DEPARTMENT OF ENERGETICS

POLITECNICO DI TORINO

Multicomponent Mass Transfer: Basic Physics and Engineering Modeling

Numerical Heat Transfer

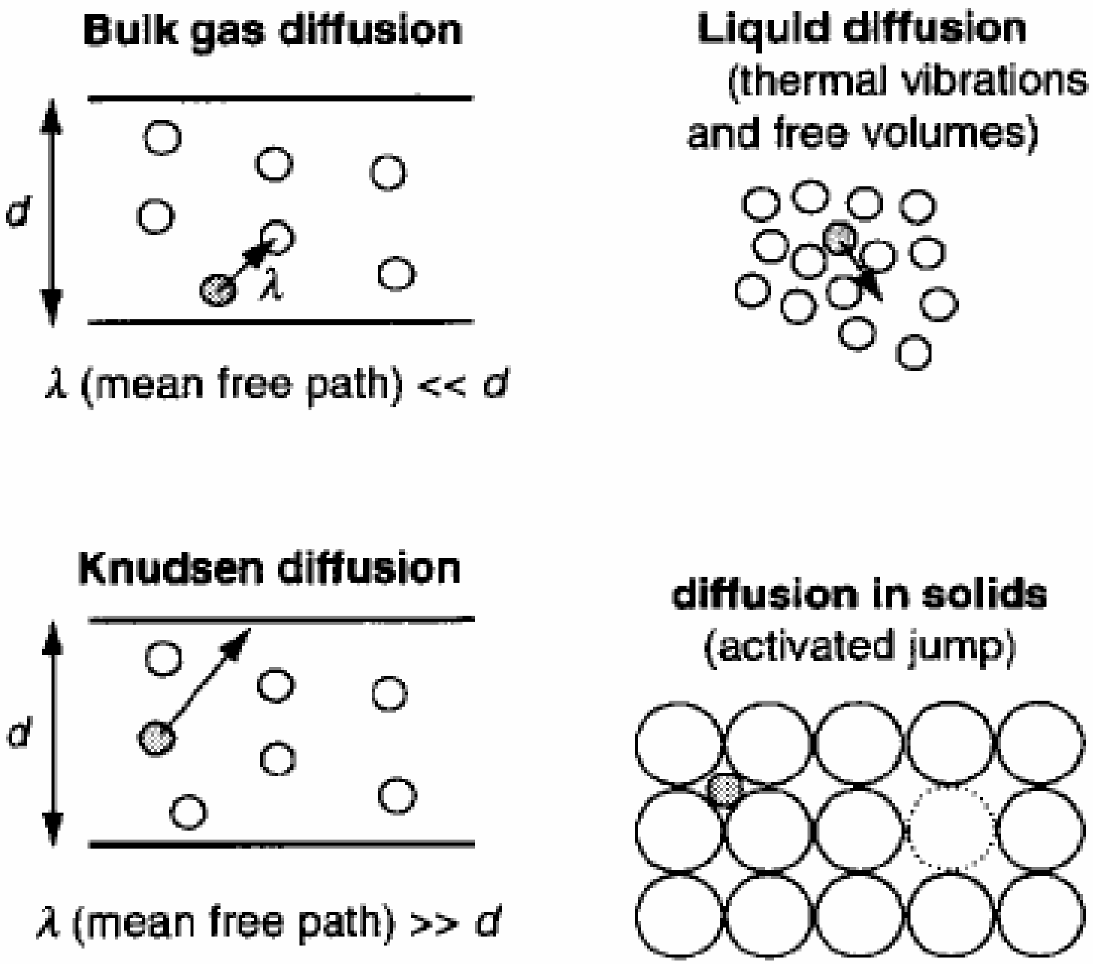
Pietro Asinari, PhD

Spring 2007, TOP – UIC Program: The Master of
Science Degree of the University of Illinois
at the ‘Politecnico di Torino’

Outline of this Section

- Multicomponent (or multi – species) fluid flows → heuristic vs. kinetic derivation
- Popular modeling approaches → Fick Model vs. Maxwell – Stefan model
- Further extensions → simultaneous heat and mass transfer; generalized driving force; fluid flow in porous media (dusty gas model)
- Reactive mixture flows → combustion: laminar reaction rates; effects due to turbulent fluctuations; brief discussion of advanced modeling issues

Isothermal Diffusion in Single Phase



Concentration Measures

Molar (or Number) Density	$c_i = \rho_i / M_i (= n_i)$
Mixture (or Total) Molar Density	$c_t = c = \sum_{i=1}^{N_s} c_i$
Mole (or Volume) Fraction of Species i-th	$x_i = c_i / c_t \rightarrow \sum_{i=1}^{N_s} x_i = 1$
Mixture (or Total) Density	$\rho_t = \rho = \sum_{i=1}^{N_s} \rho_i$
Mass Fraction of Species i-th	$\omega_i = \rho_i / \rho_t \rightarrow \sum_{i=1}^{N_s} \omega_i = 1$

Mixture Velocities

Molar Average Velocity	$\mathbf{u} = \frac{\sum c_i \mathbf{u}_i}{c} = \sum x_i \mathbf{u}_i$
Mass Average (or Barycentric) Velocity	$\mathbf{v} = \frac{\sum \rho_i \mathbf{u}_i}{\rho} = \sum \omega_i \mathbf{u}$

- It is not clear which mixture velocity is the best in order to describe the mixture dynamics → the mixture literature would be a much deal simpler if there were only one way to characterize the mixture dynamics
- By means of the previous quantities, it is possible to define the relative fluxes describing the peculiar flow of each component of the mixture

(Single Component) Diffusion Fluxes

(Absolute) Mass Flux of Species i-th	$\mathbf{n}_i = \rho_i \mathbf{u}_i \quad \mathbf{n}_T = \sum \rho_i \mathbf{u}_i = \rho \mathbf{v}$
(Absolute) Molar Flux of Species i-th	$N_i = c_i \mathbf{u}_i \quad N_T = \sum c_i \mathbf{u}_i = c \mathbf{v}$
(Relative) Mass Diffusion Flux of Species i-th	$\mathbf{j}_i = \rho_i \left(\mathbf{u}_i - \mathbf{v}\right) = \mathbf{n}_i - \rho_i \mathbf{v} = \mathbf{n}_i - \omega_i \mathbf{n}_T$
(Relative) Molar Diffusion Flux of Species i-th	$\mathbf{J}_i = c_i \left(\mathbf{u}_i - \mathbf{u}\right) = \mathbf{N}_i - c_i \mathbf{u} = \mathbf{N}_i - x_i \mathbf{N}_T$

- Clearly the relative diffusion fluxes are defined in such a way that summing over all the species is producing a zero total diffusion flux

Chemical Net Rates of Production

Molar Net Rate of Production of Species i-th

$$R_i = \sum_{r=1}^{N_r} R_{i,r}$$

Mass Net Rate of Production of Species i-th

$$r_i = M_i R_i = M_i \sum_{r=1}^{N_r} R_{i,r}$$

- If chemical reactions are considered, the total mixture mass is conserved, while this is not the case for the total number of moles of the mixture
- Each chemical net rate of production (net = production – destruction) is due to all the elementary reactions involving the considered species

Equation of Change for Species Mass

- From the Equation of Change for any conserved quantity

$$\frac{d}{dt}\int_{\mathcal{V}_i} c_i\,dV = \int_{\mathcal{V}_i} R_i\,dV$$

$$\frac{d}{dt}\int_{\mathcal{V}_i} \rho_i\,dV = \int_{\mathcal{V}_i} r_i\,dV$$

$$\frac{d}{dt}\int_{\mathcal{V}_i} \rho_i\,dV = \int_{\mathcal{V}_i} \frac{\partial \rho_i}{\partial t}\,dV + \int_{\mathcal{V}_i} \nabla\cdot\rho_i\mathbf{u}_i\,dS = \int_{\mathcal{V}_i} r_i\,dV$$

$$\frac{d}{dt}\int_{\mathcal{V}_i} \rho_i\,dV = \int_{\mathcal{V}_i} \frac{\partial \rho_i}{\partial t}\,dV + \boxed{\int_{\mathcal{S}_i} \rho_i\mathbf{u}_i\cdot\mathbf{n}\,dS} = \int_{\mathcal{V}_i} r_i\,dV$$

Species Transport Equation (STE)

$$\frac{\partial \rho_i}{\partial t} = -\nabla \cdot \mathbf{n}_i + r_i \xrightarrow{\text{summing}} \boxed{\frac{\partial \rho}{\partial t} = -\nabla \cdot \mathbf{n}_T}$$

$$\frac{\partial \rho_i}{\partial t} + \nabla \cdot (\rho_i \mathbf{v}) = -\nabla \cdot \mathbf{j}_i + r_i \xrightarrow{\text{summing}} \boxed{\frac{\partial \rho}{\partial t} + \nabla \cdot \rho \mathbf{v} = 0}$$

- The previous equation is not closed → the mass diffusion flux must be expressed as a function of the single species concentrations, which are the actual additional unknowns to be considered in mixture modeling → this relationship is sometimes called phenomenological law (or model)

Equivalent Formulations of STE

$$\rho\left[\frac{\partial \omega_i}{\partial t} + \mathbf{v}\cdot\nabla\omega_i\right] = -\nabla\cdot\mathbf{j}_i + r_i \xrightarrow{\text{summing}} \boxed{\sum r_i = 0}$$

$$\frac{\partial c_i}{\partial t} = -\nabla\cdot\mathbf{N}_i + R_i \xrightarrow{\text{summing}} \boxed{\frac{\partial c}{\partial t} = -\nabla\cdot\mathbf{N}_T + \sum R_i}$$

$$\frac{\partial c_i}{\partial t} + \nabla\cdot(c_i\mathbf{v}) = -\nabla\cdot\mathbf{J}_i + R_i \xrightarrow{\text{summing}} \boxed{\frac{\partial c}{\partial t} + \nabla\cdot c\mathbf{u} = +\sum R_i}$$

- Equivalent formulations of STE can be derived → They look similar each other if expressed in terms of single-species quantities: however summing over all the mixture components yields very different results !

