Partial exam fysische chemie 3 / advanced physical chemistry: statistical thermodynamics. April 4, 2018.

1. The frequencies of the normal modes of photons in a cubic box of edge-length L are given by

$$\upsilon = \frac{c}{2L}\sqrt{n_x^2 + n_y^2 + n_z^2}\,.$$

Here c is the speed of light and n_x, n_y, n_z are positive integers (1, 2, 3, …). Photons only have transverse modes with two polarizations.

a. [10] Show (using geometry to count the modes) that the resulting total number of normal modes of frequencies in between υ and $\upsilon + d\upsilon$ in a box with volume $V=L^3$ is given by

$$G(\upsilon)d\upsilon = \frac{8\pi V \nu^2}{c^3} d\upsilon\,.$$

b. [10] The energy levels of photons (electromagnetic oscillators) are given by $\varepsilon_n = nh\upsilon$, with n = 0, 1, 2, … The partition function of an oscillator being given by $z = \sum_{n=0}^{\infty} e^{-\varepsilon_n/kT}$, show that the average energy $\varepsilon(\upsilon)$ of a photon is given by

$$\varepsilon(\upsilon) = \frac{h\upsilon}{e^{h\upsilon/kT} - 1}\,.$$

c. [5] With $E(\upsilon)d\upsilon$ the total radiant energy in the range υ to $\upsilon + d\upsilon$, show that the spectral energy density is given by

$$E(\upsilon) = \frac{8\pi V h(\upsilon/c)^3}{e^{h\upsilon/kT} - 1}$$

d. [15] Show that the temperature of the box (the 'black body') to a good approximation is given by $T = h\upsilon_{\max}/3k$ with $\upsilon_{\max}$ the frequency where $E(\upsilon)$ has a maximum. Could this result in principle be used to estimate the temperature of the cosmic microwave background?

2. a. [15] Show that the total intermolecular interaction energy in (simple) gases and liquids is given by

$$E_{\mathrm{int}} = 2\pi N\rho \int_0^{\infty} g(r)\phi(r) r^2 dr\,,$$

with ϕ(r) the potential energy of (assumed spherical symmetric) interaction between two atoms or molecules as a function of the distance r between their centers, and g(r) the radial distribution function.

b. [15] Calculate E_{int} for a *dilute* system that interacts by a square well potential given by

$\phi(r) = \infty \quad (r < \sigma_1)$
$\quad\; -\varepsilon \quad (\sigma_1 < r < \sigma_2)$
$\quad\; 0 \quad (r > \sigma_2)$

Also, comment on the behavior of E_{int} as a function of temperature.

3. A new type of particle is postulated with the following condition on the occupation of quantum mechanical states: for each state r with energy ε_r, the allowed values of the occupation numbers are $n_r = 0, 1$, or 2.

a. [15] Show, starting from the probability that a given state r has occupation number n_r

$$p_r(n_r) = \frac{e^{-n_r(\varepsilon_r-\mu)/kT}}{\sum_n e^{-n(\varepsilon_r-\mu)/kT}} \ ,$$

that the average occupation number of the postulated particles in a single-particle state with energy ε is given by

$$< n_\varepsilon > = \frac{x(1+2x)}{1+x(1+x)},$$

with

$$x = \exp\left(-(\varepsilon-\mu)/kT\right)$$

b. [15] Under what condition(s) reduces $<n_\varepsilon>$ to Boltzmann statistics where the number of available states greatly exceeds the number of particles? Hint: translate that condition into expected value range of $<n_\varepsilon>$.

Equations for statistical thermodynamics

Taylor series: exponent: $e^x \approx 1+x$ x<<1

logarithm: $\ln(1+x) \approx x$ x<<1

Geometrical series $\sum_{n=0}^{\infty} x^n = \frac{1}{1-x}$ (x<1)

Integration over angles θ and ϕ of a volume element in polar coordinates

$$\int_{\theta=0}^{\pi}\int_{\varphi=0}^{2\pi} d\tau = \int_{\theta=0}^{\pi}\int_{\varphi=0}^{2\pi} r^2 \sin\theta d\varphi d\theta dr = 4\pi r^2 dr$$

Stirling approximation: $\ln N! \approx N\ln N - N$ (N>>1)

$$Z = \sum_j e^{-E_j/kT} \qquad A = U - TS = -kT\ln Z\,; \qquad S = -\left(\frac{\partial A}{\partial T}\right)_{V,N} = \frac{U}{T} + k\ln Z\,;$$

$$U = -T^2\left(\frac{\partial(A/T)}{\partial T}\right)_{V,N} \qquad p = -\left(\frac{\partial A}{\partial V}\right)_{T,N} \quad ; \quad \mu = \left(\frac{\partial A}{\partial N}\right)_{T,V}$$

$$\Xi(\mu,V,T) = \sum_{N=0}^{\infty} e^{\mu N/kT} Z(N,V,T)$$

Solutions.

