Chemistry 311

Physical Chemistry

Homework Assignment # 4

Due: Monday, October 11, 2004

1. The following data are given for chloroform ($CHCl_3$). Calculate its absolute entropy at 1 bar and 500 K.

$S°$ at 10 K (J K^{-1} mol^{-1})	1.142
$C_{P,m}$ of solid phase (J K^{-1} mol^{-1})	52.34
$\Delta_{fus}H°$ (kJ K^{-1} mol^{-1})	8.8 at 210.2 K
$C_{P,m}$ of liquid phase (J K^{-1} mol^{-1})	114.25
$\Delta_{vap}H°$ (kJ K^{-1} mol^{-1})	31.4 at 334.3 K
$C_{P,m}$ of gas phase (J K^{-1} mol^{-1})	$44.24 + 114.67\times10^{-3}T - 5.228\times10^{5}/T^2$

2. The area of a rectangle may be considered a function of the breadth, b, and the length l, since $a = bl$. Then, b and l are considered independent variables and a is the dependent variable. Other possible dependent variables are the perimeter $p = 2b + 2l$, and the diagonal, $d = \sqrt{b^2 + l^2}$. Evaluate the following partial derivatives in terms of b and l, or obtain a numerical answer:

(i) $\left(\frac{\partial a}{\partial l}\right)_b$, (ii) $\left(\frac{\partial p}{\partial l}\right)_b$, (iii) $\left(\frac{\partial l}{\partial b}\right)_d$, (iv) $\left(\frac{\partial l}{\partial b}\right)_p$.

3. Starting from Eq. (3-126), and making use of Eq. (C-11), show that

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

where α and κ are, respectively, the cubic expansion coefficient and the isothermal compressibility.

4. A gas obeys the equation of state

$$\left(P - \frac{a}{V_m}\right)V_m = RT.$$

Evaluate the fugacity of the gas at 500 K and 20 bar, if a = 0.786 L bar.