Fick Model

$$\mathbf{J}_A = c_A\left(\mathbf{u}_A - \mathbf{u}\right) = -c\mathcal{D}_{AB}\nabla x_A$$

$$\mathbf{J}_B = c_B\left(\mathbf{u}_B - \mathbf{u}\right) = -c\mathcal{D}_{BA}\nabla x_B$$

$$\mathcal{D}_{AB} = \frac{\mathbf{J}_A}{-c\nabla x_A} \qquad \mathcal{D}_{AB} = \mathcal{D}_{BA}$$

$$\left(\mathbf{u}_A - \mathbf{u}_B\right) = -\mathcal{D}_{AB}\nabla \log\frac{x_A}{x_B}$$

- It is a phenomenological model (or law) based on experimental studies involving binary mixtures
- D_{AB} and D_{BA} are the Fick diffusion coefficients (it is always better to refer the latter to the original models)

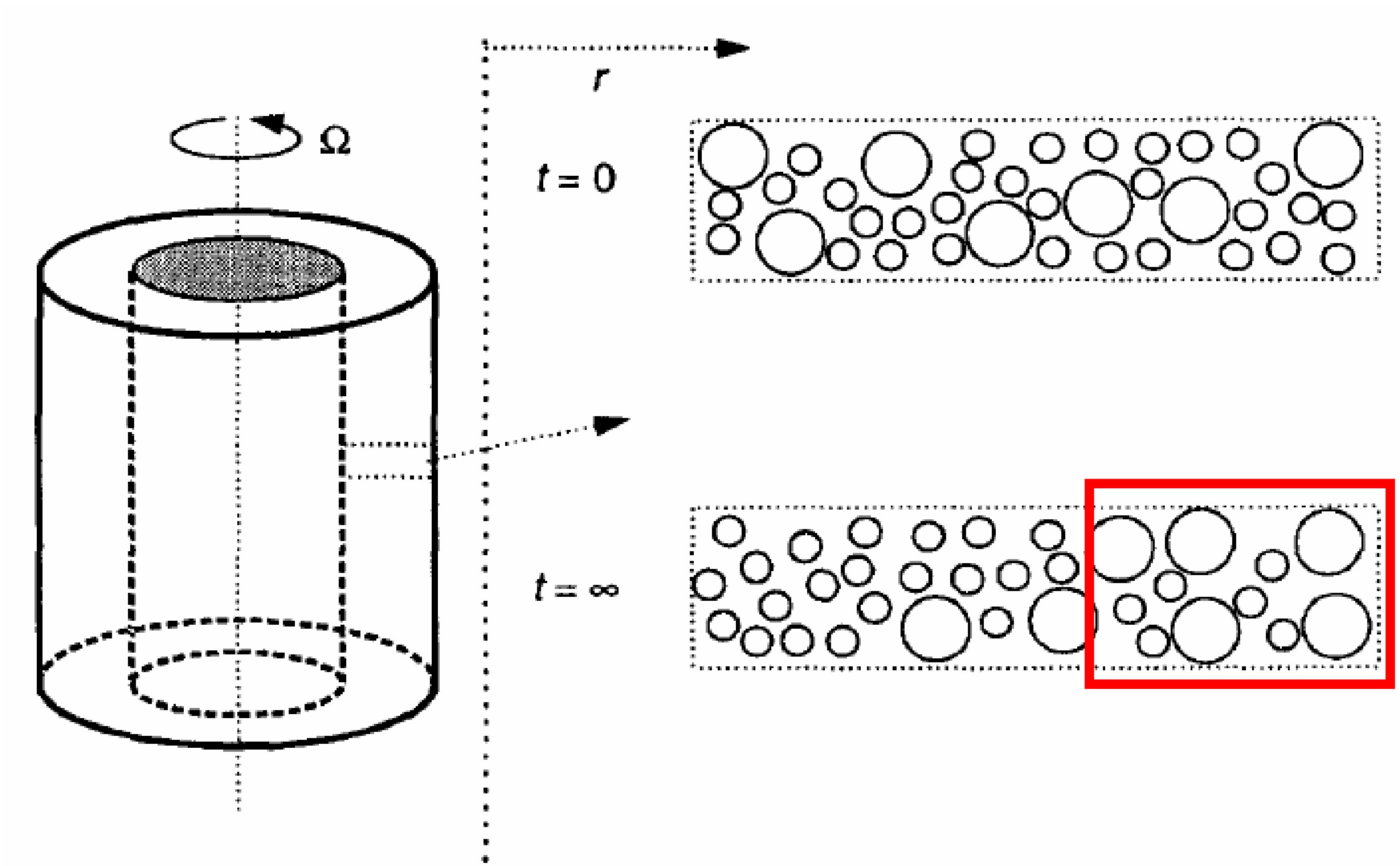
Equivalent Formulation of Fick Model

$$\mathbf{J}_A = c_A\left(\mathbf{u}_A - \mathbf{u}\right) = -c\mathcal{D}_{AB}\nabla x_A$$

$$\mathbf{j}_A = \rho_A\left(\mathbf{u}_A - \mathbf{v}\right) = -\rho\mathcal{D}^0_{AB}\nabla \omega_A$$

The constitutive relation is strictly valid only under the following set of conditions: (i) for binary mixtures or (ii) for diffusion of dilute species *i* in a multicomponent mixture, and (iii) in the absence of electrostatic or centrifugal force fields. If one takes the view that eq. (1) provides a definition of the effective Fick diffusivity of component *i* in a multicomponent mixture, then this parameter shows a complicated, often unpredictable, behaviour

Centrifugal Separation



Linearized Theory

$$\nabla \cdot \mathbf{j}_A = -\rho \mathcal{D}_{AB} \nabla^2 \omega_A \qquad \rho \mathcal{D}_{AB} \text{ costant}$$

$$\rho \left[\frac{\partial \omega_A}{\partial t} + \mathbf{v} \cdot \nabla \omega_i \right] = \rho \mathcal{D}_{AB} \nabla^2 \omega_A + r_A$$

- The linearized theory allows one to recover an advection – diffusion equation for single component mass concentration → If matrix notation is considered, a proper diffusivity tensor **D** must be defined → Exploiting the properties of the corresponding modal matrix, it is possible to make diagonal the diffusivity tensor **D** so that the problem reduces to a finite set of uncoupled advection – diffusion equations

(Fick) Diffusivity in Gasses

$$\mathcal{D}_{AB} = \sqrt{\frac{2}{\pi^3}}\,\frac{(RT)^{3/2}}{\mathcal{N} P d_{AB}^2}\left(\frac{1}{M_A} + \frac{1}{M_B}\right)^{1/2} \qquad d_{AB} = \frac{d_A + d_B}{2}$$

- Kinetic theory of gasses provides a closed expression for the binary diffusion coefficient, to be used in the Fick model → This formula is independent on composition, is inversely proportional to pressure and depends on $T^{3/2}$ → The kinetic formula depends on the considered atomic model (collision integral, molecular energy parameter, …) used to characterize the gas particle
- A number of semi–empirical correlations for estimating gaseous diffusion coefficients have been developed as well

(Fick) Diffusivity in Liquids

Stokes-Einstein $$\frac{\mathcal{D}^0_{AB}\,\mu_B}{T} = \frac{k_B}{6\pi R_A}$$

- In case of infinite dilution and if the diffusing species is very large compared to the solvent molecules, it is possible to derive a purely theoretical method of estimating the binary diffusivity (Stokes – Einstein formula) → However, the diffusion coefficients in binary mixtures of real liquids can be strong functions of composition
- Also in this case, a number of semi–empirical correlations for estimating liquid diffusion coefficients have been developed as well

Heat and Mass Transfer Analogy

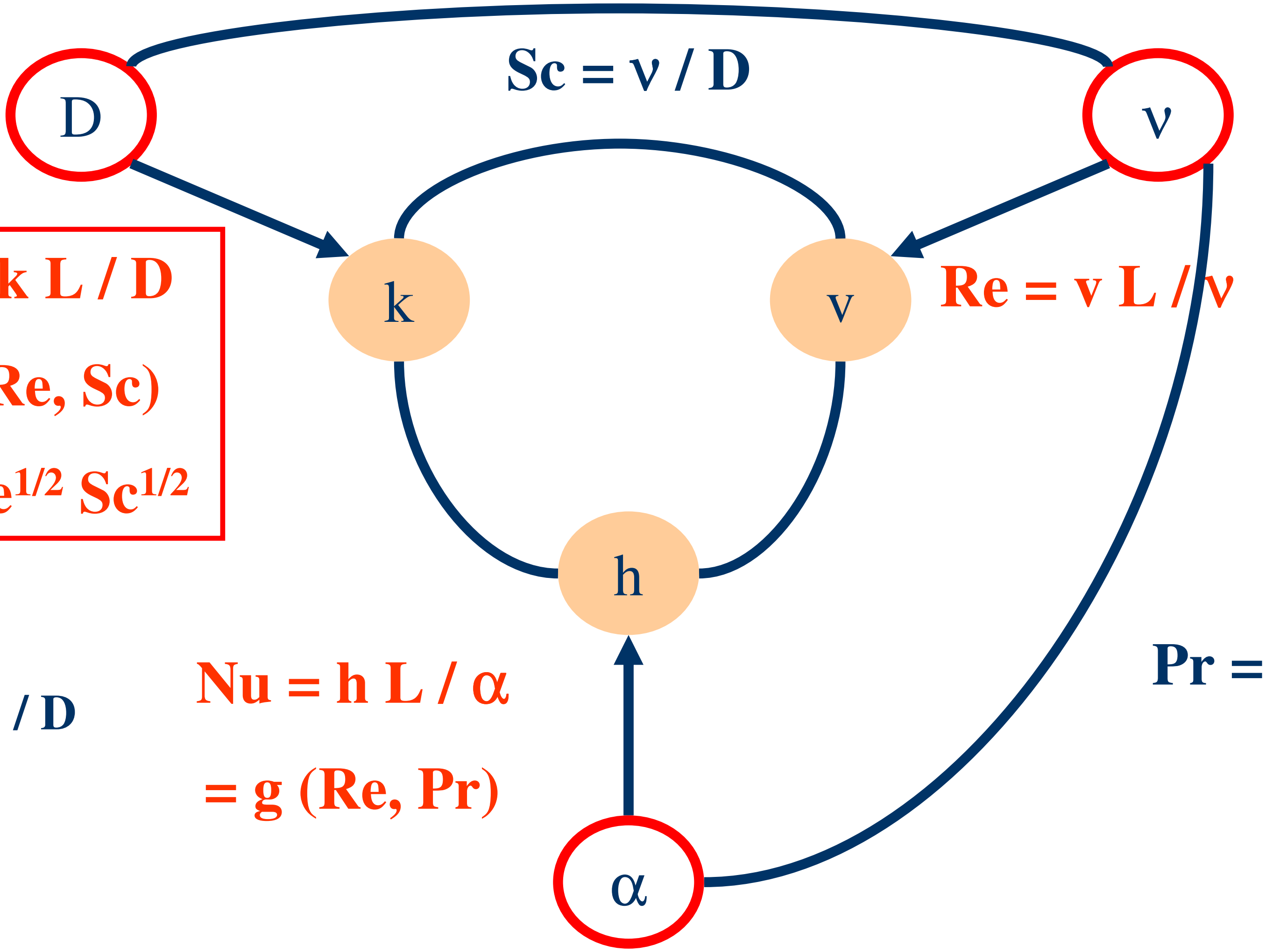
$$\rho\left[\frac{\partial \omega_A}{\partial t} + \enclose{circle}{\mathbf{v}} \cdot \nabla \omega_i\right] = \rho \mathcal{D}_{AB} \nabla^2 \omega_A$$

