

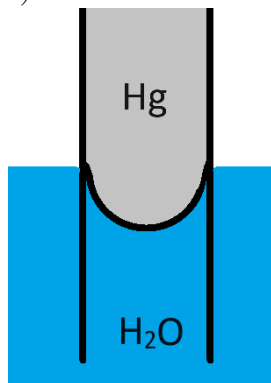
CH-242(b) - Week 5 exercise solutions

Lippmann's ΔP vs. e curve

a)

The pressure at the water side of the meniscus is just atmospheric pressure $P_o = 1 \text{ atm}$ since it is at the same elevation as the flat water-air interface. The pressure at the mercury side is $P_o + \Delta p + \rho_{\text{Hg}}gh$ where $\Delta p = 0$, $h = 750 \text{ mm}$, $g = 9.8 \text{ m s}^{-2}$, and $\rho_{\text{Hg}} = 13.5 \text{ g cm}^{-3}$ is the volumetric mass density of mercury. The pressure difference is thus $\rho_{\text{Hg}}gh$. You can plug the numbers in or note that mmHg is a unit of measure representing the hydrostatic pressure of a column of mercury 1 mm in height, with a conversion factor of $760 \text{ mmHg} = 1 \text{ atm}$ so the pressure difference at the meniscus is about 1 atm.

b)



Because the pressure in the mercury is greater than in the water, the meniscus must curve in towards the mercury. This is also consistent with the known fact that mercury does not wet glass and so will try to minimize the glass-mercury surface area by forming a low $\approx 0^\circ$ contact angle. What would happen if mercury wetted glass more strongly than water?

c)

From the Laplace-Young equation we have

$$\Delta P = 2\gamma/r$$

where, from our assumption of a zero contact angle, r represents both the radius of curvature of the meniscus as well as the radius of the capillary. Solving for r we get:

$$r = 2 \times 0.415 \text{ N m}^{-1} / 1 \times 10^5 \text{ Pa} \approx 1 \times 10^{-5} \text{ m} = 10 \mu\text{m}$$

very small!

d)

If the surface tension is 415 mN m^{-1} when $\Delta P = 750 \text{ mmHg}$, and the meniscus radius of curvature is fixed because its elevation is fixed and we always assume perfect wetting, then for an added pressure Δp of 111 mmHg at $V = 0.140 \text{ Daniell} \approx 0.154 \text{ V}$ we get a surface tension of

$$\gamma = \frac{750 \text{ mmHg} + 111 \text{ mmHg}}{750 \text{ mmHg}} 415 \text{ mN m}^{-1} \approx 746 \text{ mN m}^{-1}$$

e)

From inspection of the table:

$$\sigma = \frac{d\gamma}{d\Delta V} \approx \frac{(131 \text{ mmHg} - 111 \text{ mmHg}) \times \frac{0.415 \text{ N m}^{-1}}{750 \text{ mmHg}}}{(0.170 \text{ Daniell} - 0.140 \text{ Daniell}) \times \frac{1.1 \text{ V}}{1 \text{ Daniell}}} \approx +0.3 \text{ C m}^{-2}$$

or what amounts to roughly one elementary charge per each $7 \text{ \AA} \times 7 \text{ \AA}$ square at the interface. Considering that mercury atoms themselves have a diameter of roughly 3 \AA , this suggests a rather dense concentration of excess charge at the interface. Check the definitions of Σ and ΔV from the lecture notes to make sure the positive sign is correct. A positive surface charge density on the mercury side near $\Delta V = 0$ is consistent with selective adsorption of negatively charged anions on the aqueous side of the interface.

f)

The surface charge goes to zero at the voltage V_{pzc} when $\sigma = \frac{d\gamma}{d\Delta V} = 0$, i.e. where the curve reaches a maximum, which from inspection of the table appears to occur around 0.905 Daniell .

g)

$c_A = -\frac{d^2\gamma}{d\Delta V^2}$. This can be numerically approximated by “the change in the slope over the change in the voltage”. Picking two pairs of points near the maximum at V_{pzc} with significant slopes we get:

$$c_A = -\frac{\left(\frac{(301-353)\text{mmHg}}{(1.261-1.000)\text{Daniell}} - \frac{(356.5-314)\text{mmHg}}{(0.833-0.588)\text{Daniell}} \right) \times \frac{1 \text{ Daniell}}{1.1 \text{ V}}}{\left(\frac{1}{2} \times (1.261 + 1.000) - \frac{1}{2} \times (0.833 + 0.588) \right) \text{ Daniell} \times \frac{1.1 \text{ V}}{1 \text{ Daniell}}} \times \frac{0.415 \text{ N m}^{-1}}{750 \text{ mmHg}}$$

or

$$c_A \approx 0.41 \text{ F m}^{-2}$$

h)

If the acid solution is roughly 6 parts water to 1 part sulphuric acid by volume, and one liter of sulphuric acid is $1.83 \times 10^3 \text{ g L}^{-1} / 98 \text{ g mol}^{-1} \approx 19 \text{ mol L}^{-1}$ then the solution is roughly 3 M . If we assume that all the H_2SO_4 molecules dissociate into H^+ and HSO_4^- , then that gives a background concentration c_o of 3 M with a valency $z = 1$. To save a little work, from the notes we have, for monovalent aqueous solution at room temperature:

$$\lambda_D^{\text{H}_2\text{O}} = 3.04 \text{ \AA} / \sqrt{c_o} \approx 2 \text{ \AA}$$

A layer with such a thickness can hardly be considered “diffuse”! Forging ahead in any case, from λ_D we can get the differential capacitance c_A via

$$c_A = \varepsilon_r \varepsilon_o / \lambda_D \approx 80 \times 8.9 \times 10^{-12} \text{ F m}^{-1} / 2 \times 10^{-10} \text{ m} = 3.56 \text{ F m}^{-2}$$

which compares reasonably well with the value implied by analysis of the electrocapillary curve.

i)

From the lecture notes we have

$$\Delta\phi = \sigma \lambda_D / \varepsilon_r \varepsilon_o$$

but

$$\frac{d^2\phi}{dz^2}(z=0) = \Delta\phi / \lambda_D^2 = -F \Delta c_o / \varepsilon_r \varepsilon_o$$

so

$$\Delta c_o = -\frac{\sigma}{F \lambda_D} = -\frac{0.3 \text{ C m}^{-2}}{9.6 \times 10^4 \text{ C mol}^{-1} \times 2 \times 10^{-10} \text{ m}} \approx -15.6 \text{ M}$$

So the simplified equations derived in class predict a max deviation Δc_o that is not only not much smaller than the mean, but is in fact *larger*, in violation of the assumption $|\Delta c_o| \ll c_o$ used to derive the expression for Δc_o . We do not expect therefore to get very accurate results from application of our “linearized” equations. Interested readers can refer to section 4.2 of *Physics and Chemistry of Interfaces* by Butt et al. (3rd edition) for a more general solution to the diffuse layer problem which does not assume $|\Delta c_o| \ll c_o$.