CH-242(b) - Review questions

1. Consider a closed cylinder of radius R filled with N moles of an ideal gas in thermal contact with its surroundings which are at a temperature T. On one end of the cylinder is a plunger (or piston) which can compress or expand the cylinder volume, and on the other end is a film of soapy water with a surface tension γ. When the cylinder is a length L the pressure inside the cylinder is equal to the pressure P_o of the surroundings so that the soap film is flat. When the cylinder is compressed the pressure inside the cylinder increases and as a result the film becomes curved (see Fig. 1).

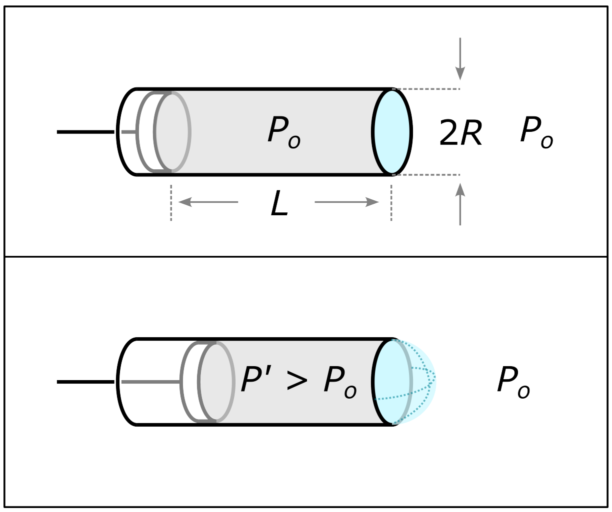


Figure 1: Plunger with soapy film on one end.

   (a) At what final volume V' will the film have the shape of a hemisphere? The expression should depend on the initial volume V_o and on the ratio $\alpha \equiv R/R_o$, where R_o is a "natural" length scale for the problem given by $R_o \equiv 4\gamma/P_o$.

   Solution: When the film has a hemispherical shape, it's radius of curvature is simply R. According to the Young-Laplace equation, this will occur when the pressure inside the cylinder exceeds that of the outside by an amount $\Delta P = 4\gamma/R$. There is a factor 4 because a soap film has two sides. For closed isothermal processes of an ideal gas we have that the product $P \times V$ is constant. Therefore, we have

$$V' = V_o \times \frac{P_o}{P'} = V_o \times \frac{P_o}{P_o + \Delta P} = V_o / \left(1 + 1/\alpha\right) = V_o \times \frac{\alpha}{1+\alpha}$$

   (b) Estimate R_o for a soapy film of surface tension $\gamma \approx 10\,\mathrm{mN\,m^{-1}}$. Assume $P_o = 1\,\mathrm{atm}$.

   Solution: Plug and chug. I end up with $R_o \approx 400\,\mathrm{nm}$.

(c) Calculate the minimum work W required to perform this compression. Express your answer in terms of units of $P_o V_o$ (or, equivalently, $N\bar{R}T$, where $\bar{R}$ is the universal gas constant). The resulting expression should depend only on α. Hint: start from the thermodynamic law stating that the minimum work W required to perform some operation on some system at fixed temperature is equal to the change ΔF in the system's Helmoltz free energy $F = U + TS$.

Solution: We begin, as suggested in the hint, by noting that

$$W = \Delta F$$

Where W is the minimum work required for some isothermal process and ΔF is the change in the system's Helmholtz free energy. This formula is in fact easily derived by start from the first law of thermodyamics:

$$\Delta W + \Delta Q = \Delta U = \Delta\left(F + TS\right) = \Delta F + T\Delta S$$

But from the second law of thermodyamics $T\Delta S \geq \Delta Q$ we have thus

$$\Delta W \geq \Delta F$$

Our system is composed of the gas G and the soap film S, so that

$$\Delta F = \Delta F_G + \Delta F_S$$

For the gas we have for closed isothermal processes:

$$dF_G = d\left(U_G - TS_G\right) = \left(TdS_G - PdV\right) - T\Delta S_G = -PdV$$

Integrating from V_o to V' we get

$$\Delta F_G = -\int_{V_o}^{V'} P(V)dV = P_o V_o \int_{\frac{\alpha}{1+\alpha}}^{1} d\ln\frac{V}{V_o} = N\bar{R}T\ln\left(1 + 1/\alpha\right)$$

For the interface we have simply (see lecture 2 notes)

$$\Delta F_S = 2\gamma\Delta A = 2\gamma\left(2\pi R^2 - \pi R^2\right) = 2\gamma\pi R^2$$

where the factor 2 comes from the fact that the film has two sides. This can be manipulated into a form that permits comparison with ΔF_G:

$$2\gamma\pi R^2 = \frac{1}{2}P_o\pi R^2 L \times \frac{4\gamma}{P_o}/R \times \frac{R}{L} = N\bar{R}T \times \frac{1}{2} \times \frac{R/L}{\alpha}$$

In fact if we consider that we can not compress the cylinder any further than $L \to 0$, then we can show that in order to obtain a hemispherical film we require

$$\frac{R}{L} \leq \frac{3}{2} \times \frac{1}{1 + 1/\alpha}$$

We leave it as a challenge to you to demonstrate that the ratio $\Delta F_S/\Delta F_G$ obtains a maximum value of $3/4$ in the limit $\alpha \to \infty$.