$$\rho c_p\left[\frac{\partial T}{\partial t} + \enclose{circle}{\mathbf{v} \cdot} \nabla T\right] = k \nabla^2 T$$

- Heat and mass transfer analogy → Sherwood number

$$\begin{array}{ll} \dfrac{|\mathbf{j}_i|_I}{\rho} = D \left|\dfrac{\partial \omega_i}{\partial n}\right|_I = k\,|\omega_\infty - \omega_I| \rightarrow & \multirow{2}{*}{$\boxed{\begin{array}{c} Sh = \dfrac{k\,L}{D} \\[2em] Nu = \dfrac{h\,L}{\lambda} \end{array}}$} \\[3em] \lambda \left|\dfrac{\partial T}{\partial n}\right|_W = h\,|T_\infty - T_W| \rightarrow & \end{array}$$

Experimental Correlations



$Sc = \nu / D$

$Sh = k L / D$

$= f (Re, Sc)$

$= a \, Re^{1/2} Sc^{1/2}$

$Re = v L / \nu$

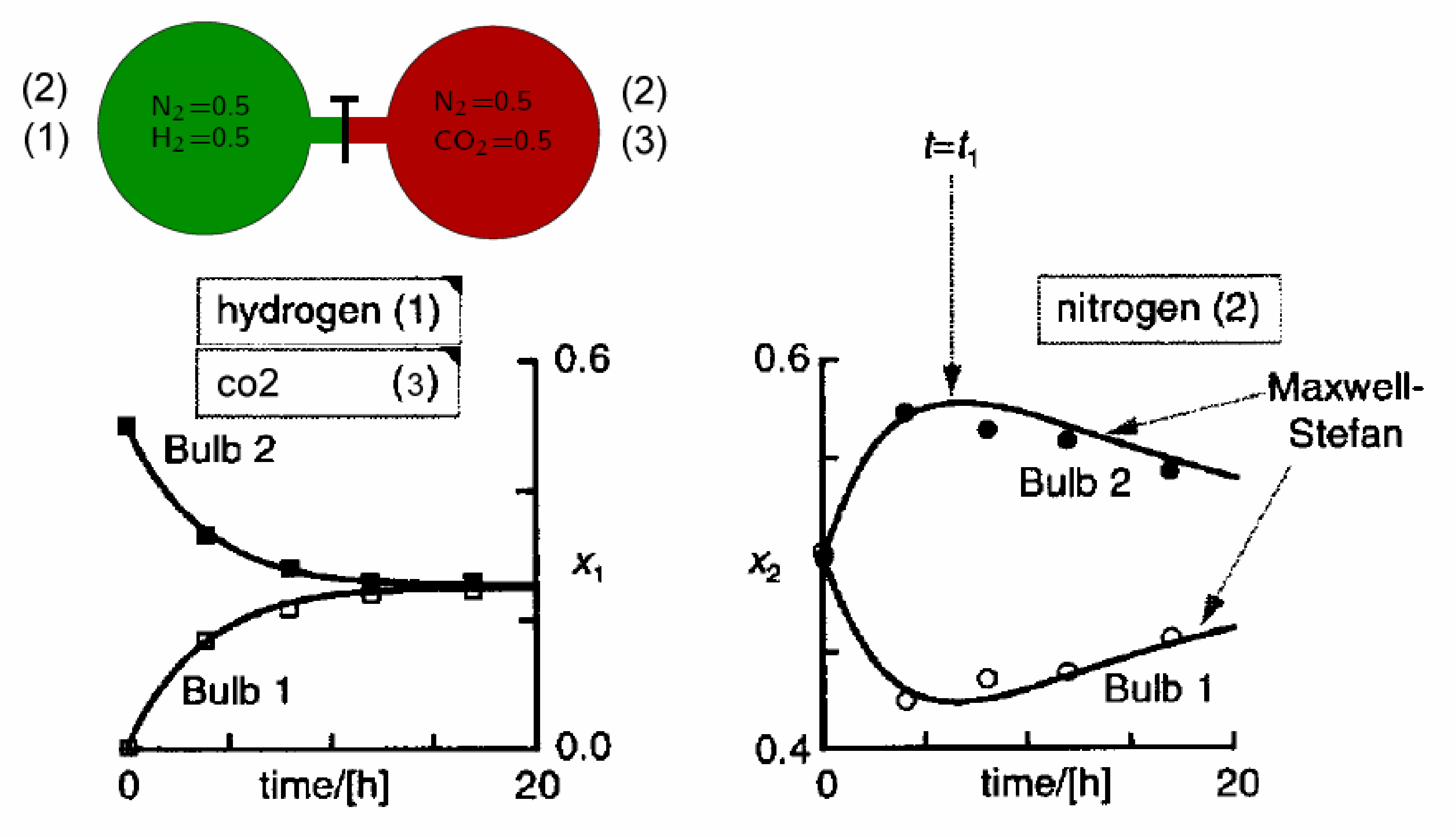
$Le = \alpha / D$

$Nu = h L / \alpha$

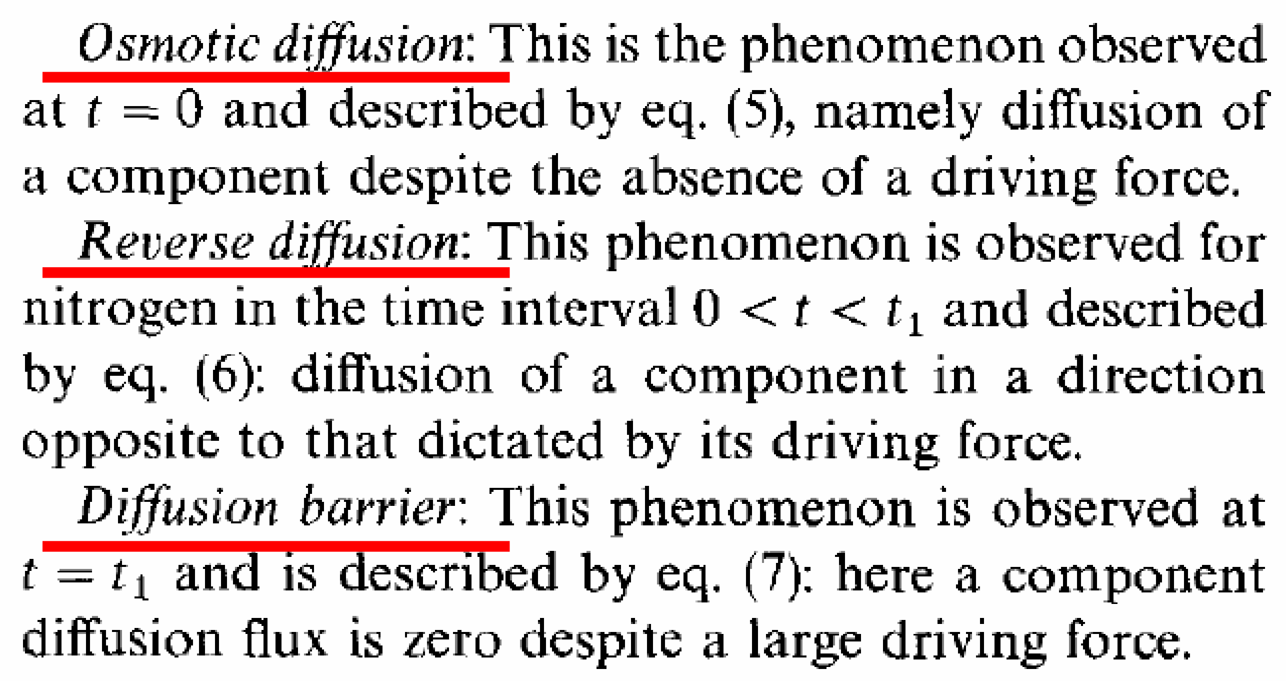
$= g (Re, Pr)$

$Pr = \nu / \alpha$

(1) Duncan & Toor Experiment (1962)



(1) Duncan & Toor Experiment: Why

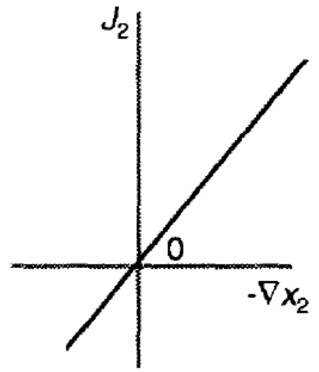


Osmotic diffusion: This is the phenomenon observed at $t = 0$ and described by eq. (5), namely diffusion of a component despite the absence of a driving force.

