ETH
Eidgenössische Technische Hochschule Zürich
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Mass Transfer (Stoffaustausch) Fall Semester 2019

Test 1 October 22nd 2019

Name:____

Legi-Nr.:____

Test Duration: 45 minutes

Test Location: A to L in HG E 1.1
M to Z in HG E 3

Permitted material:
1 calculator
1 copy of Cussler's book "Diffusion" (2nd or 3rd edition)
1 printout of the lecture script, without notes on the exercises
1 page summary

NOT permitted:
solutions of exercises (also handwritten on summary), notebooks, mobile phones

If any information or data are missing, make an assumption but justify it.

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Problem 1 (50 points)

A thin layer of nickel (Ni) coating can prevent metals from corrosion. A metallic surface is placed in a chamber with well-stirred, highly concentrated nickel tetra carbonyl ($Ni(CO)_4$) vapor mixed with carbon monoxide (CO) at 200 ℃ and $1\ atm$. Thus, Ni atoms are deposited on that surface by the following instant and irreversible reaction:

$$Ni(CO)_{4(g)} \rightarrow Ni_{(s)} + 4\ CO_{(g)}$$

Assume that $Ni(CO)_4$ diffuses against the released CO that moves away from the surface in a thin unstirred film of thickness $2\ mm$ where the mole fraction of $Ni(CO)_4$ outside of the film is constant and equal to 90%.

a) Draw a sketch of the process. (11 points)
b) Develop the differential equation describing the mole fraction of $Ni(CO)_4$ perpendicular to the surface. Start with an appropriate diffusion equation and clearly state all assumptions. (12 points)
c) Propose appropriate boundary conditions and calculate the $Ni(CO)_4$ flux on the surface. (15 points)
d) How long does it take to grow a Ni coating with a thickness of $5\ \mu m$? (6 points)
e) How much would be the thickness of the coating in (d) if we assume dilute conditions? (6 points)

<u>Additional data:</u>

Diffusion coefficient of $Ni(CO)_4$ in CO at 200 ℃: $0.2\ \frac{cm^2}{s}$

Molecular mass of $Ni(CO)_4$: $171\ \frac{g}{mol}$

Molecular mass of Ni: $59\ \frac{g}{mol}$

Molecular mass of CO: $28\ \frac{g}{mol}$

Density of Ni: $8.9\ \frac{g}{cm^3}$

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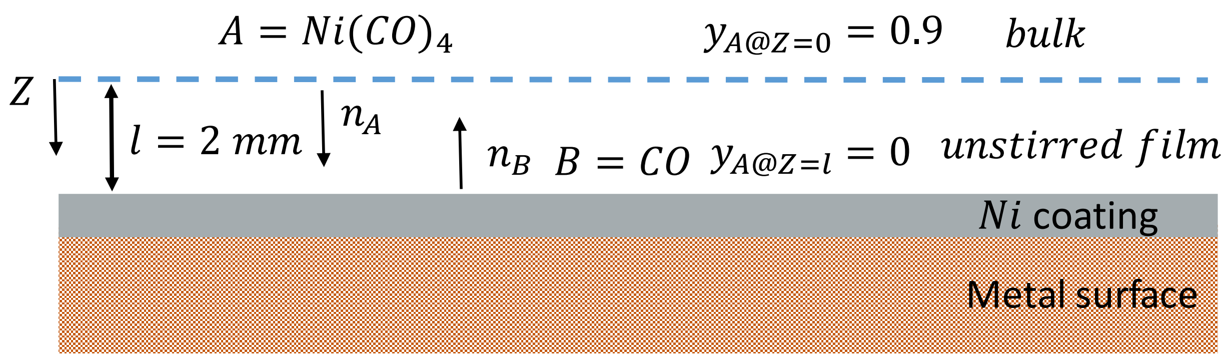
SOLUTION

a) 11 points



b) 12 points

$$n_A = j_A + c_A V^* = -D\frac{dc_A}{dz} + c_A V^*$$

$$V^* = y_A v_A + y_B v_B = \frac{n_A + n_B}{c}$$

$$n_B = -4n_A \rightarrow V^* = -\frac{3n_A}{c}$$

$$n_A = -D\frac{dc_A}{dz} - c_A\frac{3n_A}{c}$$

$$y_A = \frac{c_A}{c}$$

$$n_A = -Dc\frac{dy_A}{dz} - 3y_A n_A$$

$$n_A(1 + 3y_A) = -Dc\frac{dy_A}{dz}$$

$$\frac{dy_A}{1 + 3y_A} = -\frac{n_A}{Dc}dz$$

c) 15 points

$$\frac{\ln(1 + 3y_A)}{3})\Big|_{y_{A@z=0} = 0.9}^{y_{A@z=l} = 0} = -\frac{n_A}{Dc}\, z\Big|_{z = 0}^{z = l}$$

