

Wadham College

Second Year Tutorials: Liquids and Solutions

This week's work involves producing a summary of the topics listed below in the written work section. This can be in the form of an essay or a set of notes, whatever you feel would be most useful for you to revise from next term. This should be handed into the porters in Magdalen by 5 p.m. on the day before the tutorial. Once you have understood the material you should attempt the problems on the following pages; these are split into numerical exercises and descriptive questions. If you wish to submit your solutions to these questions at the same time as your summary I will be happy to mark them for you.

Robert Jacobs

Written Work:

Molecular Interactions: Describe how molecular properties lead to attractions and repulsions between them. For the most common interactions give equations that relate the interaction energy to their properties and the distance between the molecules.

What is a *Pair Distribution Function*? Sketch a typical distribution function for an ideal gas, a real gas, a liquid and a crystalline solid. What does the pair distribution function tell us about the structure of a liquid? Use argon, CCl_4 , benzene and water as examples to explain the factors affecting the structure of liquids.

Describe how the phase behaviour of real *solutions of non-electrolytes* differs from that of ideal solutions (define what an ideal solution is!), including the terms regular solution, upper critical solution temperature, azeotrope and eutectic.

Polymer Solutions: Give a description of a simple model of a polymer, explain how this relates to the dimensions of real polymers, and consider the effect of solvent on the dimensions of a polymer molecule in a solution.

Ions in Solution: Among the topics you should cover are the structure of hydrated ions, ion activities, Debye-Hückel theory (physical basis, assumptions, ionic atmosphere, Debye Length and the limiting law but do not give the mathematical details of the derivation), consequences of Debye-Hückel theory (e.g. the effect of ionic strength on solubility and electrode potentials), conductivity and mobility of ions.

What is meant by the surface tension of a *Liquid Surface*? How do molecules dissolved in the liquid affect the surface tension of a solution.

Bibliography:

P. W. Atkins: *Physical Chemistry*

J. N. Murrell and A. D. Jenkins: *Properties of liquids and Solutions*, 2nd Ed. (1994)
D. F. Evans and H. Wennerström: *The Colloidal Domain* (1995)
D. H. Everett: *Basic Principles of Colloid Science* (1998)
J. Israelachvilli: *Intermolecular and Surface Forces*, 2nd Ed. (1991)
R. G. Compton and G. H. W. Sanders: *Electrode Potentials* (Oxford Primer No. 41)
D. R. Crow: *Principles and applications of Electrochemistry*
J. Robbins: *Ions in Solution: an Introduction to Electrochemistry*

Numerical Exercises (Be prepared to explain your answers to these questions to the rest of the group using the white board)

- 1) The HCl bond length is 0.13 nm and its dipole moment is 1.8 D. Assuming a simple model in which the charges are localised on the atoms, calculate the partial charge on chlorine ($1\text{D} = 3.336 \times 10^{-30}$ Cm).
- 2) Chloroform (CHCl_3) is a low boiling point liquid that used to be employed as a general anaesthetic. Given that its molecular weight is 119 and its density is 1.48 g cm^{-3} , estimate the mean separation between molecules in the liquid. (Treat the molecules as spherical and either assume simple close packing or, for a more accurate answer, cubic close packing). At this separation calculate the dipole-dipole energy, dipole induced dipole energy and dispersion energy between the two molecules. ($\alpha' = 8.1 \times 10^{-30} \text{ m}^3$, $I \approx 10^6 \text{ J mol}^{-1}$, $\mu = 1 \text{ D}$, $T = 293 \text{ K}$. Take $\epsilon = 1$ in this calculation.)
- 3) Calculate the van der Waals interaction between two $1 \mu\text{m}$ diameter silica spheres separated by 100 nm in a vacuum and compare this value with the thermal energy of the particles at room temperature. $A_{11} \approx 6 \times 10^{-20} \text{ J}$ for silica. (Ignore retardation effects.) Repeat the calculation for silica in water, where $A_{131} = 0.8 \times 10^{-20} \text{ J}$.
- 4) Trouton's Rule states that $\Delta H_{\text{vap}}^\circ / T_B \approx 85 \text{ JK}^{-1} \text{ mol}^{-1}$, where $\Delta H_{\text{vap}}^\circ$ is the latent heat of vaporisation and T_B is the normal boiling point. The Lennard-Jones parameter, ϵ/k , is 520 K for Br_2 , and bromine boils at 59°C . Estimate the number of nearest neighbours in liquid Br_2 . What is the physical basis of Trouton's Rule?
- 5) Regular Solutions are one of the simplest types of non-ideal binary solutions. A general expression for the chemical potential of the components in a solution is

$$\begin{aligned}\mu &= \mu^\circ + RT \ln \gamma x_1 \\ \mu &= \mu^\circ + RT \ln \gamma x_2\end{aligned}$$

where μ° is the chemical potential of the pure liquid and γ is the activity coefficient. We can write the deviation from ideality as a power series

$$\begin{aligned}RT \ln \gamma &= \alpha x_2 + \beta x_2^2 + \dots \\ RT \ln \gamma &= \alpha x_1 + \beta x_1^2 + \dots\end{aligned}$$