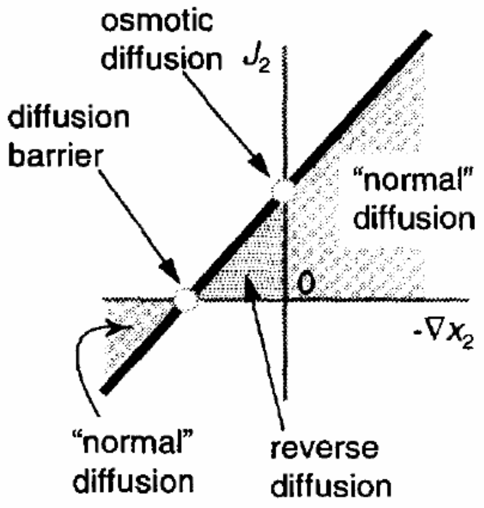
Reverse diffusion: This phenomenon is observed for nitrogen in the time interval $0 < t < t_1$ and described by eq. (6): diffusion of a component in a direction opposite to that dictated by its driving force.

Diffusion barrier: This phenomenon is observed at $t = t_1$ and is described by eq. (7): here a component diffusion flux is zero despite a large driving force.

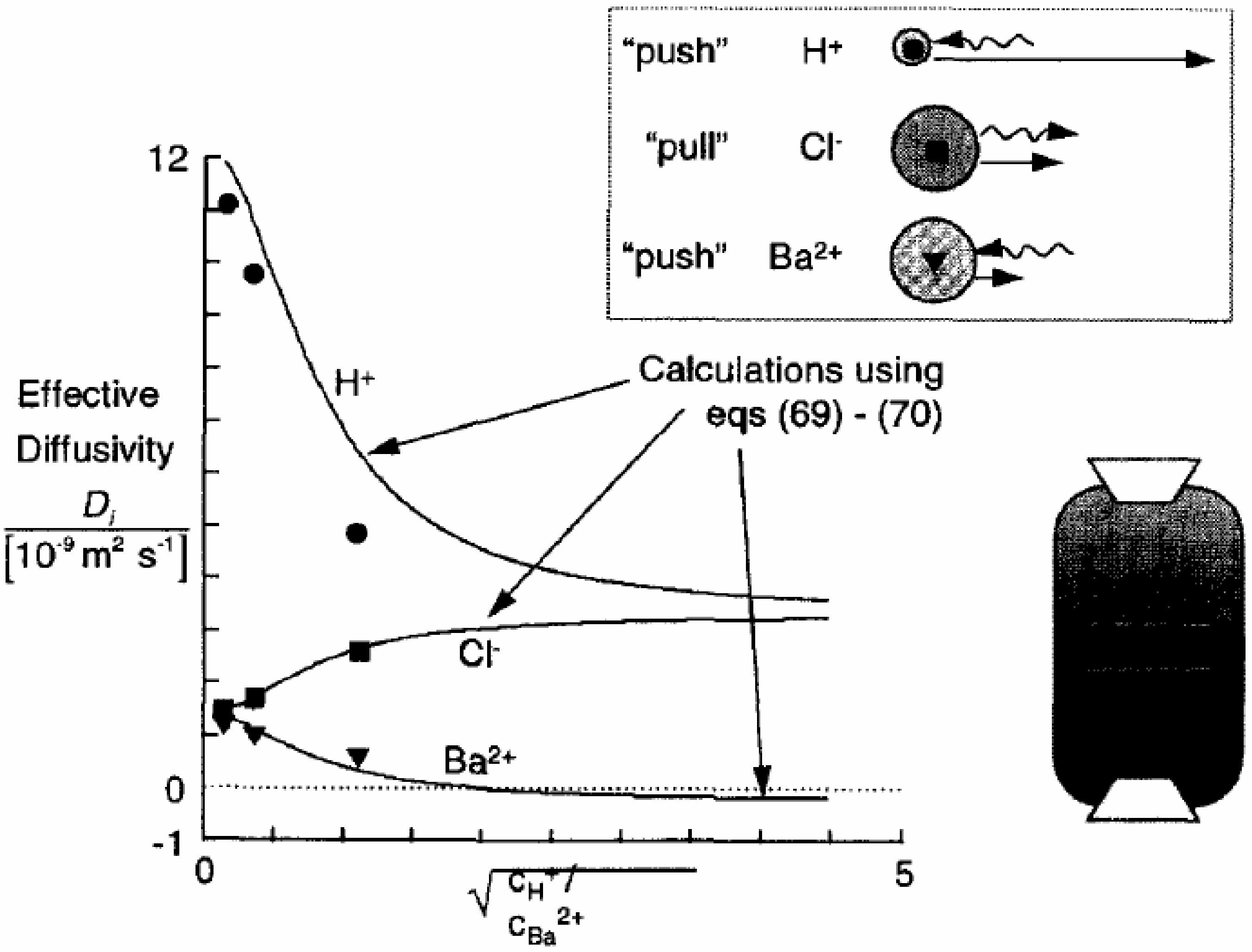
(a) binary



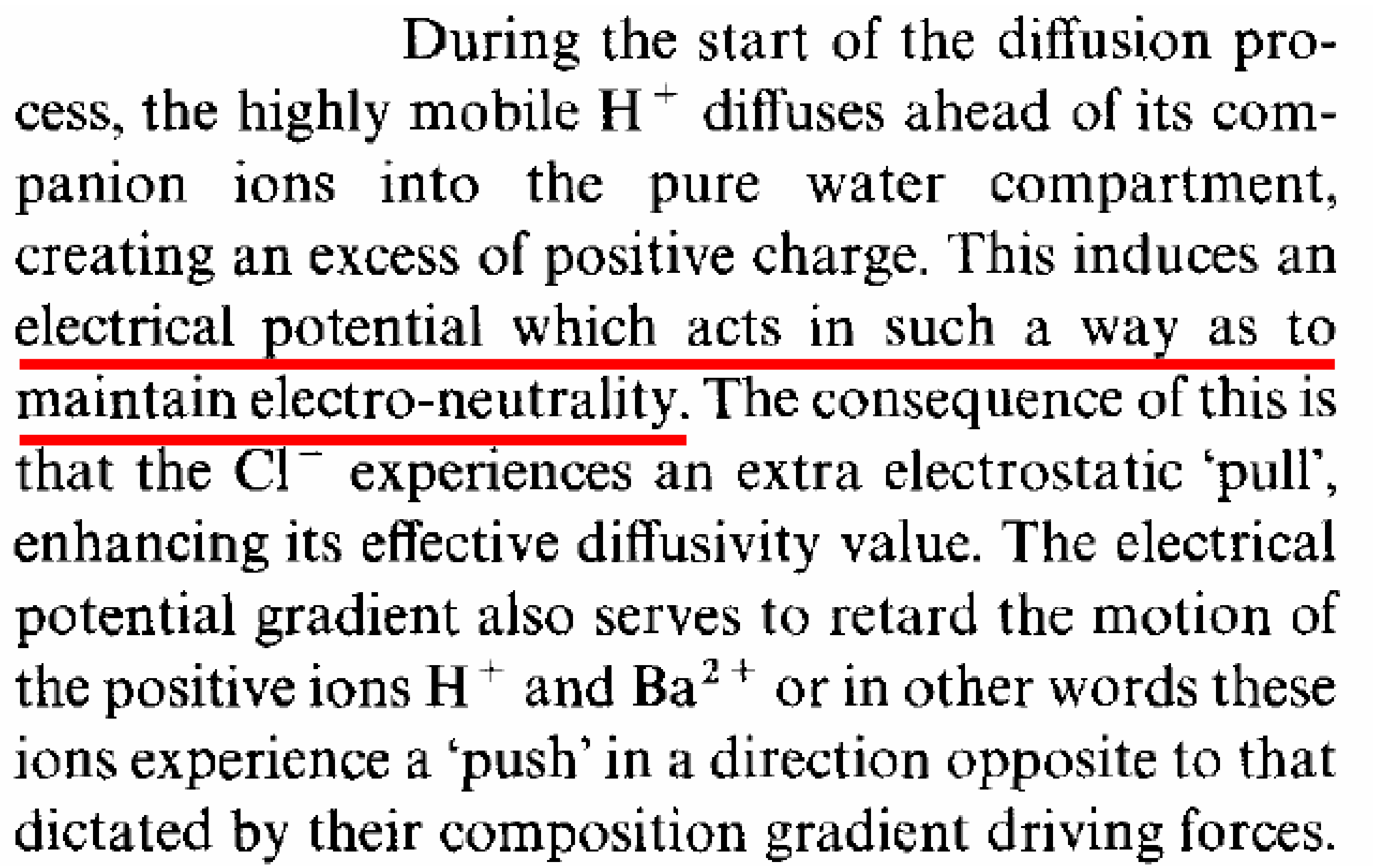
(b) ternary



(2) Vinograd & McBain Experiment (1941)

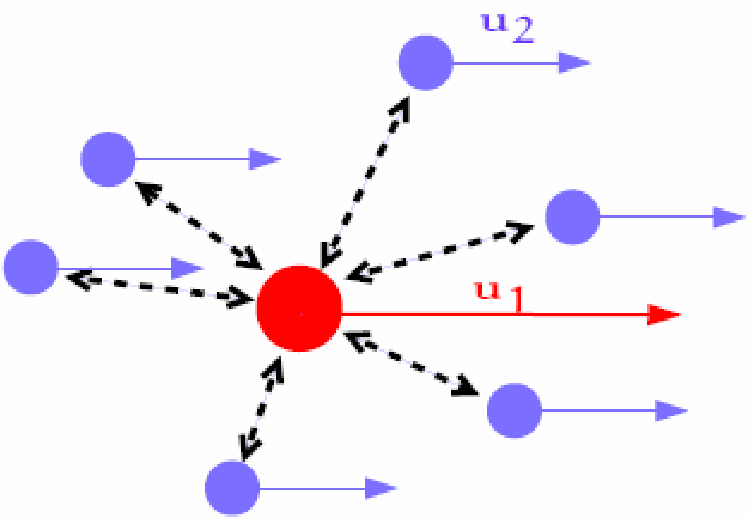


(2) Vinograd & McBain Experiment: Why



During the start of the diffusion process, the highly mobile H^+ diffuses ahead of its companion ions into the pure water compartment, creating an excess of positive charge. This induces an electrical potential which acts in such a way as to maintain electro-neutrality. The consequence of this is that the Cl^- experiences an extra electrostatic 'pull', enhancing its effective diffusivity value. The electrical potential gradient also serves to retard the motion of the positive ions H^+ and Ba^{2+} or in other words these ions experience a 'push' in a direction opposite to that dictated by their composition gradient driving forces.