1a. See Widom p. 60+61. A unit volume in n_x, n_y, n_z space refers to a single state. Thus, the total number of frequencies in between υ and $\upsilon + d\upsilon$ is the volume of a spherical shell in the positive octant of that space, that is, $G(\upsilon)d\upsilon = \frac{1}{8}4\pi R^2 dR$ Where $R = \sqrt{n_x^2 + n_y^2 + n_z^2} = \frac{2L\upsilon}{c}$, $dR = \frac{2L}{c}d\upsilon$. There is an extra factor of two because of the two transverse polarizations. Take that into account, and QED.

1b. See Widom p.67. Eq.(4.22) in Widom can be derived by starting with the definition of average energy being $\varepsilon(\upsilon) \equiv <\varepsilon(\upsilon)> = \sum_{n=0}^{\infty}\varepsilon_n p_n = \frac{1}{z}\sum_{n=0}^{\infty}\varepsilon_n e^{-\varepsilon_n/kT}$ $= \frac{-1}{z}\frac{d}{d(1/kT)}\sum_{n=0}^{\infty}e^{-\varepsilon_n/kT} = -k\ d\ln z/d(1/T)$. Using that leads to the equation that was sought.

1c. Total energy within the frequency interval is the total number of modes in that interval times the average energy per mode, and thus $E(\upsilon)d\upsilon = G(\upsilon)\varepsilon(\upsilon)d\upsilon$.
d. Set $\frac{dE(\upsilon)}{d\upsilon} = 0$, use the chain rule, and realize that at the maximum, it should be that $e^{h\upsilon_{\max}/kT} >> 1$, so that $e^{h\upsilon/kT} - 1 \approx e^{h\upsilon/kT}$.

The relation $T = h\upsilon_{\max}/3k$ is indeed being used to estimate the temperature of the cosmic microwave background. There is a potential issue with the redshift due to the expansion of the universe, but that is a relatively small effect.

2a. see Widom p. 90 + 91
2b. only the part with $\sigma_1<r<\sigma_2$ contributes to the integral so we have

$$E_{\text{int}} = 2\pi N\rho\int_{\sigma_1}^{\sigma_2} g(r)\phi(r)r^2dr = -\frac{2\pi}{3}N\rho\varepsilon e^{\varepsilon/kT}(\sigma_2^3 - \sigma_1^3)$$

Clearly E_int goes from negative values to zero upon increasing temperature in the situation of an ‘attractive’ square well, and from positive to zero for an repulsive ‘well’ – actually a ‘shoulder’. The physical reason is that upon increasing temperature the probability that the systems resides in the well becomes smaller for attractive wells and higher for repulsive wells. Thus the fraction of time spent in the wells tend to become comparable to the fraction of time spent outside the well.

3. a. Use that $< n_{\varepsilon} >= \sum_{n=0}^{2} np_{\varepsilon} = \frac{\sum_{n=0}^{2} nx^n}{\sum_{n=0}^{2} x^n} = \frac{x+2x^2}{1+x+x^2}$, with $x = \exp\left(-(\varepsilon-\mu)/kT\right)$.

b. In the Boltzmann limit where the number of states greatly exceeds the number of particles is should be that $<n_{\varepsilon}> << 1$ for all values of ε. In other words, on average most states are unoccupied in this limit. That translates into x << 1, or (ε – μ)/kT >>0. Since ε≥ it should be that μ << 0. [That will do for an answer – in fact, via $\mu = kT\ln(\Lambda^3\rho)$, with Λ the thermal de Broglie wavelength, this condition in turn translates into the (hopefully familiar) condition $\Lambda^3\rho << 1$.]