Use the Gibbs-Duhem equation to show that $\alpha = \alpha = 0$ and that $\beta = \beta$. Then show the simplest non-ideal solution thus has chemical potentials of the form

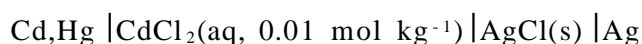
$$\begin{aligned}\mu &= \mu^\circ + RT \ln x_1 + \beta x_2^2 \\ \mu &= \mu^\circ + RT \ln x_2 + \beta x_1^2.\end{aligned}$$

Show that if the β is independent of temperature, then the entropy of mixing is ideal. Hence, show that the enthalpy of mixing is $\beta x_1 x_2$.

- 6) For a regular solution, the first and second derivatives of ΔG_{mix} with respect to the mole fraction vanish at the upper critical solution temperature. Write down an expression for ΔG_{mix} , evaluate the derivatives and hence show that $T_c = \beta 2R$. The excess free energy of mixing of an equimolar mixture of acetonitrile and CCl_4 is +1190

J mol^{-1} at 45°C . Assuming that the mixture behaves as a regular solution, calculate the UCST.

- 7) The thermodynamic solubility product for AgCl in water at 298 K is 1.78×10^{-10} . Calculate the solubility (in mol kg^{-1}) of AgCl in (a) pure water; (b) a $0.100 \text{ mol kg}^{-1}$ KNO_3 solution; (c) a $0.100 \text{ mol kg}^{-1}$ KCl solution. Comment on your answers.
- 8) The solubility product of anhydrite (CaSO_4) is 3.7×10^{-5} at room temperature. Calculate the ideal solubility in (g dm^{-3}) of anhydrite. The actual solubility of anhydrite is 2.1 g dm^{-3} . Comment on this value. (MW of anhydrite = 136)
- 9) At 298 K, the EMF of the cell



is 0.7585 V. (Cd,Hg is a cadmium-mercury amalgam.) The standard EMF of this cell is 0.5732 V. Calculate the mean ion activity coefficient of cadmium chloride in a $0.100 \text{ mol kg}^{-1}$ solution and compare it with the value obtained from the Debye-Hückel limiting law. Account for any differences in the values you obtain.

- 10) A certain polymer associates into dimers and tetramers in the molar proportions of monomers:dimers:tetramers in the ratio 4:2:1. Calculate the number average and weight average molecular weights of the mixture taking the molecular weight of the monomer to be 100000.
- 11) The following results were obtained for a globular protein:

Π/Pa	16.00	32.10	48.35	64.70	81.15
$c/\text{mg cm}^{-3}$	1	2	3	4	5

Calculate the molecular weight of the protein and its second virial coefficient.

- 12) The Radius of gyration and second virial coefficient 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
B/arb. units	-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.

- 13) The intensity of X-rays scattered by a 50 mg cm^{-3} protein solution falls by a factor of 10 when k increases from 0.1 to 1.0 nm^{-1} . If the scattering obeys the Guinier law ($\ln I = \ln I_0 - k^2 R_g^2/3$) what is the radius of gyration of the protein. How would you expect the plot to change if the concentration were increased?

Descriptive Questions (Be prepared to discuss these questions in the tutorial)

- 1) Toluene has a boiling point of 111 °C and a melting point of -95 °C. Heptane boils at 98 °C and melts at -91°C. Assuming that the mixtures of toluene and heptane are ideal (which they are not!), sketch the phase diagram for mixtures of the two liquids.
- 2) Hexane and Perfluorohexane are partially miscible below 22.7 °C. The critical concentration at the UCST is $x = 0.355$, where x is the mole fraction of Perfluorohexane. At 22.0 °C, the two solutions in equilibrium have $x = 0.24$ and 0.48, respectively, and at 21.5 °C the mole fractions are 0.22 and 0.51. Sketch the phase diagram. Describe the phase changes that occur if Perfluorohexane is added to a fixed amount of hexane at (a) 23 °C, and (b) 22 °C.
- 3) What will happen if two 200ml open beakers, one containing 50ml of a 1 mol dm^{-3} solution of LiCl(aq) the other containing 50ml of pure water, are placed in an air tight box at room temperature for a month?
- 4) Draw the interaction potential between spherical particles in a colloidal solution stabilised by NaCl. Explain the factors that determine the shape of the curve. Comment on the effect of (a) increasing the NaCl concentration; (b) adding a divalent electrode; (c) adding methanol to the solution while retaining the NaCl at the same molality.
- 5) Explain the following observations:
 - a) All liquids are partially miscible.
 - b) The melting of ice is endothermic. Nevertheless, salt melts ice on the roads.
 - c) Parsnips taste sweeter after the first frost.
 - d) Sprinkling salt on a slug rapidly kills it.
 - e) Dry ice sublimates at atmospheric pressure, rather than melting.
 - f) Deltas form where rivers meet the sea.
 - g) Soap solutions form foams but pure water does not.