Problems 2

1. (a) Describe how the short range chemical structure of a polymer is related to its conformation in solution and derive an equation relating the mean square end-to-end distance of a random flight polymer to the number of formula units in a statistical segment.
   (b) Explain what is meant by the radius of gyration of a polymer (R_g). How is it related to the end-to-end distance for a single chain polymer and what is its significance?
   (c) The R_g for polystyrene (C_8H_8) in cyclohexane at 310 K was found to be 6.2 nm for a molecular weight of 50k. Given that the length of the formula unit is about 0.3 nm, estimate the number of formula units in a statistical segment.

2. The radius of gyration R_g and second virial coefficient A_2 of a sample of polystyrene dissolved in cyclohexane were measured at a series of temperatures with the following results

T/K	305.7	307.2	311.2	318.2	328.2
R_g/nm	47.9	51.8	57.6	62.5	66.5
A_2	-0.40	-0.20	0.37	0.95	1.58

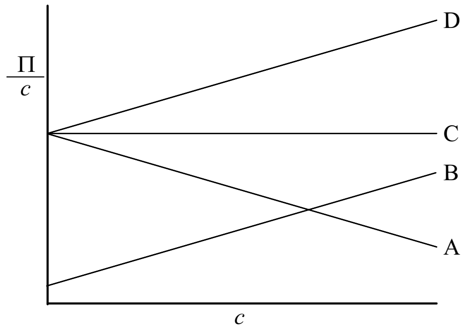
   Estimate the unperturbed root mean square end-to-end distance (empirically) and the θ-temperature in this solvent.

3. The results of a series of measurements of the osmotic pressure for a solution of polystyrene in toluene at 25°C are shown in the table below

c(polystyrene) (g/dm^3)	2.56	3.80	5.38	7.80	8.68
height of toluene (cm toluene)	0.325	0.545	0.893	1.578	1.856

   The mass density of toluene is 0.8669 g/cm^3 and the molar mass of toluene is 92.15 g/mol. The mass density of polystyrene is 1 g/cm^3.
   (a) Determine the molar mass M of the polystyrene used.
   (b) Determine the second virial coefficient of polystyrene in toluene.
   (c) Determine the Flory-Huggins-parameter. Is toluene a good solvent for polystyrene?

4. In the figure below the measured osmotic pressure, Π, is plotted as a function of the mass concentration c of the polymer for polymer solutions A, B, C and D. The temperature is constant and the solvent is always the same.



   (a) Rank the polymers according to their molar mass.
   (b) In which polymer solution is the quality of the solvent the poorest?
   (c) Which polymers could have the same chemical composition?

5. (a) Calculate the Debye length in 1.00 mM KNO_3 (the relative permittivity of water at 25°C is 78). Discuss whether the Debye length will be smaller or larger in a 1.00 mM K_2SO_4 solution.
   (b) Given that the Debye length is about 10 nm in aqueous 0.001 M KCl at room temperature, calculate its value in aqueous 0.01 M solutions of (i) KNO_3, (ii) $CaCl_2$, (iii) Na_2SO_4, (iv) $CuSO_4$ and (v) $LaCl_3$.

6. According to E.W. Neumann (*J. Am. Chem. Soc.* **54** (1932) 2195) the solubility of AgCl in the presence of KNO_3 at 25°C varies as

$c(\text{AgCl})\times10^5$ (mol/l)	1.453	1.469	1.488	1.516	1.537	1.552
$c(\text{KNO}_3)$ (mol/l)	0.013695	0.016431	0.020064	0.027376	0.033760	0.040144

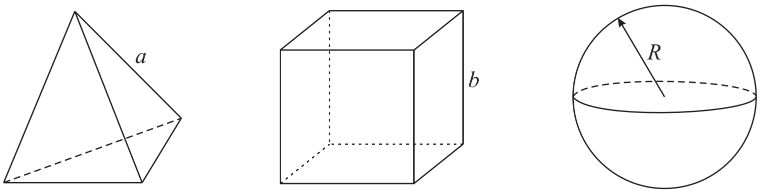
   (a) Verify whether these results are consistent with Debye-Hückel-theory.
   (b) Determine the solubility product of AgCl.

7. The degree of dissociation α of ethanoic acid, CH_3CO_2H, in aqueous solution at 298 K varies with concentration c in the following manner:

c(mol/l)	$2.801\cdot10^{-5}$	$1.532\cdot10^{-4}$	$2.414\cdot10^{-3}$	$5.912\cdot10^{-3}$
α	0.5393	0.2875	0.0829	0.054

Calculate the (thermodynamic) dissociation constant of ethanoic acid. How far do the data verify the Debye-Hückel theory?

8. Below you see a tetrahedron, a cube and a sphere with their volume V and total surface area σ.



$V=\frac{\sqrt{2}}{12}a^3$	$V=b^3$	$V=\frac{4}{3}\pi R^3$
$\sigma=\sqrt{3}a^2$	$\sigma=6b^2$	$\sigma=4\pi R^2$

   (a) Show that for a given volume the sphere has the minimal surface area.
   (b) Why are liquid surfaces with sharp edges never encountered in real life?

9. The free energy required for the formation of a liquid droplet with a radius r in a saturated vapor with pressure P is given by

$$\Delta G = \gamma 4\pi r^2 - \frac{4\pi RT}{3v_l} r^3 \ln \frac{P}{P_0}$$

where v_l is the molar volume of the liquid and P_0 the vapour pressure of the liquid with a flat surface (at the same temperature).
   (a) Sketch the free energy as a function of the radius r and explain its shape and significance.
   (b) The maximum in the free energy can be interpreted as the energy barrier for the nucleation of droplets with a radius r. Show that the critical radius r^* is given by the Kelvin equation.
   (c) Water at 0°C condensates when $P/P_0 \approx 4.2$. Calculate the critical radius r^* and hence the number of water molecules in such a critical liquid droplet.

10. For a two component system the Gibbs adsorption equation is often written as $d\gamma = -\Gamma_1 RT d\ln c_1 - \Gamma_2 RT d\ln c_2$, where γ is the surface tension, c_1 and c_2 are the concentrations of the two components, and Γ_1 and Γ_2 are the surface excess concentrations of the two components.
   (a) Show how this may be simplified by defining the Gibbs dividing surface for the solvent.
   (b) Estimate the relative surface excess concentrations of phenol in the concentration ranges of (i) 0.05 to 0.08 mole/dm^3 and (ii) 0.268 to 0.496 mole/dm^3 at the surface of an aqueous solution from the following data taken at 293 K

c_{phenol}/mole dm^{-3}	0.05	0.08	0.127	0.268	0.496
γ/mN m^{-1}	67.88	64.60	60.10	51.58	44.97

(c) Given that the cross section of a phenol molecule is about 0.4 nm^2 estimate what fraction of the surface is covered by phenol at the higher of the two concentration ranges. Suggest an explanation for the high value that you should obtain.

11. An experiment shows that ethanol adsorbs positively at the water/air interface (w/a).
    (a) Show that for a regular solution the Gibbs adsorption equation is given by

$$\frac{1}{RT}\left(\frac{\partial \gamma_{\mathrm{w/a}}}{\partial \ln x_{\mathrm{ethanol}}}\right)_T = -\Gamma^{\mathrm{w/a}}_{\mathrm{ethanol}}\left\{1 - \frac{2w x_{\mathrm{ethanol}}\left(1 - x_{\mathrm{ethanol}}\right)}{RT}\right\}.$$

    (b) Does the non-ideal behaviour of water and ethanol lead to a stronger or weaker decrease of the interfacial tension compared to ideal behaviour?