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$$\ln\left(\frac{1}{1+3y_{A@z=0}}\right) = \frac{-3n_A}{Dc} l$$

$$\rightarrow n_A = \frac{+Dc}{3l}\ln\left(\frac{1}{1+3y_{A@z=0}}\right) = \frac{+Dc}{3l}\ln\left(\frac{1}{1+3y_{A@z=0}}\right) = -0.436\frac{Dc}{l}$$

To calculate gas concentration, c, we use ideal gas law:

$$PV = nR_uT \ \rightarrow \ c = \frac{n}{V} = \frac{P}{R_uT} = \frac{1013250 \ \ dyne/cm^2}{8.315\times10^7 \ \cdot (273+200)K} = 2.58 \ \times 10^{-5} \ \frac{mol}{cm^3}$$

So

$$n_A = -0.436\frac{Dc}{l} = -0.436\frac{0.2 \ \frac{cm^2}{s}\times 2.58 \ \times 10^{-5} \ \frac{mol}{cm^3}}{0.2 \ cm} = 1.12\times10^{-5} \ \frac{mol}{cm^2 s}$$

d) 6 points

$$|n_A|\cdot\frac{MW_{Ni}}{\rho_{Ni}}\cdot time = \ thickness$$

$$\rightarrow \ time = \frac{\rho_{Ni}}{MW_{Ni}}\cdot\frac{thickness}{|n_A|} = \frac{8.9 \ \frac{g}{cm^3}}{59 \ \frac{g}{mol}}\cdot\frac{5 \ \times 10^{-4} cm}{1.12\times10^{-5} \ \frac{mol}{cm^2 s}} = 6.71 \ s$$

e) 6 points

$$\rightarrow n_{A\_Dilute} = -\frac{Dc_1}{l} = -\frac{0.2 \ \frac{cm^2}{s}\times 0.9\times 2.58 \ \times 10^{-5} \ \frac{mol}{cm^3}}{0.2 \ cm} = 2.32\times10^{-5} \ \frac{mol}{cm^2 s}$$

so the new thickness assuming dilute conditions would be $\frac{n_{A\_Dilute}}{n_A}\cdot thickness = 10.37 \ \mu m$

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Problem 2 (50 points)

Barium Vanadate ($Ba_3(VO_4)_2$) nanoparticles (NPs) are attractive as imaging material for biomedical applications. To study their stability in liquids, 10'000 of the spherical NPs (radius = 100 nm) are dispersed in water, inside a well-stirred cylindrical vial of 2 cm diameter and 8 cm height. The Ba^{2+} ions from the NPs dissolve very slowly (assume NP size constant) into the solution through a hypothetical stagnant film (an unstirred layer at the interface of the NP with the liquid) of thickness *l*. Also, 0.001 mol/L of Ba^{2+} ions are added, simulating the normal Ba^{2+} concentration in blood.

a) Make a detailed sketch of the problem including all relevant information. Additionally, make a separate sketch of the concentration profile of the Ba^{2+} concentration as a function of time. (10 points)
b) Derive an equation for the Ba^{2+} concentration in water for two cases: *l* = 10 nm and *l* = much larger than the radius of the NP (i.e., practically infinite). (20 points)
c) Calculate the Ba^{2+} concentration in water after one day for the case *l* = 10 nm. (10 points)

A researcher wants to assess whether the elevated Ba^{2+} concentrations caused by dissolution of NPs is harmful to cells. To that end, she prepares a new solution (without NPs) with $c(Ba^{2+})$ = 0.1 mol/L in an identical vial without stirring. Now, at the top of the vial, a layer of cells is added. The Ba^{2+} ions are absorbed immediately and continuously by the cells when they come in contact.

d) How much Ba^{2+} is taken up by the cells after 24 hours? (10 points)