Maxwell–Stefan (MF) for Binary Mixtures



R gas constant

$$F_1 = -(\nabla \mu_1)_{T,P} = -\frac{RT}{a_1}\nabla a_1 \xrightarrow{\text{ideal}} -\frac{RT}{x_1}\nabla x_1$$

$$F_2 = \zeta_{12} x_2 \boxed{(u_1 - u_2)}$$

$$-\nabla \mu_1 = \zeta_{12} x_2 (u_1 - u_2)$$

Maxwell–Stefan Diffusivity

Multiplying for x_1/RT

$$\left(\frac{x_1}{RT}\nabla\mu_1\right)_{T,P} = -\frac{\zeta_{12}}{RT}x_1 x_2\left(\mathbf{u}_1-\mathbf{u}_2\right) = -\frac{x_1 x_2\left(\mathbf{u}_1-\mathbf{u}_2\right)}{\text{Đ}_{12}}$$

$$c x_i \mathbf{u}_i = \mathbf{N}_i \qquad \boxed{x_2\mathbf{N}_1 - x_1\mathbf{N}_2 = x_2\mathbf{J}_1 - x_1\mathbf{J}_2}$$

$$\mathbf{d}_1 = \frac{x_1}{RT}\left(\nabla\mu_1\right)_{T,P} = -\frac{x_2\mathbf{N}_1 - x_1\mathbf{N}_2}{c\text{Đ}_{12}} = -\frac{x_2\mathbf{J}_1 - x_1\mathbf{J}_2}{c\text{Đ}_{12}}$$

Maxwell–Stefan Consistency

$$\boxed{\nabla x_1 = -\frac{x_2 \mathbf{N}_1 - x_1 \mathbf{N}_2}{c Đ_{12}} = -\frac{x_2 \mathbf{J}_1 - x_1 \mathbf{J}_2}{c Đ_{12}}}$$

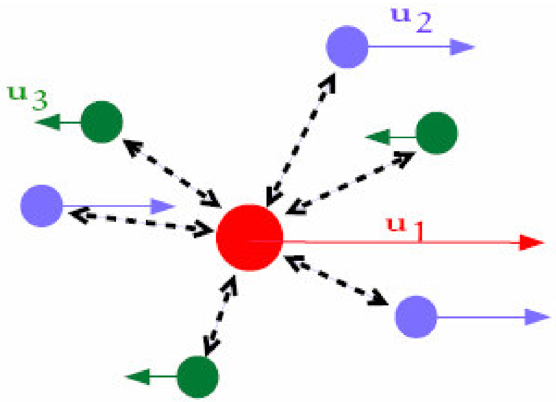
- Consistency of Maxwell – Stefan model with Fick model in case of binary mixture → $x_2 = 1 - x_1$

Stefan-Maxwell $N_1 = x_1 N_T - c Đ_{12} \nabla x_1$

Fick $N_1 = x_1 N_T - c \mathcal{D}_{12} \nabla x_1$

$$\boxed{\mathcal{D}_{12} = Đ_{12}}$$

MS for Multicomponent Mixtures



$$\mathbf{F}_i = -(\nabla \mu_i)_{T,P} = \sum_{j \neq i} \zeta_{ij} x_j \left(\mathbf{u}_i - \mathbf{u}_j\right)$$

$$\mathbf{d}_1 = \frac{x_i}{RT} \nabla \mu_i = -\sum_{j \neq i} \frac{\zeta_{ij}}{RT} x_i x_j \left(\mathbf{u}_i - \mathbf{u}_j\right) = -\sum_{j \neq i} \frac{x_j \mathbf{N}_i - x_i \mathbf{N}_j}{c \mathit{Đ}_{ij}}$$

$$\nabla x_1 = \frac{x_1 \mathbf{N}_2 - x_2 \mathbf{N}_1}{c \mathit{Đ}_{12}} + \frac{x_1 \mathbf{N}_3 - x_3 \mathbf{N}_1}{c \mathit{Đ}_{13}} + \frac{x_1 \mathbf{N}_4 - x_4 \mathbf{N}_1}{c \mathit{Đ}_{14}} + \dots$$

$$\nabla x_2 = \frac{x_2 \mathbf{N}_1 - x_1 \mathbf{N}_2}{c \mathit{Đ}_{12}} + \frac{x_2 \mathbf{N}_3 - x_3 \mathbf{N}_2}{c \mathit{Đ}_{23}} + \frac{x_2 \mathbf{N}_4 - x_4 \mathbf{N}_2}{c \mathit{Đ}_{24}} + \dots$$

Maxwell–Stefan vs. Fick Model

Fick

$$J_1 = -c\, D_{11} \nabla x_1 - c\, D_{12} \nabla x_2$$

$$J_2 = -c\, D_{12} \nabla x_1 - c\, D_{22} \nabla x_2$$

$$\boxed{(J) = -c\,[D]\,(\nabla x)}$$

$$\boxed{[D] = [B]^{-1}}$$

Maxwell -Stefan

$$\nabla x_1 = -\frac{x_1 J_2 - x_2 J_1}{c\, Đ_{12}} - \frac{x_1 J_3 - x_3 J_1}{c\, Đ_{13}}$$

$$\nabla x_2 = -\frac{x_2 J_1 - x_1 J_2}{c Đ_{12}} - \frac{x_2 J_3 - x_3 J_2}{c\, Đ_{23}}$$

$$\boxed{(J) = -c\,[B]^{-1}\,(\nabla x)}$$

Limiting Case: Solvent Species

$$\nabla x_1 = \frac{x_1 J_2 - x_2 J_1}{c\text{Đ}_{12}} + \frac{x_1 J_3 - x_3 J_1}{c\text{Đ}_{13}} \qquad \nabla x_2 = \frac{x_2 J_1 - x_1 J_2}{c\text{Đ}_{12}} + \frac{x_2 J_3 - x_3 J_2}{c\text{Đ}_{23}}$$

$$\text{Đ}_{12} \approx \text{Đ}_{13} \approx \text{Đ}_{23} \qquad c\nabla x_1 = -\frac{J_1}{\text{Đ}_{12}} \qquad D_{ii} = \text{Đ}_{12} = \mathcal{D}_{12}$$

$$\boxed{x_1 \to 0 \quad x_2 \to 0} \qquad c\nabla x_1 = -\frac{J_1}{\text{Đ}_{13}} \qquad c\nabla x_2 = -\frac{J_2}{\text{Đ}_{23}}$$

Limiting Case: Dilute Species

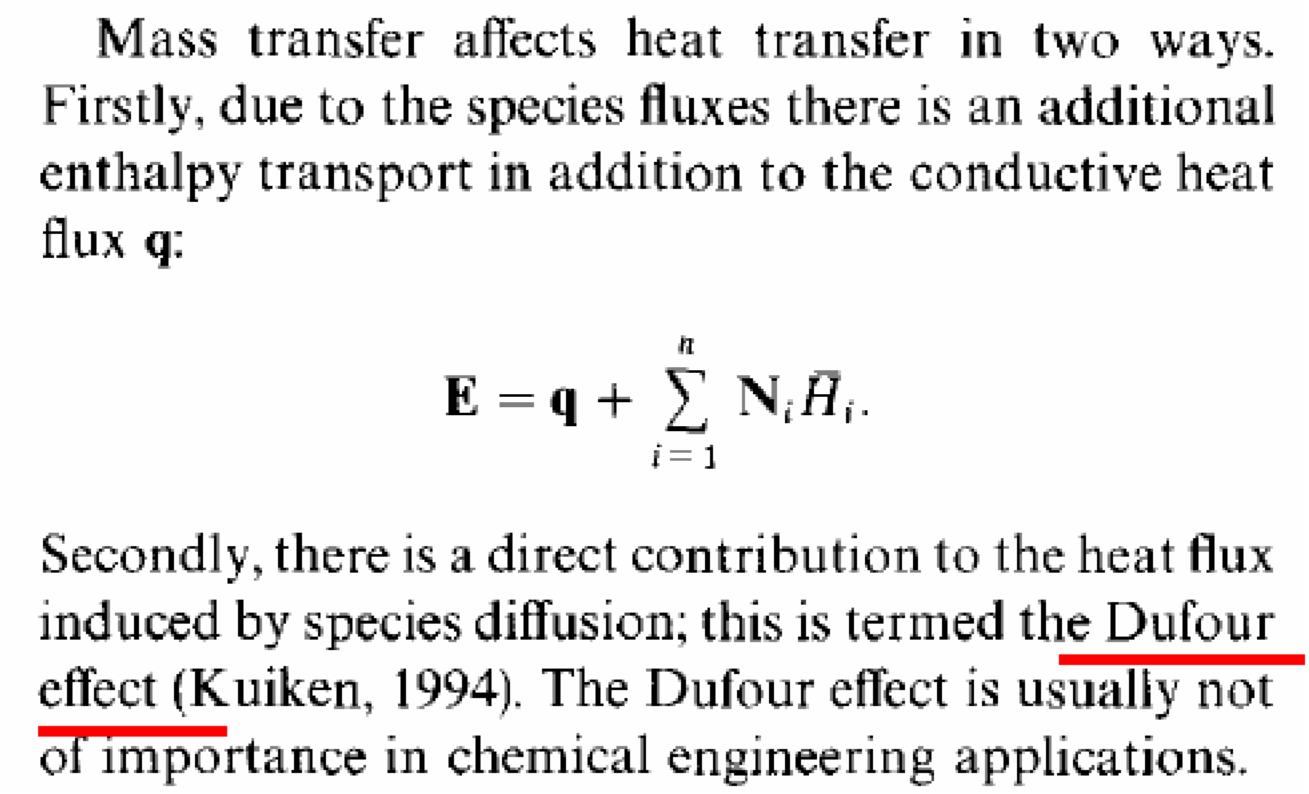
$$\mathbf{J}_1 = -c\mathcal{D}_{1,eff}\nabla x_1$$

$$\boxed{x_1 \to 0} \qquad c\nabla x_1 = -\left(\frac{x_2}{\text{Đ}_{12}} + \frac{x_3}{\text{Đ}_{13}}\right)\mathbf{J}_1$$

$$\boxed{\frac{1}{\mathcal{D}_{eff}} = \frac{x_2}{\mathcal{D}_{12}} + \frac{x_3}{\mathcal{D}_{13}}}$$

