bulk average velocity **V**:

$$\mathbf{J}_A = c_A(\mathbf{v}_A - \mathbf{V}) = \mathbf{j}_A M/(M_A M_B) = -cD_{AB}\,\nabla x_A \qquad (54)$$

In equation (54), M is the average molar mass (mass per mole of particles, also referred to as the average molecular weight) of the solution,

$$M = \rho/c = (c_A M_A + c_B M_B)/c = x_A M_A + x_B M_B \qquad (55)$$

M_A and M_B are the molar masses of A and B particles, respectively (e.g. the molar mass of water is 18 grams per mole of water molecules). Equation (54) can be derived directly from equation (52) through a rather lengthy algebraic procedure involving conversions between mass fractions and mole fractions, densities and molar concentrations. If the total molar concentration c is constant throughout the solution, irrespective of composition, c can be brought inside the gradient operator and equation (54) becomes:

$$\mathbf{J}_A = -D_{AB}\,\nabla c_A \qquad (c = \text{constant}) \qquad (56)$$

Finally, it should be emphasized that the diffusion coefficient D_{AB} in all of the above Fick's Law expressions is the same (has the same numerical value and units of length^2 /time), whether the expressions are for a mass diffusive flux or a molar diffusive flux. In the strictest interpretation, the above expressions are specialized to binary solutions in which the only gradients present are those in composition. However, as already mentioned, they in fact work quite well for dilute solutions containing more than one solute.

6. Convective Mass Transfer. Application of Fick's Law to the calculation of a diffusive mass flux requires knowledge of the composition gradient at each point in space at which the mass flux is to be determined. Further complicating the picture, there are many situations in which convective mechanisms are important in addition to diffusive ones. By convective mechanisms one means mass transfer that arises by virtue of bulk motion. For example, in the case of the total mass flux $\mathbf{n}_A$ of species *A*, equation (35) states that

$$\mathbf{n}_A = \mathbf{j}_A + \rho_A \mathbf{v} \tag{35}$$

In equation (35), $\mathbf{j}_A$ is the diffusive part of the total mass flux $\mathbf{n}_A$ (arising from the presence of thermodynamically unfavorable gradients in properties such as concentration), while $\rho_A \mathbf{v}$ is mass transfer of *A* due to bulk motion. It is this $\rho_A \mathbf{v}$ part that one is referring to as "convective" mass transfer. In the case of the molar flux $\mathbf{N}_A$, the convective part is $c_A \mathbf{V}$. This is evident from equation (36),

$$\mathbf{N}_A = \mathbf{J}_A + c_A \mathbf{V} \tag{36}$$

To obtain the total mass transfer of a species, one would need to calculate not only the diffusive portion ($\mathbf{j}_A$ or $\mathbf{J}_A$) but also the convective contribution. The sum of these two terms then leads to the total mass transfer (whether expressed in mass or molar units).

The trouble is that, for an arbitrary situation in which mass transfer may occur by diffusion as well as by convection, the necessary calculation of composition and velocity at each point inside a mixture is often simply too hard. The difficulties make calculation of mass transfer from Fick's Law and equations such as (35) or (36) virtually impossible. Therefore, another approach, based on so-called **mass transfer coefficients**, is very commonly implemented. In general, one is interested in calculating mass transfer across the boundary of some system (e.g. from a liquid into a gas, from one liquid into another liquid, etc.). Then one way to define a mass transfer coefficient k_C (units: length/time) is as follows,

$$N_A = k_C (c_{AS} - c_{A\infty}) \tag{57}$$

N_A is the molar mass transfer of *A* across the boundary (moles /(area time)), $c_{A\infty}$ is molar concentration of *A* (moles / volume) in the bulk of the system far away from the boundary (surface), and c_{AS} is the molar concentration of *A* right at the boundary but still on the same side as the bulk of the system.

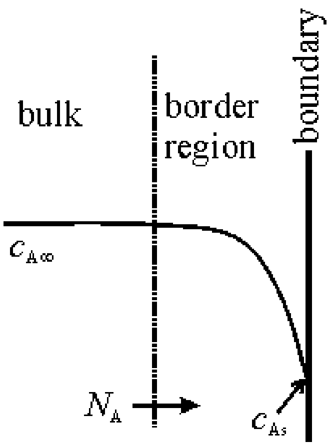

Fig. 7

Fig. 7 depicts this situation. In the figure, flux of A, N_A, is occurring from the bulk of a solution phase (system) to its boundary. The boundary could represent, for example, the interface between two immiscible fluids or between a fluid and a solid wall. The simplicity of equation (57) is achieved by two key *assumptions:* **(i)** concentration in the bulk of the system is uniform (hence $c_{A\infty}$ is well-defined), so that concentration of A only varies across a "border" (or "**film**") region next to the boundary, and **(ii)** flux of species A from the bulk to the interface is proportional to the magnitude of the concentration change across the border film region (this change being equal to c_{As} - $c_{A\infty}$). However, note that the mass transfer coefficient k_C is itself in general a function of flow geometry, temperature, concentration, and possibly other parameters. Still, relatively simple expressions for k_C can be often developed directly from experimental measurements, or from theory when possible. Use of equation (57) is supported by its often excellent success in applications.

