Assigned questions for Lecture 15 are listed below. The questions occur in the following editions of "Physical Chemistry" by P.W. Atkins:

10th edition	9th edition	8th edition

Note: The letter "P" in front of a number indicates that the question is in the "Problem" category as opposed to the "Exercise" category in Atkins' books. Updates are highlighted in yellow.

Question 15.01*

P4B.17	P4.19	P4.18

Same in all editions

P4B.17 The Clapeyron equation does not apply to second-order phase transitions, but there are two analogous equations, the *Ehrenfest equations*, that do. They are:

$$\text{(a)}\ \frac{dp}{dT}=\frac{\alpha_2-\alpha_1}{\kappa_{T;2}-\kappa_{T;1}} \qquad \text{(b)}\ \frac{dp}{dT}=\frac{C_{p,m;2}-C_{p,m;1}}{TV_m(\alpha_2-\alpha_1)}$$

where α is the expansion coefficient, κ_T the isothermal compressibility, and the subscripts 1 and 2 refer to two different phases. Derive these two equations. Why does the Clapeyron equation not apply to second-order transitions?

Note: Be sure to be able to sketch the first- and second-order phase transitions, and understand why they look the way they do - see L15, slides 1-5.

Question 15.02

16C.1	17.13	18.10

Same questions.

16C.1(a) Calculate the vapour pressure of a spherical droplet of water of radius 10 nm at 20 °C. The vapour pressure of bulk water at that temperature is 2.3 kPa and its density is 0.9982 g cm^{-3}.

16C.1(b) Calculate the vapour pressure of a spherical droplet of water of radius 20.0 nm at 35.0 °C. The vapour pressure of bulk water at that temperature is 5.623 kPa and its density is 994.0 kg m^{-3}.

Question 15.03

16C.2	17.14	18.11

Same questions.

17.14(a) The contact angle for water on clean glass is close to zero. Calculate the surface tension of water at 20°C given that at that temperature water climbs to a height of 4.96 cm in a clean glass capillary tube of internal radius 0.300 mm. The density of water at 20°C is 998.2 kg m^{-3}.

17.14(b) The contact angle for water on clean glass is close to zero. Calculate the surface tension of water at 30°C given that at that temperature water climbs to a height of 9.11 cm in a clean glass capillary tube of internal radius 0.320 mm. The density of water at 30°C is 0.9956 g cm^{-3}.

Question 15.04

16C.3	17.15	18.12

Same questions.

16C.3(a) Calculate the pressure differential of water across the surface of a spherical droplet of radius 200 nm at 20 °C.

16C.3(b) Calculate the pressure differential of ethanol across the surface of a spherical droplet of radius 220 nm at 20 °C. The surface tension of ethanol at that temperature is 22.39 mN m^{-1}.

Question 15.05

n/a	n/a	n/a

Some qualitative discussion questions - refer to notes.

(a) Discuss the processes of:
- (i) nucleation in relation to condensation and formation of droplets
- (ii) nucleation in relation to boiling and formation of cavities

(b) Why do bubbles, cavities and droplets tend to minimize their surface areas?

(c) Explain the origins of surface tension in water, and why water is a unique substance in terms of its high surface tension vs. other solvents.

Question 15.06*

n/a	n/a	n/a

New question for 2015, not in any editions.

Would the equation $\gamma = \varrho g r h/(2 \cos\theta)$ be altered for liquid mercury, which does not wet glass?

Question 15.07*

n/a	n/a	n/a

New question for 2015, not in any editions.

In a certain capillary tube at 0 °C, the mercury level was 12.8 mm below the surface of the liquid outside of the tube. What is the radius of the tube? Known values for Hg at 273 K are $\gamma = 0.476$ N m^{-1}, $\varrho = 13.6$ g cm^{-3}, and $\theta = 140^{\circ}$.

Question 15.08*

n/a	n/a	n/a

New question for 2015, not in any editions.

In an experiment to determine how well benzene wets glass, benzene was found to rise to 1.71 mm in a certain capillary tube at 20 °C. In the same tube, water rose 4.90mm at 20 °C. Calculate the contact angle for benzene. Known values at 20"C are $\varrho_{benzene} = 0.879$ g cm^{-3}, $\varrho_{water} = 0.998$ g cm^{-3}, $\gamma_{benzene} = 2.89 \times 10^{-2}$ N m^{-1}, and $\gamma_{water} = 7.28 \times 10^{-2}$ N m^{-1}.

