CHEM 331
Physical Chemistry
Fall 2009

Problem Set 10

Problems

1. At the absolute Zero of temperature, orthoHydrogen can exist in any one of nine quantum states. Calculate the residual Entropy of orthoHydrogen at the absolute Zero of temperature if the concentrations of all the different states are equal.

2. Thermodynamic properties of Diethyl Ether $(C_2H_5)_2O$ were measured from 15K to above 300K. Data include C_p over the entire temperature range and Enthalpy changes for the phase transitions. Smoothed values of C_p and numerical integration by computer gave for the crystalline solid:

   $C_p(10K) = 1.925$ Joule/K mol

   (The Debye Law holds well at 10K for Diethyl Ether.)

   Other data for the solid include:

   $\int_{10K}^{T_m} \frac{C_p^o}{T} dT$ 105.4 Joule/K mol

   and for the liquid:

   $\int_{T_m}^{T_2} \frac{C_p^o}{T} dT = 101.7$ Joule/K mol

   Phase transition data is:

   $\Delta H_{fus}(T_m, P^o) = 7190$ Joule/mol $\quad T_m = 156.92$ K

   $\Delta H_{vap}(T_2, P^*) = 27090$ Joule/mol $\quad P^* = 71770 \text{ Nm}^{-2}$

   (P^* is the equilibrium vapor pressure at T_2).

   Calculate $S^o(T)$ for the Liquid and Gas at 298K. (P^o = 1 barr)

3. If a tension *t* is applied to a one-dimensional body, the length *L* of the body will change. The Work associated with the tension is given by:

   $\delta W = tdL$

If an electric field ***E*** is applied to a material, a polarization *p* results, and the work associated is:

$$\delta W = \mathbf{E}dp$$

Under combined tension and electric field, the Internal Energy can be written as:

$$dU = TdS - PdV + \delta W_a$$

$$= TdS - PdV + tdL + \mathbf{E}dp$$

Provide a Legendre Transform of U into G, the Gibbs Free Energy, such that G is a function of intensive variables. Then write dG. Finally, show that:

$$\left(\frac{\partial L}{\partial \boldsymbol{E}}\right)_{T,P,t} = \left(\frac{\partial p}{\partial t}\right)_{T,P,\boldsymbol{E}}$$

This last relationship is important for pizoelectric materials.

4. At 25^{o}C calculate the value of ΔA for an isothermal expansion of one mole of an Ideal Gas from 10L to 40L.

5. Starting with:

$$C_p - C_v = \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]\left(\frac{\partial V}{\partial T}\right)_P$$

show that:

$$C_p - C_v = \frac{TV\alpha^2}{\kappa}$$

6. Starting with:

$$\left(\frac{\partial U}{\partial V}\right)_T = \left(\frac{\partial (A+TS)}{\partial V}\right)_T$$

show that:

$$\left(\frac{\partial U}{\partial V}\right)_T = -P + \frac{T\alpha}{\kappa}$$

Show that for a van der Waals gas:

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{a}{V^2}$$