7. Species' Balances for Systems That Obey Fick's Law.

Equations (14) and (18), the differential molar and mass balances on a species, are general in the sense that they are independent of the number of components present or any models of diffusion. For example, they do not require ordinary diffusion to obey Fick's Law. These equations are only based on the statement that the rate at which the amount of A can change at a point in space equals the rate at which A is convected into that point plus the rate at which it is generated by chemical reactions. However, in their present form,

$$\frac{\partial c_A}{\partial t} = -\nabla \cdot c_A \mathbf{v}_A + R_A \qquad (14)$$

$$\frac{\partial \rho_A}{\partial t} = -\nabla \cdot \rho_A \mathbf{v}_A + r_A \qquad (18)$$

these equations can be inconvenient because they contain the species' velocity $\mathbf{v}_A$, which must be known in order to accomplish the usual goal of solving for the mass or molar concentrations. One way to model $\mathbf{v}_A$ is to consider it as consisting of the two contributions previously encountered: **(i)** one due to bulk flow of the fluid mixture and **(ii)** one due to the diffusion of species A.

$$\mathbf{n}_A = \rho_A \mathbf{v}_A = \mathbf{j}_A + \rho_A \mathbf{v} \tag{35}$$

$$\mathbf{N}_A = c_A \mathbf{V}_A = \mathbf{J}_A + c_A \mathbf{V} \tag{36}$$

Separation of the total flux of *A* into diffusive and bulk convection contributions is motivated by convenience. The mass average velocity **v** is easy to measure, and can be obtained by direct calculation from the differential equations of fluid mechanics (e.g. Navier Stokes equations for Newtonian fluids with ρ and μ constant). Typically, the diffusive fluxes are modeled well by Fick's Law for solutions in which only ordinary diffusion is present and which are either binary or, as discussed earlier, dilute.

Equations (14) and (18) can be specialized to fluids that follow Fick's Law. One can begin by inserting (35) into (18) to obtain

$$\frac{\partial \rho_A}{\partial t} = -\nabla \cdot \mathbf{j}_A - \nabla \cdot \rho_A \mathbf{v} + r_A \tag{58}$$

$$= -\nabla \cdot \mathbf{j}_A - \mathbf{v} \cdot \nabla \rho_A - \rho_A \nabla \cdot \mathbf{v} + r_A \tag{59}$$

A vector identity was used in deriving equation (59) from equation (58) (equation (30d) from Handout 1). Substituting Fick's Law for $\mathbf{j}_A$,

$$\mathbf{j}_A = -\rho D_{AB} \nabla \omega_A \tag{60}$$

into (59) and rearranging

$$\frac{\partial \rho_A}{\partial t} = \nabla \cdot \rho D_{AB} \nabla \omega_A - \mathbf{v} \cdot \nabla \rho_A - \rho_A \nabla \cdot \mathbf{v} + r_A \tag{61}$$

The left hand side term and the 2nd term on the right can be rewritten using the material derivative notation, $\frac{\partial \rho_A}{\partial t} + \mathbf{v} \cdot \nabla \rho_A = \frac{D\rho_A}{Dt}$, and (61) becomes

$$\frac{D\rho_A}{Dt} = \nabla \cdot \rho D_{AB} \nabla \omega_A - \rho_A \nabla \cdot \mathbf{v} + r_A \tag{62}$$

Equations (61) and (62) are common forms of the differential mass balance on species *A* with Fick's Law diffusion. These equations simplify for mixtures assumed to possess a constant density, and for which the diffusion coefficient can be regarded as constant. For constant ρ, $\nabla \cdot \mathbf{v} = 0$, so the 3rd right term in equation (61) and the 2nd right term in (62) drop out. If in addition D_{AB} is also assumed constant, and recalling that $\rho\omega_A = \rho_A$, equation (61) rearranges to

$$\frac{\partial \rho_A}{\partial t} = D_{AB} \nabla^2 \rho_A - \mathbf{v} \cdot \nabla \rho_A + r_A \qquad (\rho,\ D_{AB}\ \text{constant}) \tag{63}$$

