

1. **Dissolution of a Slowly Rotating Sphere:** Consider the quasi-steady dissolution of a slowly rotating sphere of a sparingly soluble solid A in a large body of an initially pure liquid B at rest far from the sphere. The solid A has an equilibrium solubility in the liquid B of $\omega_A^{eq} \ll 1$. Presume that the solid very nearly maintains its spherical shape as it dissolves, and that the instantaneous radius of the sphere, $R(t)$, can be considered constant for the purpose of this analysis (quasi-steady assumption). Use a spherical-polar coordinate system (see Figure A-3 (b) in Appendix A of Deen). The sphere rotates slowly about the z axis with angular frequency ω ($[=] \frac{1}{T}$) low enough that the "creeping flow" (i.e. inertia-free) approximation applies for the velocity distribution

$$\mathbf{v} \simeq (0, 0, v_\phi(r, \theta))$$

$$v_\phi(r, \theta) \simeq \frac{\omega R^3}{r^2} \sin \theta$$

We want to predict the average rate of dissolution of A into the liquid phase as expressed by an average Sherwood number Sh^{ave}

$$Sh^{ave} = \frac{k^{ave} R}{\rho D_{AB}}$$

where k^{ave} is the average mass transfer coefficient, defined by

$$\int_0^\pi \int_0^{2\pi} n_{Ar}|_{r=R} R^2 \sin \theta d\theta d\phi = 4\pi R^2 k^{ave} \omega_A^{eq} \quad [=] \quad \frac{M}{T}$$

- (a) Apply the steady state FCMT model in the trace limit to this system to find the species A continuity equation in the liquid phase. Write down a set of boundary conditions, assuming local chemical equilibrium at the sphere surface and assuming axisymmetry wrt ϕ . What do these auxiliary conditions suggest about the solute mass fraction distribution $\omega_A = \omega_A(r, \theta, \phi)$? Simplify the model accordingly.
- (b) Scale the model from a). using

$$\bar{r} = \frac{r}{R}; \quad \omega = \frac{\omega_A}{\omega_A^{eq}}$$

and find a (quasi) steady solution for $\omega(\bar{r})$.

- (c) Determine Sh^{ave} . How does rotation of the sphere affect the rate of dissolution according to this model? Justify your answer..

2. **Sedimentation of Charged Colloidal Particles.** Sedimentation in aqueous media typically involves charged species. A common scenario is the sedimentation of charged colloidal particles in an aqueous electrolyte solution. Here we develop a simple model for the steady-state distribution in a gravitational field assuming $Z (> 0)$ valent colloidal particles, with $Z \gg 1$, suspended at trace levels with their monovalent counterions (anions) in water, and no additional added electrolyte (i.e. "salt free" conditions). Denote with subscripts 1, 2, and 3 the cationic colloidal particles, the anionic counterions and water, respectively. The colloidal particles ($i = 1$) are much larger than the anionic counterions or water ($\bar{V}_1 \gg \bar{V}_j$; $j = 2, 3$ where \bar{V}_j means the molar volume).

- (a) Starting with Eqns (6.32) and (6.45) in V&O for binary systems, one can develop the ff expressions for the molar diffusion fluxes of the trace solutes ($i = 1, 2$) wrt the volume average velocity \mathbf{v}^\dagger , $\mathbf{J}_i^\dagger = c_i (\mathbf{v}_i - \mathbf{v}^\dagger)$, combining ordinary diffusion, pressure diffusion and forced diffusion (migration) contributions

$$\begin{aligned} \lim_{x_1 \rightarrow 0} \mathbf{J}_1^\dagger &= -D_{13}^\infty \nabla c_1 + s_1^\infty c_1 \frac{1}{\rho} \nabla p - c_1 D_{13}^\infty \frac{ZF}{RT} \nabla \phi_{el}; \quad s_1^\infty = D_{13}^\infty \frac{\bar{V}_1}{RT} (\rho_1^0 - \rho_3^0) \\ \lim_{x_2 \rightarrow 0} \mathbf{J}_2^\dagger &= -D_{23}^\infty \nabla c_2 + s_2^\infty c_2 \frac{1}{\rho} \nabla p + c_2 D_{23}^\infty \frac{F}{RT} \nabla \phi_{el}; \quad s_2^\infty = D_{23}^\infty \frac{\bar{V}_2}{RT} (\rho_2^0 - \rho_3^0) \end{aligned}$$

where

$$\begin{aligned} \lim_{x_i \rightarrow 0} D_{i3} &= D_{i3}^\infty \text{ constant} \\ \lim_{x_i \rightarrow 0} s_i(\rho_i) &= s_i^\infty \text{ constant}; \quad s_i^\infty = D_{i3}^\infty \frac{\bar{V}_i}{RT} (\rho_i^0 - \rho_3^0) \end{aligned}$$

with ρ_i^0 meaning the density of pure i . Show that these equations are dimensionally consistent (i.e. all terms have the same units).

