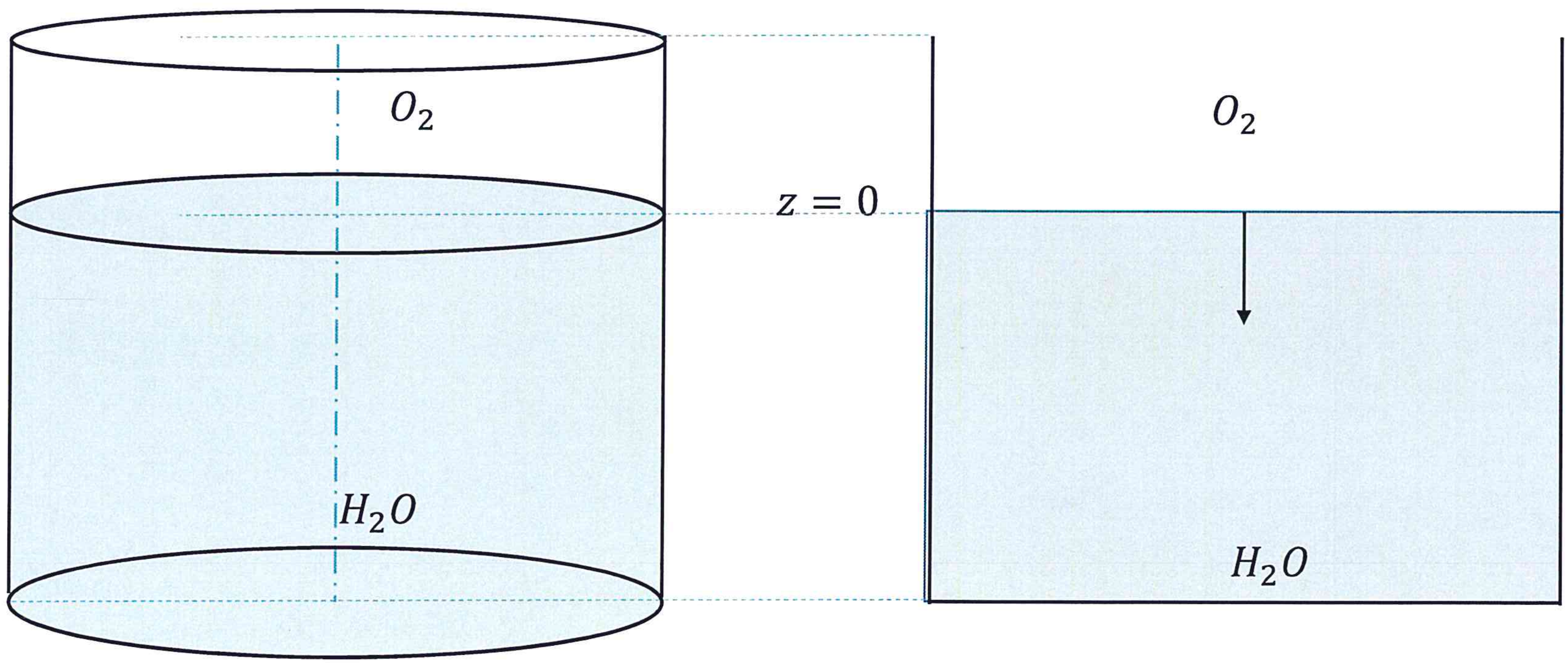
UNSTEADY STATE EXAMPLE ①

Example: A very long, very large tank of water is suddenly exposed to oxygen atmosphere. Oxygen diffuses into the water. What is the concentration profile of the oxygen in the water as a function of time?



CARTESIAN

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The **Equation of Species Mass Balance, constant ρD_{AB}.** For binary systems, and Fick's law has been incorporated. Good for dilute liquid solutions at constant temperature and pressure.

