

Homework #7
Problems (#41-#55)

Section Questions: Q8.5, Q8.9, Q8.17(typo in text), Q9.13

41. ***** (optional) E&R_{4th} P7.13 (for only 100 bar, and 500 bar)
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).
- For Na^+ (inside, 0.05M) \rightarrow Na^+ (outside, 0.20M) calculate $\Delta\mu$ approximating the ion activities by their molarity. Will the reaction proceed spontaneously?
 - What would be ΔG for 3 pumping moles of Na^+ at these concentrations?
 - What is $\Delta\mu$ if the $[Na^+]_i=[Na^+]_o$?
 - *(optional)**
For the reaction:
 $ATP + H_2O \rightarrow ADP + \text{phosphate}$ $\Delta\mu^\circ = -31.3 \text{ kJ mol}^{-1}$ at 1 atm, 310 K
 For $[ADP]/[ATP] = 0.10$, what would be the phosphate concentration $[P]$ required to yield $\Delta\mu = -40 \text{ kJ mol}^{-1}$? (assume activity coefficients are unity)
 - *(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 $3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g)$ the gaseous species have the following fugacity coefficients: $\gamma_{H_2} = 1.11$ $\gamma_{N_2} = 1.04$ $\gamma_{NH_3} = 0.968$.
 If $\Delta\bar{G}_f^0(NH_3) = -16.5 \times 10^3 \text{ J mol}^{-1}$ at 298.15K what is P_{N_2} in an equilibrium mixture where $P_{H_2} = 10^{-1} \text{ bar}$ and $P_{NH_3} = 1 \text{ bar}$?
44. [Adapted from Raff #6.1, p282]
 At 298K $\mu_f^0 = 7.2 \text{ kJ mol}^{-1}$ and $S^0 = 39.55 \text{ J mol}^{-1}$ for $Al(\ell)$. Using the data for $Al(s)$ in Appendix A, calculate the melting temperature of $Al(s)$ at $P=1 \text{ bar}$. Assume that the difference in entropies of $Al(s)$ and $Al(\ell)$ is a constant, equal to the value at 298K. Compare your result to the experimental value in Table 2.3 (p. 627) E&R_{4th}.
45. E&R_{4th} P8.1
NOTE: The critical point is at $T_c=31.1^\circ\text{C}$ and $P_c= 72.8 \text{ atm}$.
 for part b :
 b. As pressure on a cylinder containing pure CO_2 is increased from 5 to 80. atm, no interface delineating liquid and gaseous phases is observed. (note the 5 atm here differs from E&R_{4th} USE THIS VALUE, it makes more sense)

46. E&R_{4th} P8.21

47. ★(optional) E&R_{4th} P8.26 (b part only);

Note: the text's equation: $\Delta H_{sub}(T) = \Delta H_{sub}(T_0) + \Delta C_p (T - T_0)$

should be $\Delta H_{vaporization}(T) = \Delta H_{vaporization}(T_0) + \Delta C_p (T - T_0)$

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.

- 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
- Which is more ordered, A or B? Explain.

49. E&R_{4th} P8.28

50. E&R_{4th} P9.6

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

A and B form an ideal solution.

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

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

52. E&R_{4th} P9.8

Use the data in this problem

A solution is prepared by dissolving 54.0 g of a non-volatile solute in 150 g of water. The vapor pressure above the solution is 22.97 Torr and the vapor pressure of pure water is 23.76 Torr at this temperature.

but do the calculations for

- Calculate molecular mass from data in problem assuming the non-volatile solute was a molecular solute (as in text).
- What would be the molecular mass 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_{4th} P 9.29 (**part a only**)