- This limiting case suggests an idea: it is possible to use the simple Fick model by providing a proper expression for the diffusivity in such a way to recover the correct dynamics → effective diffusivity methods

Heat ← Mass Transfer



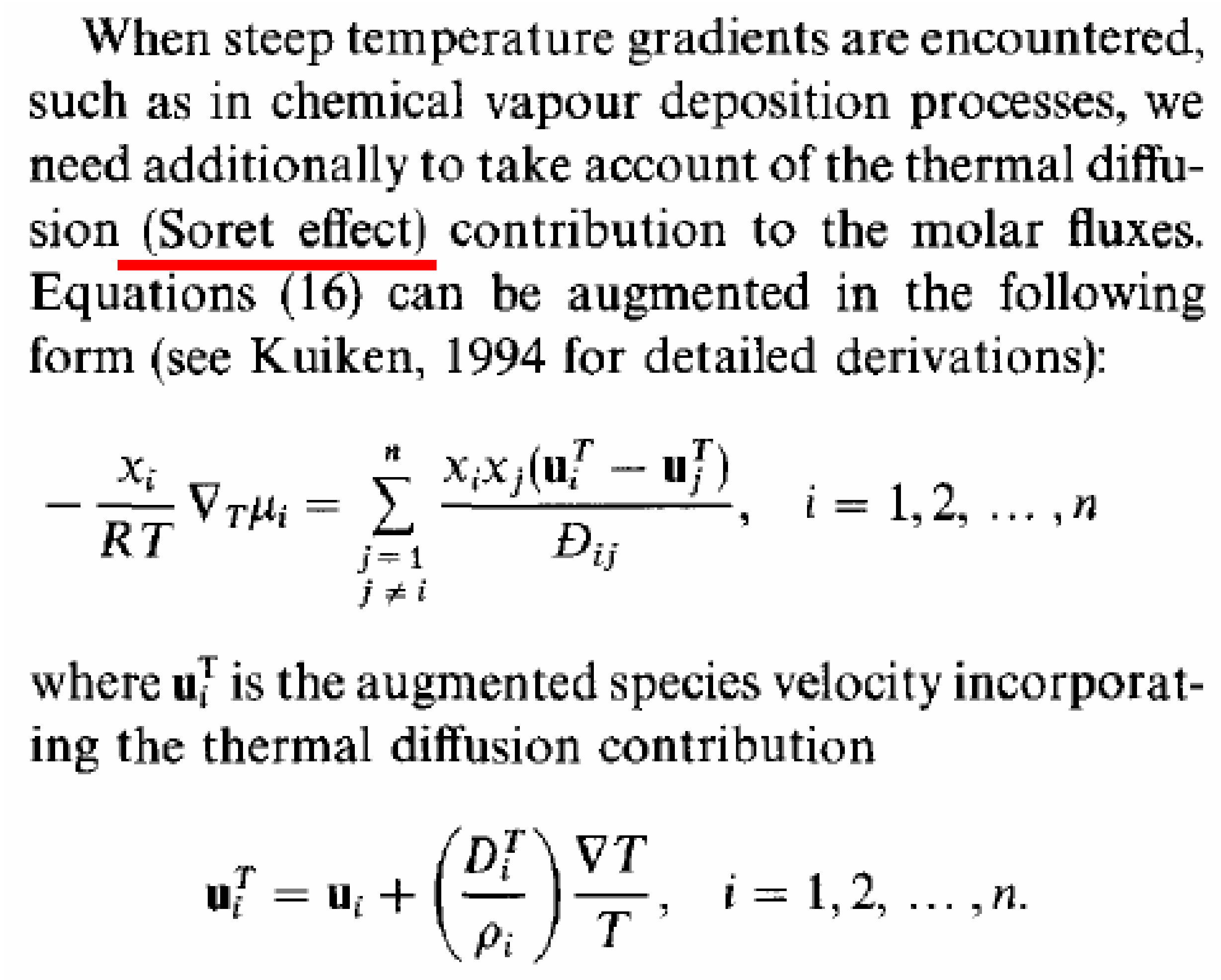
① Mass transfer affects heat transfer in two ways. Firstly, due to the species fluxes there is an additional enthalpy transport in addition to the conductive heat flux **q**:

$$\mathbf{E} = \mathbf{q} + \sum_{i=1}^{n} \mathbf{N}_i \bar{H}_i .$$

② Secondly, there is a direct contribution to the heat flux induced by species diffusion; this is termed the Dufour effect (Kuiken, 1994). The Dufour effect is usually not of importance in chemical engineering applications.

Heat → Mass Transfer

③



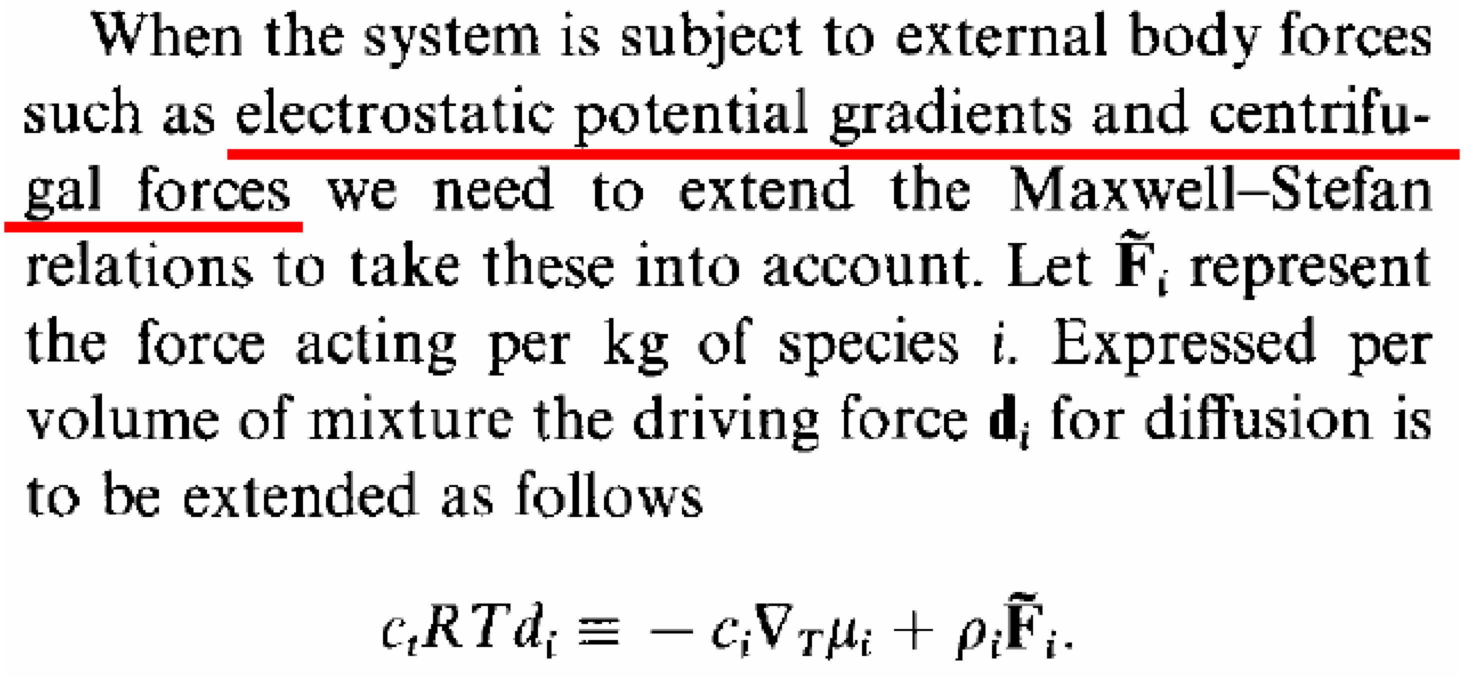
When steep temperature gradients are encountered, such as in chemical vapour deposition processes, we need additionally to take account of the thermal diffusion (Soret effect) contribution to the molar fluxes. Equations (16) can be augmented in the following form (see Kuiken, 1994 for detailed derivations):

$$-\frac{x_i}{RT}\nabla_T\mu_i = \sum_{\substack{j=1\\ j\neq i}}^{n} \frac{x_i x_j(\mathbf{u}_i^T - \mathbf{u}_j^T)}{\text{Đ}_{ij}}, \quad i = 1, 2, \ldots, n$$

where $\mathbf{u}_i^T$ is the augmented species velocity incorporating the thermal diffusion contribution

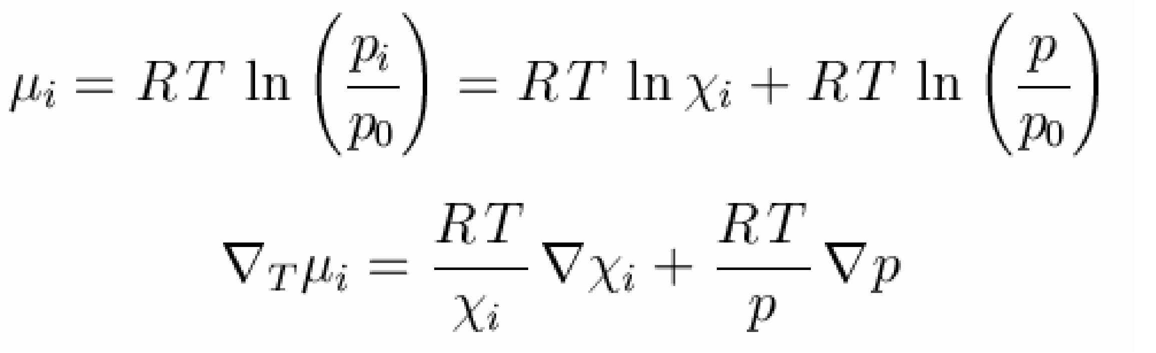
$$\mathbf{u}_i^T = \mathbf{u}_i + \left(\frac{D_i^T}{\rho_i}\right)\frac{\nabla T}{T}, \quad i = 1, 2, \ldots, n.$$

