Homework 5 Advanced Thermodynamics
Due Tuesday September 29, 2020

In class we discussed the activity coefficient as a measure of the thermodynamics of mixtures.

a) Jin, Weiliang, Qian, Xiaohong, Saijun and Jun, *Thermodynamics of Liquid Bi-Pb alloys - Experimental vs Modeling* Int. J. Electrochem. Sci., **15** 3836 – 3845 (2020), model and measure the miscibility of bismuth-lead alloys which is used as a heat transfer fluid in nuclear reactors. They used the electromotive force to measure the activity coefficients. For this case the Gibbs free energy can be expressed as

$$dG = -SdT + VdP + \mathcal{E}dQ$$

where Q = Fn is the charge (F is the Faraday constant and n is the number of electrons) and E is the potential or electromotive force dW/dQ. Figure 1 shows an electrochemical cell used to measure the open circuit voltage as a function of composition of the alloy in the right cup number 10. In equation (1) identify the entropic and enthalpic terms. Compare the equation with the Hildebrand model and explain any differences and similarities.

b) Equations (2) and (3) are polynomial models for the activity coefficient. Compare these equations with the equations presented in class. From what was done in class, what is the activity coefficient at infinite dilution? How are equations (4) and (5) obtained?

c) Explain the origin of equation (8). Use the free energy expression given above at constant temperature and pressure.

d) Luo, Chen, Wu, Cao, Luo and Shi, *Molecular Dynamics Simulation Study on Two-Component Solubility Parameters of Carbon Nanotubes and Precisely Tailoring the Thermodynamic Compatibility between Carbon Nanotubes and Polymers* Langmuir **36** 9291−9305 (2020) used the Hildebrand and Hansen solubility parameters to quantify the compatibility between polymers and carbon nanotubes. They used molecular dynamics simulations and the COMPASS force field. The solubility parameter is obtained from $\delta = \sqrt{CED} = \sqrt{(E_{coh}/V)}$ and E_{coh} for various interactions are calculated and averaged using a quadratic mean, $x_m^2 = x_a^2 + x_b^2$ from the simulation results. The solubility parameters are compared with those obtained from the Flory-Huggins equation as described in reference 46. The smaller the R value the better the dispersion of SWNT in the polymer. Explain how the solubility parameter is related to the enthalpy of interaction. Interactions can be attractive or repulsive, how is this accounted for in the solubility parameter approach?

e) Explain the relationship between the Hildebrand, Hansen and the potentials available from the COMPASS simulations. How do these parameters relate to the Flory-Huggins interaction parameter, χ?