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SEPARATION-IRREVERSIBLE THERMO A UNIFIED THEORY OF SEPARATION PROCESSES BASED ON

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A UNIFIED THEORY OF SEPARATION PROCESSES BASED ON IRREVERSIBLE THERMODYNAMICS

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The theory of Irreversible Thermodynamics (IT), in particular the Generalized Maxwell–Stefan relations for describing the relative motion of species in a multicomponent mixture, is used to develop the fundamental basis for separation processes. The IT approach, and formulation, is shown to be indispensible in the estimation of the mass diffusivities of thermodynamically non-ideal fluid mixtures, description of separation processes in the region of the critical point, prediction of mass transfer rates and stage efficiencies in multicomponent separation processes, and for the correct modelling of separation processes involving more than one driving force. Use of the "dusty" fluid model allows the IT formulation to be consistently extended to the treatment of separation processes involving porous barriers of membranes.

KEYWORDS   Irreversible thermodynamics   Separation   Processes   Mass transfer   Diffusivity   Multi component.

1. INTRODUCTION

There are two basic steps involved in developing a separation process:

(1) The first step is to effect *relative* motion of the molecular species present in the mixture to be separated. To achieve this, a force must be exerted on each of the species; the various separation possibilities differ in the type of force exerted and by the manner in which this force is "created".

(2) The next step is to determine the rates at which the relative motion takes place. The knowledge of these rates is essential in the sizing of the separation equipment.

The theory of Irreversible Thermodynamics (IT) identifies the various driving forces which can cause relative motion of molecular species. Also, the IT formulation provides a relationship between the driving force exerted on the species and the velocities at which these species are caused to move in relation to the mixture. IT therefore offers a potential of being used to develop a unified theory of separation processes.

The starting point in the theory of IT is the expression for the rate of entropy production caused by the relative motion of species set up during separation (see

Lightfoot (1974) and Standart *et al.* (1979) for derivation):

$$\sigma = -\frac{1}{T}\sum_{i=1}^{n} c_i RT \mathbf{d}_i \cdot (\mathbf{u}_i - \mathbf{u}) \geq 0 \tag{1}$$

where $c_i RT \mathbf{d}_i$ represents the driving force exerted on species i *per unit volume of the mixture*, which tends to move species i *with respect to the mixture* with a relative velocity given by $(\mathbf{u}_i - \mathbf{u})$. This relative motion is the essence of separation. In the absence of any driving force there is no relative motion between the various species; the mixture is at thermodynamic equilibrium:

$$\sigma = 0; \qquad \mathbf{d}_i = 0 \quad \text{(thermodynamic equilibrium)} \tag{2}$$

When finite driving forces $\mathbf{d}_i$ are exerted on the species, the rate of entropy production is positive definite (cf. Eq. (1)), signifying the fact that energy must be expended in achieving separation. It remains to identify the various driving forces $\mathbf{d}_i$ and to relate the $\mathbf{d}_i$ to the $(\mathbf{u}_i - \mathbf{u})$.

2. DRIVING FORCES AND CONSTITUTIVE RELATIONS

From the theory of IT the driving force for relative motion of molecular species i with respect to the mixture is seen to be the sum of three constituent driving forces:

1. driving force arising out of chemical potential gradients which are created in the system; these forces are *always* present in separation processes even though they need not be the "initial" cause for separation to occur.

2. driving forces arising out of pressure gradients generated in the system. For pressure gradients to be effective in separation of a mixture there must be a difference in molecular weights of the species to be separated or put another way, there must be difference between the volume fraction and the mass fraction of the mixture.

3. for electrically charged species, application of an electrostatic potential gradient will cause the species to be set in relative motion.

The general expression for the overall driving force $\mathbf{d}_i$ has been conveniently put in the following form by Lightfoot (1974):

$$\mathbf{d}_i = \frac{x_i}{RT}\nabla_{T,p}\mu_i + \frac{(\phi_i - \omega_i)}{c_i RT}\nabla p + x_i z_i \frac{F}{RT}\nabla\Phi \tag{3}$$

In a mixture of uniform composition there will be no chemical potential gradients. To this mixture the application of a pressure gradient, for example, will set up a finite driving force $\mathbf{d}_i$ (provided the volume fraction ϕ_i differs from the mass fraction ω_i) causing relative motion of molecular species. This motion in turn will cause chemical potential gradients to be created which will act in a way to counter the pressure gradient till a dynamic equilibrium is reached (with $\mathbf{d}_i = 0$). There is a useful composition difference which exists at this equilibrium condition and separation is achieved.

Having identified the three basic constituents of the driving force $\mathbf{d}_i$, it now remains to relate the (relative) velocities of motion of species to this driving force. This relationship, called the constitutive relationship, is most conveniently written in the following two *equivalent* forms (see Lightfoot (1974) and Standart, Taylor and Krishna (1979) for derivation):

$$\mathbf{d}_i = \sum_{\substack{j=1 \\ j \neq i}}^{n} \frac{x_i x_j (\mathbf{u}_j - \mathbf{u}_i)}{\mathcal{D}_{ij}} \equiv \sum_{\substack{j=1 \\ j \neq i}}^{n} \frac{(x_i \mathbf{N}_j - x_j \mathbf{N}_i)}{c_t \mathcal{D}_{ij}}, \qquad i = 1, 2, \ldots, n \qquad (4)$$

The constitutive relation (4) is called the Generalized Maxwell–Stefan (GMS) equation and is the most convenient flux-driving force relation from a practical point of view. Equations (3) and (4) form the basis of our unified approach to the theory of separation processes. In their complete form they do appear awesome and before proceeding further it is instructive to deal with a few limiting cases, in order to emphasise the utility of the generalized approach.

First, let us consider the simplest case of separation of a binary mixture in the absence of pressure gradients and electrostatic potential gradients. The GMS equations take the form:

$$\mathbf{d}_1 = \frac{x_1}{RT} \nabla_{T,p} \mu_1 = \left(1 + x_1 \frac{\partial \ln \gamma_1}{\partial x_1}\right) \nabla x_1$$

$$= -\frac{\mathbf{J}_1[\equiv \mathbf{N}_1 - x_1(\mathbf{N}_1 + \mathbf{N}_2)]}{c_t \mathcal{D}_{12}} \qquad (5)$$

or

$$\mathbf{J}_1 = -c_t \mathcal{D}_{12} \Gamma \nabla x_1 = -c_t D_{12} \nabla x_1 \qquad (6)$$

where D_{12} is the Fickian diffusion coefficient which is related to the GMS diffusivity $\mathcal{D}_{12}$ by

$$D_{12} = \mathcal{D}_{12} \Gamma; \qquad \Gamma \equiv \left(1 + x_1 \frac{\partial \ln \gamma_1}{\partial x_1}\right) \qquad (7)$$

The thermodynamic factor Γ is a strong function of composition and, as a consequence the Fickian diffusivity D shows a strong composition dependence. Figure 1 shows the strong variation of the Fickian diffusivity of triethylamine(1)-water(2). The GMS diffusivity $\mathcal{D}_{12}$, calculated as D_{12}/Γ, shows a much simpler variation with composition. This goes to show that the GMS diffusivity more closely reflects the "kinetic" nature of the diffusion process whereas the commonly used Fickian diffusivity reflects both the "kinetic" and "thermo-dynamic" factors. Separation of these two factors is useful from the point of view of calculation of the transfer rates. From Figure 1 it can be seen that $\log \mathcal{D}_{12}$ varies with x_1 in a linear fashion. This (empirical) observation has been confirmed for a variety of systems by Vignes (1966). Acceptance of this allows calculation of $\mathcal{D}_{12}$ from a knowledge of the infinite dilution diffusivities. The Fick's law diffusivity can then be calculated from the GMS diffusivity by use of Eq. (7). The use of the GMS constitutive relation, in preference to the conventionally used

FICKIAN DIFFUSION COEFFICIENT
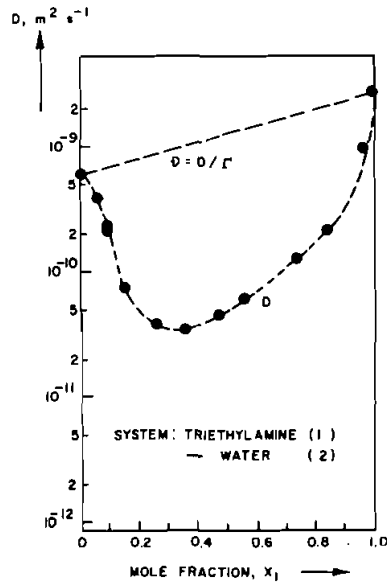
FIGURE 1   Variation of the Fickian diffusivity D and the GMS diffusivity with composition. Dudley and Tyrrell (1973).

Fickian formulation, provides a convenient practical treatment of mass transport phenomena in non-ideal fluid mixtures.

