Statistical Mechanics WS 2013/14 Sheet 8

Please hand in your solutions (in pairs) before the Monday lecture.

Problem 1 Triple point (20 points)

The vapour pressure of solid and liquid ammonia (in mm Hg = 133.32 Pa) is given by $\ln(p) = 23.03 - \frac{3754}{T}$ and $\ln(p) = 19.49 - \frac{3063}{T}$.

a) What is the temperature of the triple point?

b) What is the latent heat of sublimation and vaporization at the triple point?

c) What is the latent heat of fusion at the triple point?

Problem 2 Osmotic pressure (20 points)

Obtain the osmotic pressure of the following equimolar solutions

a) glucose

b) potassium chloride (KCl)

c) sodium sulfide (Na_2S)

In which solution do you measure the largest osmotic pressure?

d) The osmotic pressure of a glucose solution at 20° C is 2 bar. How large is the osmotic pressure after diluting the solution to 10 times its original volume?

Problem 3 Solid-liquid phase transition (20 points)

We want to consider a substance with the free energy of the liquid phase

$$F_l(V,T) = \frac{aN^2}{2TV} \tag{1}$$

and the free energy of the solid phase

$$F_s(V,T) = \frac{bN^3}{3TV^2}, \tag{2}$$

where a and b are constants, V is the total volume of the system, T is the temperature and N is the total number of particles.

a) Calculate the pressure P_m at which the substance melts.

b) Calculate the densities of the liquid and the solid phase at the phase transition point.

c) Calculate the entropy change per particle at the phase transition point.

d) Use the Clausius-Clapeyron equation and your results in parts b) and c) to calculate $\frac{dP_m(T)}{dT}$. Compare the result with the result in part a).

Problem 4 Melting (20 points)

a) An ice cube ($m = 300$g, $T = 273.15$ K) is thrown into a lake ($\theta = 0°C$), where it melts. What will be the final temperature of the lake? What happens to the internal energies U_{ice} and U_{lake}? What happens to the entropy of the ice cube and the lake?

   Notes: The heat required for melting one mol of ice is $Q_{fus} = 6.01$kJ. Assume that the molar heat capacity of water is $c_V = 75.3$ J mol^{-1} K^{-1} and that it does not change within the temperature range considered here.

b) 27g of ice ($T_A = 273.15$K, system A) are mixed with 150g of water ($T_B = 353.15$K, system B) at constant volume. The container isolates perfectly and its heat capacity can be neglected.

What will be the final temperature T_E of the mixture after reaching equilibrium? Calculate the quantities

$$\Delta S_A = \frac{Q_{\text{fus}}}{T_A} + \int_{T_A}^{T_E} \frac{\delta Q_{\text{rev}}}{T} = \frac{Q_{\text{fus}}}{T_A} + \int_{T_A}^{T_E} \frac{nc_V dT}{T} \tag{3}$$

and

$$\Delta S_B = \int_{T_B}^{T_E} \frac{nc_V dT}{T} \tag{4}$$

How large is $\Delta S_{\text{tot}} = \Delta S_A + \Delta S_B$?

Problem 5 Solid-Gas Phase (20 points)

Consider molecules *coexist* in gas-solid phases (N_g gas molecules in $V_g \approx V$, and N_s solid molecules in V_s) in the system.

a) (10 points) Express N_g in terms of z_g and z_s. Here, z_g and z_s are single-molecule partition functions for the gas and solid phases, respectively. Assume the thermodynamic limit, and that gas molecules are indistinguishable while solid molecules are distinguishable.

b) (10 points) In three-dimension, regarding the gas as ideal gas, and the solid as quantum harmonic oscillators with an additive absorption energy $-\epsilon$ per molecule, calculate the number of the gas molecules.

You do not need to hand in this exercise again if you did already, but I will be discussed in the next tutorial.