Exercise 2

1

a. The work of adhesion for Hg on a solid surface (s) is: $W_{a,Hg/s} = 236\ mJ/m^2$. Calculate the contact angle of a drop of Hg on this surface when the work of cohesion for Hg is: $W_{c,Hg} = 970\ mJ/m^2$.

b. The work of adhesion between Hg and water is $W_{Hg/w} = 183\ mJ/m^2$. The surface tension of water is $\gamma = 72 mN/m$. Set up an expression for the change in surface free energy for spreading of water on Hg and calculate the spreading coefficient. Will water spread on Hg?

c. Based on the answer of b, what can you say about the intermolecular forces?

a) $W_c = 2\gamma_{Hg}$

$\Rightarrow \gamma_{Hg} = 485\ mJ/m^2$

$W_A = \gamma_{Hg} + \gamma_s - \gamma_{Hg,s} = 236\ mJ/m^2 \Rightarrow \gamma_s - \gamma_{Hg,s} = W_A - \gamma_{Hg} = 236 - 485 = -249\ mJ/m^2$

Youngs eq

$$\gamma_s = \gamma_{Hg,s} + \gamma_{Hg} \cdot \cos\theta$$

$$\cos\theta = \frac{\gamma_s - \gamma_{Hg,s}}{\gamma_{Hg}} = \frac{-249\ mJ/s}{485\ mJ/s}$$

$$\theta = \cos^{-1}\left(\frac{-249}{485}\right) = 120{,}9^\circ$$

b) $\Delta G_{W/Hg} = \gamma_{Hg/s} + \gamma_W - \gamma_{Hg}$

$W_A = \gamma_{Hg} + \gamma_W - \gamma_{Hg/W} = 183$

$\Rightarrow \gamma_{Hg/W} = \gamma_{Hg} + \gamma_W - 183 = 485 + 72 - 183 = 374$

$S_{W/Hg} = -\Delta G_{W/Hg} = \gamma_{Hg} - \gamma_{Hg/W} - \gamma_W = 485 - 374 - 72 = 39\ mN/m^2$

$S > 0 \Rightarrow$ It will spred $\Rightarrow$ The intermolecular forces between Hg and water are stronger than between water molecules

c) For Hg on water, $S_{Hg/w} < 0 \Rightarrow$ No spreading

2

At 20 °C the surface tensions of water and n-octane are 72.8 and 21.8 mN/m, respectively. The interfacial tension between n-octane and water is 50.8 mN/m. Calculate:

a. The work of adhesion between n-octane and water
b. The work of cohesion for i) n-octane and ii) water
c. The spreading coefficient of n-octane on water. Will octane spread on water?

a) $W_A = \gamma_n + \gamma_w - \gamma_{n,w} = 21{,}8 + 72{,}8 - 50{,}8 = \underline{43{,}8\ mN/m}$

b) i) $W_{C,n} = 2 \cdot \gamma_n = 2 \cdot 21{,}8 = \underline{43{,}6\ mN/m}$

ii) $W_{C,w} = 2 \cdot \gamma_w = 2 \cdot 72{,}8 = \underline{145{,}6\ mN/m}$

c) $S_{n/w} = \gamma_w - \gamma_{w,n} - \gamma_n = 72{,}8 - 50{,}8 - 21{,}8 = \underline{0{,}2\ mN/m}$

S>0 => Octane will spread over water => False

3

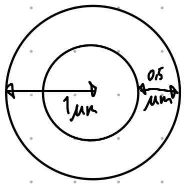
The vapour pressure for a curved surface is given as:

$$RT\, ln(\frac{p}{p_0}) = \gamma \overline{V_L} (\frac{1}{R_1} + \frac{1}{R_2})$$

The walls inside a cylindrical pore with radius 0,1 μm is covered with a film of water with thickness 0,05 μm. T = 293K.
The normal vapour pressure for water at this temperature: p_0 = 2307 Pa. The surface tension of water is $\gamma = 72 mN/m$. R = 8,314 J/mol·K.

a. What is the vapour pressure of water inside the pore?
b. Explain what the calculated value of the vapour pressure of water inside the pore means physically for this system

a) We have a cylinder:



$R_1 = 0{,}1 - 0{,}05 = 0{,}05\ \mu m = 5 \cdot E-8$

$R_2 = \infty$

$\overline{V_L} = \frac{M}{\rho} = \frac{18 g/mol}{1000 kg/m^3} = 1{,}8 \cdot 10^{-5}\ m^3/mol$

$RT \ln \frac{p}{p_0} = \gamma \overline{V_L} \left(\frac{1}{R_1} + \frac{1}{R_2}\right)$

$p = p_0 \cdot \exp\left(\gamma \frac{\overline{V_L}}{RT} \left(\frac{1}{R_1} + \frac{1}{R_2}\right)\right)$

$p = 2307\ Pa \cdot \exp\left(72 \cdot 10^{-3}\ N/m \cdot \frac{1{,}8 \cdot 10^{-5}\ m^3/mol}{8{,}314\ J/mol K \cdot 293 K} \cdot \frac{1}{-0{,}05 \cdot 10^{-6}\ m}\right)$

Negative radius as the curvature is towards the liquid

$\underline{p = 2282{,}6\ Pa}$

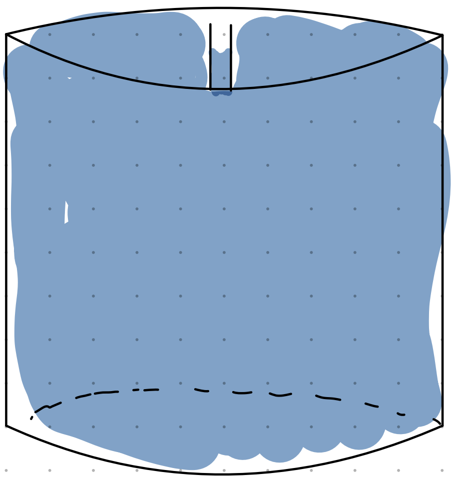
b)

As the vapor pressure is lower inside the capillary, than the normal vapor pressure. The liquid film in the capillaries is evaporating at a lower rate than water in a large container at these conditions will.

4

A cylindrical glass capillary is put vertically into a beaker with pure water at $25°C$. The diameter of the capillary is 1 mm. The water completely wets the capillary.

Water will evaporate both from the beaker and from the water meniscus within the capillary. At which place will the evaporation rate per unit area be largest? Justify your answer.



As the curvature of the liquid is curved towards the liquid (gas has highest pressure) then the radius should be negative in the Klevin equation. The meniscous is circular, meaning that R1 = R2 = Rs. This gives the Kelvin equation provided:

$$RT \ln\left(\frac{P}{P_0}\right) = \frac{-2\gamma V_L}{R_S}$$

As the water completely wets the capillary, the radius of the capillary is equal to Rs. It is a finite value. For the beaker, the Rs is much larger (towards infinity). Looking at Kelvins equation, the vapor pressure increases when Rs increases. This means that the evaporation is largest for the surface of the beaker.