In physical terms, equation (63) states that the rate at which mass density of *A* changes at a point (left hand side) equals the rate at which mass of *A* diffuses to that point due to concentration gradients (first term on right), plus the rate at which mass of *A* is convected to that point by bulk motion **v** of the fluid (second term on right), plus the rate at which mass of *A* is generated at that point by all chemical reactions (third term on right). In the material derivative notation, equation (63) becomes

$$\frac{D\rho_A}{Dt} = D_{AB}\,\nabla^2\rho_A + r_A \qquad (\rho,\ D_{AB}\ \text{constant}) \qquad (64)$$

Recall that the term $\frac{D\rho_A}{Dt}$ includes a local rate of change, $\frac{\partial \rho_A}{\partial t}$, plus change due to motion through a gradient of ρ_A, $\mathbf{v}\cdot\nabla\rho_A$. Equation (64) states: the rate at which the mass density ρ_A changes inside a fluid element moving with the mass average velocity **v** (left hand side) equals the rate at which mass of *A* diffuses into the fluid element (first term on right) plus the rate at which mass of *A* is generated inside the fluid element by chemical reactions (second term on right). Compared to equation (63), the difference lies in interpretation of the term $\mathbf{v}\cdot\nabla\rho_A$. For a stationary point through which a fluid flows, as in equation (63), this term represents the change in amount of species *A* due to bulk convection that brings to that point species *A* at a different rate than the rate at which it removes *A*. In contrast, when thinking not in terms of a stationary point but a fluid element that moves with the flow, $\mathbf{v}\cdot\nabla\rho_A$ represents change in composition that an observer in the fluid element would observe due to motion through a gradient of ρ_A; i.e. from an area of one concentration of *A* to another.

Expressed in Cartesian, cylindrical, and spherical coordinate systems, equation (63) becomes

$$\frac{\partial\rho_A}{\partial t} = D_{AB}\left(\frac{\partial^2\rho_A}{\partial x_1^2}+\frac{\partial^2\rho_A}{\partial x_2^2}+\frac{\partial^2\rho_A}{\partial x_3^2}\right) - v_1\frac{\partial\rho_A}{\partial x_1} - v_2\frac{\partial\rho_A}{\partial x_2} - v_3\frac{\partial\rho_A}{\partial x_3} + r_A \quad \text{(Cartesian)} \qquad (65)$$

$$\frac{\partial\rho_A}{\partial t} = D_{AB}\left(\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial\rho_A}{\partial r}\right)+\frac{1}{r^2}\frac{\partial^2\rho_A}{\partial\theta^2}+\frac{\partial^2\rho_A}{\partial z^2}\right) - v_r\frac{\partial\rho_A}{\partial r} - \frac{v_\theta}{r}\frac{\partial\rho_A}{\partial\theta} - v_Z\frac{\partial\rho_A}{\partial z} + r_A$$

(cylindrical) (66)

$$\frac{\partial\rho_A}{\partial t} = D_{AB}\left(\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\rho_A}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\rho_A}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2\rho_A}{\partial\varphi^2}\right) - v_r\frac{\partial\rho_A}{\partial r} - \frac{v_\theta}{r}\frac{\partial\rho_A}{\partial\theta} - \frac{v_\varphi}{r\sin\theta}\frac{\partial\rho_A}{\partial\varphi} + r_A$$

(spherical) (67)

Equations (65) to (67) are specialized to the case of constant ρ and D_{AB}.

The above equations were obtained by taking the general differential *mass* balance on species *A*, separating the total flux $\rho_A\mathbf{v}_A$ of species *A* into bulk convection and diffusion contributions, and using Fick's Law to model the diffusion flux. Instead, had one started from the differential *molar* balance, equation (14),

$$\frac{\partial c_A}{\partial t} = -\nabla \cdot c_A \mathbf{v}_A + R_A \tag{14}$$

and separated the total molar flux $c_A\mathbf{v}_A$ into bulk and diffusive contributions according to equation (36), $c_A\mathbf{v}_A = \mathbf{J}_A + c_A\mathbf{V}$, the result would be

$$\frac{\partial c_A}{\partial t} = -\nabla\cdot \mathbf{J}_A - \nabla\cdot c_A\mathbf{V} + R_A = -\nabla\cdot \mathbf{J}_A - c_A\nabla\cdot\mathbf{V} - \mathbf{V}\cdot\nabla c_A + R_A \tag{68}$$

