

Physical Chemistry of Interfaces: Exercises

Série 2 - Solutions

2.1 (following 1.3) The droplets of mercury are deposited on the glass plate. What is the vapor pressure over the droplets at $T = 20\text{ }^{\circ}\text{C}$ if their diameter is equal to 1 mm, 0.01 mm or 0.0001 mm?

$$(\gamma_{Hg} = 484\text{ mNm}^{-1}\text{ at } T = 20\text{ }^{\circ}\text{C}, M_{Hg} = 200.6\text{ gmol}^{-1}, \rho_{Hg} = 13.5\text{ gcm}^{-3},$$

$$p_{Hg}^* = 0.1713\text{ Pa at } T = 20\text{ }^{\circ}\text{C})$$

Solution:

From the lecture notes we have for the Kelvin equation:

$$p_g = p^* \exp\left(\frac{2\gamma V_{m,l}}{rRT}\right) = p^* \exp\left(\frac{2\gamma M_{m,l}}{rRT\rho_l}\right) .$$

Therefore, the vapor pressure over the mercury droplet at $T = 20\text{ }^{\circ}\text{C}$ is:

if $r = 0.5\text{ mm}$,

$$p_g = 0.1713\text{ Pa} \times \exp\left(\frac{2 \times 484\text{ mNm}^{-1} \times 200.6\text{ gmol}^{-1}}{0.5\text{ mm} \times 8.314\text{ JK}^{-1}\text{mol}^{-1} \times 293\text{ K} \times 13.5\text{ gcm}^{-3}}\right) = 0.1713\text{ Pa} \times$$

$$\exp(1.18 \times 10^{-6}) = 0.1713\text{ Pa} ;$$

If $r = 0.005\text{ mm}$, $p_g = 0.1715\text{ Pa}$;

if $r = 0.00005\text{ mm}$, $p_g = 0.1928\text{ Pa}$.

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2.2 Soap bubbles are formed from the air which is slightly warmer than the ambient air. Determine the minimal temperature difference at which the bubbles can rise in the air if:

a) the liquid weight is neglected;

b) weight of the liquid film is taken into account; suppose the thickness $\varepsilon=50$ nm and density equal to the water density.

Given values: $T_{amb} = 298$ K, $p_{amb} = 1$ bar, radius of the bubble $r=1$ cm, surface tension of the soap solution $\gamma = 0.04$ J/m². We assume that the air obeys the ideal gas law.

Solution:

a) Ideal gas law: $pV = nRT = \frac{m}{M}RT$ (where m =weight of the gas et M =molar mass)

The specific weights of the gas inside and outside of the bubble with volume V are:

$$\rho_{amb} = \frac{m_{amb}}{V} = \frac{p_{amb}M}{RT_{amb}} \approx 1.18 \text{ kg/m}^3 \quad \rho_{int} = \frac{m_{int}}{V} = \frac{p_{int}M}{RT_{int}}$$

Where the inner pressure of the bubble (2 interfaces!!) is given by:

$$p_{int} = p_{amb} + \frac{4\gamma}{r}$$

When we neglect the liquid weight, the bubble rises if $\rho_{int} < \rho_{amb}$:

$$\frac{p_{int}}{T_{int}} < \frac{p_{amb}}{T_{amb}} \Rightarrow T_{int} > \frac{p_{int}T_{amb}}{p_{amb}}$$

where:

$$\frac{p_{int}}{p_{amb}} = \frac{p_{amb} + \frac{4\gamma}{r}}{p_{amb}} = 1 + \frac{4\gamma}{rp_{amb}}$$

Therefore:

$$T_{int} > T_{amb} \left(1 + \frac{4\gamma}{rp_{amb}} \right)$$

and:

$$\Delta T = T_{int} - T_{amb} > T_{amb} \frac{4\gamma}{rp_{amb}}$$

b) The volume of the liquid and its mass are appprox. given as:

$$V_l = 4\pi r^2 \varepsilon \quad m_l = 4\pi r^2 \varepsilon \rho_{H_2O}$$

The weight of the gas in the bubble is $m_{int} = \rho_{int} V$ and the total weight of the bubble is $m_{tot} = m_{int} + m_l$. $m_{amb} = \rho_{amb} V$.