EXAM COVER PAGE

COURSE:	**Physical Chemistry 3 / Advanced Physical Chemistry**
COURSE CODE:	**SK-BFYC3 / SK-MPC3**
EXAM:	interfaces
TIME:	07-03-2018 from 17:00 to 19:30
LENGTH:	2h30m (plus 25m extra time=2h55m for students with disabilities)
PLACE:	Educatorium Beta

IMPORTANT
- PLACE YOUR ID CARD (WITH PHOTO) ON THE TABLE
- WRITE YOUR NAME AND STUDENT NUMBER ON EVERY ANSWER SHEET

EXAM SPECIFICS

- This exam counts for 33% of the final grade.
- There is no minimum score required for each of the three parts of the course. However, if one fails (average below 5.5), one MUST re-do parts where the grade was less than 5.0 and one CAN re-do the other parts. See the Course Manual @BB for further details.
- Max. number of points are given after each question.
- When answering the questions, please take the following into account:
  a. Answers in English or Dutch are permitted.
  b. Make sure that the answers are explained with clear arguments, **only yes or no is not enough**!
  c. Unreadable or poorly readable handwriting could result in a lower grade.

PERMITTED EQUIPMENT
calculator

GOOD LUCK!

Andrei Petukhov

GENERAL EXAMINATION RULES

- You are not allowed to leave the exam room in the first 30 minutes. Latecomers are allowed in up to 30 minutes after the start time.
- All electronic equipment needs to be switched off (including mobile phones), with the exception of electronic equipment allowed by the examiner.
- Your coat and closed bag are placed on the ground.
- Raise your hand when you need to go to the bathroom. 1 person at a time. Place your mobile phone visibly on your table just before you go.
- Raise your hand if you have a question about the exam, or need extra paper, etc.
- Not following the instructions of the examiner or surveillant can lead to exclusion from the exam.
- When fraud is suspected the exam will be confiscated immediately. The examiner will act according to the Education and Exam Regulations and will inform the Exam Committee and the Education Manager in writing within one work day.
- Upon receiving your result you can request the examiner for access to your graded exam. Possibly, a collective meeting will be organized.

Problem 1

(a) What is the Gibbs dividing plane and how is it defined? [1 point]

(b) Explain how the surface coverage of certain species can be negative and give an example. [1 point]

Problem 2

The critical micelle concentration of a homologue series of sodium alkyl-sulphates, $H(CH_2)_nCOSO_3^-\ Na^+$ at 40°C is given in the table below as a function of chain length, *n*.

n	8	10	12	14	16
c.m.c., mmol/l	140	???	8.6	2.1	0.5

(a) Is micelle formation driven by hydrophilic heads or hydrophobic tails of these molecules? Explain why c.m.c. is smaller for larger *n*. [1 point]

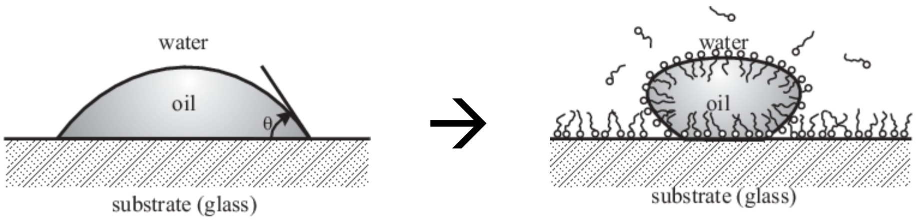
(b) The c.m.c. value for *n*=10 is missing. Using the given data, predict the missing value. [2 points]

Problem 3

(a) Describe what happens when a drop of hexanol $H(CH_2)_6OH$ (h) is applied to a clean water (w) / air (a) interface, given γ_{wh} = 6.8 mN/m, γ_{ha} = 24.8 mN/m, γ_{wa} = 72.8 mN/m for a clean water surface and γ_{wa}^* = 28.5 mN/m for a saturated hexanol solution in water. [2 points]

(b) Why the water/air interfacial tension strongly reduces ($\gamma_{wa}^* \ll \gamma_{wa}$, see question (a) above) when a small amount of hexanol dissolves in water? [1 point]

Problem 4



(a) Using the sketch above and Young's law explain how a soap helps with cleaning dishes and other kitchenware. Using Young's law and Gibbs adsorption equation explain why it is important to ensure adsorption of soap at the solid-water interface? What can happen if this condition is not met? [2 points]

Possibly useful formulas and constants

Gibbs adsorption equation $d\gamma = -\sum_{i>1} \Gamma_i^{(1)} d\mu_i$.