- (b) Use the diffusion flux laws from a). to model the steady final state of one directional sedimentation of the charged particles in a closed vertical column of height H . Employ a Cartesian coordinate system with origin on the bottom of the column and the x direction pointing upwards against gravity. Assume no volume change on mixing, and local electrical neutrality. Find the differential equations governing the steady density distributions of the colloidal particles $c_1(x)$ and their counter-ions, $c_2(x)$. Give a sufficient set of auxiliary conditions needed to solve for $c_1(x)$, $c_2(x)$ and $\phi_{el}(x)$.
- (c) Scale the system resulting from part b). using

$$\bar{x} = \frac{x}{H}; \quad \bar{c}_i = \frac{c_i}{c_{i0}}; \quad \bar{\phi} = \frac{\phi_{el} F}{RT}$$

where c_{i0} are the initial uniform (trace) concentrations of the colloidal particles and counterions (note $Zc_{10} = c_{20}$) and show that

the scaled colloid particle density distribution, $\bar{c}_1(\bar{x})$ for $Z \gg 1$ is very nearly

$$\bar{c}_1 \simeq \frac{Pe_2}{1 - e^{-Pe_2}} e^{-Pe_2 \bar{x}} ; Pe_2 = \frac{s_2^\infty gH}{D_{23}^\infty} = \frac{\bar{V}_2}{RT} (\rho_2^0 - \rho_3^0) gH$$

How does this result compare with the case of uncharged colloidal particles, i.e. does the charge on the colloidal particles increase or decrease the extent of segregation of the particles? Justify your answer. (*Hint: what is Z for the uncharged case?*)

3. **Limiting Current in a Well-Stirred Galvanostatic EC Cell with an Ionic Liquid Electrolyte:** Consider a galvanostatic EC cell with a ternary ionic liquid electrolyte consisting of $i = 1$ inert cation ($Z_1 = 1$), $i = 2$ inert anion ($Z_2 = -1$) and $i = 3$ reactive cation ($Z_3 = 1$). Assume the cell is well stirred with "bulk" mole fractions $x_{i,\infty}$, except for a stagnant layer of thickness δ adjacent to the cathode surface where a heterogeneous reduction occurs $I_{3,solution}^+ + e \rightarrow I_{3,solid}$ associated with the (experimentally controlled) current \mathbf{i} . Assume a one directional steady-state process and use RCC with the origin on cathode and δ_x pointing into the ionic liquid.

- (a) Employ the Stefan Maxwell constitutive laws to work this problem. These are developed in section 6.5 of V&O where the following "linear phenomenological force-flux" relations are given for a ternary mixture of uncharged fluids under isothermal, isobaric conditions

$$\begin{aligned} -\frac{1}{RT} \nabla \mu_1 &= \frac{x_2}{\mathfrak{D}_{12}} (\mathbf{v}_1 - \mathbf{v}_2) + \frac{x_3}{\mathfrak{D}_{13}} (\mathbf{v}_1 - \mathbf{v}_3) \\ -\frac{1}{RT} \nabla \mu_2 &= \frac{x_1}{\mathfrak{D}_{12}} (\mathbf{v}_1 - \mathbf{v}_2) + \frac{x_3}{\mathfrak{D}_{23}} (\mathbf{v}_1 - \mathbf{v}_3) \end{aligned}$$

Here the μ_i are molar (local) chemical potentials, and the three independent \mathfrak{D}_{ij} are the Stefan-Maxwell diffusivities. To adapt these to a ternary ionic liquid mixture and include migration effects, one can, in principle, substitute the molar electrochemical potential

$$\mu_i \rightarrow \mu_i^e = \mu_i + \bar{\phi}_i = \mu_i + Z_i F \phi^e$$

where Z_i is the valence and F is Faraday's constant. A necessary condition for the validity of this substitution is that μ_i^e obey the Gibbs Duhem equation. Show that this is true for an electrically neutral mixture.

- (b) If we adopt that chemical part of μ_i^e obeys

$$\mu_i = RT \ln [x_i \gamma_i] + \mu_i^0(T, p)$$

with constant γ_i show that

$$\begin{aligned} -\left[\nabla \ln x_1 + Z_1 \frac{F}{RT} \nabla \phi^e \right] &= \frac{x_2}{\mathfrak{D}_{12}} (\mathbf{v}_1 - \mathbf{v}_2) + \frac{x_3}{\mathfrak{D}_{13}} (\mathbf{v}_1 - \mathbf{v}_3) \\ -\left[\nabla \ln x_2 + Z_2 \frac{F}{RT} \nabla \phi^e \right] &= \frac{x_1}{\mathfrak{D}_{12}} (\mathbf{v}_1 - \mathbf{v}_2) + \frac{x_3}{\mathfrak{D}_{23}} (\mathbf{v}_1 - \mathbf{v}_3) \end{aligned}$$

- (c) Show that for the 1-d steady EC cell, the equations in b) reduce to

$$\begin{aligned} \frac{d}{dx} \ln x_1 + \frac{F}{RT} \frac{d}{dx} \phi^e &= \frac{i_x}{c \mathfrak{D}_{13} F} \\ \frac{d}{dx} \ln x_2 - \frac{F}{RT} \frac{d}{dx} \phi^e &= \frac{i_x}{c \mathfrak{D}_{23} F} \end{aligned}$$

Use these, with c assumed constant, appropriate boundary conditions, and local electrical neutrality, to find that the limiting current obeys

$$i_x^l = c \frac{\mathfrak{D}_{13}\mathfrak{D}_{23}}{(\mathfrak{D}_{23} + \mathfrak{D}_{13})\delta} F \ln(1 - 2x_{3,\infty})$$

Discuss the limiting cases

$$\begin{aligned} x_{3,\infty} &\rightarrow 0 \\ x_{3,\infty} &\rightarrow \frac{1}{2} \end{aligned}$$