Inserting in Fick's Law for $\mathbf{J}_A$, $\mathbf{J}_A = -cD_{AB}\nabla x_A$, leads to

$$\frac{\partial c_A}{\partial t} = \nabla\cdot cD_{AB}\nabla x_A - c_A\nabla\cdot\mathbf{V} - \mathbf{V}\cdot\nabla c_A + R_A \tag{69}$$

If the total concentration c and diffusion coefficient D_{AB} are constant (i.e. c and D_{AB} do not vary from point to point irrespective of variations that may be present in temperature, pressure, *or* composition), equation (69) becomes

$$\frac{\partial c_A}{\partial t} = D_{AB}\nabla^2 c_A - c_A\nabla\cdot\mathbf{V} - \mathbf{V}\cdot\nabla c_A + R_A \qquad (c,\ D_{AB}\ \text{constant}) \tag{70}$$

Even though the total molar concentration c was assumed constant, the divergence of the molar average velocity, $\nabla\cdot\mathbf{V}$, will in general not be zero and therefore the 2nd right term in (70) cannot be dropped. This is in contrast to the case of constant ρ, for which $\nabla\cdot\mathbf{v}$ equals zero. One could show that

$$\nabla\cdot\mathbf{V} = R/c \qquad (c = \text{constant}) \tag{71}$$

where

$$R = \sum_{i=1}^{n} R_i \tag{72}$$

R is the total production rate of particles, in units of moles/volume, due to chemical reactions. Equation (71) was stated here without proof, but can be derived by summing equation (70) over all of the components of a mixture. What is the value of R? For a reaction such as

$$B \rightarrow A$$

$R = R_A + R_B = 0$ since one B molecule is converted to exactly one A molecule, so that $R_B = -R_A$ and the total number of molecules does not change. However, for a reaction such as

$$B \rightarrow 2A$$

$R = R_A + R_B = R_A/2$ since only one molecule of *B* is consumed for two molecules of *A* produced (i.e. $R_B = - R_A/2$).

Equations (61) and (69) assumed that the solution is either binary or, if more than two components are present, sufficiently dilute. The key point here is that the diffusion of a molecule of *A* should occur as if through pure *B*; this will be true even if other species are present (i.e. in addition to *A* and *B*) as long as the concentrations of the additional species are very dilute. If the concentrations are not dilute, then the diffusion term is usually modified by defining additional “diffusion coefficients” responsible for coupling the diffusion flux of a species to compositional gradients of all the other components. Of course, for a strictly binary solution of *A* and *B*, equations (61) and (69) hold over the entire range of composition, dilute as well as concentrated.

8. The Bulk Reference Velocity and the Dilute Solution Limit.

The preference for choosing to work in mass units ($\mathbf{n}_A$, $\mathbf{j}_A$, $\mathbf{v}$, ρ_A) or molar units ($\mathbf{N}_A$, $\mathbf{J}_A$, $\mathbf{V}$, c_A) is based on convenience. Often, convenience has to do with handling of the bulk convection terms; these are the terms involving the bulk average velocities $\mathbf{v}$ or $\mathbf{V}$. For example, if one expects $\mathbf{V}$ but not $\mathbf{v}$ to be zero, one may choose (69) instead of (61) because the species mass balance would be simpler. An example of a scenario in which $\mathbf{V}$ is zero is **equimolar counterdiffusion**. This situation often arises in the interdiffusion of ideal gases in the absence of forced or natural convection. In equimolar counterdiffusion, the two components have molar fluxes that are equal in magnitude but opposite in direction, so that the total molar flux is zero,

$$\mathbf{N}_A = - \mathbf{N}_B \tag{73}$$

$$\text{total molar flux} = \mathbf{N}_A + \mathbf{N}_B = c\mathbf{V} = 0 \tag{74}$$

In equation (74), identification of $c\mathbf{V}$ as the total molar flux, which equals the sum of the molar fluxes $\mathbf{N}_i$, follows from the definition $\mathbf{V} = \sum_{i=1}^{n} x_i \mathbf{v}_i$:

$$\text{total molar flux} = \sum_{i=1}^{n} \mathbf{N}_i = \sum_{i=1}^{n} c_i \mathbf{v}_i = c \sum_{i=1}^{n} x_i \mathbf{v}_i = c\mathbf{V} \tag{75}$$