Another interesting observation concerns the variation of the diffusivity of a binary mixture with temperature in the region of the critical solution temperature (LCST or UCST), as shown in Figure 2. The Fickian diffusivity falls sharply in
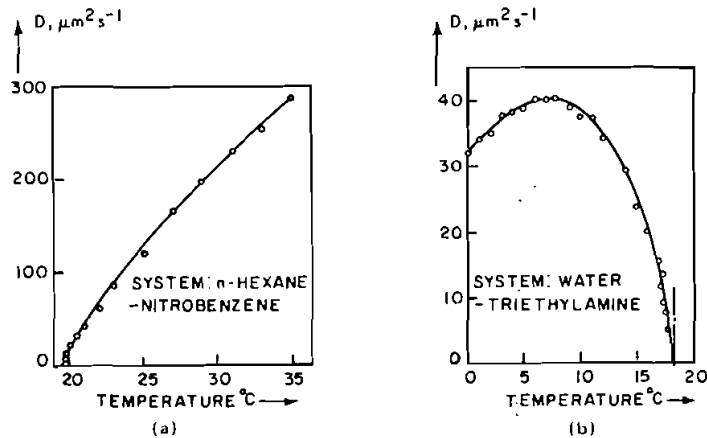
FIGURE 2   (a) Fickian diffusivity of the system n-hexane-nitrobenzene as a function of temperature, $x_1 = 0.58$. (b) Fickian diffusivity of the system triethylamine-water, $x_1 = 0.087$. Data from Haase and Siry (1968).

value to zero as the CST is approached! Again, with the application of IT theory this "strange" behaviour of the Fickian diffusivity can be understood. The reasoning is as follows. From considerations of thermodynamic stability, the determinant of the Hessian matrix $|G|$ must be positive definite (see Modell and Reid (1983) for more detailed discussions), i.e.

$$|G| \geq 0 \tag{8}$$

where the elements of the matrix $[G]$ are given by

$$G_{ij} = \frac{\partial(\mu_i - \mu_n)}{\partial x_j} = G_{ji} = \frac{\partial(\mu_j - \mu_n)}{\partial x_i} = \frac{\partial^2 G}{\partial x_i \, \partial x_j} \tag{9}$$

where G is the molar Gibbs free energy. At the critical point itself we have

$$|G| = 0 \tag{10}$$

It follows from Eq. (7) that the Fickian diffusivity must vanish at the critical point for a binary system. A few separation processes, such as liquid-liquid extraction could operate close to the critical point (the plait point in L–L systems) and the IT formulation is indispensible for the estimation of the transfer rates. The recent paper by Krishna *et al.* (1985) emphasised the need for using a rigorous IT formulation in describing the interphase mass transfer rates in L–L extraction.

Having demonstrated the utility of the GMS formulation in describing mass transport in non-ideal fluid mixtures, and in the region of the critical point, let us turn our attention to ideal gas mixtures. In this case the GMS Eqs (3) and (4) reduce to

$$\mathbf{d}_i = \nabla x_i + \frac{(x_i - \omega_i)}{p} \nabla p = \sum_{\substack{j=1 \\ j \neq i}}^{n} \frac{x_i \mathbf{N}_j - x_j \mathbf{N}_i}{c_t \mathcal{D}_{ij}} \tag{11}$$

where we have omitted the electrostatic potential gradient term, usually not of importance in gaseous separation. Also, for ideal gas mixtures the mixture molar density $c_t = p/RT$ and the volume fraction ϕ_i equals the mole fraction x_i. For ideal gas mixtures the GMS diffusivity $\mathcal{D}_{ij}$ equals the Fickian diffusivity of the corresponding binary pair and these are composition independent. Equations (11), which are called the Maxwell-Stefan equations, are consistent with the kinetic theory of gases. The Maxwell-Stefan equations (11) are thus a special case of the IT theory.

It is important to appreciate that even for mixtures of ideal gases the diffusivities of the binary pairs $\mathcal{D}_{ij}$ are, in general, unequal to one another. In fact in the sweep diffusion process for separation, as we shall see later, it is the *difference* in the diffusivities of the binary pairs which is harnessed for the purposes of achieving separation. The IT formulation takes this effect into account quite routinely. In the modelling of the mass diffusion process it is quite tempting to use Occam's Razor "Pluralitas non est ponenda sine necessitae" or in free translation "Do not complicate things beyond necessity". With this approach let us assume all pair diffusivities are (nearly) equal to one another leading to the
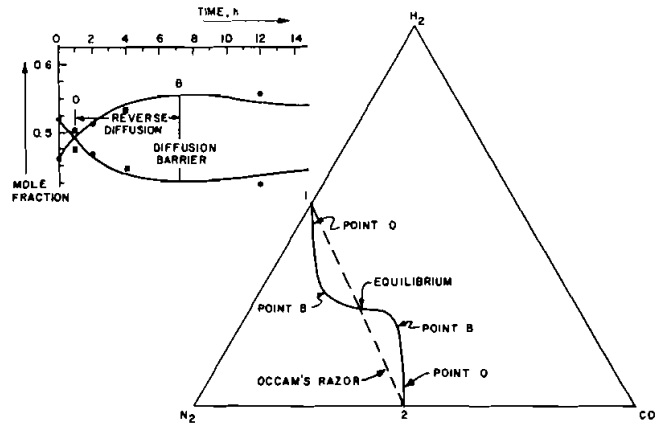
FIGURE 3 Diffusion in a two-bulb diffusion cell (Bulbs 1 and 2). For the particular starting compositions 1 and 2 denoted on the triangular diagram, N_2 experiences osmotic diffusion at O, diffusion barrier at B and reverse diffusion between O and B. The dashed lines - - - - denote the composition path that would have been followed if Occam's Razor Eq. (12) were to be employed. Data of Duncan and Toor (1962).

simplification (cf. Eq. (11)):

$$J_i \equiv N_i - x_i N_t = -c_t \mathcal{D} d_i, \qquad i = 1, 2, \ldots, n \tag{12}$$

or in other words the diffusion flux J_i of component i, with respect to the mixture is proportional to its *own* driving force d_i. Duncan and Toor (1962) studied diffusion in the ideal gas system $N_2-H_2-CO_2$ in a two-bulb diffusion cell. Of particular interest are the composition profiles of N_2, shown in the inset to Figure 3. At point 0, the compositions of N_2 in the two bulbs are the same; nevertheless the diffusion of N_2 continues to take place. Between the points O and B the composition of N_2 in bulb 1 continues to increase at the expense of the composition in bulb 2; in this region diffusion of N_2 takes place from a region of low composition (bulb 2) to a region of higher composition (bulb 1). At point B the composition profiles in both bulbs 1 and 2 are flat, which signifies that no diffusion takes place at B despite the existence of a large composition difference driving force. The three peculiar phenomena noted have been respectively termed osmotic diffusion (at point 0), reverse diffusion (between O and B) and diffusion barrier (at point B). Beyond point B, diffusion of N_2 takes place "normally". The diffusion behaviour of this *ideal* gas mixture cannot be described by use of the Occam's Razor model Eq. (12), wherein each flux is taken to be proportional to its own driving force, with equal diffusion coefficient for each component. As shown by Duncan and Toor (1962), the Maxwell–Stefan Eq. (11) is able to "model" the diffusion process quantitatively. In separations involving gaseous mixtures with widely varying molecular weights the complete form of the MS equations must therefore be used. Generally speaking, gaseous mixtures with H_2 as one of the components will fall into this category.

One further point regarding the two-bulb diffusion experiment of Duncan and Toor (1962) needs special mention. Does the phenomenon of reverse diffusion

violate the second law of thermodynamics? The answer is an emphatic NO. The positive definite condition for the rate of entropy production, Eq. (1) only requires the total system entropy production to be positive definite. N_2 can consume entropy in experiencing reverse diffusion *provided* the other two species H_2 and CO_2 produce entropy at such a rate that the total rate of production for the system as a whole is positive. These two species are in effect pumping N_2 uphill. IT helps in rationalizing the experimental observations.

If in the two-bulb diffusion experiment, the transfer of N_2 were to be modelled using the "effective" diffusivity concept, then this effective diffusion coefficient for N_2 will assume values ranging from negative (in the region of reverse diffusion) to zero (at the point of diffusion barrier). Such "odd" behaviour of the effective diffusivity is characteristic of multicomponent systems, i.e. systems having three or more species. The GMS pair diffusivity $Đ_{ij}$ is always positive definite. This can be seen by combining Eq. (1) and (4) which gives the following expression for the rate of entropy production:

$$\sigma = \frac{c_t R}{2} \sum_{i=1}^{n} \sum_{\substack{j=1 \\ j \neq i}}^{n} \frac{x_i x_j}{Đ_{ij}} (\mathbf{u}_i - \mathbf{u}_j)^2 \geq 0 \tag{13}$$

The positive definite condition for σ can only be met if the $Đ_{ij}$ are individually positive definite, i.e.

$$Đ_{ij} \geq 0 \tag{14}$$

The neat and compact form of Eq. (13), which contains no thermodynamic factors, also suggest the fundamental and superior basis of the GMS formulation of IT theory. Equation (13) was first derived by Standart, Taylor and Krishna (1979).

Having set up the theoretical framework for dealing with separation processes, let us first attempt to classify separation processes in a logical and systematic manner using this IT framework.

3. CLASSIFICATION OF SEPARATION PROCESSES

Relative motion between the species in a mixture can be caused by the action of one, or more, of the following (cf. Eq. (3))

1. chemical potential gradients
2. pressure gradients
3. electrostatic potential gradients (effective only for charged species)

The above gradients may be created or made to act upon a system consisting of:

- a single phase (G, L or S), or
- a two phase system (V–L, G–L, L–L, G–S, L–S, G–PS, L–PS), or
- a system consisting to two phases separated by a porous barrier or membrane (Fluid—M–Fluid; where Fluid = G, V or L)

where we use the notation: G = gas; V = vapour; L = liquid; S = solid; PS = porous solid; M = membrane or porous barrier.

The first scheme of classifying separation processes is based on the *type* of gradients (chemical potential, pressure or electrostatic potential) created in the system and whether these gradients are created in a (i) single phase, or (ii) a two phase system, or (iii) a system consisting of two fluid phases separated by a membrane or porous barrier.

The second scheme of classifying separation processes is according to whether the primary cause for separation is difference in the system (usually two-phase) composition at *equilibrium* or whether we rely on differences in *transport rates* of the species to achieve the desired separation. Thus we have:

(i) *Equilibration separation processes.* Here we have a useful composition difference between the two phases at equilibrium ($\sigma = 0$; $d_i = 0$) and our efforts are devoted to promoting the approach to equilibrium. IT is useful in predicting the actual approach to equilibrium (by use of Eqs. (3)–(4)), i.e. in predicting stage efficiencies or heights of transfer units. By operating industrial contactors with a high degree of turbulence, the rates of equilibration can be enhanced because of the additional, parallel, mechanism of turbulent mass transport.