Additional data

Diffusion coefficient of Ba^{2+} ions in water: $10^{-5}\,\frac{cm^2}{s}$

Solubility of Ba^{2+} in water: 0.1 $\frac{mol}{L}$

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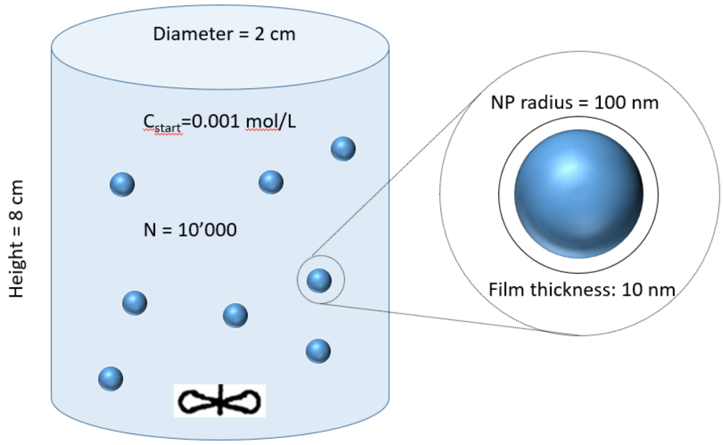
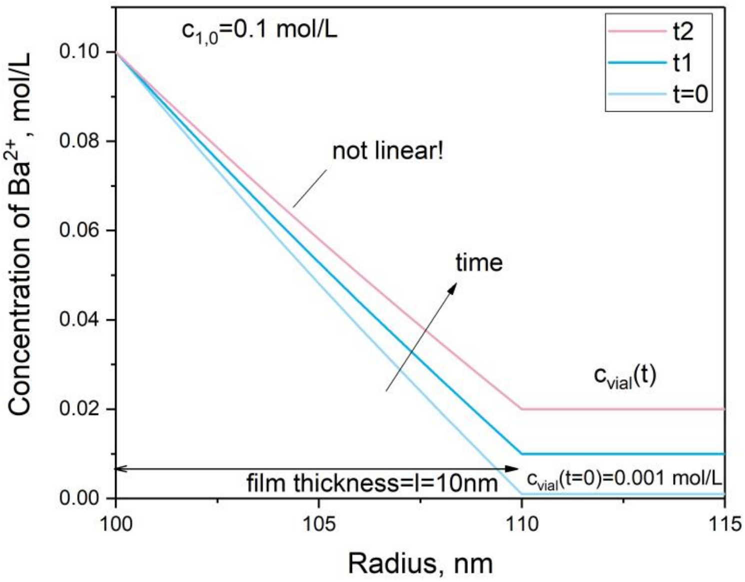
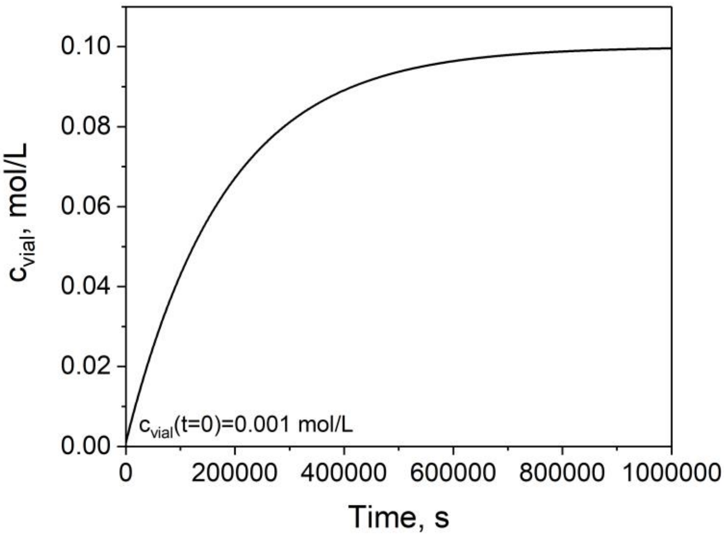
SOLUTION

a) 10 points







b) 20 points

This is a "thin film" problem, similar to the problem in Cussler Chapter 2.4.2 (Steady Dissolution of a Sphere).

