

Taken from Thomas Group Website, Problems 1. The answers are up on the web (which you might be interested in!). It's the working I am interested in seeing, and what you understand from this course.

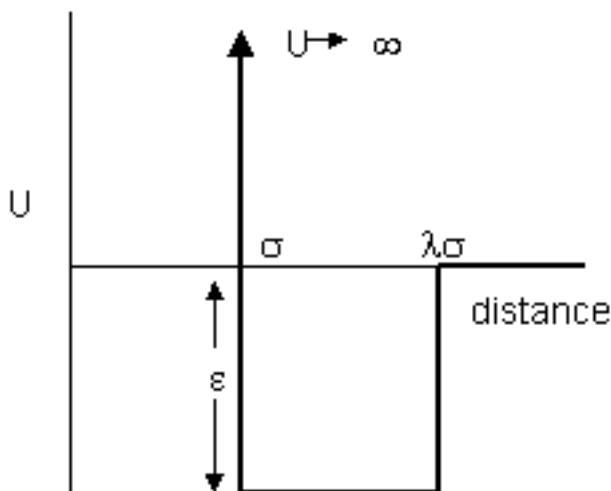
<http://physchem.ox.ac.uk/~rkt/lectures/liqsolns/problems1.html>

Question 1

- Write down a form of virial equation for describing the relation between the pressure, temperature and volume of a gas.
- The second virial coefficient B of a gas is related to the intermolecular potential U between two molecules at a distance r by

$$B = 2\pi \int_0^{\infty} \left[1 - \exp\left(-\frac{U}{kT}\right) \right] r^2 dr$$

- Show that for molecules that behave like hard spheres of radius σ ($U = \infty$ when $r < \sigma$, $U = 0$ when $r > \sigma$) the virial coefficient is given by $B_0 = 2\pi \sigma^3/3$
- For real molecules there is also an attractive interaction. An approximate representation of the attraction potential can be made using the square well potential shown below.



Show that the expression for the virial coefficient now becomes

$$B = \frac{2\pi\sigma^3}{3} \left[\lambda^3 + (1 - \lambda^3) \exp\left(-\frac{\epsilon}{kT}\right) \right]$$

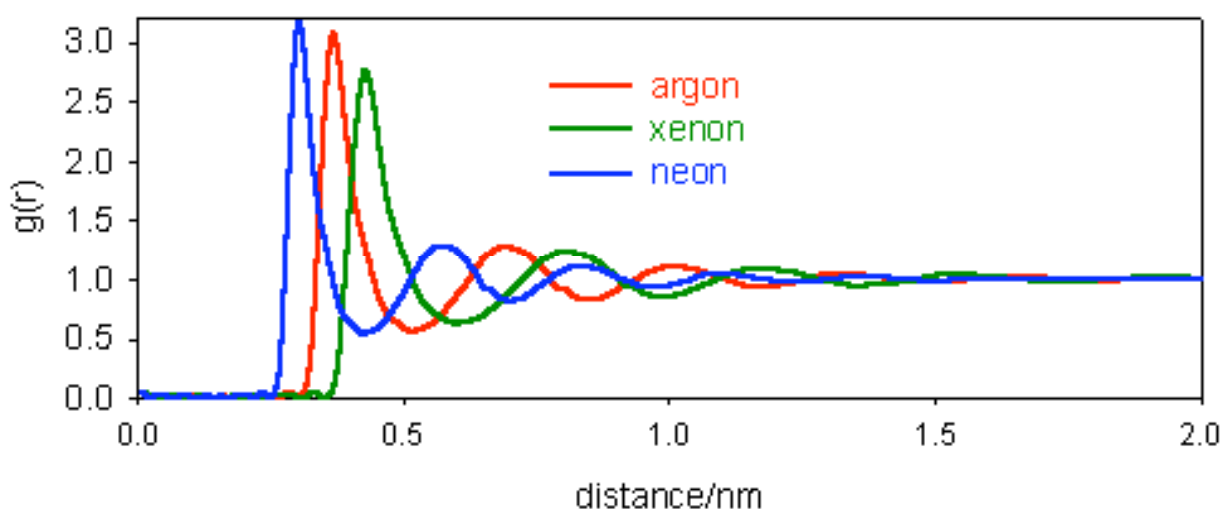
- The temperature at which N_2 behaves like an ideal gas (the Boyle temperature) is 325 K. Given that the ratio λ is 1.58 for N_2 use the value of the Boyle temperature to calculate the depth ϵ of the square well potential.

