Homework #8
Problems (#41-#55)

41. ✶E&R P7.7 **(for only 150 bar, and 550 bar)**
For a gas at a given temperature, the compression factor is described by the empirical equation:

$$z = 1 - 8.50\times10^{-3}\frac{P}{P^0} + 3.50\times10^{-5}\left(\frac{P}{P^0}\right)^2$$

where P°=1bar. . Calculate the fugacity coefficient for P=150., 250., 350., 450., and 550. bar. For which of these values is the fugacity coefficient greater than 1 ?

42. *(adapted from Physical Chemistry by Tinoco, Sauer, Wang, and Puglisi, pub by Prentice-Hall)* In living biological cells the sodium ion concentration inside the cell $[Na^+]_i$ is kept at a lower concentration than that outside $[Na^+]_o$ by an active transport pump powered by ATP hydrolysis. The mechanism of the pump requires that each mol of ATP discharge 3 moles of Na^+. In the following questions assume that T=310K (37C).

   a. For Na^+ (inside, 0.05M) → Na^+ (outside, 0.20M) calculate $\Delta\mu$ approximating the ion activities by their molarity. Will the reaction proceed spontaneously?

   b. What would be ΔG for 3 pumping moles of Na^+ at these concentrations?

   c. What is $\Delta\mu$ if the $[Na^+]_i=[Na^+]_o$?

   d. ***(optional)**
   For the reaction:
   $ATP + H_2O \rightarrow ADP + \text{phosphate}$ $\quad \Delta\mu° = -31.3$ kJ mol^{-1} at 1 atm, 310 K
   For [ADP]/[ATP] = 0.10 , what would be the phosphate concentration [P] required to yield $\Delta\mu = -40$ kJ mol^{-1} ? (assume activity coefficients are unity)

   e. ***(optional)** Would the free energy of hydrolysis of 1 mole of ATP under the conditions of part d, be sufficient to account for the transport of Na^+ in part b?

43. For the reaction $3H_2(g) + N_2(g) \rightleftarrows 2NH_3(g)$ the gaseous species have the following fugacity coefficients: $\gamma_{H_2} = 1.11 \quad \gamma_{N_2} = 1.04 \quad \gamma_{NH_3} = 0.968$.
If $\Delta\bar{G}_f^0\left(NH_3\right) = -16.5\times10^3\ J\ mol^{-1}\ at\ 298.15K$ what is P_{N_2} in an equilibrium mixture where $P_{H_2} = 10^{-1}\ bar\ and\ P_{NH_3} = 1\ bar$?

44. [Adapted from Raff #6.1, p282]
At 298K $\mu_f^0 = 7.2\ kJ\ mol^{-1}\ and\ S^0 = 39.55\ J\ mol^{-1}\ for\ Al(\ell)$. Using the data for Al(s) in Appendix A, calculate the melting temperature of Al(s) at P=1 bar. Assume that the difference in entropies of Al(s) and Al(ℓ) is a constant, equal to the value at 298K. Compare your result to the experimental value in Table 2.3 (p. 555) E&R.

45. E&R P8.5
Within what range can you restrict the values of P and T if the following information is known about CO_2? Use Figure 8.12 to answer this question.
NOTE: The critical point is at T_c=31.1°C and P_c= 72.8 atm.
   a. As the temperature is increased, the solid is first converted to the liquid and subsequently to the gaseous state.
   b. An interface delineating liquid and gaseous phases is observed throughout the pressure range between 6 and 65 atm.
   c. Solid, liquid, and gas phases coexist at equilibrium.
   d. Only a liquid phase is observed in the pressure range from 10. to 50. atm.
   e. An increase in temperature from -80.° to 20.°C converts a solid to a gas with no intermediate liquid phase.

