

## 020425 Quiz 5 Properties

- a) The osmotic pressure relates a polymer solution to the pure solvent.  
**-Explain** how the osmotic pressure is measured.  
 -In this measurement, **what thermodynamic feature** is identical in the solution and the solvent at equilibrium?  
**-How is** this similar to an ideal gas?

- b) The Flory-Huggins expression for free energy is used to calculate and equate the thermodynamic feature of question b.  
**-Give the Flory Huggins** expression and  
**-explain** the major assumptions associated with it.  
**-Explain all terms** in the expression including the type of free energy to which it is associated and the structural unit to which it corresponds.  
**-How** can the Gibbs free energy for a solution be obtained from this expression?  
**-Give (do not derive)** an expression for the osmotic pressure based on this free energy.

- c) des Cloiseaux developed a scaling expression based on scaling limits to osmotic pressure in the semidilute regime,

$$\pi = (kT / N) (\phi / \phi^*)^{1/(3 - \chi)}$$

- Use** this expression and the Flory expression (question b) to obtain a molecular weight and composition dependence to **the interaction parameter,  $\chi$** ,  
**-and the second virial coefficient,  $A_2$** .  
**-Are such** molecular weight and composition dependences compatible with your answer to question b?

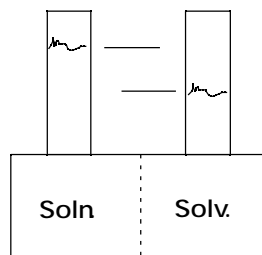
- d) The following are reported interaction parameters for PDMS in benzene at several volume fractions at 25°C (Physical Properties of Polymers Handbook, ed. J. E. Mark 1996). The values of  $\chi$  are independent of molecular weight.

p	12
0	0.5
0.2	0.56
0.5	0.66
0.8	0.75
1	0.82

- What** are the problems with this data compared to your assumptions and answer in question b?

## Answers: 020425 Quiz 5 Properties

a)



Semi-permeable  
Membrane

The chemical potential of the solvent is equal in the two chambers at equilibrium. In an ideal gas the gas molecules move by Brownian motion, have no volume but have mass so they can attain at equilibrium  $kT$  energy. This energy is imparted to the walls of the vessel enclosing the gas and results in the ideal pressure. The molecules in solution can also be considered volumless particles with  $kT$  energy that move by Brownian motion. The osmotic pressure is the excess pressure over that of the solvent associated with these Brownian particles, just as the ideal gas molecules impart pressure by molecular collision of free particles.

b)  $f_m = \frac{1}{N} \ln \dots + (1 - \dots) \ln(1 - \dots) + \dots (1 - \dots)$

Gaussian chains, random mixing, no structural changes in the polymer such as blobs.  $\phi$  is the volume fraction,  $N$  is the chain length,  $\chi$  is the site-site interaction parameter. This is a Helmholtz (volumetric) free energy per lattice site (persistence unit) per  $kT$ . To convert to  $F_m$ , the Helmholtz free energy of the solution, you need to multiply by the number of lattice sites in the system,  $V_c$ .

To convert  $F_m$  to the Gibbs Free energy you add  $PV$ .

$$= kT \frac{1}{V_c} (1/N + A_2 \phi^2), \quad A_2 = (1/2 - \chi \phi)$$

c) At high concentrations the Flory expression gives  $\chi = A_2 kT \phi^2 / V_c$ . The des Cloiseaux expression is  $\chi = (kT \phi^2 / N) (\chi^*)^{-5/4}$  and  $\chi^*$  has a  $N^{-4/5}$  dependence.

Then  $A_2$  has no molecular weight dependence consistent with its definition.

$A_2 = (1/2 - \chi \phi)$  depends on  $\phi^{1/4}$ . This is not predicted by the Flory definition of an interaction parameter. The apparent dependence on volume fraction is do to the incorrect assumption that the chain is Gaussian in the Flory-Huggins equation. If the Flory-Huggins expression is used in a forced fit of the data a composition dependence for  $\chi$  will be observed, even though it does not exist.

e) The interaction parameter should not depend on composition at all by the classic definition.

Values of the interaction parameter larger than 0.5 lead to problems with expressions of the type  $(1/2 - \chi \phi)$  which are positive by definition. The data for 0.2 and 0.8 come close to following the  $\phi^{1/4}$  estimate above indicating that the calculation of  $\chi$  was in error.