Generalized Driving Force



When the system is subject to external body forces such as electrostatic potential gradients and centrifugal forces we need to extend the Maxwell–Stefan relations to take these into account. Let $\tilde{\mathbf{F}}_i$ represent the force acting per kg of species i. Expressed per volume of mixture the driving force $\mathbf{d}_i$ for diffusion is to be extended as follows

$$c_t RT d_i \equiv -c_i \nabla_T \mu_i + \rho_i \tilde{\mathbf{F}}_i.$$



$$\mu_i = RT \ln\left(\frac{p_i}{p_0}\right) = RT \ln \chi_i + RT \ln\left(\frac{p}{p_0}\right)$$

$$\nabla_T \mu_i = \frac{RT}{\chi_i} \nabla \chi_i + \frac{RT}{p} \nabla p$$

Incorporating Mechanical Equilibrium

$$c_iRT\mathbf{d}_i \equiv -c_i\nabla_T\mu_i + \rho_i\tilde{\mathbf{F}}_i + \rho_i\left(\frac{1}{\rho}\nabla p - \sum_{k=1}^{n} \omega_k\tilde{\mathbf{F}}_k\right)$$

For ideal gas mixtures

$$-\nabla x_i - \frac{1}{p}(x_i-\omega_i)\nabla p + \frac{\rho_i}{p}\left(\tilde{\mathbf{F}}_i - \sum_{k=1}^{n} \omega_k\tilde{\mathbf{F}}_k\right) = \sum_{\substack{j=1\\ j\neq i}}^{n} \frac{x_j\mathbf{N}_i - x_i\mathbf{N}_j}{c_t\mathcal{D}_{ij}}, \quad i=1,2,\ldots,n.$$

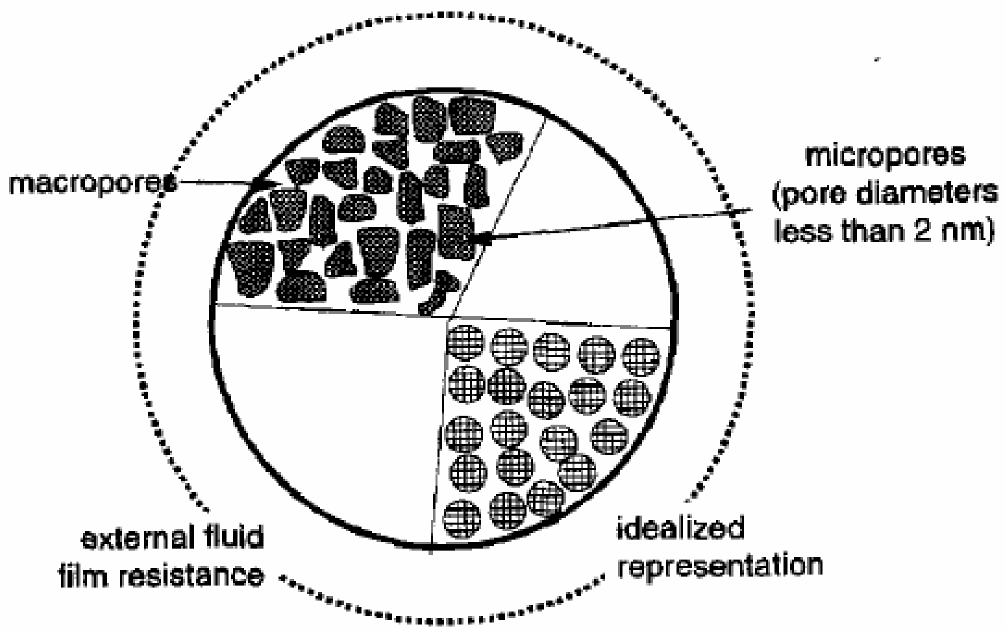
If the body forces $\mathbf{F}_i$ represent the force acting per mole of species i, the corresponding relations are

$$-\nabla x \boxed{-\frac{1}{p}(x_i-\omega_i)\nabla p} + \boxed{\frac{1}{p}\left(c_i\mathbf{F}_i - \omega_i\sum_{k=1}^{n} c_k\mathbf{F}_k\right)} = \sum_{\substack{j=1\\ j\neq i}}^{n} \frac{x_j\mathbf{N}_i - x_i\mathbf{N}_j}{c_t\mathcal{D}_{ij}}, \quad i=1,2,\ldots,n.$$

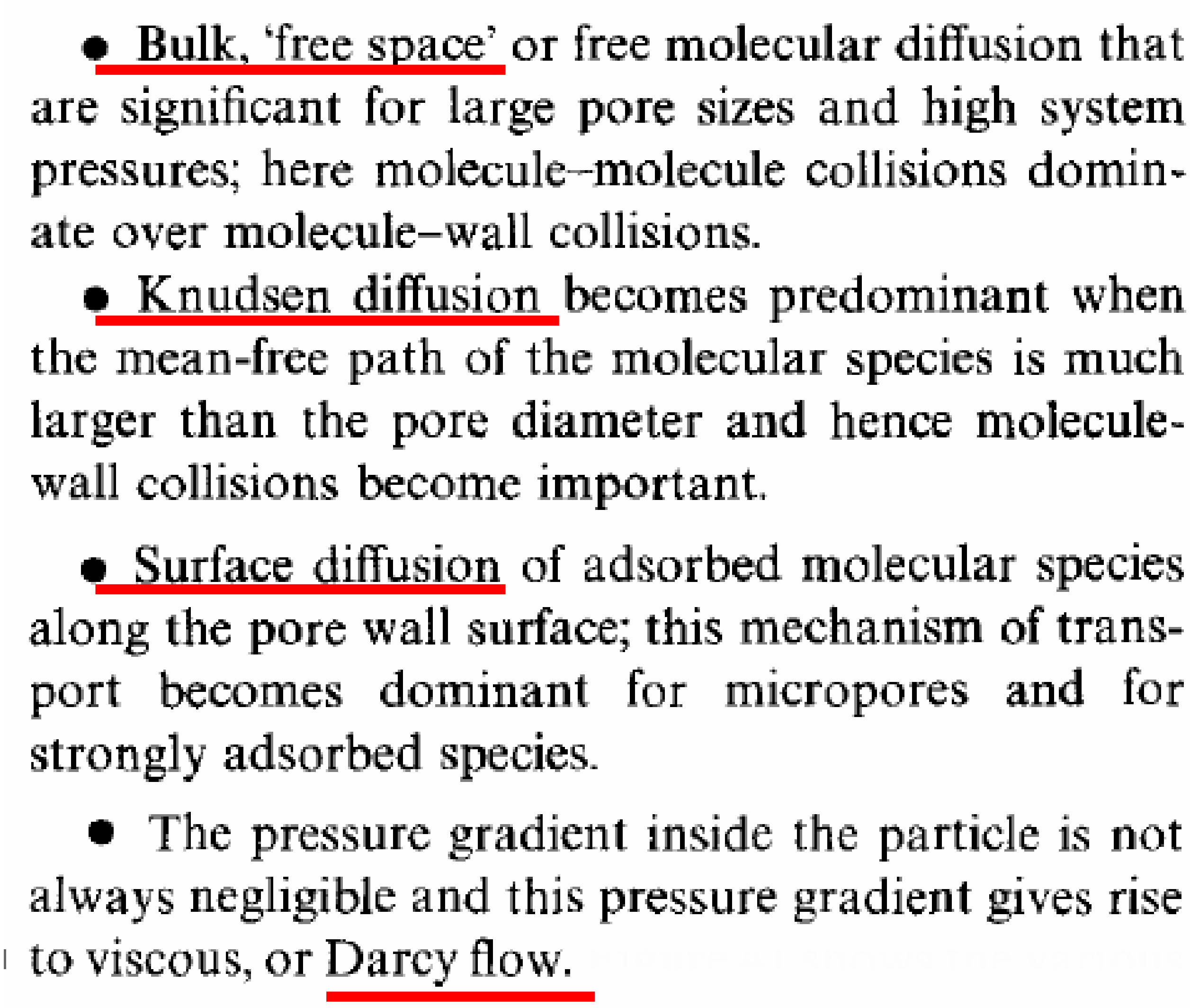
- Two important body forces:
  - electrostatic potentials (ionic systems)
  - centrifugal forces (centrifugal separation)

Fluid Flow in Porous Media

- Sometimes it is convenient to model the fluid flow through a porous medium by means of the average flow properties and skipping the actual microscopic details (homogenization problem) → Upscaling?