2. Take a look at Fig. 2 showing the "Wilhelmy plate" used for measuring surface tension. Using force analysis, derive an expression for the surface tension γ of the liquid in terms of

- the width W of the plate,

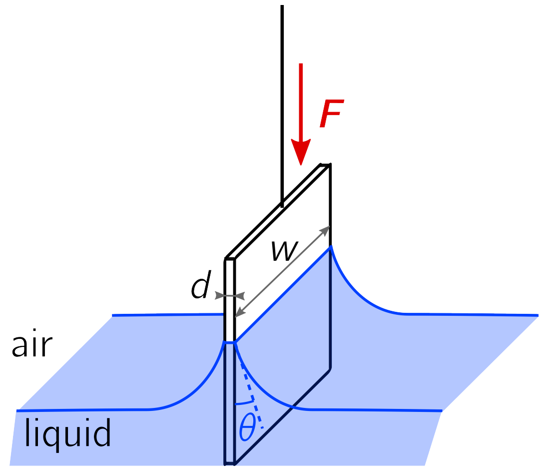
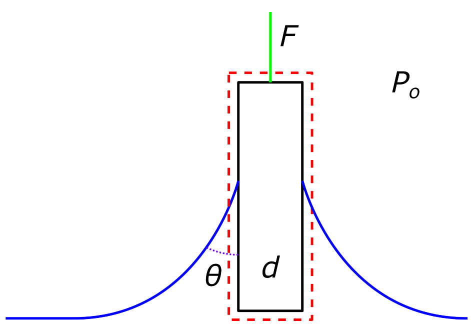


Figure 2: The Wilhelmy plate

- the contact angle θ of the interface, and
- the force F required to hold the plate up.

Assume $d \to 0$ so that you can neglect the weight of the plate, and assume further that the plate is inserted only just below the meniscus formed between the liquid and the plate.

Solution: Construct, as we have done in lecture, a virtual surface (shown in dashed red) around the plate on which we can do a force analysis. In this case our virtual surface is a box, constructed to just barely enclose the plate:



We must consider external forces acting inside the volume as well as forces acting at the boundary. Gravity will act on the mass inside the volume, but, since we presume the plate is extremely thin, this gravitation force can be neglected.

There will then be forces due to pressure from the gas and liquid outside the volume acting at the boundaries of the virtual surface. It is clear from the symmetry of the problem that there is no net force arising from the pressure applied on the four side walls, since the force applied on one side will be exactly cancelled by the force acting on the opposite side. The force $F_{top} = P_o wl$ acting on the top face will be different than the force $F_{bot} = (P_o + \rho g \Delta h)\, wl$ applied by the liquid on the bottom face, where Δh is the difference in elevation between the bottom of the plate and the liquid level (below the meniscus where the liquid becomes flat) and ρ is the density of the liquid. The net force $\Delta F = F_{top} - F_{bot}$ is, like the force acting inside the virtual surface, gravitation in origin, and so is negligible in the limit $l \to 0$. In any case we assume that we have positioned the depth of the plate so that $\Delta h \approx 0$ so $\Delta F \approx 0$ even when $l \neq 0$.

There is in addition the force due to the surface tension γ at the liquid-gas interface. It acts along the perimeter of a rectangle of dimension $w \times l$ where the interface intersects our virtual surface. For each infinitessimal line element dl along this rectangle there will be a force $dF_{\parallel} = dl\gamma\cos\theta$ acting downwards and a force $dF_{\perp} = dl\gamma\sin\theta$ acting horizontally. The horizontal force of each line element will be cancelled by an opposing force from the corresponding line element on the opposite side. The vertical forces for all the line elements all act upwards and so do not cancel, giving an overall force $F_{\gamma} = (w + l + w + l)\,\gamma\cos\theta \to 2\gamma w\cos\theta$ acting downwards.