Start with a mass balance for total Ba^{2+} in the vial

$$\frac{dc_{vial}(t)}{dt} = -\frac{\left(-j_1\big|_{r=R_0}\right)\cdot A_{1,sphere}\cdot N_{spheres}}{V_{vial}}$$

Vial volume:

$$V_{vial} = \left(\frac{d}{2}\right)\cdot \pi \cdot h = 1cm^2 \cdot \pi \cdot 8cm = 25.13cm^3$$

Total NP surface area:

$$A_{1,sphere}\cdot N_{spheres} = 4\pi r^2 \cdot N_{spheres} = 4\cdot\pi\cdot(100\cdot 10^{-7}cm)^2\cdot 10^4 = 1.26\text{x}10^{-5}cm^2$$

For each sphere, we calculate the flux, starting with a mass balance in a thin shell around the sphere

$$0 = \frac{1}{r^2}\frac{d}{dr}\left(r^2 j_1\right)$$

Using Fick's law and integrating yields

$$c_1 = A - B\frac{1}{r}$$

For Case A: Thin film of thickness *l*

Boundary conditions:

$$r = R_0 = 100nm, \quad \rightarrow c_1 = c_{1,0} = 0.1\frac{mol}{L}$$
$$r = R_0 + l, \quad \rightarrow c_1 = c_{vial}(t)$$

Plugging the boundary conditions in and subtracting the two equations, we can solve for B (we don't care about A, as for the flux only B is relevant)

$$B = R_0\cdot\left(1+\frac{R_0}{l}\right)\cdot\left(c_{vial}(t) - c_{1,0}\right)$$

Flux:

$$j_1\big|_{r=R_0} = -D\frac{dc_1}{dr}\bigg|_{r=R_0} = -D\cdot\left(-\frac{B}{r^2}\right)\bigg|_{r=R_0} = \frac{D}{R_0}\cdot\left(1+\frac{R_0}{l}\right)\cdot\left(c_{vial}(t)-c_{1,0}\right)$$

For Case B: Infinite film thickness (*l* >> *R*0)

Boundary conditions:

$$r = R_0 = 100nm, \rightarrow c_1 = c_{1,0} = 0.1\frac{mol}{L}$$
$$r = \infty \qquad \rightarrow c_1 = c_{vial}(t)$$

Plugging the BC in and solving for B

$$B = R_0\cdot\left(c_{vial}(t)-c_{1,0}\right)$$

Flux:

$$j_1\big|_{r=R_0} = -D\frac{dc_1}{dr}\bigg|_{r=R_0} = -D\cdot\left(-\frac{B}{r^2}\right)\bigg|_{r=R_0} = \frac{D}{R_0}\cdot\left(c_{vial}(t)-c_{1,0}\right)$$

Comparison of the two cases (not asked):

$$j_{1,CaseA} = j_{1,CaseB}\cdot\left(1+\frac{R_0}{l}\right)$$

Conclusion*:* For large layer thickness (*l* → infinity), the two equations become the same, as expected!!!

Now, we can plug in the flux in the mass balance for Ba^{2+} from the top

$$\frac{dc_{vial}(t)}{dt} = -\frac{\left(-j_1\big|_{R_0}\right)\cdot A_{1,sphere}\cdot N_{spheres}}{V_{vial}} = -\frac{D}{R_0}\cdot\left(1+\frac{R_0}{l}\right)\cdot\left(c_{vial}(t)-c_{1,0}\right)\cdot\frac{A_{1,sphere}\cdot N_{spheres}}{V_{vial}}$$

Separate the variables and integrate

$$\int_{c_{start}}^{c_{vial}(t)}\frac{dc_{vial}}{c_{vial}-c_{1,0}} = -\int_0^t\frac{D}{R_0}\cdot\left(1+\frac{R_0}{l}\right)\cdot\frac{A_{1,sphere}\cdot N_{spheres}}{V_{vial}}\,dt = -\int_0^t M\,dt$$

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where we have defined the characteristic (inverse time) constant or rate of transport:

$$M = \frac{D}{R_0} \cdot \left(1 + \frac{R_0}{l}\right) \cdot \frac{A_{1,sphere} \cdot N_{spheres}}{V_{vial}}$$