Chemical potential of a solute in a dilute solution $\mu_i = \mu_i^\circ + RT \ln c_i$

Critical micelle mole fraction $x_{\text{cmc}} = \exp\left(\frac{\mu_n - n\mu_1}{(n-1)RT} \right) = \exp\left(\frac{\Delta\mu}{RT} \right)$.

Young's law $\gamma_{SG} = \gamma_{SL} + \gamma_{LG} \cos\theta$

Adsorption energy of a spherical particle at an oil-water interface $\Delta U_{\text{ad}} = -\frac{\pi}{4} D^2 \gamma_{\text{ow}} \left(1 \mp \cos\theta\right)^2$

Area of a circle with diameter *D*: $A_{\text{circle}} = (\pi / 4) D^2$

Surface area of a sphere with diameter *D*: $A_{\text{sphere}} = \pi D^2$

Volume of a sphere $V_{\text{sphere}} = (\pi / 6) D^3$

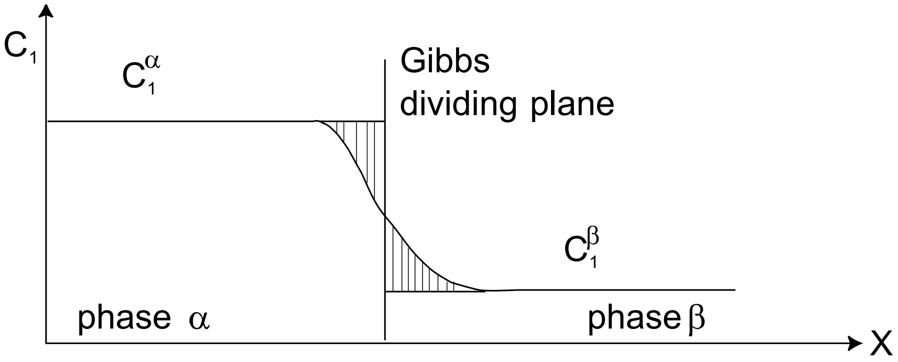
Avogadro number N_{av} = 6 10^{23} mol^{-1}.

Boltzmann constant k_B = 1.38 × 10^{-23} J/K.

Ideal gas constant R = k_B N_{av} = 8.31 J mol^{-1} K^{-1}.

Problem 1

(a) What is the Gibbs dividing plane and how is it defined? [1 point]



The concentration of the molecules is varying smoothly through the interface from its bulk value in one phase to that in the other as illustrated in the sketch above. The Gibbs dividing plane is defined such that there is no excess molecules of at the surface. It means that the overestimation of the number of molecules in the phase α (shaded region on the left-hand side of the Gibbs dividing plane) is exactly compensated the underestimation of the number of molecules in the phase β (shaded region on the right-hand side). For solutions the position of the Gibbs dividing plane is defined using the profile of the solvent molecules.

(b) Explain how the surface coverage of certain species can be negative and give an example. [1 point]

For solutions the Gibbs dividing plane is usually defined for solvent molecules. The (positive or negative) excess number of solute molecules is then introduced relative to the Gibbs dividing plane for solvent. This excess number can be negative when the solutes are depleted (e.g., ions) from the near-surface region.

Problem 2

The critical micelle concentration of a homologue series of sodium alkyl-sulphates, $H(CH_2)_nCOSO_3^-\ Na^+$ at 40°C is given in the table below as a function of chain length, *n*.

n	8	10	12	14	16
c.m.c., mmol/l	140	???	8.6	2.1	0.5

(a) Is micelle formation driven by hydrophilic heads or hydrophobic tails of these molecules? Explain why c.m.c. is smaller for larger *n*. [1 point]

The hydrophobic tails are responsible for micelle formation as they can win free energy by coming together and reducing the contact with water. The longer the tail, the stronger is the energy gain $\Delta\mu$ and the smaller is the c.m.c.

(b) The c.m.c. value for *n*=10 is missing. Using the given data, predict the missing value. [2 points]

The c.m.c. values exponentially depend on the change of the standard chemical potential $\Delta\mu$ (see the formula provided). One can assume that $\Delta\mu(n)$ linearly depends on the chain length *n*. The c.m.c. for *n*=10 can be estimated as follows. As described above, one can assume $\Delta\mu(10) = \left[\Delta\mu(8) + \Delta\mu(12)\right]/2$. Because of the exponential relation between x_{cmc} and $\Delta\mu$, $x_{cmc}(10) \approx \sqrt{x_{cmc}(8)x_{cmc}(12)} = 35$ mmol/l. This estimated value is indeed very close to the experimental result $x_{cmc}(10) = 33$ mmol/l [see Exercise 2a on page 27 of the lecture notes].