- iv. Experimentally determined values of the second virial coefficient of N_2 at lower temperatures are given below. Using the value of ϵ and/or λ you have obtained in (iii) show that the square well potential accounts accurately for the data in the table above. Use the data to calculate σ .

T/K	100	125	175	250
B/cm ³ mol ⁻¹	-163.6	-104.8	-50.1	-16.2

Question 2

- a) Describe what is meant by the pair distribution function of a liquid. How does it differ from the pair distribution functions of solids and gases?
- b) The pair distribution functions for the liquid states of Ne, Ar and Xe are shown in the diagram below. Comment on the general pattern of $g(r)$ and estimate the distance between nearest neighbours in each case.



- c) The interaction between a pair of inert gas atoms is given by

$$U = \frac{3\alpha'^2 I}{4r^6}$$

where the electronic polarizabilities α' and ionization potentials I of the inert gases are as given in the table below. Explain the origins of this formula and calculate the values of U for the three gases at the distance at which they are separated in the liquid, using the nearest neighbour distances you have estimated in (b).

Inert gas	Ionization energy/kJ mol ⁻¹	α' /nm ³
Ne	2085	0.4×10^{-3}
Ar	1524	1.6×10^{-3}
Xe	1173	4.0×10^{-3}

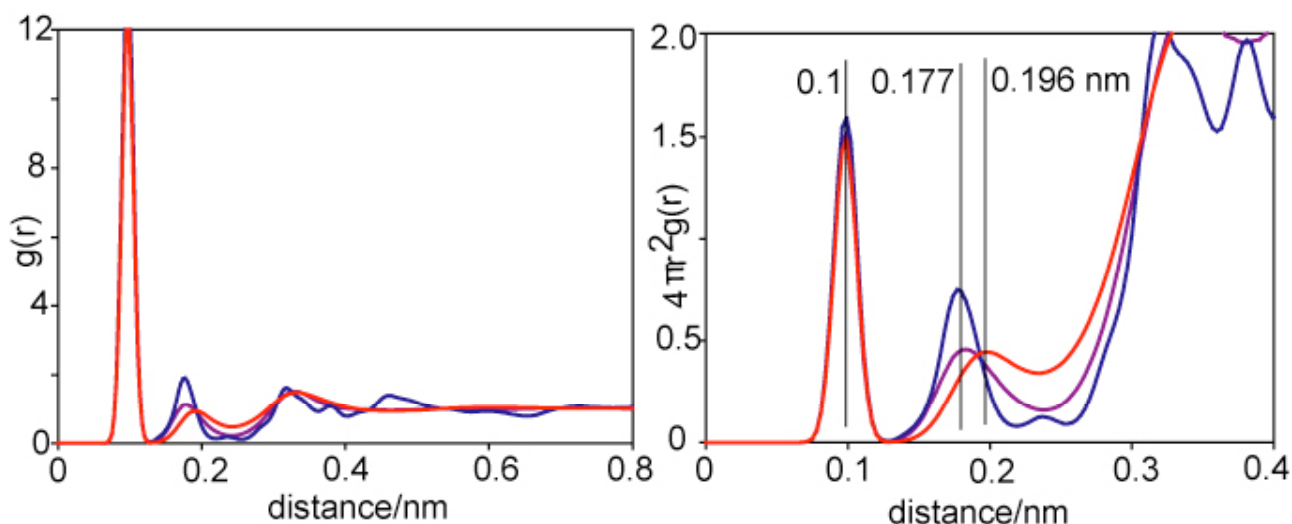
- d) Taking the entropy of vaporization of liquid xenon to be $80 \text{ J K}^{-1} \text{ mol}^{-1}$ and the boiling point to be 166 K, calculate the enthalpy of vaporization of Xe. Assuming

that there is insignificant difference between the enthalpy (H) and energy (U) of vaporization use your value of U for xenon to estimate the coordination number in liquid xenon.

- e) Applying the same approximations and assuming that the entropy of vaporization is the same for all three inert gases estimate the boiling points of Ar and Ne.

Question 3

The radial distribution g_{OH} and $4\pi r^2 g_{OH}$ are shown for ice (blue), water at 273 K (purple) and superheated water at 473 K (red) below.