(*ii*) *Rate governed separation processes.* Here we have no separation occurring at equilibrium e.g. a single phase system of homogeneous composition at equilibrium or it may be that an unfavourable equilibrium exists in a heterogeneous system. This situation is modified by the rate process so that we operate in a manner to prevent equilibration. The key to the separation is the different rates of transfer of the component species in the non-equilibrium situation. Essentially we rely here on the differences in the fluxes N_i created within a single phase or across phase boundaries. IT plays a vital role here in the calculation of the transfer fluxes N_i, by use of Eqs. (3) and (4). If we were to rely only on the differences in the GMS pair diffusivities to ensure differences in the rates of transfer N_i, then the separation factors α_{ij}:

$$\alpha_{ij} = (y_i/y_j)/(x_i/x_j) \tag{15}$$

(here y and x denote mole fractions in the two product streams) will be close to unity (except in exceptional cases). Therefore in practice the separation factors (or selectivities) of the process are enhanced by use of selective barriers (or membranes) which allow predominantly the passage of one component. The membranes may take different forms: porous diaphragm, metal perforated screens, polymeric films with or without charged species, liquid surfactant films etc.

Combining the two classification schemes above we may cite the following examples of industrial importance:
Single Phase Separation Processes
– Equilibration separation process: centrifugation
– Rate governed separation process: electrolysis, thermal diffusion
Two-Phase Separation Processes
– Equilibration separation process:
  V–L: distillation, partial condensation

G–L: absorption, desorption, stripping, evaporation, gas extraction
L–L: extraction
G–S: sublimation, desublimation
L–S: crystallization, zone melting, freezing
G–PS: adsorption
L–PS: adsorption, ion exchange, leaching

– Rate governed separation process:
condensation of azeotrope vapours through inert gas; evaporation of azeotrope liquid into an inert gas

Membrane Separation Processes

– Equilibration separation process:
osmosis

– Rate governed separation process:
gas diffusion through barriers, mass or sweep diffusion, permeation of fluids through polymeric films or liquid surfactant films, reverse osmosis, ultrafiltration, dialysis, electrodialysis, pervaporation.

We now take up the discussions of separations under the above three main categories and shall see how IT can be useful in the modelling and design of the separation process.

4. SINGLE PHASE SEPARATION PROCESSES

4.1 Centrifugation

Consider a binary system made up of uncharged species and subjected to a pressure gradient. Provided the volume fraction ϕ_i is different from the mass fraction, the two species will experience a different force (cf. Eq. (3)) and relative motion between the species will result. Due to the composition difference arising out of this relative motion a chemical potential gradient will be set up which will act in a "direction" tending to equalize the composition differences. Eventually a thermodynamic equilibrium condition will be attained wherein the two forces (due to chemical potential and pressure gradients) will balance each other. At equilibrium, $d_1 = 0$, the composition distribution of component 1 will be given by (cf. Eq. (3))

$$\Gamma \frac{dx_1}{dr} = \frac{(\omega_1 - \phi_1)}{c_t RT} \frac{dp}{dr} \tag{16}$$

which shows that "dense" molecules for which the mass fraction is greater than the volume fraction will tend to move preferentially down the pressure gradient. For an aqueous solution of component 1, for example, an indication of the magnitude of the pressure gradient necessary to cause separation can be gleaned from the fact that $c_t RT = 138\,\mathrm{MN/m^2}$ and therefore pressure gradients of the order of a few thousand atmospheres must be set up across the system in order to achieve measurable separations. In practice, large pressure gradients can be

developed in a centrifuge for which

$$\frac{dp}{dr} = \rho\Omega^2 r \tag{17}$$

where Ω is the angular velocity ($\Omega = 2\pi f$ which f is the rotational speed in revolutions per second) and r is the radius of the centrifuge. Many thousand rotations per minute are required to induce the necessary gradients of pressure.

For an ideal gas mixture, the separation factor α_{12} (defined by Eq. (15)) can be obtained by integration of Eq. (16)–(17) and works out to

$$\alpha_{12} = \exp\left[(M_1 - M_2)\frac{\Omega^2 r^2}{2RT}\right] \tag{18}$$

Ultracentrifugation is the industrially used technique for the separation of the isotopes of uranium: $U^{235}F_6$ ($M_1 = 349.15$) and $U^{238}F_6$ ($M_2 = 352.15$). Even at a rotational speed of 40,000 rpm the separation factor, calculated from Eq. (18) taking $r = 60$ mm, works out to only 1.0396. For commercial operation to achieve the desired throughput and separation, many thousand centrifuges are required.

4.2 Single Phase Separations involving Ionic Species

Consider an aqueous solution of electrolytes. The mixture consists of the ionized species (both + and − vely charged) and the "solvent" water. If an electrostatic potential is applied to the solution then the $+ve$ ions will move towards the $-ve$ electrode and the $-ve$ ions will move in the opposite direction towards the $+ve$ electrode. For *dilute* electrolyte solutions, Eqs. (3) and (4) reduce to the following expression for each ionic species i:

$$\mathbf{N}_i = -c_i\DJ^0_{in}\nabla x_i - c_i z_i \DJ^0_{in}\frac{F}{RT}\nabla\Phi + c_i\mathbf{u}_n \tag{19}$$

where the subscript n denotes the "solvent" water. Equation (19) is usually referred to as the Nernst–Planck equation and as we see it is only a special case of the GMS formulation of IT. The charge on each ionic species, z_i, can be positive or negative (e.g. $z_{H^+} = +1$; $z_{Cl^-} = -1$) and so the electrostatic force can act either in the same or opposite direction to the composition gradient.

Even when no electrostatic potential is imposed on the system, Eq. (19) must be used to describe ionic mass transport because when diffusion of ionic species takes place there will be a charge separation due to the fact that the ions have different intrinsic diffusivities (e.g. $\DJ^0_{H^+} = 9300$; $D^0_{Cl^-} = 2000$; $D^0_{Ba^{++}} = 850\,\mu m^2 s^{-1}$). In the bulk solution there will be a tendency to maintain electro-neutrality:

$$\sum_{i=1}^{n} c_i z_i = 0 \tag{20}$$

To maintain electroneutrality an electrostatic force will be created on each of the ionic species. This effect can best be explained in terms of the data of Figure 4.
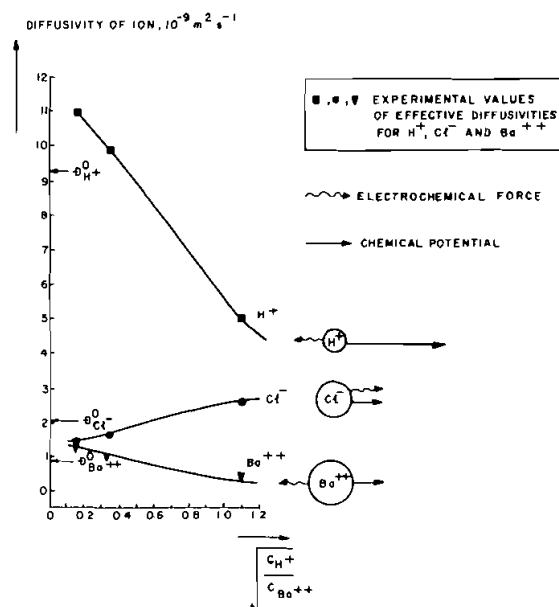
FIGURE 4 Diffusion in mixed electrolyte systems. The effective diffusivity of an ion is strongly influenced by the electrostatic force "pull" or "push" exerted on it. Data from Vinograd and McBain (1941). See also Krishna (1987a).

Here we see that the "effective" diffusion coefficient of H^+ ion is lowered considerably due to the presence of other ions. The electrostatic force tends to act as a "leash" tending to impede the transfer of H^+ in the interests of maintaining electroneutrality. On the other hand the relatively sluggish Cl is made to move "faster" by the electrostatic "pull". The, even more sluggish, Ba^{++} is slowed down even further by the electrostatic leash, as pictured in Figure 4. For separation processes involving ionic species, such as ion exchange and metals extraction, the correct modelling of the transfer process using the IT formulation is essential. For further details see Krishna (1987a). We shall be touching on this later on in this paper but the principles behind the phenomena are those described above.

4.3 Thermal Diffusion

In setting up the GMS Eq. (4) we had ignored the effect of thermal diffusion, i.e. diffusion induced by a temperature gradient. Thermal diffusion is usually unimportant in practice, but in a few cases this phenomenon can be used to effect separation. To take account of thermal diffusion, the term on the right hand side of Eq. (4) has to be augmented to include the effect of a temperature gradient. For a binary system, for example, we may write (cf. Eq. (6)):

$$J_1 = -c_t \mathcal{D} \Gamma (\nabla x_1 + k_{1T} \nabla \ln T) \tag{21}$$

where k_{1T} is the thermal diffusion ratio. The greater the value of k_{1T}, the greater is the separation achievable by thermal diffusion. When k_{1T} is $+ve$, species 1 moves down the temperature gradient; when k_{1T} is $-ve$, component 1 moves up the temperature gradient to the warmer region. k_{1T} is usually one or two orders of magnitude smaller than unity and therefore the separation factors achieved by thermal diffusion are close to unity. For successful practical application the small separations achieved can be enhanced by thermal convection as is done in the thermogravitational thermal diffusion column of Clusius and Dickel (1938). In gaseous mixtures at normal temperatures the heavier molecules usually diffuse down the temperature gradient, leading to a higher composition in the colder region.

The thermal diffusion ratio is more sensitive than any of the other transport coefficients to the *nature* of the intermolecular forces. Whereas viscosity, thermal conductivity and molecular diffusivity are first order effects depending primarily on the occurrence of molecular collisions and only secondarily on the *nature* of these collisions, thermal diffusion effect arises from a second order process and the values of the thermal diffusion coefficient may be positive, zero or negative according to the nature of the molecular interactions. Commercial application of the thermal diffusion phenomena is mainly for the separation of isotopes which show differences only at a second order level; see Rutherford (1975).