Problem 3

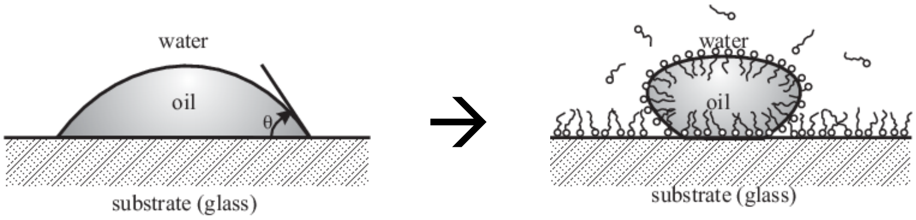
(a) Describe what happens when a drop of hexanol $H(CH_2)_6OH$ (h) is applied to a clean water (w) / air (a) interface, given γ_{wh} = 6.8 mN/m, γ_{ha} = 24.8 mN/m, γ_{wa} = 72.8 mN/m for a clean water surface and γ_{wa}^* = 28.5 mN/m for a saturated hexanol solution in water. [2 points]

A droplet of hexanol will initially spread over the water surface since it is energetically favorable to replace the water/air interface (γ_{wa} = 72.8 mN/m) with water/hexanol and hexanol/air interfaces ($\gamma_{wh} + \gamma_{ha}$ = 6.8 + 24.8 = 31.6 < 72.8 mN/m). However, in equilibrium hexanol will partially dissolve in water. This will significantly reduce the water/air interfacial tension and the spreading coefficient will become negative: $S = 28.5 - (24.8 + 6.8) = -3.1$ mN/m. The droplet will therefore stay on the water surface in a form of a thin “lens”.

(b) Why the water/air interfacial tension strongly reduces ($\gamma_{wa}^* \ll \gamma_{wa}$, see question (a) above) when a small amount of hexanol dissolves in water? [1 point]

Hexanol molecules possess a relatively long hydrophobic tail, which leads to their low solubility in water. However, they can effectively adsorb at the air-water interface by sticking out the tails into the gas phase and keeping the polar group in water. According to Gibbs adsorption equation, positive adsorption leads to lower surface tension.

Problem 4



(a) Using the sketch above and Young’s law explain how a soap helps with cleaning dishes and other kitchenware. Using Young’s law and Gibbs adsorption equation explain why it is important to ensure adsorption of soap at the solid-water interface? What can happen if this condition is not met? [2 points]

Cleaning oil droplets from a solid surface will be much more efficient if the contact angle at the oil-water-solid contact line is increased towards 180°. According to Young's law, $\cos\theta = (\gamma_{SW} - \gamma_{SO}) / \gamma_{WO}$. An obvious effect is the adsorption of soap at the oil/water interface, which will reduce γ_{WO}. However, if this is not accompanied by a reduction of γ_{SW} and making $\gamma_{SW} - \gamma_{SO} < 0$, a reduction of γ_{WO} will shift $\cos\theta$ towards a larger positive value. On the left sketch (no soap) $\theta < 90^\circ$ and, therefore, $\gamma_{SW} - \gamma_{SO} > 0$! For $\cos\theta \to 1$ the contact angle will reduce, which will lead to an even better spreading of oil over the solid surface. To fulfil the condition $\gamma_{SW} - \gamma_{SO} < 0$, one needs to reduce γ_{SW}. According to Gibbs adsorption equation, this can happen if soap strongly adsorbs at the sold-water interface.