Similarly, the total mass flux, given by the sum of all the mass fluxes $\mathbf{n}_i$, equals $\rho\mathbf{v}$,

$$\text{total mass flux} = \sum_{i=1}^{n} \mathbf{n}_i = \sum_{i=1}^{n} \rho_i \mathbf{v}_i = \rho \sum_{i=1}^{n} \omega_i \mathbf{v}_i = \rho\mathbf{v} \tag{76}$$

Relations (75) and (76) often come in useful when manipulating mass transfer expressions. While $\mathbf{V}$ is a good choice for some problems, in other situations $\mathbf{v}$ may be constant or zero, e.g. if $\mathbf{n}_A = - \mathbf{n}_B$. In general, deciding whether $\mathbf{v}$ or $\mathbf{V}$ is more convenient as the bulk average velocity may not always be transparent and may require prior experience with solving mass transfer problems. Fortunately, this decision is entirely eliminated in an important class of mass transfer problems in which *bulk convection is negligible*. Let's consider the requirements for neglecting bulk convection.

Bulk convection is represented by the terms involving the bulk average velocities in the above equations (for example, 2nd term on the right in equations (58) and (68)). These terms will be zero if $\mathbf{v} = \mathbf{0}$ and $\mathbf{V} = \mathbf{0}$. In general, both the mass and molar bulk average velocities will be zero when **(i)** there is no forced convection, **(ii)** there is no free convection, and **(iii)** the solution is dilute. **Forced convection** refers to convection "forced" by pressure gradients, shaft work, and forces such as may arise from external potentials such as gravity. Most often, forced convection is driven by machinery – e.g. pumps, impellers. **Free convection** refers to the specific case when convection is caused by variation of fluid density. Free convection occurs because, in the presence of a gravitational field, less dense fluid will rise to the top. The rising of hot air through colder air is an example of free convection. Free convection is also known as **natural convection**.

Even if forced and free convection are not present, diffusion itself can still engender convection. This ability of diffusion to create bulk convection is why the solution is stipulated to be dilute (condition **(iii)** in previous paragraph). To illustrate how diffusion can create bulk convection, let us consider again the two bulb apparatus encountered earlier (Fig. 8). For the purposes of this illustration it is assumed that pure species *A* (in the left bulb) is denser than pure species *B* (in the right bulb), and the question is whether bulk convection of mass is ($\mathbf{v} \neq \mathbf{0}$) or is not ($\mathbf{v} = \mathbf{0}$) present when *A* and *B* mix. Initially there must be more mass on the left than on the right, since *A* is denser than *B*. When the valve is opened, a final state is reached in which the composition inside both bulbs will be the same. In the final state, right and left bulbs both contain equal amounts of mass – therefore, mass was moved from left to right on passage from the initial state (in which more mass was present in the left bulb) to the final state (in which both bulbs contain equal mass). This movement was by bulk convection, since there was not just mixing of *A* and *B*, but also a net transfer of mass from left to right. This convection was not driven by a pressure gradient, shaft work, or body forces – it was engendered by the interdiffusion of *A* and *B* species. Thus, the above thought experiment proves that diffusion can engender bulk convection of mass. This was an example of mass transfer in a concentrated solution since the amount of *A* and *B* present in the two bulb apparatus was comparable.

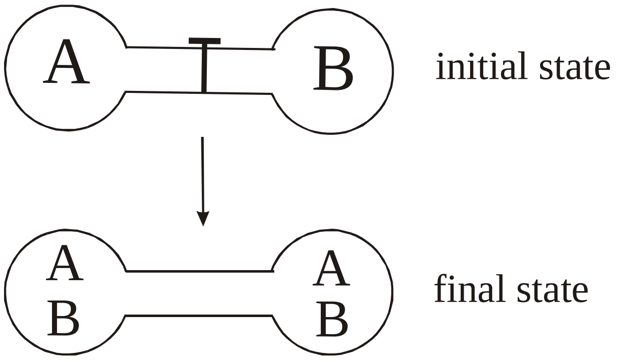

Fig. 8.

Next, imagine the same apparatus. However, while the right bulb is again filled with pure *B*, the left bulb is filled with a dilute solution of *A* solute in a vast excess of *B* solvent. For concreteness, imagine that the right bulb has 10000 *B* molecules, while the left bulb has 9900 *B* molecules and 100 *A* molecules. Since *A* is again denser than *B*, more mass is present on the left than on the right. However, because the *A* concentration is so dilute, this initial difference in mass between the two bulbs is very slight, almost imperceptible. On passage from the initial to the final state, we expect about 50 molecules of *A* to flow from left to right so that at equilibrium, on average, the composition inside both bulbs is the same (9950 *B* molecules and 50 *A* molecules in each bulb – note that *B* has to flow from right to left to "make room" for the *A* molecules going from left to right). Clearly, the bulk convection of mass will be much, much less than for the concentrated case discussed above, since the two bulbs were very similar in mass to begin with.