5. TWO PHASE SEPARATION PROCESSES

In this class of separation processes two phases are created from the original mixture either by the input of energy (heating or cooling) or by the addition of a separating agent; this agent may take the form of a liquid, a gas or porous solid. Most of the processes in this category are equilibration separation processes and thus rely on the fact that at equilibrium there is a useful composition difference between the two phases. For the two phases I and II, the condition of thermodynamic equilibrium, Eq. (2), leads to the condition:

$$\ln\left(\frac{\gamma_{iI}x_{iI}}{\gamma_{iII}x_{iII}}\right) + \frac{(\bar{V}_i)_{avg}}{RT}(p_I - p_{II}) + \frac{z_i F}{RT}(\Phi_I - \Phi_{II}) = 0 \qquad (22)$$

wherein we have noted that the volume fraction $\phi_i = c_i \bar{V}_i$ where $\bar{V}_i$ is the partial molar volume of species i. Equation (22) is the generalized expression for equilibrium between two phases, which follows nicely from a general IT theory. The treatment of phase equilibria and their prediction from a knowledge of the molecular properties and functional groups as discussed in the excellent texts of Praustnitz (1969) and Reid, Prausnitz and Sherwood (1977).

Most industrial contactors operate under steady-state conditions; here the gradients in composition in either phase are dictated by the operating conditions *and* the equilibrium composition distribution (satisfying Eq. (22)). The GMS formulation Eqs. (3)–(4) is useful in determining the steady-state transfer rates and hence stage efficiencies.

In the class of two-phase separation processes distillation is by far the most
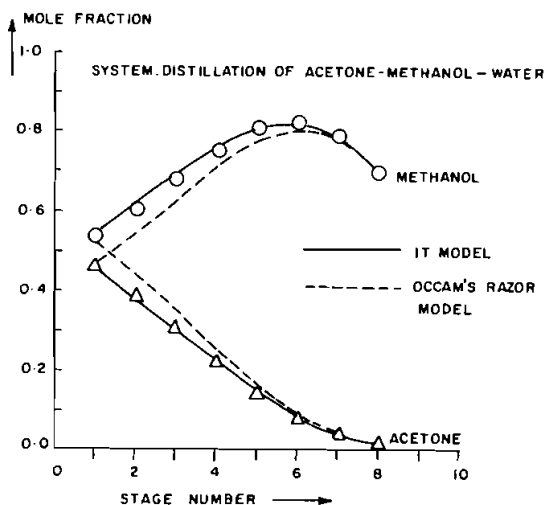
FIGURE 5 Composition profiles in a distillation tray column. Comparison of the experimentally measured profiles with predictions of: (1)——— IT theory, Eqs (3)–(4), (2) - - - - Occam's Razor, Eq. (12). Comparative study carried out by Krishnamurthy and Taylor (1985).

widely used. It is surprising therefore that it is only recently that it has been realized that for highly non-ideal mixtures it is absolutely necessary to use the GMS formulation for estimation of the transfer efficiencies on trays. Figure 5 compares the experimentally measured composition profiles for the system acetone-methanol-water with the theoretical predictions based on two different approaches: (1) based on the GMS formulation of IT theory, Eqs. (3)–(4), and (2) based on the Occam's Razor "model" Eq. (12), which is equivalent to assuming equal component transfer efficiencies for each individual component in the multicomponent mixture. The results given in Figure 5 demonstrate the clear superiority of the GMS formulation of IT; see Krishnamurthy and Taylor (1985).

The results of Figure 5 only show the superiority of the IT formulation in *simulation* of experimental distillation results. The effect of differing constituent binary pair $Ð_{ij}$, in both vapour and liquid phases, can also be very significant in column design calculations. Krishnamurthy and Taylor (1985) studied four cases of column design using both the GMS formulation and the Equal Efficiency (i.e. Occam's Razor) approach. Their key results in separation are given in Table I.

The results show that the Occam's Razor approach is adequate for thermodynamically ideal mixtures of compounds with small differences in molecular size while for highly non-ideal mixtures the use of Occam's Razor approach could lead to severe underdesign and it is essential to use the GMS formulation of IT.

Similar conclusions in favour of the IT approach to the modelling of distillation and absorption separations in continuous contacting apparatuses (e.g. packed and wetted-wall columns) have been reached in other studies carried out; see Krishna and Taylor (1986) for a summary of these findings.

We had earlier pointed out the need to use the IT formulation to describe diffusion in the region of the critical point such as the plait point in $L-L$ systems.

TABLE I

Number of distillation trays required for specified separation

System	Equal efficiency assumption	GMS formulation of IT
1. Methanol–isopropanol–water	30	41
2. Acetone–methanol–water	80	105
3. Ethanol-*t* butanol–water	79	121
4. C_1–C_5 hydrocarbons	33	32

Krishna *et al.* (1985) have recently reported the results of transient composition profiles measured in a batch stirred cell with the *L–L* system: acetone-glycerol-water. The equilibration trajectory in both liquid phases (glycerol-rich towards the right and acetone-rich towards the left of Figure 6) are highly curvilinear while the Occam's Razor approach would predict equilibration along a *linear* (dashed in Fig. 6) approach to equilibrium. Use of the IT formulation for diffusion in either phase is able to successfully "model" the experimental results (Krishna *et al.* (1985)). The *L–L* behaviour portrayed in Figure 6 is the exact analog of the two-bulb gas diffusion experiment of Duncan and Toor (1962) seen earlier; cf. Fig. 3.

In the foregoing we have demonstrated the utility of using the GMS formulation in describing the interphase mass transfer processes in the widely
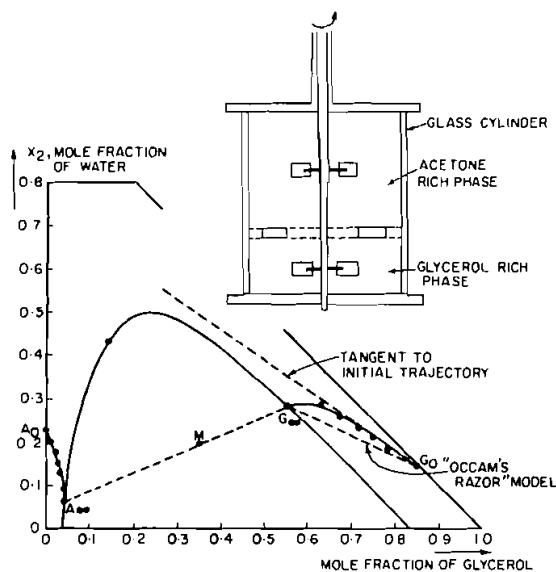

FIGURE 6 Composition trajectories in the *L–L* system: acetone–glycerol–water. Results of Krishna *et al.* (1985). It is interesting to observe that the tangent to the initial traject in the glycerol-rich phase misses the binodal curve completely! Occam's Razor approach is hopelessly inadequate.

used separation processes of distillation and extraction. Conventionally used design procedures for such equipment still use the equivalent of the Occam's Razor formulation: Eq. (12), which can be expected to be in serious error in some cases. Let us turn our attention to another important separation process of partial condensation of a vapour mixture.

Separation is achieved when a vapour mixture is cooled below the dew point of the vapour mixture. Industrial condensers are usually operated in a manner that the composition of the liquid condensate is dictated by the transfer fluxes of the components at the point in question:

$$\frac{x_i}{x_j} = \frac{\mathbf{N}_i}{\mathbf{N}_j} \tag{23}$$

Also in practice the mass transfer limitations are increased due to the presence of inert gases such as air. Accurate estimation of the transfer fluxes $\mathbf{N}_i$, using the GMS formulation of IT, is required in the design of condensation equipment, as has been emphasized in the review of Krishna and Taylor (1986). In an extreme example of condensation of acetone-benzene in the presence of helium, the work of Krishna (1981) has shown that use of a simple-minded Occam's Razor formulation could lead to a wrong anticipation of the *direction* of transfer of acetone; see Figure 7. Under the conditions of the experiment described in Figure 7 reverse diffusion of acetone takes place, a phenomenon earlier signalled during our discussions of the diffusion behaviour of multicomponent gas mixtures.
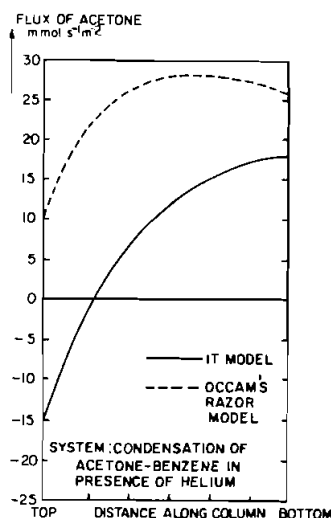
FIGURE 7   Condensation of acetone–benzene vapour mixture in the presence of inert gas helium. Experiments carried out in a wetted wall column. For specified inlet conditions at the top of the column, the Figure 7 shows the acetone fluxes predicted by (1) IT model and (2) Occam's Razor model. Use of Occam's Razor predicts +ve fluxes (i.e. condensation of acetone) all along the column. It was observed experimentally that there was net vaporization of acetone in the column, which situation can only be anticipated by the IT model. Results of Krishna (1981).

One reason why the GMS formulation of IT is not used in routine design calculations of separation equipment is possibly due to the (apparent) complexity of the diffusion equations (3)–(4). However, it has been shown by Krishna and Taylor (1986) that the GMS diffusion equations can be solved in an efficient manner to yield interfacial transfer fluxes and that these rigorous formulations can be incorporated straightforwardly into efficient computer algorithms for the design of separation equipment. Also, with the use of efficient computational techniques for the solution of the set of design equations (representing mass and energy balances, interfacial mass and energy transfer relations and interfacial equilibrium) the IT approach does *not* require more time than the Occam's Razor approach!