The bubble ascends if $m_{tot} < m_{amb}$:

$$\begin{aligned} m_{tot} &= \rho_{int} V + 4\pi r^2 \varepsilon \rho_{H_2O} < \rho_{amb} V = m_{amb} \\ \rho_{int} &< \rho_{amb} - \rho_{H_2O} \frac{3 \cdot 4\pi r^2 \varepsilon}{4\pi r^3} = \rho_{amb} - \rho_{H_2O} \frac{3\varepsilon}{r} \\ \frac{\rho_{int}}{\rho_{amb}} &= \frac{p_{int} T_{amb}}{p_{amb} T_{int}} < 1 - \frac{3\varepsilon \rho_{H_2O}}{r \rho_{amb}} \end{aligned}$$

From which:

$$\Delta T = T_{int} - T_{amb} > T_{amb} \left(\frac{p_{int} \rho_{amb} r}{p_{amb} (r \rho_{amb} - 3\varepsilon \rho_{H_2O})} - 1 \right)$$

Numeric results:

$$\text{a) } \Delta T > 4.8 \cdot 10^{-2} \text{ K}$$

$$\text{b) } \Delta T > 3.9 \text{ K}$$

The mass of the liquid thus cannot be neglected!

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2.3 Capillary condensation and pore size measurement

(see next page)

CH-242(b) - Homework 2.3

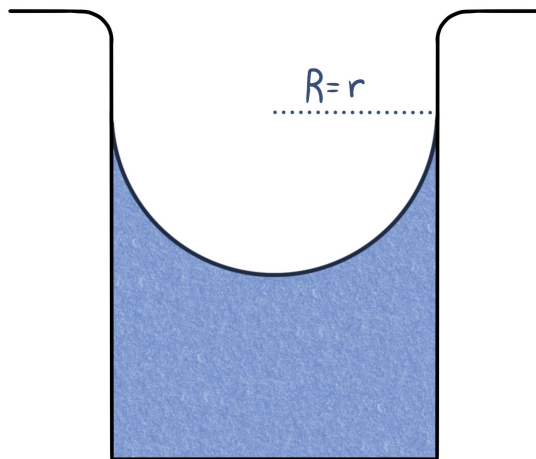
Capillary condensation and pore size measurement

Part A

At what pressure P'_o will gaseous vapor begin to completely fill up the nanopore? Express your answer in terms of the surface tension γ of the fluid, the vapor pressure P_o of the flat interface, the molar volume V_m of the liquid, and the ambient temperature T of the nanopore. Assume that the nanopore is wetting with respect to the fluid so that the liquid makes a contact angle $\theta = 0^\circ$ at the nanopore. Draw a diagram with the fluid half-way filling the nanopore.

Solution:

The nanopore will start to fill up once a stable meniscus is able to span across the pore:



Since the contact angle is zero, the radius of curvature $-R$ of the meniscus spanning the pore is equal to the pore radius r . According to the Kelvin equation, such a meniscus is in equilibrium with an ambient pressure P'_o when

$$P'_o = P_o e^{-R_o/r} \quad (1)$$

where

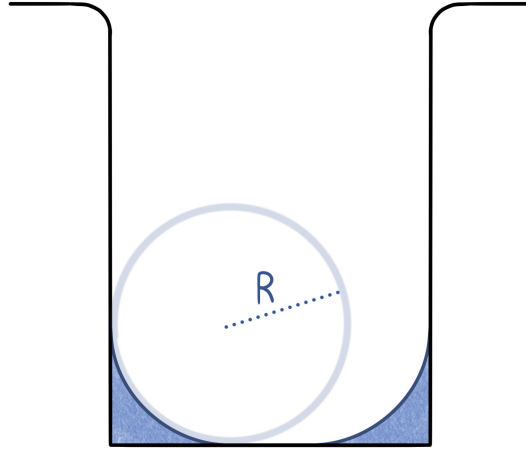
$$R_o = 2\gamma V_m / \bar{R}T \quad (2)$$

Part B

At pressures below P'_o , will there be any liquid in the nanopore? If so, draw a diagram illustrating the distribution of liquid in the nanopore.

