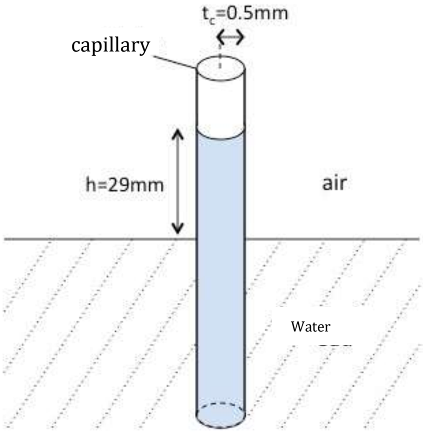
Physical Chemistry of Interfaces: Exercises

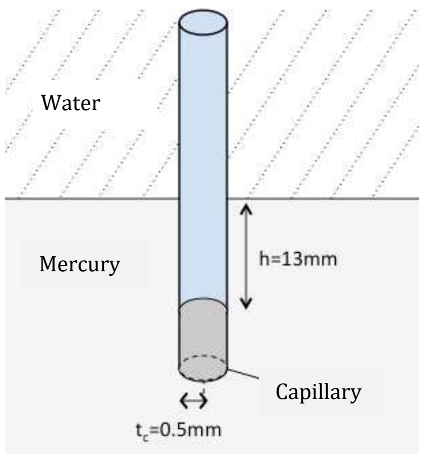
3rd session

3.1 Capillary rise/fall

a) A glass capillary is immersed in water. The water in the capillary rises 29 mm (as demonstrated in the figure below). Suppose that water perfectly wets glass surface and contact angle between water and inside of the capillary is zero. The radius of capillary is 0.5 mm. Estimate the surface tension of water. Tip: Neglect the weight of water meniscus.



b) Consider a water phase on top of mercury phase. The glass capillary is immersed in mercury. This time the capillary fall is observed. The mercury level in capillary is 13 mm lower compared to the plane interface between water and mercury. The radius of capillary is 0.5 mm. Suppose that contact angle between mercury and inner capillary wall is 180°. Calculate the surface tension between water and mercury. The density of mercury is 13.6 g/cm^3. Tip: Neglect the weight of liquid meniscus.



3.2 Surface thermodynamics

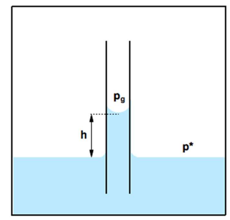
Surface tension of 1-butanol was measured as a function of temperature at constant pressure p=1 atm:

T [°C]	10	25	50	75	100
γ [mN/m]	25.28	24.13	22.13	20.03	17.83

Estimate quantities $\gamma = G^s,\ S^s,\ H^s, C_p^s$ of 1-butanol at T=50°C.

(Data: CRC Handbook of Chemistry & Physics).

3.3 Capillary ascension and Kelvin equation.



A cylindrical capillary is immersed of radius r_c in a wetting liquid.

In this case the height of capillary rise h is expressed by the following relation:

$$h = \frac{2\,\gamma\,\cos\theta}{\rho\,g\,r_c}$$

According to simplified Kelvin equation the pressure above flat interface between liquid p^* and gas and the pressure above curved interface (meniscus) p_g are not equal. The relation between these pressures is expressed as follows:

$$p_g = p^*\,exp\left(\pm\frac{2\,\gamma\,\cos\theta\;V_{m,l}}{R\,T\,r_c}\right)$$

here γ is the surface tension, ρ is liquid density, $V_{m,l}$ is molar volume of liquid and θ contact angle between solid/liquid/gas).

a) What is the correct sign in the equation above? What is the relation between sign and contact angle θ ?

c) Express the relation between h and $\frac{p^* - p_g}{p^*}$.

d) Estimate the h and $\frac{p^* - p_g}{p^*}$ for quartz capillary immersed in water :
$T = 25°C, \gamma = 72.7\ mNm^{-1}, \theta = 0°, \rho = 997\ kg\ m^{-3}, M_{H_2O} = 18\ g\ mol^{-1}, r_c = 0.2\ mm,$
$R = 8.314\ Jmol^{-1}K^{-1}, g = 9.81\ ms^{-2}$.

3.4 The surface tension of aqueous solutions of surfactant CTAB (hexadecyltrimethylammonium bromide) at 25 ° C. was measured:

C [M]	$1.0x10^{-4}$	$1.6x10^{-4}$	$4.0x10^{-4}$	$6.3x10^{-4}$	$1.0x10^{-3}$	$1.6x10^{-3}$	$2.5x10^{-3}$	$4.0x10^{-3}$
γ [mN/m]	64	59	51	45	37.8	38.3	38.2	38

Estimate for this surfactant the critical micelle concentration (CMC), the surface excess for concentrations close to the CMC, as well as the effective area occupied by a molecule at the air / solution interface. Considering that the aggregation number is ν = 93 for this surfactant, what are the fractions of the surfactant molecules that are on the surface, and in the form of monomer or micelle in the solution, for a total concentration of $C = 2 \cdot 10^{-3}$ M. Assume that the system is of the form of a 10cm x 10cm x 10cm cube, so that the area of the gas-liquid interface is $100 cm^2$.