The important question is whether bulk convection can be made so small, under sufficiently dilute conditions, that it can be neglected in comparison with diffusion. More precisely, can the 2nd right term (bulk convection) in equation (58) (note: there are no reactions in the example under discussion so $r_A = 0$)

$$\frac{\partial \rho_A}{\partial t} = \nabla \cdot \rho D_{AB} \nabla \omega_A - \nabla \cdot \rho_A \mathbf{v} \tag{58}$$

be ignored to yield the simpler equation

$$\frac{\partial \rho_A}{\partial t} = \nabla \cdot \rho D_{AB} \nabla \omega_A \tag{59}$$

which retains only the diffusive term on the right. The answer is YES; i.e. bulk convection can be neglected for sufficiently dilute solutions. For example, for binary mixtures of *A* solute in *B* solvent, the total flux of *A*, $\mathbf{n}_A$, is given by

$$\mathbf{n}_A = \rho_A \mathbf{v}_A = \mathbf{j}_A + \rho_A \mathbf{v} = \rho_A(\mathbf{v}_A - \mathbf{v}) + \rho_A \mathbf{v}$$

As stated earlier, $\mathbf{j}_A = \rho_A(\mathbf{v}_A - \mathbf{v})$ is diffusive mass flux and $\rho_A \mathbf{v}$ is flux of *A* due to bulk convection. The ratio of bulk convection to diffusion is

$$\text{(bulk convection) / diffusion} = \rho_A \mathbf{v} / \mathbf{j}_A = \rho_A \mathbf{v} / [\rho_A(\mathbf{v}_A - \mathbf{v})] = \mathbf{v} / (\mathbf{v}_A - \mathbf{v})$$

Using the definition of $\mathbf{v}$ for a binary solution, $\mathbf{v} = \omega_A \mathbf{v}_A + \omega_B \mathbf{v}_B$, leads to

$$\text{(bulk convection) / diffusion} = \rho_A \mathbf{v} / \mathbf{j}_A = (\omega_A \mathbf{v}_A + \omega_B \mathbf{v}_B)/(\mathbf{v}_A - \omega_A \mathbf{v}_A - \omega_B \mathbf{v}_B)$$

In the dilute limit, solute (species *A*) vanishes. Therefore, $\omega_A \rightarrow 0$ and $\omega_B \rightarrow 1$, leading to

$$\text{(bulk convection) / diffusion} = \rho_A \mathbf{v} / \mathbf{j}_A = \mathbf{v}_B / (\mathbf{v}_A - \mathbf{v}_B) \tag{77}$$

If $\mathbf{v}_B << \mathbf{v}_A$, then (77) simplifies to

$$\rho_A \mathbf{v} / \mathbf{j}_A \approx \mathbf{v}_B / \mathbf{v}_A << 1 \tag{78}$$

Inequality (78) shows that, for $\mathbf{v}_B \ll \mathbf{v}_A$, the bulk convection term is much less than the diffusion term. This inequality will always hold for sufficiently dilute solutions. Let's return to the previous thought experiment in which 50 molecules of *A* were transported from the left to the right bulb. To make room for the incoming *A* molecules, the *B* solvent molecules must be simultaneously displaced in the opposite direction. However, because there are so many more *B* molecules than *A* molecules, on average a *B* molecule only needs to travel a short distance; in other words, it is the *summed displacement* of 10000 *B* molecules that must counterbalance the addition of just 50 *A* molecules. On average, a *B* molecule will only need to be displaced by a fraction, ≈ 50/10000 = 1/200, in the direction opposite to that of the *A* molecules. This means that the velocity of a typical *B* molecule will only be about 1/200 that of a typical *A* molecule during the mixing process. Thus, $\mathbf{v}_B / \mathbf{v}_A \approx 0.005 \ll 1$, satisfying the inequality (78) and demonstrating that bulk convection could indeed be neglected compared to diffusion. Put differently, if one adds a grain of sugar (species *A*) to a bathtub of stationary water (species *B*), the water is not displaced very much even as the sugar disperses through the entire bathtub. Thus the average velocity of the sugar, $\mathbf{v}_A$, must be much greater than the average velocity of a typical water molecule, $\mathbf{v}_B$, during this mixing process. Therefore, in this dilute, binary sugar solution it would also be appropriate to neglect bulk convection since $\mathbf{v}_B / \mathbf{v}_A \ll 1$.

