# Chem 531: Problem Set #6

Due in class: Thurs, October 26th

**(1)** For $CH_4$ at –50ºC, measured $\bar{V}$ values as a function of $P$ are

| $\bar{V}$ (in cm$^3$/mol) | 18224 | 1743 | 828 | 366 |
|---|---|---|---|---|
| P (in atm) | 1 | 10 | 20 | 40 |

| $\bar{V}$ (in cm$^3$/mol) | 207 | 128.7 | 91.4 | 76.3 |
|---|---|---|---|---|
| P (in atm) | 60 | 80 | 100 | 120 |

Find the fugacity and fugacity coefficient of $CH_4$ at –50ºC and 120 atm (Hint: use the above data in a polynomial fit of (Z–1)/P ). Please show all work (including plots).

**(2)** When two phases are in equilibrium, their chemical potentials are equal (for fixed $T$ and $P$).

**(a)** Show that as the temperature is varied at constant $P$ from the transition temperature by $\Delta T$, the difference in chemical potentials between the two phases is equal to $-\Delta\bar{S}\Delta T$ . Where $\Delta\bar{S}$ is the difference in molar entropies of the two phases. Assume the molar entropies are independent of $T$.

**(b)** then by what amount does the chemical potential of water exceed that of ice at –5.00º C ?

**(c)** likewise by what amount does the chemical potential of water exceed that of steam at 105.00º C?

**(3)** Carbon tetrachloride melts at 250 K. The vapor pressure of the liquid is 10,539 Pa at 290 K and 74,518 Pa at 340 K. The vapor pressure of the solid is 270 Pa at 232 K and 1092 Pa at 250 K.

**(a)** Calculate $\Delta H_{vap}$ and $\Delta H_{sub}$

**(b)** Calculate $\Delta H_{fus}$

**(c)** Calculate the <u>normal</u> boiling point and $\Delta S_{vap}$ at the boiling point

**(4)** The normal melting point of $H_2O$ is 273.15 K and $\Delta H_{fus}$ = 6008 J/mol. Calculate the decrease in the normal freezing point at 500 bar assuming that the densities of the liquid and solid phases remain constant at 997 and 917 kg $m^{-3}$, respectively.

**(5)** Using the integrated forms of the Clapeyron and Clausius-Clapeyron equations, construct the

**(a)** solid-liquid

**(b)** solid-gas

**(c)** liquid-gas

portions of the phase boundaries for pure benzene around its triple point ($P_{trip}$=36 torr and $T_{trip}$=278.5 K) by calculating the changes in pressure when the temperature is raised and/or lowered by 2 K around $T_{trip}$. For benzene, $\Delta H_{fus}$=10.6 kJ/mol, $\Delta H_{vap}$=30.8 kJ/mol, $\Delta H_{sub}$=41.4 kJ/mol, $\rho$(s)=0.891 g/cm$^3$, and $\rho$(l)=0.879 g/cm$^3$.