[At 0.25 nm $4\pi r^2 g_{OH}$ runs red, purple, blue, from top to bottom for those in black and white]

- What is the average hydrogen bond length (O-O distance) in the three situations shown?
- Assuming that each oxygen in ice is hydrogen bonded to exactly four other oxygens, estimate the number of intact hydrogen bonds in water at 273 K and at 473 K, given that the heights of the second peak in the distributions shown on the right above are respectively 0.75, 0.46 and 0.45 for ice, water at 273 K and water at 473 K.
- The enthalpy of fusion of ice is 6 kJ mol^{-1} . Use this value together with your answer from (b) to estimate the average strength of a hydrogen bond (assume that this does not change between ice and water and that the coordination number for water molecules is about 4).
- Use the value from (c) and the mean number of hydrogen bonds per water molecule to estimate how much hydrogen bond energy is lost when water boils. The difference between this value and the observed latent heat of vaporization of water of 40.6 kJ mol^{-1} can be attributed to dispersion forces between water molecules. Using a coordination number of four estimate the mean dispersion forces between a pair of water molecules in liquid water.

Question 4

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.

Question 5

A certain solvent, Y, freezes at 278.400 K and has $\Delta H_{\text{fus}} = 10.0 \text{ kJ mol}^{-1}$. 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.

Question 6

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?

Question 7

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

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

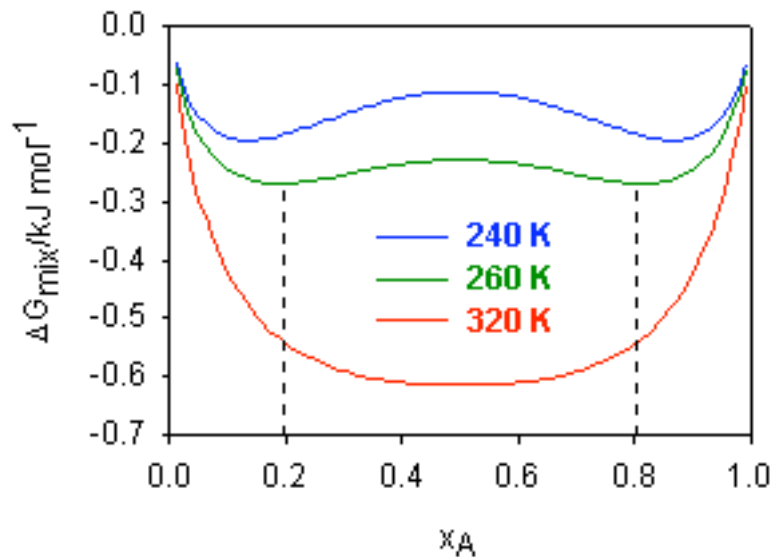
Show that the data is consistent with benzoic acid being almost completely associated to a dimer in the benzene (you may neglect any possibility of dissociation of the monomer in water).

Question 8

- Explain what is meant by the term regular solution.
- Write down expressions for the entropy of mixing when two components are mixed to form a regular solution.
- Show how the enthalpy of mixing, ΔH_{mix} , in a regular solution of two components, A and B, may be related to the pairwise interactions between its components, H_{AA} , H_{BB} and H_{AB} , via an equation of the form $\Delta H_{\text{mix}} = \beta x_{\text{A}}x_{\text{B}}$ where β depends on H_{AA} , H_{BB} and H_{AB} .
- For a regular solution, the first and second derivatives of ΔG_{mix} with respect to mole fraction vanish at an upper critical solution temperature (UCST). Use your results from parts (b) and (c) to write an expression for ΔG_{mix} in terms of x_1 . 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 450°C . Assuming that the mixture obeys regular solution theory, calculate the UCST.

Question 9

The figure below shows a plot of the free energy of mixing, ΔG_{mix} , for a two component system, over the full range of molar composition, $x_{\text{A}} = 0 \rightarrow 1$ and a range of temperatures.



- Over what range of compositions will the mixture be immiscible when the temperature is 260 K?
- At this temperature, the mixture was found to behave as a regular solution. Write down an expression for ΔG_{mix} in terms of x_A ; hence calculate the enthalpy of mixing of the two components at the composition $x_A = 0.1$.
- Calculate the upper critical solution temperature of the mixture; assuming the solution remains regular up to this temperature.