To oppose this force we must therefore apply a force F in the upwards direction, i.e. $F = F_{\gamma}$. Therefore

$$\gamma = \frac{F}{2w\cos\theta} \quad .$$

3. Take a look at Fig. 3 showing the solubility products and points of zero charge for different silver halides.

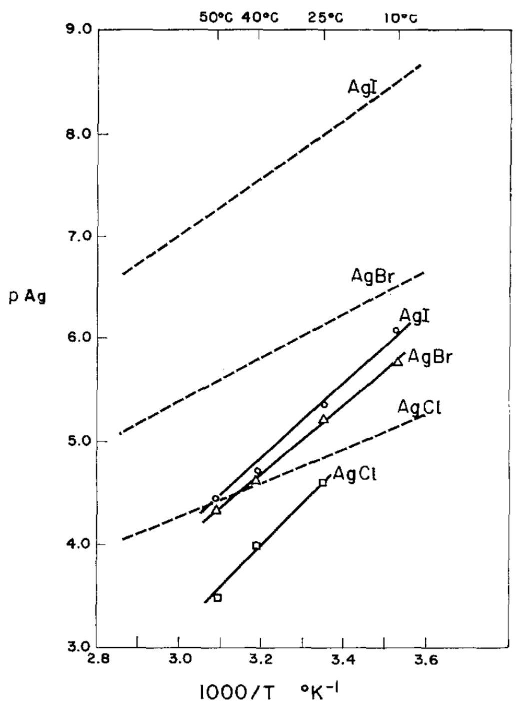


Figure 3: Plot showing the square root of the solubility product (dashed lines) and points of zero charge (solid lines) for different silver halides. Units are in molar, and the scale is inverted and logarithmic so that a pAg of, e.g., 8 correponds to a Ag^+ concentration of 10^{-8}M. From H. A. Hoyen and R. M. Cole, Journal of Colloid and Interface Science 41, 93 (1972).

(a) Large silver iodide particles are placed into water that is initially pure and equilibrium is chemical equilibrium is established between the solution and the particles. How does the interfacial electric potential change as the temperature is raised from 10 °C to 50 °C?

Solution: From the Nernst equation we have for the interfacial potential $\Delta\phi$

$$\Delta\phi = \frac{RT}{F}\ln\frac{[\mathrm{Ag}^+]}{[\mathrm{Ag}^+]_{\mathrm{pzc}}} = 0.43\frac{RT}{F}\log_{10}\frac{[\mathrm{Ag}^+]}{[\mathrm{Ag}^+]_{\mathrm{pzc}}}$$

For a neutral solution containing only Ag^+ and I^- ions, the concentration $[Ag^+]$ of cations will be equal to the square root of the AgI solubility product. From inspection of the graph, we see that the vertical separation between the dashed and solid lines for the AgI data increases with increasing temperature. This in turn implies that the value of $|\log_{10}\frac{[Ag^+]}{[Ag^+]_{pzc}}|$ increases with T. Since T of course also increases with T, we can conclude that $|\Delta\phi|$ will increase with temperature. Since from lecture we know that $\Delta\phi < 0$ for AgI at 25 °C (this can also be read from the graph), we can conclude that $\Delta\phi$ will become increasingly negative with increasing temperature.

(b) Among the halides represented in the graph, which binds most strongly to the silver halide interface?

Solution: The strength of binding of the halide anion can be measured by the concentration $[Ag^+]$ of silver counterions (adjusted by, say, addition of $AgNO_3$ to solution) required to establish a neutral interface, relative to the concentration $[Aq^+]$ of the pure silver halide solution (i.e. the square root of the solubility product). The logarithm $\log_{10}\frac{[Ag^+]}{[Ag^+]_{pzc}}$ of this ratio is simply measured by the vertical distance between the dashed and solid lines of each silver halide. It is clearly the AgI solution with the largest separation between its dashed and solid lines, indicating that the I^- iodide anion that binds more strongly to the AgI/aqueous interface than the Br^- or Cl^- ions to their respective interfaces.

4. (a) To what extent must air at room temperature be supersaturated with water vapor to permit nucleation on aerosol particles that are 11 nm in size? Express your answer in terms of a "supersaturation ratio" $\alpha = P/P_o$, where P is the required partial pressure of water and P_o is the partial pressure of water at 100 % humidity.

Solution: From the Kelvin equation

$$P_o' = P_o e^{R_o/R}$$

where $R_o \approx 1.1\,\text{nm}$ for water at room temperature, if we assume the aerosol particles to be roughly spherical than the vapor pressure for a film of water on the surface of the aerosol will be

$$P_o' \approx P_o \exp\left(\frac{1.1\,\text{nm}}{11\,\text{nm}}\right) \approx (1 + 1/10)\,P_o = 1.1P_o$$

where P_o is the vapor pressure of water at room temperature at a flat air-water interface, which corresponds to the partial pressure of water at 100 % humidity. Therefore

$$\alpha \approx 1.1$$

(b) Why will water vapor at $\alpha = 1.0$ fail to nucleate on aerosol particles?