46. E&R P8.14
You have collected a tissue specimen that you would like to preserve by freeze drying. To ensure the integrity of the specimen, the temperature should not exceed –5.00 °C . The vapor pressure of ice at 273.16 K is 624 Pa. (at the temperatures $\Delta \boldsymbol{H}^0_{fusion} = 6.004\, \boldsymbol{kJ\ mol}^{-1}$ and $\Delta \boldsymbol{H}^0_{vaporization} = 40.054\, \boldsymbol{kJ\ mol}^{-1}$)
What is the maximum pressure at which the freeze drying can be carried out?

47.★(optional) E&R P8.21 (**b part only**);
Benzene (ℓ) has a vapor pressure of 0.1269 bar at 298.15 K and an enthalpy of vaporization of 30.72 kJ mol $^{-1}$.The $\overline{\boldsymbol{C}}_{\boldsymbol{P}}$ of the vapor and liquid phases at that temperature are 82.4 and 136.0 J K^{-1}, respectively. Calculate the vapor pressure of $C_6H_6(\ell)$ at 340.0 K assuming
   a. ~~that the enthalpy of vaporization does not change with temperature.~~
   b. that the enthalpy of vaporization at temperature T can be calculated from the equation $\Delta \boldsymbol{H}_{vaporization}(\boldsymbol{T}) = \Delta \boldsymbol{H}_{vaporization}(\boldsymbol{T}_0) + \Delta \boldsymbol{C}_p\left(\boldsymbol{T} - \boldsymbol{T}_0\right)$ assuming that ΔC_P does not change with temperature.

48. [Adapted from Raff #6.28, p285]
Two crystalline forms, A and B, of a compound are in equilibrium. The density of A is greater than the density of B. The conversion of A to B is exothermic.
   a. If one wishes to shift the equilibrium towards crystal B, should one raise or lower the temperature? Should one raise or lower the pressure? Explain
   b. Which is more ordered, A or B? Explain.

49. E&R P8.24
The vapor pressure of an unknown solid is given by,
$\ln\left(P_{VP\ of\ solid}/Torr\right) = 22.413 - 2211\left(K/T\right)$, and the vapor pressure of the liquid phase of the same substance is approximately given by
$\ln\left(P_{VP\ of\ LIQUID}/Torr\right) = 18.352 - 1736\left(K/T\right)$.
   a. Calculate $\Delta H_{vaporization}$ and $\Delta H_{sublimation}$.
   b. Calculate ΔH_{fusion}.
   c. Calculate the triple point temperature and pressure

50. E&R P9.19
A and B form an ideal solution. At a total pressure of 0.720 bar, $y_A = 0.510$ *and* $x_A = 0.420$. Using this information, calculate the vapor pressure of pure A and of pure B.

51.★(optional) [adapted from Raff #8.3, p403]

A and B form an ideal solution.
   a. Derive an equation in terms of $P_A^\bullet$ *and* $P_B^\bullet$ that gives the mole fraction $X_A^{(\ell)}$ at which $P_A=P_B$.
   b. Show that the total pressure, P_T, over a solution with $P_A=P_B$ is

$$P_T = \frac{2P_A^\bullet P_B^\bullet}{P_A^\bullet + P_B^\bullet}$$

52. E&R P9.25
Use the data in this problem
A solution is prepared by dissolving 45.2 g of a non-volatile solute in 119 g of water. The vapor pressure above the solution is 22.51Torr and the vapor pressure of pure water is 23.76 Torr at this temperature.
but do the calculations for
   a. Calculate molecular weight from data in problem assuming the non-volatile solute was a molecular solute (as in text).
   b. What would be the molecular weight if the solute was an ionic salt $M^{2+}(X^-)_2$ and was completely dissociated?

53. [Adapted from Raff #8.13]
Seventy-five grams of CCl_4 are mixed with 10 grams of $CHCl_3$ at 298K to form a solution. If the solution is ideal, calculate ΔG_{mixing}, ΔS_{mixing}, ΔH_{mixing}, ΔU_{mixing}, ΔV_{mixing}, and ΔA_{mixing}.

54.★(optional) Prove that for a mixture of two substances A and B, the maximum entropy of mixing occurs for $X_A = 0.5$.

55. E&R P 9.15 ***(part a only)***