EXAM COVER PAGE

COURSE: **Fysische Chemie 3 / Advanced Physical Chemistry**
COURSE CODE: **SK-BFYC3 / SK-MPC3**
EXAM: partial exam on Colloids and Polymers
TIME: 13-04-2018 from 13.30h to 16.30h
LENGTH: 3h00m (no students with extra time)
PLACE: Beatrixgebouw

IMPORTANT

- **PLACE YOUR ID CARD (WITH PHOTO) ON THE TABLE – Show your ID when you hand in the exam.**
- **WRITE YOUR NAME AND STUDENT NUMBER ON EVERY ANSWER SHEET**
- **WHEN YOU HAND IN YOUR EXAM, YOU CAN TAKE THE QUESTIONS AND SCRATCH PAPER HOME**

EXAM SPECIFICS

- This exam counts for 1/3 of the final grade.
- The average score for all three partial exams of the course needs to be at least 5.5 to prevent a re-exam. In order to be allowed to take a re-exam, the final grade for the course needs to be at least 4.0 and at most 5.4.
- This exam has 3 pages including this cover page.
- Points per question are distributed as follows: see number of points at the start of each question.
- In grading your answers, the lecturer will evaluate (a) whether you have understood the question, (b) whether you know in part or fully which approach should lead to a proper answer (formulas, argumentation, schematics if necessary), and (c) which answer you reach (in the case of calculations, also show the units of the quantities with which you calculate).
- When answering the questions, please take the following into account: answer either in English or in Dutch and write legibly.

PERMITTED EQUIPMENT

A calculator is required (graphical or not, with an empty memory); except for that, no electronic devices are allowed, no books, no notes of any kind.

SUCCESS!
Ben Erné

GENERAL EXAMINATION RULES

- You are not allowed to leave the exam room in the first 30 minutes. Latecomers are allowed in up to 30 minutes after the start time.
- All electronic equipment needs to be switched off (including mobile phones), with the exception of electronic equipment allowed by the examiner.
- Your coat and closed bag are placed on the ground.
- Raise your hand when you need to go to the bathroom. 1 person at a time. Place your mobile phone visibly on your table just before you go.
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- When fraud is suspected the exam will be confiscated immediately. The examiner will act according to the Education and Exam Regulations and will inform the Exam Committee and the Education Manager in writing within one work day.
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Polyethylene glycol (PEG) is a polymer of ethylene glycol (EG; molar mass: 62 g/mol; density: ~1 g/cm^3). Solutions of “PEG-4000” (4000 g/mol, ~1 g/cm^3) in water (18.0 g/mol, 1.00 g/cm^3, 1.0 mPas) have an osmotic pressure given by the following equation:

$$\Pi = Ac + Bc^2$$

where Π is the osmotic pressure in Pa, *A* is a constant, *B* = 27.2 Pa per (g/L)^2, and *c* is the concentration in g/L. Except if the question asks to find a (critical) temperature, assume a temperature of 300 K.

1. [10] Predict the value of *A*.

2. [10] Is water a good solvent for PEG? (no points are given for just “yes” or “no”)

3. [20] From the given information, predict the minimum temperature above which PEG-4000 should be fully miscible with water.

4. [10] Calculate the mixing *enthalpy* and the mixing *entropy* of a solution with 4.00 g of PEG-4000 and 180 g of water.

5. [10] Without necessarily performing the calculations, explain how you expect that the answers will change if questions 1, 2, 3, and 4 are asked about the monomer (ethylene glycol) rather than about polymer?

PEG-4000 can be chemically attached to nanoparticles of iron oxide (5.2 g/cm^3) with a diameter of 10.0 nm, to promote their sterical stabilization. This can for instance be done by modifying the uncharged PEG molecules with a negatively charged phosphate end group, so that strong adsorption occurs to the positively charged bare surface of iron oxide in acidic solution. Including polymer layer, the hydrodynamic diameter is measured to be ~30 nm.

6. [10] The iron oxide nanoparticles have a magnetic dipole moment *m* equal to 1.0×10^{-19} Am^2. As a result, they are drawn toward a magnet by a magnetic force equal to *mB′*, where *B′* is the magnetic field gradient. Calculate the speed at which the particles will move magnetophoretically in water toward a magnet, assuming a constant magnetic field gradient *B′* of 1.0 tesla per meter (1.0 T/m, with T = JA^{-1}m^{-2}).

7. [20] At magnetophoresis-diffusion equilibrium, for each nanoparticle at each distance from the magnet, the magnetic force is balanced by the gradient in the approximately ideal chemical potential of the nanoparticles. Using the information in question 6, estimate across which distance the concentration of nanoparticles will change by a factor of e = 2.718… at magnetophoresis-diffusion equilibrium. You may first need to find an expression for the concentration profile, in a derivation similar to that for sedimentation-diffusion equilibrium.

8. [10] At high salt concentrations, the colloidal stability in acidic solution is very poor for bare iron oxide particles but excellent after chemical anchoring of PEG-4000 to their surface. Explain these observations.