Solution:

$$\frac{c_{vial}(t) - c_{1,0}}{c_{vial}(0) - c_{1,0}} = \exp(-M \cdot t)$$

Rearrange:

$$\boxed{\begin{aligned} c_{vial}(t) &= c_{1,0} - \left(c_{1.0} - c_{vial}(0)\right)\exp(-M \cdot t) \\ &= c_{1.0} \cdot \left(1 - \exp(-M \cdot t)\right) + c_{vial}(0) \cdot \exp(-M \cdot t) \end{aligned}}$$

c) 10 points

Value of the inverse time constant *M*:

For case A (*l* = 10 nm):

$$M = \frac{D}{R_0} \cdot \left(1 + \frac{R_0}{l}\right) \cdot \frac{A_{1,sphere} \cdot N_{spheres}}{V_{vial}} = \frac{10^{-5}\,\frac{cm^2}{s}}{10^{-5}\,cm} \cdot \left(1 + \frac{100}{10}\right) \cdot \frac{1.26\text{x}10^{-5}\,cm^2}{25.13\,cm^3} = 5.515\text{x}10^{-6}\,\frac{1}{s}$$

For Case B (*l* >> R_0): **(NOT ASKED)**

$$M_B = \frac{D}{R_0}\left(1 + \frac{R_0}{l}\right)\frac{A_{1sphere} N_{sphere}}{V_{vial}} = \frac{10^{-5}\,\frac{cm^2}{s}}{10^{-5}\,cm} \cdot (1 + 0) \cdot \frac{1.26\text{x}10^{-5}\,cm^2}{25.13\,cm^3} = 0.501\text{x}10^{-6}\,\frac{1}{s}$$

Vial Concentration after one day (time *t* = 24 x 60 x 60 = 86,400 s):

For case A:

$$
\begin{aligned}
c_{vial,caseA}(1\ day) &= 0.1\frac{mol}{L}\left(1-\mathrm{e}^{-5.515\mathrm{x}10^{-6}\cdot 86400}\right)+0.001\frac{mol}{L}\mathrm{e}^{-5.515\mathrm{x}10^{-6}\cdot 86400} \\
&= 0.1\frac{mol}{L}\left(1-\mathrm{e}^{-0.4752}\right)+0.001\frac{mol}{L}\mathrm{e}^{-0.4752} \\
&= 0.1\frac{mol}{L}\left(1-0.6217\right)+0.001\frac{mol}{L}0.6217 \\
&= 0.0378\frac{mol}{L}+0.00062\frac{mol}{L} \\
&= 0.0384\frac{mol}{L}
\end{aligned}
$$

For case B **(NOT ASKED)**

$$
\begin{aligned}
c_{vial,B}(1\ day) &= 0.1\frac{mol}{L}\left(1-\mathrm{e}^{-0.501\mathrm{x}10^{-6}\cdot 86400}\right)+0.001\frac{mol}{L}\mathrm{e}^{-0.501\mathrm{x}10^{-6}\cdot 86400} \\
&= 0.1\frac{mol}{L}\left(1-\mathrm{e}^{-0.0433}\right)+0.001\frac{mol}{L}\mathrm{e}^{-0.0433} \\
&= 0.1\frac{mol}{L}\left(1-0.958\right)+0.001\frac{mol}{L}0.958 \\
&= 0.0042\frac{mol}{L}+0.00096\frac{mol}{L} \\
&= 0.0051\frac{mol}{L}
\end{aligned}
$$

d) 10 points

Now, this is a semi-infinite slab problem.

$$J = A\cdot j_1\big|_{z=0} = A\cdot\sqrt{\frac{D}{\pi t}}\cdot\left(c_{1,0}-c_{1,l}\right) = -A\cdot\sqrt{\frac{D}{\pi t}}\cdot c_{1,l}$$

Integrate from 0 to 24 hours

$$n = \int_0^{24hours} J\,dt = -2A\cdot\sqrt{\frac{Dt}{\pi}}\cdot c_{1,l}$$

Plugging-in all the numbers:

$$
\begin{aligned}
n &= -2\cdot\left(1cm^2\cdot\pi\right)\cdot\sqrt{\frac{10^{-5}\,\frac{cm^2}{s}\cdot 86400\ s}{\pi}}\cdot\frac{10^{-3}L}{cm^3}\cdot 0.1\,\frac{mol}{L} \\
&= -3.29\mathrm{x}10^{-4}\ mol
\end{aligned}
$$