Answer 15.01*

P4B.17	P4.19	P4.18

Same in all editions 16C.1 The surface tensions of a series of aqueous solutions of a surfactant A were measured at 20 °C, with the following results:

$[A]/(\text{mol dm}^{-3})$	0	0.10	0.20	0.30	0.40	0.50
$\gamma/(\text{mN m}^{-1})$	72.8	70.2	67.7	65.1	62.8	59.8

Calculate the surface excess concentration.

Some b-list answers:

E17.13(b) $V_m = \frac{M}{\rho} = \frac{18.02 \text{ g mol}^{-1}}{0.9940 \text{ g cm}^{-3}} = 18.13 \text{ cm}^3$

$p = p^* e^{2\gamma V_m(1)/rRT}$ [17.51, the Kelvin eqn]

$$= (5.623 \text{ kPa}) \times \exp\left\{\frac{2 \times (72.75 \times 10^{-3} \text{ N m}^{-1}) \times (18.13 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1})}{(20.0 \times 10^{-9} \text{ m}) \times (8.3145 \text{ J K}^{-1} \text{mol}^{-1}) \times (308.15 \text{ K})}\right\}$$

$$= \boxed{5.92 \text{ kPa}}$$

E17.14(b) $\gamma = \frac{1}{2}\rho g r h$ [17.40]

$$= \frac{1}{2} \times (995.6 \text{ kg m}^{-3}) \times (9.80665 \text{ m s}^{-2}) \times (0.320 \times 10^{-3} \text{ m}) \times (9.11 \times 10^{-2} \text{ m})$$

$$= 0.142\overline{3} \text{ kg s}^{-2} = \boxed{142 \text{ mN m}^{-1}}$$

E17.15(b) $p_{in} - p_{out} = \frac{2\gamma}{r}$ [17.38, the Laplace eqn] $= \frac{2 \times (22.39 \times 10^{-3} \text{ N m}^{-1})}{220 \times 10^{-9} \text{ m}}$

$$= 2.04 \times 10^5 \text{ N m}^{-2} = \boxed{204 \text{ kPa}}$$

Pressure differentials for small droplets are quite large.

Answer 15.06*

n/a	n/a	n/a

New question for 2015, not in any editions.

The equation would not be altered; its derivation does not depend upon the nature of the liquid or whether the liquid is repelled or attracted by glass. The level of Hg in the electrode would be lower than the outside, so *h* would be negative.

Answer 15.07*

n/a	n/a	n/a

New question for 2015, not in any editions.

$$r = \frac{2\gamma \cos\theta}{g\rho h} \qquad \rho = 13.6 \times 10^3 \text{ kg m}^{-3} \qquad h = -12.8 \times 10^{-3} \text{ m}$$

Then
$$r = \frac{2(0.476 \text{ N m}^{-1})(\cos 140^\circ)}{(9.81 \text{ m s}^{-2})(13.6 \times 10^3 \text{ kg m}^{-3})(-12.8 \times 10^{-3} \text{ m})} = 4.27 \times 10^{-4} \text{ m} = 0.427 \text{ mm}$$

Answer 15.08*

n/a	n/a	n/a

New question for 2015, not in any editions. Eq. 19-19 here is just the contact angle equation in L15, slide 23.

Solution: This situation is slightly complicated because the radius of the capillary is not given but must be found from the calibration with water. You could derive one large expression, but it is simpler to find *r* first, at least as a set-up calculation. First, rearrange Eq. (19-19) to

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

Then from the data for water,
$$r = \frac{2(7.28 \times 10^{-2})(\cos 0)}{9.81(0.998 \times 10^3)(4.90 \times 10^{-3})}$$

Don't calculate those terms that will cancel when you substitute in Eq. (19-19) for benzene, i.e., 10^{-2}, g, and 2.

Then
$$r = \left(\frac{2 \times 10^{-2}}{g}\right)(1.49)$$

Now rearrange Eq. (19-19) to get $\cos\theta$ and put *r* on the end:

$$\cos\theta = \left(\frac{g\rho h}{2\gamma}\right) r$$

Thus, for benzene

$$\cos\theta = \frac{g(0.879 \times 10^3)(1.71 \times 10^{-3})}{2(2.89 \times 10^{-2})}\left[\frac{(2 \times 10^{-2})(1.49)}{g}\right] = \frac{0.879(1.71)(1.49)}{2.89} = 0.775$$

So $\theta = 39.2^\circ$