Equations and constants for colloids & polymers

$\Pi V = nRT$ $\chi = w/(RT)$ $\chi_C = \left(1+\sqrt{r}\right)^2/2r$ $\phi_C = \left(1+\sqrt{r}\right)^{-1}$

$\Pi = \frac{RT}{M_2}c_2 + \frac{RT}{\rho_2^{\,2}v_1}\left(\frac{1}{2}-\chi\right)c_2^{\,2}$ $\Delta G = (n_1 + rn_2)RT\chi\phi_1\phi_2 + RT[n_1 \ln\phi_1 + n_2 \ln\phi_2]$

$\phi_1 = n_1/(n_1+rn_2)$ $\phi_2 = rn_2/(n_1+rn_2)$ $\mu_1 = \mu_1^{\,0} + k_B T\left[\ln(1-\phi) + \left(1-\frac{1}{r}\right)\phi + \chi\phi^2\right]$

R = 8.314 JK^{-1}mol^{-1} g = 9.8 m/s^2 $k_B \approx 1.38\times10^{-23}$ JK^{-1} 1 atm = 101325 Pa

$\mu = \mu^0 + k_B T\ln(c)$ $P=\rho gh$ $F = \Delta mg$ $E = \Delta mgh$ $F = 6\pi\eta au$

$\eta = (F/A)\,/\,(V/h)$ $D = k_B T/(6\pi\eta a)$ $V = (4/3)\pi a^3$ $f = f_0 \exp[-U/(kT)$

Fysische Chemie 3 (SK-BFYC3) / Advanced Physical Chemistry (SK-MPC3)

Answers to the questions on the partial exam on Colloids & Polymers of April 13, 2018

The value of B for PEG-4000 is from *Plant Physiol.* <u>91</u>, 766 (1989), one of the publications provided as a "context paper" on BlackBoard.

1. $A = \frac{\Pi \text{ in Pa}}{c \text{ in g/L}} = \frac{RT}{M_2} \text{in Pa per g/L}$

   $$A = \frac{(8.314\ \mathrm{JK^{-1}mol^{-1}})(300\ \mathrm{K})}{(4000\ \mathrm{g\ mol^{-1}})} \frac{\mathrm{Nm}}{\mathrm{J}} \frac{\mathrm{Pa}}{\mathrm{Nm^{-2}}} \frac{1000\ \mathrm{L}}{\mathrm{m^3}} = 623.6\ \text{Pa per g/L}$$

2. The nonideal term in the equation for the osmotic pressure is positive:

   $$B = \frac{RT}{(\rho_2)^2 v_1}\left(\frac{1}{2} - \chi\right) > 0$$

   The sign is determined by the factor $\left(\frac{1}{2} - \chi\right)$, as all other factors are positive.

   The osmotic pressure is higher than in the ideal case, corresponding to a good solvent.

3. First, we must find the value of χ.

   From $\frac{RT}{(\rho_2)^2 v_1}\left(\frac{1}{2} - \chi\right) = 27.2\ \text{Pa per}\ \left(\frac{\mathrm{g}}{\mathrm{L}}\right)^2$ it follows that $\chi = \frac{1}{2} - \frac{\left[27.2\ \text{Pa per}\ \left(\frac{\mathrm{g}}{\mathrm{L}}\right)^2\right](\rho_2)^2 v_1}{RT}$.

   $$\chi = \frac{1}{2} - \frac{\left[27.2\ \text{Pa per}\ \left(\frac{\mathrm{g}}{\mathrm{L}}\right)^2\right]\left(1000\frac{\mathrm{g}}{\mathrm{L}}\right)^2 [18.0 \times 10^{-6}\ \mathrm{m^3 mol^{-1}}]}{(8.314\ \mathrm{JK^{-1}mol^{-1}})(300\ \mathrm{K})} = 0.304$$

   The next step is to find the critical temperature above which no more demixing is expected.

   $T_c = w/(\chi_c R)$ where $w = \chi RT = (0.304)R(300\ \mathrm{K})$ and $\chi_c = \left(1 + \sqrt{r}\right)^2/(2r)$=0.632, with $r = (4000\ \mathrm{gmol^{-1}})/(62\ \mathrm{gmol^{-1}}) \cong 64.5$. On this basis,

   $T_c = (0.304)(300\ \mathrm{K})/(0.632) = 144\ \mathrm{K}.$

   In reality, aqueous solubility of PEG-4000 at 20 °C is not complete but 66 weight percent, indicating that the previous calculations underestimate the critical temperature.