In summary, when **(i)** there is no forced convection, **(ii)** there is no free convection, and **(iii)** the solution is dilute, bulk convection terms in the species' balance equations can be neglected. Thus equations (68) and (58) become

$$\frac{\partial c_A}{\partial t} = \nabla \cdot c D_{AB} \nabla x_A + R_A \qquad \text{(no bulk convection)} \qquad (79)$$

$$\frac{\partial \rho_A}{\partial t} = \nabla \cdot \rho D_{AB} \nabla \omega_A + r_A \qquad \text{(no bulk convection)} \qquad (80)$$

If c, D_{AB}, and ρ are constant, then

$$\frac{\partial c_A}{\partial t} = D_{AB} \nabla^2 c_A + R_A \qquad (c,\ D_{AB} \text{ constant; no bulk convection}) \qquad (81)$$

$$\frac{\partial \rho_A}{\partial t} = D_{AB} \nabla^2 \rho_A + r_A \qquad (\rho,\ D_{AB} \text{ constant; no bulk convection}) \qquad (82)$$

For the case of no chemical reactions (R_A and $r_A = 0$), equations (81) and (82) are known as **Fick's Second Law of Diffusion**.

There are some additional, special conditions under which bulk convection can be neglected. For instance, equation (63), which holds for the case of constant ρ and D_{AB}, will reduce to equation (82) if the vectors $\mathbf{v}$ and $\nabla \rho_A$ are perpendicular so that $\mathbf{v} \cdot \nabla \rho_A = 0$. Thus incompressible flows in which bulk convection (forced or natural) is perpendicular to the direction of diffusion also obey (82).

9. Common Boundary and Initial Conditions in Mass Transport.

9.i Conditions on Concentration. The concentration of a chemical species can be specified at a point in space or time. Examples are:

$$\rho_A(x_1 = 0) = \rho_{Ao} \quad (83)$$
$$\rho_A(t = 0) = \rho_{Ao} \quad (84)$$

where the value of ρ_{Ao} is given. Often, a condition on concentration may appear in the form of a partition coefficient or a Henry's Law constant. For example, imagine two phases in contact, both of which contain species *A* (Fig. 9). In phase I, the concentration of *A* is known, and the goal is to solve for the concentration profile of *A* in phase II. A common practice in these types of problems is to assume that, at the interface between the two phases, **local equilibrium** applies. Local equilibrium means that the concentrations of *A*, immediately on the two sides of the interface, are in equilibrium. This condition can be specified by an equilibrium **partition coefficient** H_c, for example

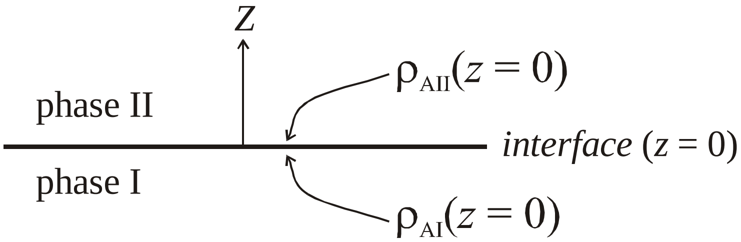

Fig. 9

$$\rho_{AII}(z = 0) = H_c\, \rho_{AI}(z = 0) \quad (85)$$

In equation (85), $\rho_{AII}(z = 0)$ is the concentration of *A* at the interface immediately inside phase II and $\rho_{AI}(z = 0)$ is the concentration of *A* at the interface immediately inside phase I. In essence, the partition coefficient accounts for the relative preference of *A* particles to be dissolved inside the two phases. If H_c and $\rho_{AI}(z = 0)$ are known, then $\rho_{AII}(z = 0)$ can be calculated and used as the boundary condition on ρ_A inside phase II.

A closely related concept is **Henry's law**,

$$p_A = H x_A \quad (86)$$

where p_A is partial pressure of *A* in a gas phase, x_A is its mole fraction in a liquid that is in equilibrium with the gas, and *H* is **Henry's Law constant**. Henry's law works well for dilute solutions; i.e. small x_A. For example, if a gas mixture containing oxygen at a partial pressure p_{O2} is in contact with a water phase then, assuming local equilibrium, the mole fraction of oxygen in the water phase immediately at the water-gas interface would be

$$x_{O2}(z = 0) = p_{O2}/H \quad (87)$$

If p_{O2} and *H* are known, the mole fraction $x_{O2}(z = 0)$ can be calculated and used as a boundary condition in solving for the oxygen concentration profile in the water phase. Note that the value of *H* will depend on the specific system considered. For ideal solutions obeying **Raoult's Law**, H equals the saturation pressure p_{ASat} of the partitioning species A.