In the foregoing examples of fluid-fluid separation processes, the major, and only, driving force causing relative motion of species (separation) was due to the chemical potential gradients. If the species being separated are charged then the motion of the species will automatically *set* up an electrostatic potential gradient within each of the fluid phases, which gradient will exert a "pull" or a "push" on the ions depending on the charge and the direction of motion. Neglect of the electrostatic effects can lead to significant errors in the calculation of the transfer rates, as has been shown by Tunison and Chapman (1976) for the case of L-L extraction of metals; see also Figure 8. The IT formulation Eqs. (3), (4) and (19) affords a consistent approach of modelling this process.

In L-S separation processes such as crystallization, the knowledge of diffusion coefficients in supersaturated solutions is of importance in the prediction of the rates of crystal growth. Diffusivity data show a very rapid decline in the Fickian diffusivity with increasing concentration in the super-saturated region (Myerson *et al.* (1984), (1986)). This behaviour is analogous to the behaviour noted in L-L systems in the region of CST (Haase and Siry (1968)) and the IT approach is essentially for a proper description of the transport process. Compare Figures 2 and 9.

Let us now turn our attention to another important class of two-phase separation processes in which a fluid is brought into contact with a *porous* solid;

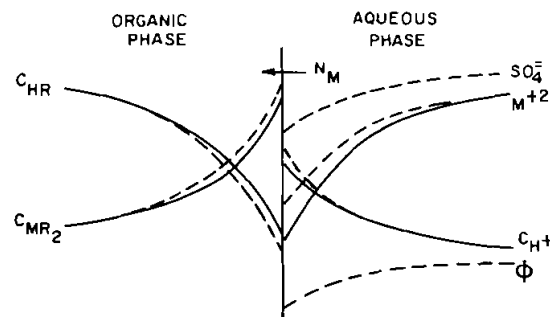FIGURE 8   Concentration profiles during metals extraction: $M^{+2} + 2HR = MR_2 + 2H^+$ in which an aqueous metal ion, such as copper or nickel is exchanged for hydrogen ions by an organic phase solute HR to form an organic soluble metal MR_2. – – – – denotes concentration profiles taking electrostatic effects into account; —— denotes profiles ignoring such effects. See Tunison and Chapman (1976).
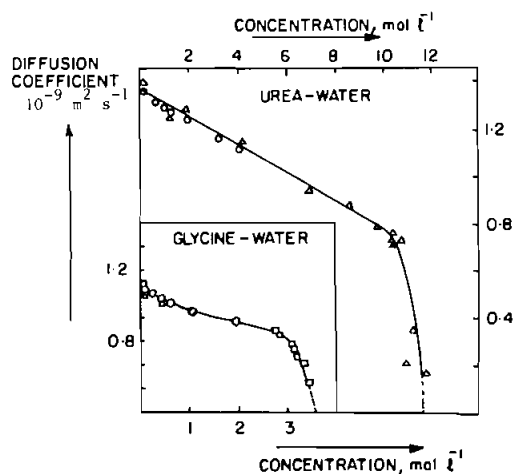
FIGURE 9   Diffusion coefficients in the system urea–water and glycine–water. Data from Myerson *et al.* (1984, 1986).

adsorption and ion exchange fall into this broad category.

Components in both gases and liquids may be separated by selective adsorption on such materials as activated carbon, silica or alumina gel, zeolites etc. Adsorption can be carried out on both fixed and moving beds of solid adsorbent. Applications of adsorption include the drying of gaseous streams by use of silica gel, separation of organic mixtures by adsorption on zeolites, removal of organic pollutants from waste water streams by adsorption on activated carbon, water treatment using ion exchange resins, etc.

The most common form of operation is with use of a fixed bed of adsorbent particles. The fluid feed is made to run through the bed until the bed becomes nearly saturated and small quantities of adsorbate begins to "break through". Then the bed must be regenerated to restore its adsorptive capacity and to recover the adsorbed material. Similarly synthetic ion-exchange resins or some naturally occurring clays will adsorb ions from aqueous solutions displacing other ions originally present in the resin matrix until the resin becomes nearly saturated with the feed stream. Regeneration then follows.

Both adsorption and regeneration are collectively termed "sorption" processes. Fixed bed sorption processes are fundamentally non-steady state and the concentrations in the fluid and solid phases inside the bed depend on position and time. When equilibrium between the fluid and solid phases is reached, the bed loses its sorptive capacity and allows the fluid to pass through the bed unchanged in composition. The knowledge of the fluid-sorbent equilibria, commonly termed the "sorption isotherm", is a key factor in the choice of a suitable absorbent and for design of the bed. The height of the adsorbent bed required for a specified 'on stream' time is determined by the fluid-solid equilibrium relationship and by the mass transport processes taking place both outside the solid phase and in the pores. The modelling of the mass diffusion process on the outside of the adsorbent is best carried out using the GMS equations (3)–(4) which reduce to

Eqs. (11) for ideal gas mixtures. For transport of mass inside the pores of the solid some additional mechanisms of mass transport have to be reckoned with. We first take up the problem of describing mass diffusion of an ideal gas multicomponent mixture inside porous media and will later extend the treatment to include diffusion of non-ideal liquid mixtures.

Transport of a gaseous component inside the porous medium is by the following mechanism:

(i) viscous flow through the pores; this mechanism is non-separative. It may be noted that this viscous flow mechanism, acting *along* the direction of diffusion, is not present when the fluid mixture is not constrained by the walls of the porous medium, i.e. the diffusion takes place in "open" space.

(ii) Separative, diffusive, transport of the gaseous component through the pores of the medium. In this case due to the presence of the "inert" wall of the solid, molecular-wall collisions will occur in addition to molecule-molecule collisions, the latter only being present for diffusion in open space. When the diameter of the pore is less than the mean free path of the gaseous molecule, collisions at the wall "controls" and the mechanism of transport is termed Knudsen diffusion. On the other hand when the pore diameter is much greater than the mean free path of the gaseous molecules, the collisions are mainly between the gas molecules, and "Bulk" gas diffusion mechanism prevails, as in open space.

Figure 10 shows a schematic of the mechanisms of transport inside the pores using the analogy with electrical networks; see Jackson (1977) and Mason and Malinauskas (1983) for further conceptual discussions. The "total" transfer flux of component i is the sum of the viscous and diffusive contributions:

$$\mathbf{N}_i = \mathbf{N}_i^{viscous} + \mathbf{N}_i^{diffusive} \tag{24}$$

The viscous contribution to the total flux $\mathbf{N}_i^{viscous}$ can be calculated from

$$\mathbf{N}_i^{viscous} = -x_i \frac{B_0 p}{\eta RT} \nabla p \tag{25}$$

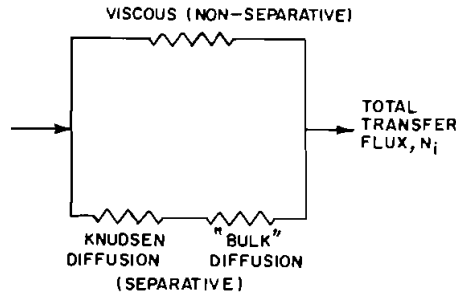where B_0 is the permeability of the medium; $B_0 = r_0^2/8$ for a cylindrical pore of

FIGURE 10   Electric analogue circuit as a mnemonic device for combining different mechanisms for transport of gaeous species inside porous medium.
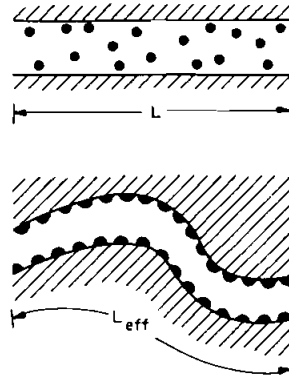
FIGURE 11   Schematic ways of visualizing the dusty-gas model for gaseous transport inside porous medium (Mason (1983)).

radius r_0. The non-separative character of viscous transport is evident from Eq. (25).

Let us now consider the modelling of the diffusive process inside the pores. How do we take the constraints of the walls consistently into account in our IT formulation? Eq. (11) is valid for ideal gas mixtures diffusing in open space only. An elegant way of extending the IT formulation to include the molecule wall interactions is to consider the wall (porous medium) as the (pseudo)$(n + 1)$th component in the mixture, the so-called "dust" molecule (Jackson (1977), Mason (1983)). These dust species are giant molecules ($M_{n+1} \rightarrow \infty$), uniformly distributed in space ($\nabla c_{n+1} = 0$), and are held motionless ($\mathbf{N}_{n+1} = 0$) by unspecified external forces acting on them. The precise origin of this external force does not matter in the mathematical treatment; in practice it would usually arise from whatever clamping device holds the porous body stationary. The particular arrangement of the dust particles in space does not matter either, since such geometric characteristics are absorbed into the transport coefficients as the multiplicative factor $\varepsilon/\tau = \text{porosity/tortuosity}$ of the medium. Thus it is unimportant how one chooses to visualize the dust—literally as a random array of large spheres stuck in space, as irregular blobs on the surface of a tortuous capillary, as indicated in Figure 11, or in some other fashion. See the excellent texts of Jackson (1977) and Mason and Malinauskas (1983) for a detailed discussion of the Dusty Gas model. One major advantage of the use of the Dusty Gas model is that the Knudsen diffusion coefficient, reflecting the molecule-wall interactions, follows naturally from the kinetic gas theory and is given by:

$$D_{iK}^{\varepsilon} = \frac{\varepsilon}{\tau} \frac{2}{3} r_0 \left(\frac{8RT}{\pi M_i} \right)^{1/2} \tag{26}$$

which is seen to be independent of pressure in contrast to the GMS molecular diffusivity of the pair $i - j$, $\mathcal{D}_{ij}$, which is inversely proportional to the pressure. The final working relations for the "total" flux $\mathbf{N}_i$, from both viscous and

diffusive contributions is obtained as:

$$\mathbf{d}_i = \nabla x_i + x_i\left(1 + \frac{B_0 p}{\eta D_{iK}^2}\right)\frac{\nabla p}{p} = \sum_{\substack{j=1 \\ j \neq i}}^{n}\frac{x_i\mathbf{N}_j - x_j\mathbf{N}_i}{c_t \mathcal{D}_{ij}^e} - \frac{\mathbf{N}_i}{c_t D_{iK}^e} \tag{27}$$