4. The *enthalpy* of mixing is:

   $\Delta H = (n_1 + rn_2)RT\chi\phi_1\phi_2$

   with $\phi_2 = \frac{rn_2}{n_1 + rn_2} = \frac{(64.5)(0.00100\ \mathrm{mol})}{(10.0\ \mathrm{mol}) + (64.5)(0.00100\ \mathrm{mol})} = 0.0064$

   (since 4.00 g of PEG-4000 is 0.00100 mol and 180 g of water is 10.0 mol).

   $= [(10.0\ \mathrm{mol}) + (64.5)(0.00100\ \mathrm{mol})](8.314\ \mathrm{JK^{-1}mol^{-1}})(300\ \mathrm{K})(0.304)(0.9936)(0.0064)$
   $= 48.5\ \mathrm{J}$

   The *entropy* of mixing is:

   $-R[n_1 \ln\phi_1 + n_2 \ln\phi_2]$
   $= -(8.314\ \mathrm{JK^{-1}mol^{-1}})[(10.0\ \mathrm{mol})\ln(0.9936) + (0.00100\ \mathrm{mol})\ln(0.0064)] = 0.58\ \mathrm{JK^{-1}}$

5. The value of *A* would be higher by a factor of *r* = 64.5, so 40.2 kPa per g/L.

   Water will also be a good solvent for EG, since the critical temperature would be even lower ($T_c = 2w/(R)$ for a regular solution (*r* = 1), so it would be lower by a factor 2/0.632 (46 K).

   The mixing enthalpy would remain unchanged, as χ, the volume fractions, and the number of moles of solvent and of polymer *segments* (now all separate from each other) remain the same.

   The mixing entropy would go up (to 3.24 JK^{-1}), since 4.00 g of EG is 64.5 times as many moles as 4.00 g of PEG-4000.

6. This is a variation on the theme of calculating the sedimentation rate (which can in this case be calculated to be about 8×10^{-11} ms^{-1}). The magnetic force on the particles should be put equal to the viscous force and one can solve for the speed of the magnetophoresis:

$$u = \frac{mB'}{6\pi\eta a_H} = \frac{(1.0 \times 10^{-19}\ \mathrm{Am^2})\left(1.0\ \frac{\mathrm{T}}{\mathrm{m}}\frac{\mathrm{JA^{-1}m^{-2}}}{\mathrm{T}}\right)}{6\pi(0.00100\ \mathrm{Pa\cdot s})(15.0 \times 10^{-9}\ \mathrm{m})} = 3.5 \times 10^{-10}\ \mathrm{m/s}$$

7. Putting the words into mathematical expressions gives:

$$-mB' = \frac{\mathrm{d}\mu}{\mathrm{d}x} = k_B T \frac{\mathrm{d}\ln(c)}{\mathrm{d}x}$$

   where ideality of the chemical potential of nanoparticles was assumed via:

$$\mu = \mu^0 + k_B T \ln(c)$$

   Integrating from x_0 to x, with $c(x_0)=c_0$ and $c(x)=c$, we get:

$$c = c_0 \exp\left[-\frac{mB'(x - x_0)}{k_B T}\right]$$

   This implies that the characteristic distance (where the exponent is –1) is equal to:

$$\frac{k_B T}{mB'} = \frac{(1.38 \times 10^{-23}\ \mathrm{J/K})(300\ \mathrm{K})}{(1.0 \times 10^{-19}\ \mathrm{Am^2})\left(1.0\ \frac{\mathrm{T}}{\mathrm{m}}\frac{\mathrm{JA^{-1}m^{-2}}}{\mathrm{T}}\right)} = 0.04\ \mathrm{m}$$

8. The answer might use a schematic illustration of a total interaction potential (potential energy versus distance between outer surfaces of the iron oxide crystals). The main point is that the attractions (Van der Waals and magnetic) start to operate at a certain distance that is shorter than the distance at which sterical repulsion from attached PPEG is already effective and that is longer than the distance at which repulsion due to surface charges starts to act. As a result, the total pair potential in the presence of a sterical stabilization layer is repulsive at each distance between iron oxide crystals, whereas for the bare crystals, the attraction is already winning at the short distances where repulsion due to surface charge starts to become significant.