In terms of Diffusivity, D_{AB}

Microscopic species mass balance, constant thermal conductivity; Gibbs notation

$$\rho\left(\frac{\partial \omega_A}{\partial t} + \underline{v}\cdot\nabla\omega_A\right) = \rho D_{AB}\nabla^2\omega_A + r_A$$

Microscopic species mass balance, constant thermal conductivity; Cartesian coordinates

$$\rho\left(\frac{\partial \omega_A}{\partial t} + v_x\frac{\partial \omega_A}{\partial x} + v_y\frac{\partial \omega_A}{\partial y} + v_z\frac{\partial \omega_A}{\partial z}\right) = \rho D_{AB}\left(\frac{\partial^2 \omega_A}{\partial x^2} + \frac{\partial^2 \omega_A}{\partial y^2} + \frac{\partial^2 \omega_A}{\partial z^2}\right) + r_A$$

Microscopic species mass balance, constant thermal conductivity; cylindrical coordinates

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

$v_z = 0$ — wide — deep — no homogeneous rxn

Microscopic species mass balance, constant thermal conductivity; spherical coordinates

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

$cx_A = c_A = \frac{1}{M_A}(\rho_A) = \frac{1}{M_A}(\rho\omega_A)$ $\left(\text{units: } c[=]\frac{mol\ mix}{vol\ soln}; \rho[=]\frac{mass\ mix}{vol\ soln}; c_A[=]\frac{mol\ A}{vol\ soln}; \rho_A[=]\frac{mass\ A}{vol\ soln}\right)$

$\underline{j}_A \equiv$ mass flux of species A relative to a mixture's mass average velocity, $\underline{v}$ $\left(\text{units: } \underline{j}_A[=]\frac{mass\ A}{area\cdot time}\right)$

$= \rho_A(\underline{v}_A - \underline{v})$

$\underline{j}_A + \underline{j}_B = 0$, i.e. these fluxes are measured relative to the mixture's center of mass

$\underline{n}_A \equiv \rho_A\underline{v}_A = \underline{j}_A + \rho_A\underline{v} =$ combined mass flux relative to stationary coordinates

$\underline{n}_A + \underline{n}_B = \rho\underline{v}$

$\underline{v}_A \equiv$ velocity of species A in a mixture, i.e. average velocity of all molecules of species A within a small volume

$\underline{v} = \omega_A\underline{v}_A + \omega_B\underline{v}_B \equiv$ mass average velocity; same velocity as in the microscopic momentum and energy balances

Reference: R. B. Bird, W. E. Stewart, and E. N. Lightfoot, *Transport Phenomena*, 2nd edition, Wiley, 2002.
(p. 515, 584)

or CYLINDRICAL ③

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Microscopic species mass balance, constant thermal conductivity; Cartesian coordinates

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Microscopic species mass balance, constant thermal conductivity; cylindrical coordinates

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Microscopic species mass balance, constant thermal conductivity; spherical coordinates

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no θ variation; $v_z = 0$; 1D mass xfer; no homogeneous rxn

$cx_A = c_A = \frac{1}{M_A}(\rho_A) = \frac{1}{M_A}(\rho\omega_A)$ (units: $c[=]\frac{mol\ mix}{vol\ soln}$; $\rho[=]\frac{mass\ mix}{vol\ soln}$; $c_A[=]\frac{mol\ A}{vol\ soln}$; $\rho_A[=]\frac{mass\ A}{vol\ soln}$)

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$$\left(\frac{1}{M_A}\right)\rho \frac{\partial w_A}{\partial t} = \rho D_{AB} \frac{\partial^2 w_A}{\partial z^2} \left(\frac{1}{M_A}\right)$$

← multiply by $1/M_A$ (both sides)

$$\boxed{\frac{\partial c_A}{\partial t} = D_{AB} \frac{\partial^2 c_A}{\partial z^2}}$$

IC: $t = 0$ $\quad c_A = c_{A0}$ $\quad \forall z$

BC: $z = 0$ $\quad c_A = c_{AS}$ $\quad \forall t > 0$

$z = \infty$ $\quad c_A = c_{A0}$ $\quad \forall t > 0$

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O_2 Diffusion Solution:

The oxygen concentration as a function of time and depth into the water is given by:

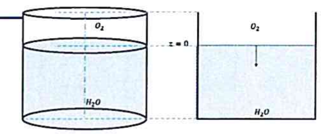
$$\frac{c_{As}-c_A}{c_{As}-c_{A0}} = \mathrm{erfc}\left(\frac{z}{2\sqrt{D_{AB}t}}\right) = \mathrm{erfc}\,\zeta$$

$$\zeta \equiv \frac{z}{2\sqrt{D_{AB}t}}$$

Solution is from WRF (or text) or the literature.

