First Year

Trinity Term 2002

Physical Chemistry

Tutorial on Thermodynamics of Solutions

Frank Schreiber

Please hand the work in to my pigeon hole in Wadham by 6:00 p.m. on Wednesday of week 3 (8 May 2002).

We will meet for the tutorial in three groups on Friday of week 3 (10 May 2002) at 2:15, 3:45, and 5:15 p.m. in Library Court 6.

Literature
R K Thomas, Handouts for lecture on this subject and related WWW material
Atkins, Physical Chemistry

Keywords
Ideal solutions
Non-ideal solutions
Osmotic pressure
Chemical potential
Raoult's law
Henry's law
Activity and activity coefficients

Revision and Background

1. Write down *briefly* the definitions / most important facts / equations related to the above keywords.
2. Explain *briefly* the origin of the entropy of mixing for an ideal solution and what changes you expect for a non-ideal solution.
3. Explain *briefly* the reason for the effect of freezing point depression.

Problem 1 Solubility

The solubility of trinitrotoluene in benzene at different temperatures is

x	0.279	0.382	0.493	0.622
T/K	303	313	323	333

where x is the mole fraction of trinitrotoluene. Assuming that the solutions are ideal, calculate ΔH_{fus} and T_{fus} for trinitrotoluene.

Problem 2 Freezing Point Depression and Molecular Weight

A certain solvent, Y, freezes at 278.400 K and has $\Delta H_{fus} = 10.0$ kJ mol^{-1}. A solution of 0.12 g of substance X in 0.10 mole Y freezes at 278.122 K. Find the molecular weight of X.

Problem 3 Solubility of Sulphur

The solubility of monoclinic sulphur at 298.3 K in various solvents (benzene, diethyl ether, ethyl bromide, ethanol) is always 1.28 times that of rhombic sulphur. In these solvents freezing point measurements show that sulphur is always present as S_8 molecules. Find ΔG for the change of monoclinic to rhombic sulphur at 298.3 K. Which of the two forms is more stable at this temperature?

Problem 4 Osmotic Pressure

The concentration of glucose in the bloodstream of a diabetic person was measured to be 1.80 g dm^{-3}, whereas for a non-diabetic person the concentration of glucose in the bloodstream was 0.85 g dm^{-3}. Calculate the difference in the osmotic pressure of the blood in the diabetic and non-diabetic. (Body temperature = 310 K, RMM of glucose = 180)

Problem 5 Benzene / Benzoic Acid / Water

The following data refer to the concentration of benzoic acid in layers of benzene and water, which are in equilibrium

c_{water}/g dm^{-3}	2.89	1.95	1.50	0.98	0.79
$c_{benzene}$/g dm^{-3}	97.0	41.2	25.2	10.5	7.4

Which of the following two hypotheses is most consistent with the data? (i) benzoic acid is almost completely dissociated in the water, (ii) benzoic acid is almost completely associated to a dimer in the benzene. The pKa for benzoic acid in water is 4.19. Does this help to distinguish between the two hypotheses?

Problem 6 Osmotic Pressure and Molecular Weight

For proteins and polymers the behaviour of the osmotic pressure, which is widely used for molecular weight determination, is usually not ideal and the osmotic pressure equation is written as a virial expansion

Π/N m^{-2} $= RTc_B(1/M_B + Bc_B + ...)$

where c_B is the concentration of solute in g cm^{-3} and the second term in the brackets accounts for the deviation from ideal behaviour. The following results were obtained for a globular protein:

Π/N m^{-2}	16.00	32.10	48.35	64.70	81.15
c/g cm^{-3}	10^{-3}	2x10^{-3}	3x10^{-3}	4x10^{-3}	5x10^{-3}

Devise a suitable graphical procedure for determining the molecular weight M_B of the protein from the data and hence calculate the molecular weight of the protein.