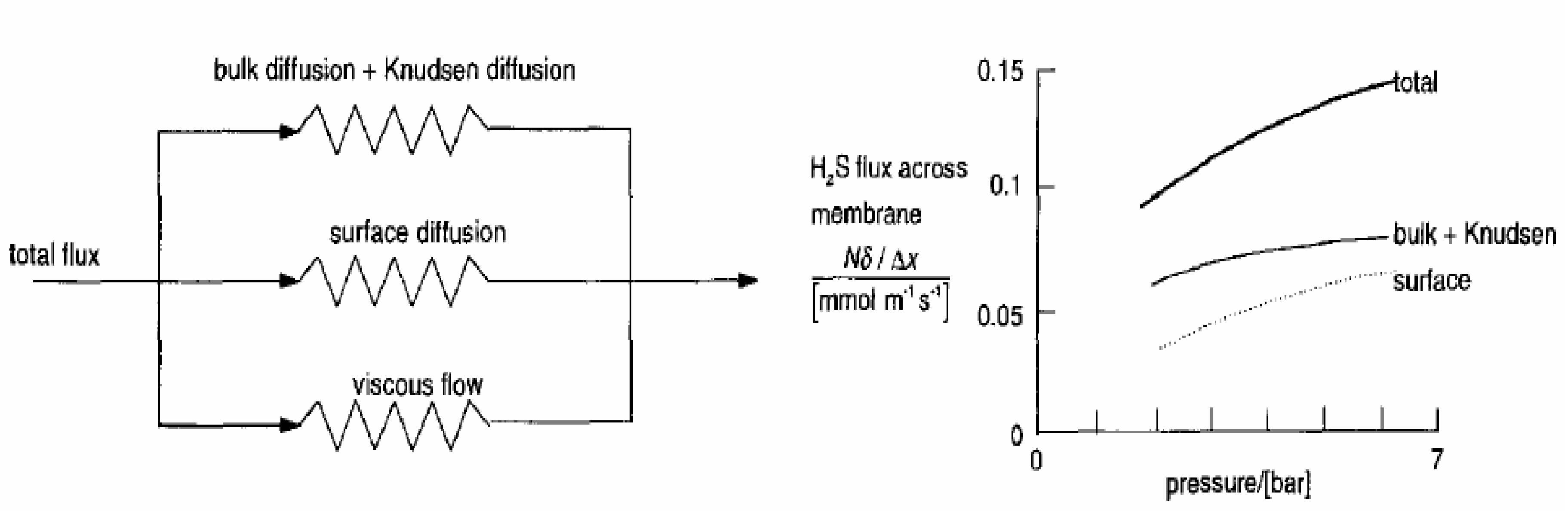


Diffusion Mechanisms in Porous Media



- Bulk, 'free space' or free molecular diffusion that are significant for large pore sizes and high system pressures; here molecule–molecule collisions dominate over molecule–wall collisions.
- Knudsen diffusion becomes predominant when the mean-free path of the molecular species is much larger than the pore diameter and hence molecule-wall collisions become important.
- Surface diffusion of adsorbed molecular species along the pore wall surface; this mechanism of transport becomes dominant for micropores and for strongly adsorbed species.
- The pressure gradient inside the particle is not always negligible and this pressure gradient gives rise to viscous, or Darcy flow.

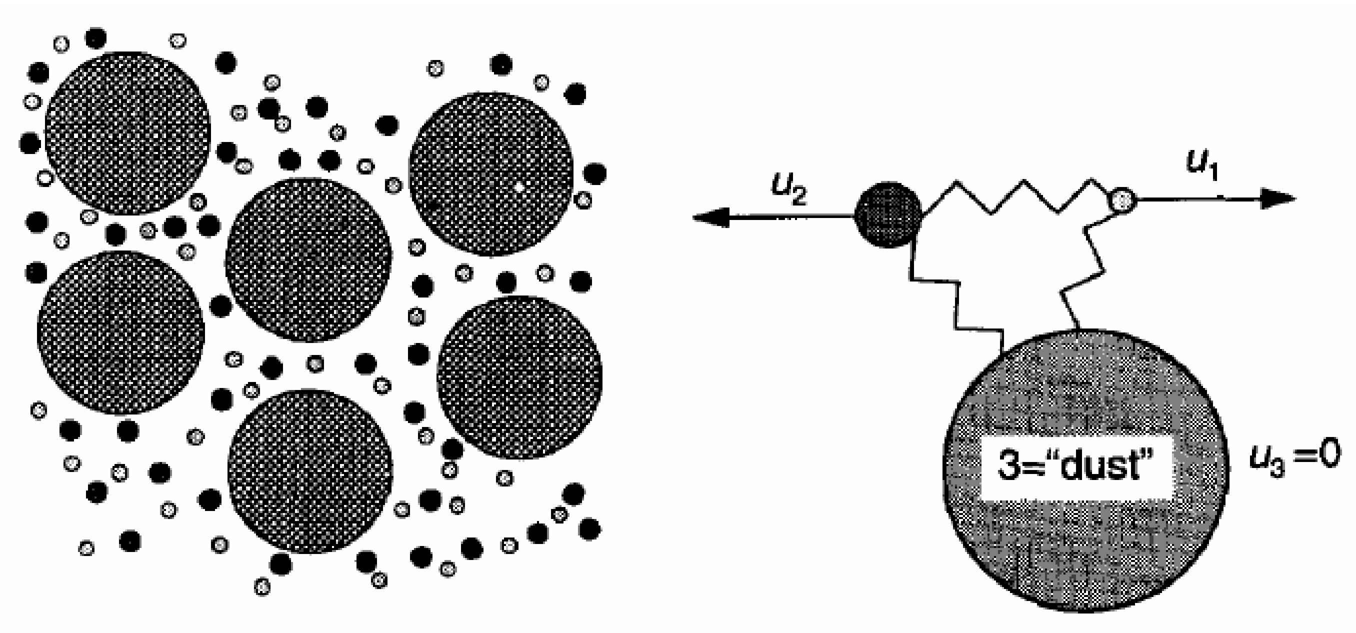
Electric Analogue Circuit



- Bulk and Knudsen diffusion mechanisms occur together and it is better to take both mechanisms into account → the distinction between them depends only on the actual size of the pores through which the mixture is flowing

Dusty Gas Model

- Straightforward application of the Maxwell–Stefan diffusion equations → let us consider the porous medium (solid phase) as consisting of giant molecules (dust) uniformly distributed in space



Starting Equation of Dusty Gas Model

$$-\nabla x_i' - \frac{(x_i' - \omega_i')}{p'}\nabla p' + \frac{1}{p'}\left(c_i\mathbf{F}_i - \omega_i'\sum_{i=1}^{n+1} c_i\mathbf{F}_i\right)$$

$$= \sum_{j=1}^{n+1}\frac{x_j'\mathbf{N}_i - x_i'\mathbf{N}_j}{c_i'\text{Đ}_{ij}'}, \quad i = 1, 2, \ldots \boxed{, n+1.}$$

- The primed quantities appearing in the previous equation refer now to the pseudo–mixture which includes the dust molecules → the quantities of physical interest are those which refer to the mixture only (free–gas) → some simplifications must be considered

Assumptions of Dusty Gas Model

- The dust concentration is spatially uniform
- The dust is motionless, so that $\mathbf{N}_{n+1}=0$
- The molecular weight of the dust molecule is large

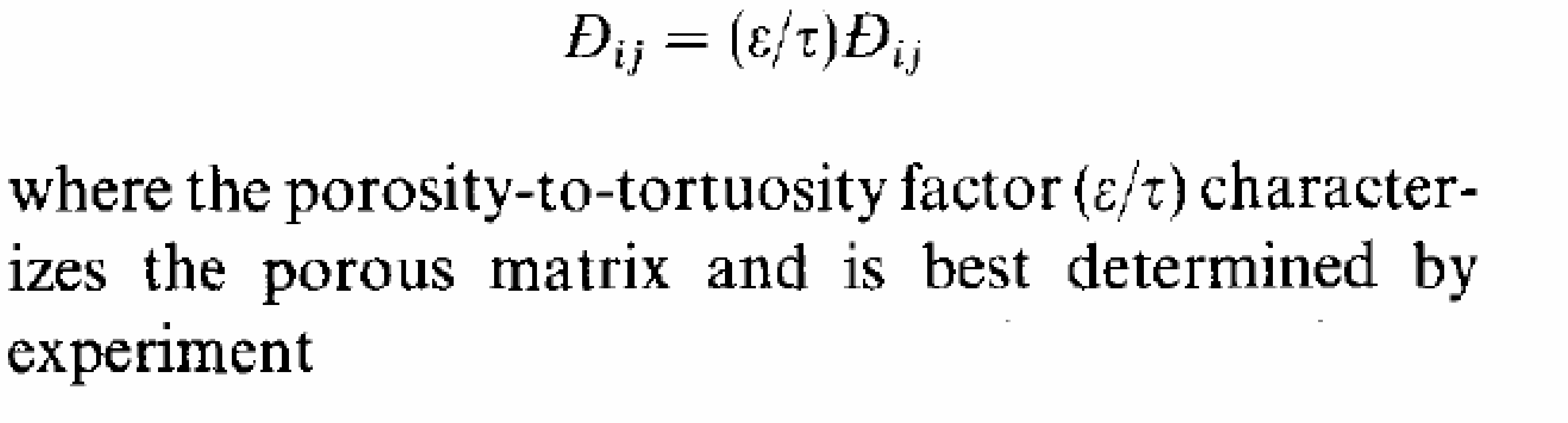
$$-\nabla x_i' - \frac{(x_i' - \omega_i')}{p'}\nabla p' - \frac{\omega_i'}{p'} c_{n+1}' \mathbf{F}_{n+1}$$

$$= \sum_{j=1}^{n} \frac{x_j'\mathbf{N}_i - x_i'\mathbf{N}_j}{c_i' \text{Đ}_{ij}'} + \frac{x_{n+1}'\mathbf{N}_i}{c_i' \text{Đ}_{i,n+1}'}, \quad i = 1, 2, \ldots \boxed{, n.}$$

$$-\frac{1}{RT}\nabla p_i = \sum_{j=1}^{n} \frac{x_j\mathbf{N}_i - x_i\mathbf{N}_j}{\boxed{\text{Đ}^e_{ij}}} + \frac{N_i}{\boxed{\text{Đ}^e_{iM}}}; \quad i = 1,2, \ldots \boxed{, n.}$$

Effective Diffusion Coefficients

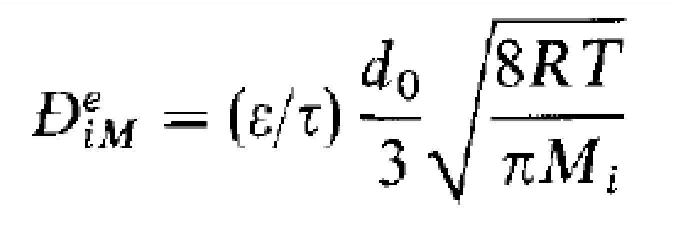
- Effective binary pair diffusion coefficients



$$\text{Đ}_{ij} = (\varepsilon/\tau)\text{Đ}_{ij}$$

where the porosity-to-tortuosity factor (ε/τ) characterizes the porous matrix and is best determined by experiment

- Effective Knudsen coefficients



$$\text{Đ}^{e}_{iM} = (\varepsilon/\tau)\,\frac{d_0}{3}\sqrt{\frac{8RT}{\pi M_i}}$$