

Homework #7 Problems (#41-#55)

41. ***E&R P7.7 (for only 150 bar, and 550 bar)** [numbers different than 2nd ed]
For a gas at a given temperature, the compression factor is described by the empirical equation:
- $$z = 1 - 8.50 \times 10^{-3} \frac{P}{P^0} + 3.50 \times 10^{-5} \left(\frac{P}{P^0} \right)^2$$
- where $P^0=1\text{bar}$. . 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 $[\text{Na}^+]_i$ is kept at a lower concentration than that outside $[\text{Na}^+]_o$ 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 $T=310\text{K}$ (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 $[\text{Na}^+]_i=[\text{Na}^+]_o$?
 - *(optional)**
For the reaction:
 $\text{ATP} + \text{H}_2\text{O} \rightarrow \text{ADP} + \text{phosphate}$ $\Delta\mu^\circ = -31.3 \text{ kJ mol}^{-1}$ at 1 atm, 310 K
For $[\text{ADP}]/[\text{ATP}] = 0.10$, what would be the phosphate concentration $[\text{P}]$ 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 $3\text{H}_2(\text{g}) + \text{N}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$ the gaseous species have the following fugacity coefficients: $\gamma_{\text{H}_2} = 1.11$ $\gamma_{\text{N}_2} = 1.04$ $\gamma_{\text{NH}_3} = 0.968$.
If $\Delta\bar{G}_f^\circ(\text{NH}_3) = -16.5 \times 10^3 \text{ J mol}^{-1}$ at 298.15K what is P_{N_2} in an equilibrium mixture where $P_{\text{H}_2} = 10^{-1} \text{ bar}$ and $P_{\text{NH}_3} = 1 \text{ bar}$?
44. [Adapted from Raff #6.1, p282]
At 298K $\mu_f^\circ = 7.2 \text{ kJ mol}^{-1}$ and $S^\circ = 39.55 \text{ J mol}^{-1}$ for $\text{Al}(\ell)$. Using the data for $\text{Al}(\text{s})$ in Appendix A, calculate the melting temperature of $\text{Al}(\text{s})$ at $P=1 \text{ bar}$. Assume that the difference in entropies of $\text{Al}(\text{s})$ and $\text{Al}(\ell)$ is a constant, equal to the value at 298K. Compare your result to the experimental value in Table 2.3 (p. 555) [Table 2.2 (p 541)]_{2nd} E&R.

45. E&R P8.5 [Parts (b) and (d) differ from 2nd ed]
 Within what range can you restrict the values of P and T if the following information is known about CO₂? Use Figure 8.12 [Figure 8.10 2nd ed] to answer this question.
 NOTE: The critical point is at T_c=31.1°C and P_c= 72.8 atm.
- As the temperature is increased, the solid is first converted to the liquid and subsequently to the gaseous state.
 - An interface delineating liquid and gaseous phases is observed throughout the pressure range between 6 and 65 atm.
 - Solid, liquid, and gas phases coexist at equilibrium.
 - Only a liquid phase is observed in the pressure range from 10. to 50. atm.
 - 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 [numbers differ from 2nd ed]
 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 $\Delta H_{fusion}^0 = 6.004 \text{ kJ mol}^{-1}$ and $\Delta H_{vaporization}^0 = 40.054 \text{ kJ mol}^{-1}$)
 What is the maximum pressure at which the freeze drying can be carried out?
47. ★(optional) E&R P8.21 (b part only); [differs from 2nd ed]
 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 \bar{C}_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 C₆H₆(ℓ) at 340.0 K assuming
- ~~that the enthalpy of vaporization does not change with temperature.~~
 - that the enthalpy of vaporization at temperature T can be calculated from the equation $\Delta H_{vaporization}(T) = \Delta H_{vaporization}(T_0) + \Delta C_p(T - T_0)$ 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.
- 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 P8.24 [numbers differ from 2
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The vapor pressure of an unknown solid is given by,

$$\ln\left(\frac{P_{VP\ of\ solid}}{Torr}\right) = 22.413 - 2211\left(\frac{K}{T}\right),$$

and the vapor pressure of the liquid phase of the same substance is approximately given by

$$\ln\left(\frac{P_{VP\ of\ LIQUID}}{Torr}\right) = 18.352 - 1736\left(\frac{K}{T}\right).$$

- Calculate $\Delta H_{\text{vaporization}}$ and $\Delta H_{\text{sublimation}}$.
 - Calculate ΔH_{fusion} .
 - Calculate the triple point temperature and pressure
50. E&R P9.19 [numbers differ from 2nd ed]
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.

- 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

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

52. E&R P9.25 [numbers differ from 2
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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 22.51 Torr and the vapor pressure of pure water is 23.76 Torr at this temperature.

but do the calculations for

- Calculate molecular weight from data in problem assuming the non-volatile solute was a molecular solute (as in text).
 - 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**) [same as 2nd ed]