The superscript e on the GMS pair diffusivity $\mathcal{D}_{ij}^e$ serves to emphasize the fact that for bulk diffusion inside the porous medium

$$\mathcal{D}_{ij}^e = \frac{\varepsilon}{\tau}\mathcal{D}_{ij} \tag{28}$$

Taking note of the fact that for an ideal gas mixture $c_t = p/RT$, Eq. (27) shows that Knudsen and Bulk diffusion "regimes" exhibit a different behaviour with regard to the influence of the total system pressure: for operation in the Knudsen regime, the magnitude of the flux $\mathbf{N}_i$ will *increase* with p whereas in the Bulk diffusion regime, $\mathbf{N}_i$ remains independent of the system pressure. This point is illustrated by the data presented in Figure 12, obtained by Mason and co-workers (1983), for diffusion of He-Ar in a low permeability graphite septum. At low pressures Knudsen diffusion controls and the fluxes of He and Ar are proportional to the pressure. With increasing system pressure, the mean free path length of the gaseous molecules decreases and at high enough pressures bulk gas diffusion mechanism predominates in which case the fluxes are pressure independent.

Another interesting effect which arises in porous medium gas diffusion is the influence of the pressure gradient, which will act in a "direction" to help the diffusion of one of the species while countering the diffusion process of the other species (acting as a "pull" or "push"). Figure 13 shows the influence of the pressure difference across the graphite septum on the fluxes of He and Ar. With a positive Δp, the He flux is descreased while the Ar flux is increased in
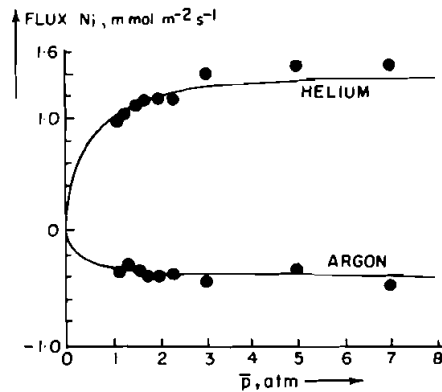

FIGURE 12   Influence of system pressure $\bar{p}$ on the fluxes of He and Ar across low permeability graphite septum Mason (1983). The experimental results are compared with theoretical predictions of a simplified, linearized, solution to the dusty gas model Eq. (27); see Krishna (1987b).
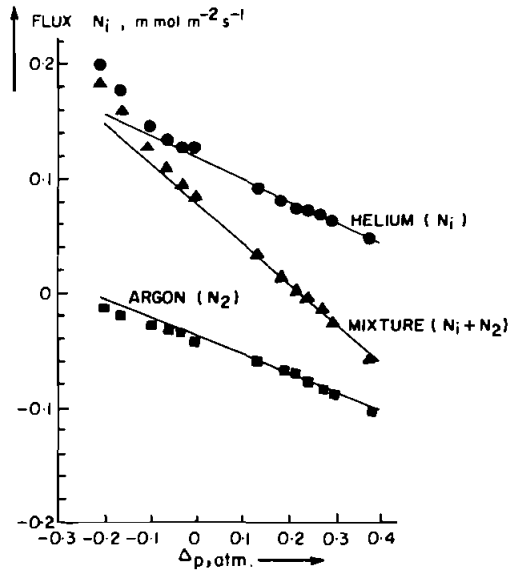
FIGURE 13   Influence of pressure difference across the graphite septum on the fluxes of He and Ar; experimental data from Mason (1983). The experimental results are compared with the theoretical predictions of a simplified, linearized, solution to the dusty gas model, Eq. (27); see Krishna (1987b) for details.

magnitude. The Dusty Gas Model Eq. (27), following IT, models this behaviour properly; see Krishna (1987b).

The Dusty Gas Model Eq. (27) is most useful in describing the transport rates during separation of gaseous mixtures using porous membranes, as we shall see later. Let us now consider the extension of this approach for treating diffusion of *ideal gas* multicomponent mixtures in porous media to *non-ideal* liquid mixtures. The starting point should, needless now to stress, be the GMS Eqs. (3)–(4). By parallel treatment to the Dusty Gas approach, but now including the electrostatic potential gradient term, we obtain (for discussions and derivations see Mason and Malinauskas (1983) and Krishna (1987b)).

$$\mathbf{d}_i = \frac{x_i}{RT} \nabla_{T,p} \mu_i + \frac{x_i \bar{V}_i}{RT} \nabla p + \frac{x_i B_0}{\eta D_{iM}^e} \nabla p + x_i z_i \frac{F}{Rt} \nabla \Phi$$

$$= \sum_{\substack{j=1 \\ j \neq i}}^{n} \frac{x_i \mathbf{N}_j - x_j \mathbf{N}_i}{c_t \mathcal{D}_{ij}^e} - \frac{\mathbf{N}_i}{c_t D_{iM}^e} \tag{29}$$

which equations may be said to be the Dusty Fluid Model Equations. Though Eq. (29) is the formal non-ideal liquid analog of Eq. (27), there are some fundamental differences in interpretation of the transport coefficients which must be realised. Firstly, the GMS pair diffusivities $\mathcal{D}_{ij}^e$ within the porous medium is no longer simply proportional to the free-space diffusion coefficient $\mathcal{D}_{ij}$, as in the relation (28). In addition the Knudsen diffusion coefficients of the Dusty Gas Model are
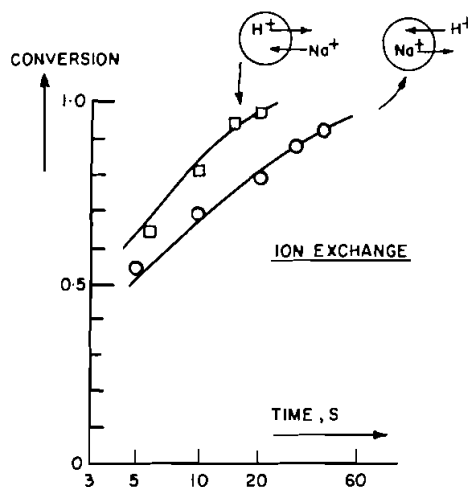
FIGURE 14 Exchange rates of H^+ and Na^+ in an ion exchange column are seen to be strongly dependent on the direction of ion transport; results of Helfferich (1962).

replaced by D^e_{iM}, the medium or membrane coefficients in order to avoid the connotation of long mean free paths of gaseous molecules. The coefficients $Ð^e_{ij}$ and $Ð^e_{iM}$ are parameters to be determined from experimental data but understanding the basis of these coefficients can be expected to aid in the interpretation of observations. The Dusty Fluid formulation Eq. (29) is to be credited to Mason (1983) and is the most useful form of the rate relations for porous liquid phase mass transport. There are many alternative formulations to be found in the literature (Mason (1983)) and all of these can be shown to be a special case of Eq. (29) above. In particular, the formulation due to Lightfoot (1974) is equivalent to Eq. (29) but with the viscous transport term $(x_iB_0/_\eta D^e_{iM})\ \nabla p$ merged into the transport coeffieients $Ð^e_{ij}$ and D^e_{iM} (Mason (1983)).

The electrostatic potential gradient term plays a very important role in the description of the transport phenomena within ion exchange "beads" or particles. On the basis of the previous discussions of transport of ions it should be clear that the rate of transfer of an ion should be very much dependent on the direction in which the ion moves; this directional dependency is due to the electrostatic "pull" or "push" on the ionic species (cf. Figure 4). If the ion exchange transfer process is modelled using an "effective" diffusivity without taking account of the electrostatic potential gradient term, then the results can be significantly in error. Figure 14 shows some experimental data which show that loading and regeneration rates occur at significantly different rates (Helfferich (1962)).

6. MEMBRANE SEPARATION PROCESSES

Membrane separation processes, with the exception of osmosis, rely on the differences in the rates of the transfer across the membrane, N_i, to achieve the

desired selectivities. There are many ways of classifying membrane processes. From the point of view of understanding the underlying principles, it is best to classify these into two broad categories: (i) porous membranes and (ii) non-porous membranes in which the mechanism of transport across the membrane is "dissolution" of the component(s) in the membrane phase (which could be a swollen polymeric film or a liquid phase stabilized by a surfactant) and transport of the dissolved species across the membrane phase.

6.1 Porous Membrane Separation Processes

Let us consider separation of a gaseous mixture. The transport of the individual species is governed by the Dusty Gas Model Eq. (27). The overall objective is to achieve the desired separation with high selectivities (which means fewer stages) and at lowest possible pressure drop (i.e. low compression costs). How these, conflicting, requirements are satisfied in practice is often a question of compromise. For example, to achieve high selectivities it is best to operate in the Knudsen diffusion regime. An industrially important example is the separation of the isotopes of uranium $U^{235}F_6$ from $U^{238}F_6$ by use of metal barriers which are porous. The separation factor α_{12}, defined by Eq. (15), is

$$\alpha_{12} = (M_2/M_1)^{1/2} \tag{30}$$

which works out to only 1.0043. Many thousand stages, with interstage compression, are required to meet the separation requirements.