9.ii Conditions on Fluxes. Boundary and initial conditions can also express statements about the flux of a species. The most obvious example is perhaps that of an impermeable boundary, across which there can be no transport of a species. Since diffusion of species A across the boundary must be zero,

$$j_{\mathrm{A}\perp}(z = 0) = 0 \qquad \text{(impermeable boundary)} \qquad (88)$$

The "$\perp$" subscript indicates diffusion perpendicular to (i.e. across) the boundary. For ordinary diffusion obeying Fick's Law, equation (88) becomes

$$j_{\mathrm{A}\perp}(z = 0) = -\rho D_{AB}\left(\frac{\partial \omega_A}{\partial z}\right)_{z=0} = 0 \quad \text{so that} \quad \left(\frac{\partial \omega_A}{\partial z}\right)_{z=0} = 0 \qquad (89)$$

z is the coordinate perpendicular to the boundary, as in Fig. 9. While equation (89) is written in terms of the mass diffusive flux, an analogous statement can be made regarding the molar diffusive flux. For the molar flux, the gradient of mole fraction x_{A} with respect to z vanishes at $z = 0$.

In contrast, at a permeable boundary species A can cross from phase I to phase II. If steady state applies, then A cannot accumulate at the boundary. Under these conditions,

$$n_{\mathrm{A}\perp,\mathrm{I}}(z = 0) = n_{\mathrm{A}\perp,\mathrm{II}}(z = 0) \qquad \text{(steady state; permeable boundary)} \qquad (90)$$

$n_{\mathrm{A}\perp,\mathrm{I}}$ and $n_{\mathrm{A}\perp,\mathrm{II}}$ are mass fluxes of A perpendicular to the permeable boundary. Equation (90) states that the mass flux $n_{\mathrm{A}\perp,\mathrm{I}}$ of A to the boundary from phase I must equal the flux $n_{\mathrm{A}\perp,\mathrm{II}}$ of A from the boundary into phase II – otherwise A would accumulate at the boundary and the condition of steady state would be violated.

When bulk convection perpendicular to the interface is negligible (this implies dilute solutions – see earlier discussion), $n_{\mathrm{A}\perp} = j_{\mathrm{A}\perp}$ and, assuming diffusion obeys Fick's Law, boundary condition (90) can be recast as

$$\rho_{\mathrm{I}} D_{\mathrm{I}} \left.\frac{\partial \omega_{A\mathrm{I}}}{\partial z}\right|_{z=0} = \rho_{\mathrm{II}} D_{\mathrm{II}} \left.\frac{\partial \omega_{A\mathrm{II}}}{\partial z}\right|_{z=0} \qquad \text{(steady state; permeable boundary; no bulk convection across boundary)} \qquad (91)$$

D_{I} and D_{II} are diffusion coefficients of A in phase I and II, respectively, and ρ_{I} and ρ_{II} are the corresponding total densities of the two phases. Equation (91) enforces continuity of the diffusion flux of A across the interface – the diffusive flux of A to the boundary from phase I equals that away from the boundary into phase II.

9.iii Conditions Involving Heterogeneous Reactions. When a chemical reaction occurs at a boundary or an interface, it is referred to as a **heterogeneous** reaction. Heterogeneous reactions typically appear in mass transport problems in the form of boundary conditions. For example:

(a). Infinitely rapid, irreversible consumption of A at a surface located at $z = 0$:

$$\rho_A(z = 0) = 0 \tag{91}$$

In (91), the reaction is assumed to occur so fast that concentration of A at the surface is effectively zero. In other words, as soon as a particle of A arrives at the surface, it reacts and therefore is eliminated.

(b). Steady-state, slow consumption of A at a surface located at $z = 0$:

$$n_{A\perp}(z = 0) = r_A^S \tag{92}$$

Since steady state applies, A cannot accumulate at the surface. Therefore, as stated in equation (92), the rate r_A^S (units: mass / (area time)) at which mass of A is consumed by the heterogeneous surface reaction must equal the flux $n_{A\perp}$ at which mass of A arrives at the surface.

The above examples of boundary conditions were expressed using the mass units. Any of these conditions could just as well be written in molar units. For example, in molar units equation (92) would become

$$N_{A\perp}(z = 0) = R_A^S \tag{93}$$

where R_A^S is the rate (units: moles / (area time)) at which A is consumed by the surface reaction and $N_{A\perp}$ is the molar flux of A perpendicular to the surface.