Unsteady State Mass Transport

Unsteady State Diffusion in a Semi-Infinite Slab



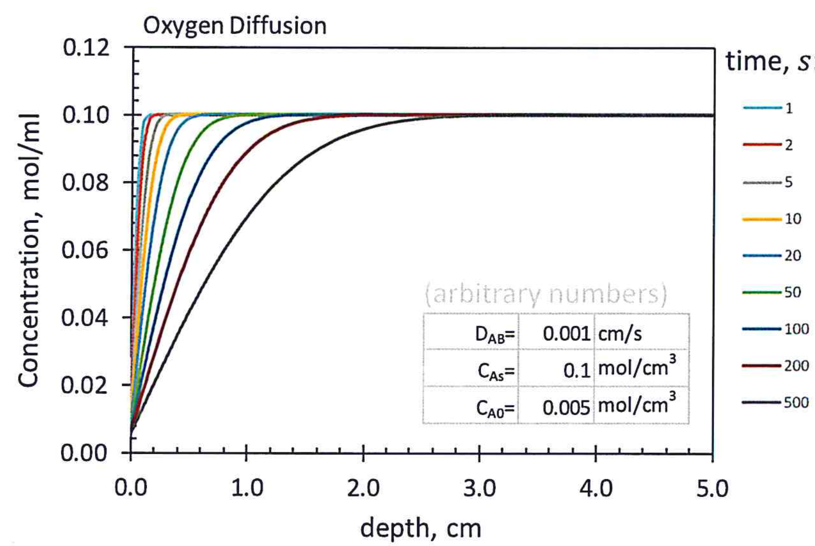
$$\frac{\partial c_A}{\partial t} = D_{AB}\left(\frac{\partial^2 c_A}{\partial z^2}\right)$$

Initial condition: $t=0 \quad c_A = c_{A0} \quad \forall\ z$

Boundary conditions:

$x=0 \quad c_A = c_{As} \quad t>0$

$x=\infty \quad c_A = c_{A0} \quad \forall\ t$



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This solution was a resource in the Danckwertz model for mass transfer; the short penetration time meant that the diffusion direction looked "infinite."

Unsteady State Mass Transport

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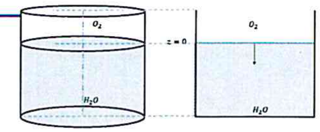


$$\frac{\partial c_A}{\partial t} = D_{AB}\left(\frac{\partial^2 c_A}{\partial z^2}\right)$$

Initial condition: $t = 0 \quad c_A = c_{A0} \quad \forall\, z$

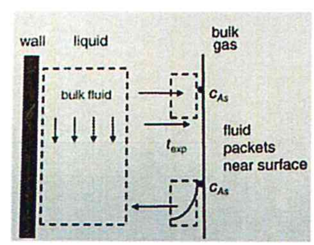
Boundary conditions:

$x = 0 \quad c_A = c_{As} \quad t > 0$

$x = \infty \quad c_A = c_{A0} \quad \forall\, t$

Mass Transport "Laws"

Another physical picture associated with penetration theory is "surface renewal" (Danckwerts)



$$k_c = \sqrt{\frac{4D_{AB}}{\pi t_{exp}}}$$

- Turbulent flow
- Diffusing species only penetrates a short distance
- Due to chem rxn or short time of contact, t_{exp}
- Model as unsteady state molecular transport
- Danckwerts: bulk motion brings fresh liquid eddies from interior to the surface
- At the surface A is transferred as though B were stagnant and infinitely deep
- Works for falling film