Porous membranes have one great advantage over non-porous membranes in that the latter is usually made of a polymeric material and are thus restricted to operating temperatures below about 100°C. On the other hand porous membranes can also be manufactured from inorganic materials (ceramics, metals, glass) and thus be employed at temperatures of several hundred degrees. Thus porous membranes could conceivably be applied in processes where non-porous membranes fail and the positive separation properties of polymers can no longer be utilized, for example, for the separation of process gases of light molecules which are formed at low pressures and high temperatures; see Eickmann and Werner (1985) for further discussions. In particular, the development of a highly porous Al_2O_3 membrane with an average pore radius of 2 to 3 nm by Leenaars et al., cited in Eickmann and Werner (1985), appears to make high temperature applications possible.

The desire to obtain high transfer fluxes and high selectivities requires the following membrane conditions (see Eickmann and Werner (1985)):

– smallest possible pore diameter of the membrane (less than 100 nm)
– maximum number of pores per unit area
– small membrane thickness
– low system pressure level
– high process temperature

In another type of porous membrane separation process, separation is effected
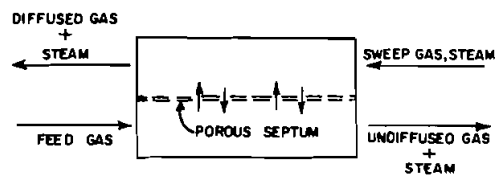
FIGURE 15   Schematic of sweep or mass diffusion process.

by allowing the components to be separated to diffuse into a third component, called a separating agent, and relying on the differences in the GMS pair diffusivities $Đ_{13}$ and $Đ_{23}$, to obtain the desired selectivities. The separating agent usually used is steam which is later condensed to recover the desired product. The terms Mass and Sweep diffusion are used to describe this process. The components to be separated are made to flow across porous screens, along which we have the flow of the separating agent. The role of the porous screen is incidental to the process and is *not* the basis for separation; see Pratt (1967) and Cichelli *et al.* (1951) for futher details. The process is pictured in Figure 15.

The principle of the mass or sweep diffusion process can be best understood on the basis of the Dusty Gas Model Eq. (27). We choose a membrane such that bulk diffusion prevails and the pressure gradients are not significantly large. Using subscripts 1, 2 to represent the components to be separated and 3 for the sweep species, it can be shown that for the case in which $N_1 = N_2$, the separation factor α_{12} works out to be

$$\alpha_{12} = \exp\left[\frac{N_2\delta}{c_t}\left(\frac{1}{Đ_{23}} - \frac{1}{Đ_{13}}\right)\right]$$ (31)

which shows that large differences in binary pair diffusivities of components 1 and 2 in the sweep gas 3 lead to high separation factors. Practical applications of the sweep diffusion process is the use of steam as separating agent to separate He–Ne, H_2–CO, H_2–Natural Gas mixtures.

Shuck and Toor (1963) have demonstrated the use of the sweep diffusion technique for separations involving a liquid mixture of methyl alcohol–n-propyl alcohol–isobutyl alcohol. Equation (29) are the starting point in the estimation of the interfacial transfer rates.

6.2   Non-porous Membrane Separation Processes

The separation factors obtained using porous membranes, see Eqs. (30) and (31), are limited. Higher selectivities are obtained by use of polymeric membranes of surfactant-stabilized liquid membrane films. The selectivities in non-porous membrane transport arise out of one or more of the following factors:

(i) differences in solubility of the components to be separated in the membrane phase. For example, a mixture of benzene and n-heptane can be separated by use of an aqueous surfactant liquid membrane in which the solubility of the aromatic compound is many hundred times larger than the solubility of the saturated
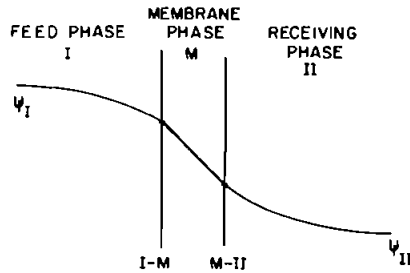
FIGURE 16 Typical profiles of overall potential Ψ_i for membrane separation.

hydrocarbon. Thus by interposing an aqueous layer between the feed mixture and the receiving phase (also a hydrocarbon), selective removal of the aromatic compound from the feed mixture can be achieved. The profile of the overall potential Ψ_i (where $\nabla\Psi_i = \mathbf{d}_i$, the overall driving force) for any component i is as shown typically in Fig. 16. At the interfaces I-M and M-II equilibrium is usually assumed to prevail and say at I-M we have (cf. Eq. (22)):

$$\ln\left(\frac{\gamma_{i1}x_{i1}}{\gamma_{iM}x_{iM}}\right) + \frac{(\bar{V}_i)_{\text{avg}}}{RT}(p_1 - p_M) + \frac{z_iF}{RT}(\Phi_1 - \Phi_M) = \Psi_1 - \Psi_M = 0 \qquad (32)$$

By choosing the membrane phase M such that the activity coefficient γ_{iM} is large the component i can be effectively "excluded" from the membrane and the desired selectivity can be achieved for the other component(s). The transfer fluxes N_i can be determined from Eqs. (3)–(4) applied to the fluid phases or from Eq. (29) for intra-membrane transport.

In the sub-section (i) under consideration here only the first term of Eq. (32), i.e. the chemical potential term, is relevant.

Use of polymeric membranes for gas separations include:

- O_2 enrichment from air (using ethyl cellulose, silicone rubber membrane)
- CO_2 enrichment from air (silicone rubber membrane)
- He separation from natural gas (membrane = cellulose acetate, PTFE, FEP)
- H_2, He recovery from refinery gases (membrane = asym. polysulphone with silicone, polylimide PET)

It needs to be stressed again here that the difference between non-porous and porous membranes is that in the former the permeating species "interacts" with the membrane phase and so the intra-membrane diffusivities of the permeating components have to be determined experimentally. In practice, effective permeability data are measured and reported for a particular gaseous mixture–membrane system. The Dusty Fluid Model Eq. (29) will help in interpreting the permeability data.

Examples of separation of liquid mixtures using polymeric membranes are: methanol-benzene, benzene-isopropanol, methanol–water, isopropanol–water, ethyl acetate–carbon tetrachloride, o- m- and p-xylenes, ethanol–acetone; see Rogers et al. (1972) for a more complete listing of separation possibilities.

(ii) In (i) above the main "driving force" for separation was the chemical potential gradient. In reverse osmosis and ultrafiltration examples, the major driving force is the pressure gradient term. Let us consider an aqueous salt solution separated by a membrane which is permeable only to water and not to the salt. If we further assume that there are no electrostatic potential gradients present, we get from Eq. (22), for water transport

$$\ln\left(\frac{a_{wI}}{a_{wII}}\right) + \frac{\hat{V}_w}{RT}(p_I - p_{II}) = 0 \tag{33}$$

where we have integrated across the membrane (cf. Figure 16) and a_w represents the activity of water. Since the membrane is permeable only to water the downstream side of the membrane will have only pure water and if we choose the standard state as the one of pure water at pressure p_{II}, it follows that

$$p_I - p_{II} = -\frac{RT}{\hat{V}_w}\ln a_{wI} \tag{34}$$

Since water behaves nearly ideally we may write Eq. (34) as

$$\pi = p_I - p_{II} = \frac{RT}{\hat{V}_w}\ln\frac{p_{wII}^s}{p_{wI}^s} \cong \frac{RT}{\hat{V}_w}\frac{(p_{wII}^s - p_{wI}^s)}{p_{wI}^s} \tag{35}$$

where p_w^s represents the vapour pressure of water. The osmotic pressure π, defined as $p_I - p_{II}$ is thus seen to be proportional to the fractional reduction of vapour pressure due to the salt. The constant of proportionality $RT/\hat{V}_w$ has a large value, 138 MN/m^2 at 25°C. This means that even modest vapour pressure lowerings produce a measurable osmotic pressure.

It follows from the above analysis that when an aqueous solution of a salt is separated from pure water by a membrane permeable only to water, water will tend to flow from the region of higher activity (pure water) to the region of lower activity (salt solution) till Eq. (33) is satisfied. The movement of solvent water is called osmosis; this is an equilibration process and the separation principle can be used for dehydration of food liquids, for example. If a pressure difference exceeding π is applied across the membrane from the side of the salt solution then the water begins to flow from the solution of lower activity to the one of higher activity. This process is reverse osmosis. The retained solute in this case is of the order of <0.1 nm in size. On the other hand if the retained solute is a macromolecule of the order of >1 nm in size, the process is called ultrafiltration. The mechanism of ultrafiltration is predominantly one of sieving.

The water flux N_w is usually taken to be equal to a permeability times the effective pressure difference: $\Delta p - \pi$.

(iii) In this third category of non-porous membrane separation processes the electrostatic potential gradient plays a key role, as in electrodialysis. When an ionic solution is subjected to an electric force field then the ions will move according to the flux relation Eq. (19). A membrane is interposed in the path of diffusion such that only positive ions or negative ions are allowed to pass through the membrane. This ion exclusion from the membrane phase is achieved by

incorporating fixed charges on to the polymeric chains making up the membrane. Thus even though the membrane may be physically "porous", the interactions of the diffusing components with the membrane matrix are such that the intramembrane transport must be modelled, using Eq. (29), taking the membrane-solution to be a homogenous phase. If the two types of membranes (allowing $+ve$ and $-ve$ ions respectively) are placed in alternate fashion in a battery, then it is possible to concentrate the cations and anions in one of the compartments in the battery; in the adjacent compartment the ions be in a depleted state. This is the principle of electrodialysis (pressure gradients are usually unimportant here) and the process has been used for the desalination of water, preparing boiler feed water, recovery of brine from brackish water, deashing of sugar solution and deacidification of fruit juices.