Solution:

At pressures below P'_o we can only form menisci with absolute mean curvature greater than $1/r$. Such menisci can form at the corners of the core, roughly as so:



Note that these menisci are not spherical in they have a different radius of curvature along the circumferential direction than along the direction perpendicular (denoted R in the figure above). Some thought should convince you that the circumferential radius of curvature at the vertical wall is $-r$, so that the absolute mean curvature $\frac{1}{2}(1/r + 1/R)$ is still greater than $1/r$ for $R < r$, so that it will indeed only be stable for ambient pressures $P < P'_o$.

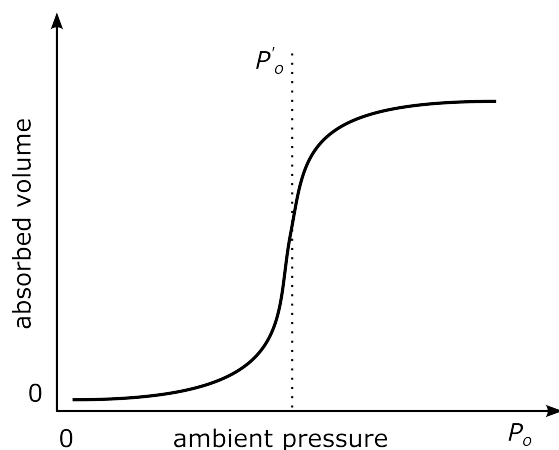
Part C

Assuming the height h of the nanopore is much larger than the nanopore radius r , make a qualitative graph describing the volume of liquid absorbed in the nanopore as a function of the ambient pressure P , with $0 < P < P_o$. Assume that $P'_o = \frac{1}{2}P_o$.

Solution:

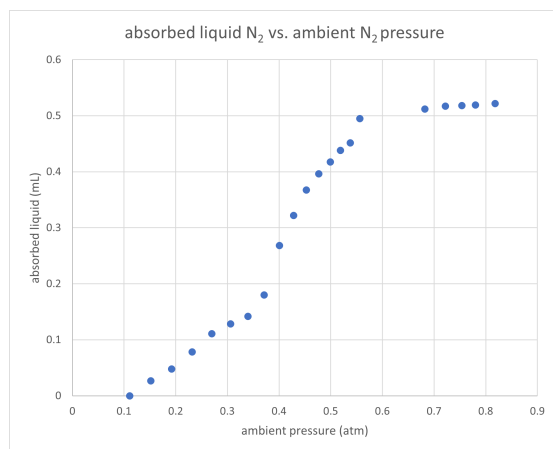
If the height of the nanopore is much taller than the radius, then we will not start to significantly fill the pore until the ambient pressure exceeds the critical pressure P'_o . At P'_o the nanopore will fill up entirely. Increasing the ambient pressure beyond this will therefore not produce a significant increase in absorbed volume, until we reach P_o at which point volume can accumulate

indefinitely. Restricting consideration to pressures below P_o we therefore expect the following qualitative behavior:



Part D

Here is a graph¹ of the volume liquid nitrogen absorbed by a sample silica particles as a function of the ambient pressure of (gaseous) nitrogen:



Suppose that the nanopore is held at a temperature of -198.5°C , which is boiling point of liquid nitrogen at a pressure of 1 atm. Given that the surface tension of liquid nitrogen is 9 mN m^{-1} and its density is 0.8 g mL^{-1} , estimate the average nanopore radius of the silica particles.

¹D. Dollimore and G. R. Heal, Journal of Applied Chemistry 14, 109 (1964).

Solution:

Inspecting the graph, we notice a sudden jump in the absorbed volume around an ambient pressure of about 0.4 atm. Setting this equal to the critical pressure we determined in part A, we can solve for the nanopore radius r :

$$r = \frac{R_o}{\ln P_o/P'_o} = \frac{2 \times 9 \times 10^{-3} \text{ N m}^{-1} \times \left(\frac{28 \text{ g}}{\text{mol}} \times \frac{1 \times 10^{-6} \text{ m}^3}{0.8 \text{ g}} \right)}{0.64 \times 10^3 \text{ J mol}^{-1} \times \ln \frac{1 \text{ atm}}{0.4 \text{ atm}}} \approx 10 \text{ \AA}$$

In reality at dimensions this small one must carefully take into consideration the effect of the microscopic film of nitrogen molecules that will be “adsorbed” over the entire silica surface. Later in the course we will discuss the phenomenon associated with adsorption of gases on solid surfaces. When one takes into account these effects one arrives at a average nanopore diameter closer to 20 Å.