

University of Washington
Department of Chemistry
Chemistry 452/456
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Lecture 14 7/26/13

A. Surface Phenomena: Surface Tension

- When a molecule is removed from a bulk liquid and transferred to the vapor phase, work is required to overcome intermolecular interactions in the liquid. Therefore, the process of vaporization requires energy. Similarly, work is required to move a molecule from the interior of a liquid to the surface of a liquid. This is because a molecule has fewer interactions with other molecules when it is at the surface of a liquid versus in the interior of a liquid. Because it requires energy to place molecules at the surface of a liquid, liquids tend to minimize their surface areas.
- The work done in reversibly expanding the surface σ by an amount $d\sigma$ is $dw = \gamma d\sigma$ where γ is the surface tension.
- Surface tension has units of energy/area (Joules/meter²) or force/length (Nt/m).

<u>Liquid</u>	<u>Surface Tension (N/m)</u>
acetone	0.0237
n-hexane	0.0184
ethanol	0.0223
ethyl ether	0.0170
mercury	0.487
water	0.0725

- To expand the surface area σ of a liquid requires work. The amount of energy required to increase the surface area of a liquid by a unit amount is called the surface tension γ .
- The surface tension can be incorporated into the general energy and free energy expressions: Starting with $dU = TdS - PdV + \gamma d\sigma$ and using the definition $dA = dU - d(TS) = -SdT - PdV + \gamma d\sigma$
- At constant volume the Helmholtz energy reduces to

$$dA = -SdT + \gamma d\sigma$$

and insofar as dA is an exact differential $-\left(\frac{\partial S}{\partial \sigma}\right)_T = \left(\frac{\partial \gamma}{\partial T}\right)_A$

- As temperature increases surface tension decreases and disappears at the normal boiling point. Therefore $\left(\frac{\partial \gamma}{\partial T}\right)_\sigma < 0$. Now we calculate the change in U with σ :
- Start with

$$dU = TdS + \gamma d\sigma$$

Then differentiate wrt σ : $\left(\frac{\partial U}{\partial \sigma}\right)_T = T\left(\frac{\partial S}{\partial \sigma}\right)_T + \gamma = -T\left(\frac{\partial \gamma}{\partial T}\right)_\sigma + \gamma$

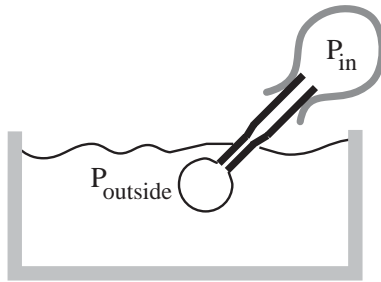
- To get the change in enthalpy you can take the following approach. At constant pressure:

$$dG = -SdT + \gamma d\sigma \Rightarrow \left(\frac{\partial G}{\partial \sigma}\right)_T = \gamma$$

- $\therefore \gamma = \left(\frac{\partial G}{\partial \sigma}\right)_T = \left(\frac{\partial}{\partial \sigma}\right)_T (H - TS) = \left(\frac{\partial H}{\partial \sigma}\right)_T - T\left(\frac{\partial S}{\partial \sigma}\right)_T$
 $\therefore \left(\frac{\partial H}{\partial \sigma}\right)_T = \gamma + T\left(\frac{\partial S}{\partial \sigma}\right)_T = \gamma - T\left(\frac{\partial \gamma}{\partial T}\right)_\sigma = \left(\frac{\partial U}{\partial \sigma}\right)_T$

B. How Surface Tension makes Drops and Cavities

- The “Laplace pressure” describes the difference in pressure between the inside of a bubble and the outside of a bubble due to the surface tension, σ . We will derive the Laplace pressure for a sphere:



- Imagine using an eyedropper to make a spherical bubble just under the surface of some water. The difference in pressure between the inside of the bubble (P_{inside}) and the atmospheric pressure outside ($P_{outside}$) will determine the radius r of the drop. Assume that the volume of water is big compared to the volume of the bubble so that the height of the water and the temperature stay approximately constant. Considering just the bubble:

$$dw_{\text{surface tension}} = dw_{\text{Pressure-volume}}$$

$$\gamma d\sigma = (P_{inside} - P_{outside}) dV$$

$$\begin{aligned} \text{For a sphere, Area} &= 4\pi r^2. & d\sigma &= 8\pi r dr. \\ \text{Volume} &= 4/3 \pi r^3. & dV &= 4\pi r^2 dr. \end{aligned}$$

Substituting above,

$$\gamma(8\pi r dr) = (P_{inside} - P_{outside})(4\pi r^2 dr)$$

$$2\gamma = (P_{inside} - P_{outside})r$$

$$\text{So then, } (P_{inside} - P_{outside}) = \frac{2\gamma}{r}$$

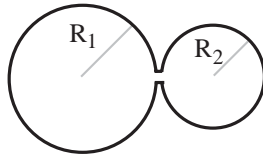
The signs of Laplace pressures are such that pressure is higher on the *concave* side of the surface. For small radii, the difference in pressure can get quite large. For a small air bubble of radius of 0.1 micron submerged in water, with $\gamma = 0.07$ N/m, then $P_{inside} - P_{outside} = 1.4 \times 10^6$ Pa = 14 atm!