We have discussed above the three main driving forces which are used to effect transfer of a component across a non-porous membrane. The selectivity is achieved by choosing the membrane phase which, generally speaking, "interacts" with the feed mixture in such a way that one or more species in the solution are excluded from the membrane phase, for example by use of electrostatic repulsion (as in electrodialysis). In addition the transfer of the "desired" component to be transported may be enhanced by preferential "complexing" with an "active" chemical species present within the membrane phase. This active species serves to transport the desired material with 100% selectivity across the membrane in a kind of shuttle service because the original compound gets released at the other end of the membrane phase. The scope for ingenuity in choosing the proper membrane is almost unlimited. As we did in the case of porous membranes, let us list the desirable set of features for non-porous membrane transport:

– highest possible selectivity of membrane
– maximum surface area of membrane in a given volume of module (this is achieved in practice by use of ultra-thin hollow fibre membranes, liquid membranes with tiny microdroplets of about 1–5 μm in diameter, etc.)
– small membrane thickness (this is necessary for increasing the flux N_i)

SELECTIVE TRANSPORT BY DIFFUSION
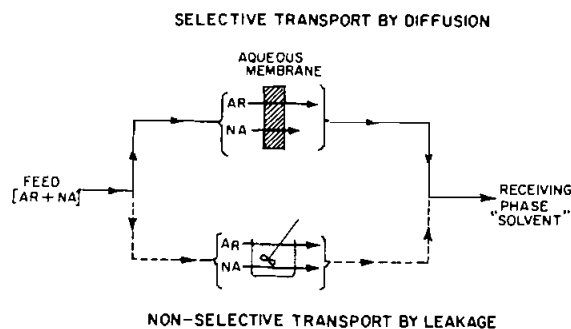
NON–SELECTIVE TRANSPORT BY LEAKAGE

FIGURE 17 Separation of aromatics (A) from non-aromatics (NA) using liquid membranes (Krishna and Goswami (1986)). Model taking leakage due to emulsion breakage into account.

– the membrane must be stable and not have "pinhole defects", "leaks" etc. (such "leakage" will lead to non-selective transport across the membrane and the overall selectivity is thus reduced).

It is interesting to note here that non-selective transport across a non-porous membrane caused by leakage is exactly analogous to the mechanism of non-separative viscous flow which occurs within a porous membrane; see Fig. 10. In a recent paper Krishna and Goswami (1986) modelled liquid membrane transport as a parallel step mechanism; see Fig. 17. This model can be extended to non-porous membranes in general.

7. CONCLUDING REMARKS

In this paper we have shown that the Generalized Maxwell–Stefan formulation of the mass diffusion rate relations, based on Irreversible Thermodynamics, Eqs. (3)–(4), provide a general basis for understanding and describing both equilibration and rate governed separation processes.

Specifically, the benefits of adopting a fundamental IT approach have been shown to be the following:

(i) the IT formulation afforts a consistent and correct approach to the description of non-ideal liquid phase transport; in particular the influence of solution thermodynamics on the Fickian diffusivity is made "transparent"

(ii) the IT formulation is indispensible in describing the transport behaviour in the region of the critical point; this is particularly important in the design of processes involving phase transitions such as crystallization

(iii) the various driving forces causing relative motion of species, i.e. separation are clearly identified. This identification will aid the screening of alternative separation routes in a systematic manner. In future computer based synthesis of separation schemes can be developed using the IT formulation

(iv) the Generalized Maxwell–Stefan Eqs (3)–(4), yield as special cases the widely accepted Maxwell–Stefan equations for ideal multicomponent gas diffusion and the Nernst–Planck equations for dilute electrolyte transport. There is no need for *ad hoc* modelling of special cases.

(v) the generalized phase equilibrium relationship Eq. (22), derived from the GMS equations, provides the correct starting point for describing phase equilibrium for equilibration separation processes.

(vi) the GMS formulation, can be extended in a logical manner to the treatment of diffusion inside porous media, by modelling the medium as giant "dust" species. For gaseous transport, this approach is particularly rewarding while for liquid phase transport inside porous media, the Dusty Fluid Model will help in the modelling and interpretation of experimental data.

(vii) The GMS approach has been shown to be absolutely necessary in a few cases involving ,multicomponent mixtures. Simple minded approaches based on the Occam's Razor approach (i.e. equal transport facility for all components in a fluid mixture) have been shown to lead to significant deviations from experimen-

tal observations. In a few extreme cases the Occam's Razor approach has been shown to predict the wrong "direction" of transfer. One separation process, viz. Mass or sweep ·diffusion *relies* on the multicomponent diffusion "effects" to achieve separation.

(viii) Most of the commonly used, simplified, flux expressions used for membrane transport processes have been shown to be special cases of the GMS formulation; this leads to a better understanding of the limitations of the simplified approaches.

Finally, it may be expected that with a thorough fundamental approach to the theory of separation processes, the development of "novel" separation techniques could be "systematized".

NOMENCLATURE

a_i	activity of component i in solution, $a_i = \gamma_i x_i [-]$
a_w	activity of water $[-]$
B_0	permeability of the porous medium $[m^2]$
c_i	molar concentration of species i $[kmol\ m^{-3}]$
c_t	mixture molar concentration $[kmol\ m^{-3}]$
$\mathbf{d}_i$	generalized driving force for the motion of species i relative to mixture $[m^{-1}]$
$\mathcal{D}_{ij}$	GMS diffusivity of $j-j$ pair in multicomponent mixture $[m^2\ s^{-1}]$
$\mathcal{D}$	GMS diffusivity taken equal for all components in the diffusing mixture $[m^2\ s^{-1}]$
$\mathcal{D}^e_{ij}$	effective GMs diffusivity of pair $i-j$ in porous medium $[m^2\ s^{-1}]$
D^e_{iK}	effective Knudsen diffusion coefficient of gaseous component i in porous medium $[m^2\ s^{-1}]$
D^e_{iM}	effective "membrane" diffusivity of component i in porous medium $[m^2\ s^{-1}]$
f	rotational speed of centrifuge $[s^{-1}]$
F	Faraday's constant $[9.65 \times 10^7\ C\ kgequiv^{-1}]$
G_{ij}	elements of the Hessian matrix $[G]$, with elements given by Eq. (9) $[J\ kmol^{-1}]$
$[G]$	Hessian matrix of the molar Gibbs free energy $[J\ kmol^{-1}]$
$\mathbf{J}_i$	molar diffusion flux of i with respect to molar average mixture velocity $[kmol\ m^{-2}\ s^{-1}]$
k_{iT}	thermal diffusion ratio of component i $[-]$
M_i	molar mass of species $[kg\ kmol^{-1}]$
n	number of species in the mixture $[-]$

$\mathbf{N}_i$ molar flux of species i in a fixed coordinate reference frame $[\mathrm{kmol\,m^{-2}\,s^{-1}}]$

$\mathbf{N}_t$ mixture molar flux in a fixed coordinate reference frame $[\mathrm{kmol\,m^{-2}\,s^{-1}}]$

p system pressure $[\mathrm{N\,m^{-2}}]$

p_w^s vapour pressure of water $[\mathrm{N\,m^{-2}}]$

r radial coordinate $[\mathrm{m}]$

r radius of ultracentrifuge $[\mathrm{m}]$

r_0 pore radius $[\mathrm{m}]$

R gas constant $[8314.4\,\mathrm{J\,kmol^{-1}\,K^{-1}}]$

T absolute temperature $[\mathrm{K}]$

$\mathbf{u}_i$ velocity of diffusing species i in a fixed coordinate reference frame $[\mathrm{m\,s^{-1}}]$

$\mathbf{u}$ molar average velocity of mixture in fixed coordinate reference frame $[\mathrm{m\,s^{-1}}]$

$\bar{V}_i$ partial molar volume of species i $[\mathrm{m^3\,kmol^{-1}}]$

x_i mole fraction of species i in "x" phase $[-]$

y_i mole fraction of species i in "y" phase $[-]$

z_i charge on species i $[-]$

Greek Letters

α_{ij} separation factor in a single stage for the pair of components $i - j$ $[-]$

γ_i activity coefficient of species i in solution $[-]$

Γ thermodynamic correction factor, defined by Eq. (7) $[-]$

δ length of diffusion path $[\mathrm{m}]$

ε porosity of medium $[-]$

η viscosity of fluid mixture $[\mathrm{Pa\,s}]$

μ_i molar chemical potential of species i $[\mathrm{J\,kmol^{-1}}]$

π osmotic pressure $[\mathrm{N\,m^{-2}}]$

ρ_i mass density of component i $[\mathrm{kg\,m^{-3}}]$

ρ mixture mass density $[\mathrm{kg\,m^{-3}}]$

σ rate of entropy production $[\mathrm{J\,m^{-3}\,s^{-1}\,K^{-1}}]$

τ tortuosity of porous medium $[-]$

ϕ_i $= c_i \bar{V}_i$, volume fraction of species i $[-]$

Φ electrostatic potential $[\mathrm{V}]$

Ψ_i generalized potential for mass diffusion; $\nabla \Psi_i = \mathbf{d}_i$ $[-]$

ω_i	mass fraction of component i [$-$]
Ω	angular velocity of rotation of centrifuge [$-$]

Subscripts

avg	average over the diffusion path
i, j	referring to species i, j in multicomponent mixture
K	Knudsen diffusion coefficient
M	membrane coefficient
n	referring to nth species in the multicomponent mixture
$n+1$	referring to the medium which is modelled as a giant "dust" molecule fixed in space
T, p	evaluated at constant temperature and pressure conditions
w	water
1, 2, 3	referring to species 1, 2, 3 in ternary mixture
I	referring to phase I
II	referring to phase II

Superscripts

diffusive	diffusive contribution to the transfer flux N_i
e	effective coefficient inside porous medium
viscous	viscous contribution to the transfer flux N_i
0	denotes infinite dilution value
$^-$	overbar denotes molar value

Vector Notation

∇	gradient operator
$\cdot$	dot product between two vectors

Operators

$\sum$	summation over n species
Δ	difference operator
$\dfrac{d}{dr}$	gradient in r direction

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