CHEM 331
Physical Chemistry
Fall 2010

Problem Set 9

Problems

1. The temperature of one mole of an Ideal Gas in increased from 100K to 300K; $C_v = 3/2R$.

   a) Calculate ΔS if the volume is constant.
   b) Calculate ΔS if the pressure is constant.

2. One mole of a van der Waals Gas at 27^oC expands isothermally and reversibly from $0.020\ m^3$ to $0.060\ m^3$. For the van der Waals gas:

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

   with $a = 0.556$ Pa m^6/mol^2 and $b = 64 \times 10^{-6}\ m^3/mol$. Calculate ΔS for the transformation.

3. Caculate the Standard Molar Entropy for Ethane gas at 500K; $S^o(500K)$. Also, calculate S(500K) at 40 Torr.

   Data:
   $S^o(298.15) = 229.60$ Joule/K mol.
   $C_p^o = 9.404 + (159.836 \times 10^{-3})\ T + (-426.28 \times 10^{-7})\ T^2$ Joule/K mol

   [Ans. 263.29 J/K mol, 287.66 J/K mol]

4. Calculate the Molar Entropy of $CO_2(g)$ at 298.15K at 1 atm and 100 atm. For the Eq. of State, use the Virial Equation truncated at the 2nd Virial Coefficient. (van der Waals constants available in a previous handout.)

   The Standard Entropy of a Gas is defined as:

$$S^o(T) = \lim_{P'\to 0}\left[S(T,P') - R\ln\left(\frac{P^o}{P'}\right)\right] = S_{Ideal}(T,P^o)$$

5. For liquid Ethanol at 25^oC:

   $M = 46.07$ g/mol
   $\rho = 0.785\ g/cm^3$
   $\alpha = 1.18 \times 10^{-3}\ K^{-1}$
   $S^o = 160.7$ Joule/K mol

Calculate S(298.15, 100 atm) and $\left(\frac{\partial S}{\partial P}\right)_T$ for liquid Ethanol.

6. 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.

7. 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 $\quad P^* = 71770\ Nm^{-2}$

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

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

8. Compute the entropy of mixing in producing a mole of Methane-Helium mixture that is 75% Helium at 298K and 101.3 kPa.