If the bubble were an ellipse (or another shape with two radii of curvature) rather than a sphere,

$$P_{Laplace} = P_{inside} - P_{outside} = \gamma \left(\frac{1}{R_1} + \frac{1}{R_2} \right)$$

B. Stability of Drops and Bubbles: Coarsening

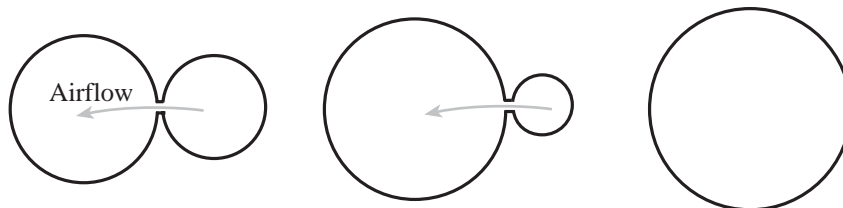
Consider two air bubbles of liquid with the same surface tension, σ , one with a large radius R_1 , and one with a small radius R_2 . There is a uniform pressure outside the bubbles.



What happens (can you guess?) The Laplace pressures are:

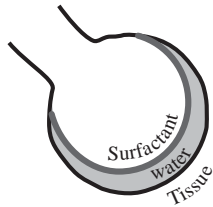
$$P_1 = \frac{2\gamma}{R_1} \quad \text{and} \quad P_2 = \frac{2\gamma}{R_2}$$

The pressure inside bubble 2 (with respect to some common exterior pressure) is greater than in bubble 1, so air will flow from bubble 2 to bubble 1 until the second bubble disappears entirely. In foams this is called “coarsening” or “Ostwald Ripening” (especially in crystals).



Aveoli, the small air sacs in lungs, act as connected bubbles of radius 0.1-0.5mm in a liquid.

If the aveolar surface were simply an air-water interface, the change in Laplace pressure would cause small aveoli to coarsen, leading to lung collapse. Nature solves this problem by adding a layer of surfactant (lipids and protein) to the aveolar surface. The surfactant layer greatly reduces σ , which is proportional to the concentration of surfactants at the aveolar surface (see below).



$$\Delta P = \frac{2\gamma(c_1)}{R_1} - \frac{2\gamma(c_2)}{R_2}$$

$$\Delta P \text{ is small if } \gamma(c_1) \approx \gamma(c_2) \frac{R_1}{R_2}$$

Lung surfactant is compromised in smokers and in premature babies. The age limit at which premature babies live is related to when they can produce lung surfactant. This is an active area of research, especially to produce a synthetic lung surfactant. Currently, many therapies for premature babies use lung surfactant derived from cows and there are concerns about transferring diseases among species. I don't know if any therapy is currently available for adults who have degraded their lung surfactant by smoking (other than advising the patient to stop smoking).

C. How Surface Tension Affects the Vapor Pressure of Small Drops

- Various commercial products are based on the idea of cooling people, places, and/or things with cooled water. In fact an excellent approach to cooling with water involves exposing the warm object to a fine mist of water droplets. Here we explore the physical basis for these "mistifiers".

- The condition for mechanical equilibrium of a small drop with radius of curvature $1/r$ is $P'' - P' = \frac{2\gamma}{r}$ where P' is the vapor pressure, P'' is the corresponding pressure exerted by the liquid phase, and γ is the surface tension. We can take the differential of both sides of this equation to get...

$$dP'' - dP' = d\left(\frac{2\gamma}{r}\right) = 2\gamma d\left(\frac{1}{r}\right)$$

- The condition for phase equilibrium is $\mu'' = \mu'$ or $d\mu'' = d\mu'$. At constant

$$\text{pressure this is } \bar{V}''P'' = \bar{V}'P' \Rightarrow P'' = \frac{\bar{V}'}{\bar{V}''}P' \dots \therefore dP'' = \frac{\bar{V}'}{\bar{V}''}dP'$$

- The two equations are combined to eliminate dP'' and to get

$$\left(\frac{\bar{V}' - \bar{V}''}{\bar{V}''}\right)dP' = 2\gamma d\left(\frac{1}{r}\right).$$

- Now because the molar volume of the vapor is much greater than the molar volume of the liquid phase $\left(\frac{\bar{V}' - \bar{V}''}{\bar{V}''}\right) dP' \approx \frac{\bar{V}'}{\bar{V}''} dP' = 2\gamma d\left(\frac{1}{r}\right)$
- Assuming the vapor behaves ideally $\bar{V}' = \frac{RT}{P'} \Rightarrow d\left(\frac{1}{r}\right) = \frac{RT}{2\gamma\bar{V}''} \frac{dP'}{P'} = \frac{\rho RT}{2\gamma M} \frac{dP'}{P'}$
where ρ is the density, M is the molecular weight, so that $\bar{V}'' = \frac{M}{\rho}$

- Now we integrate both sides of the equation. Specifically we integrate the l.h.s. from a flat surface where $1/r=0$ to a radius of curvature $1/r$. The r.h.s. is correspondingly integrated from a normal vapor pressure of P^0 to P.
- Whence

$$\int_0^{\frac{1}{r}} d\left(\frac{1}{r}\right) = \frac{\rho RT}{2\gamma M} \int_{P^0}^P \frac{dP'}{P'} \Rightarrow \frac{1}{r} = \frac{\rho RT}{2\gamma M} \ln\left(\frac{P}{P^0}\right)$$

$$\therefore \ln\left(\frac{P}{P^0}\right) = \frac{2\gamma M}{r\rho RT}$$

- This equation states that the vapor pressure of a droplet increases as the radius of the drop decreases.

C. How Surface Tension Affects the Physical Properties of Drops