

12.11: Chapter 12 Problems

An underlined problem number or problem-part letter indicates that the numerical answer appears in Appendix I.

12.1

Consider the heterogeneous equilibrium $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$. Table 12.3 lists pressures measured over a range of temperatures for this system.

12.14

The method described in Prob. 12.13 has been used to obtain high-precision values of the Henry's law constant, $k_{\text{H,B}}$, for gaseous methane dissolved in water (Timothy R. Rettich, Y. Paul Handa, Ruben Battino, and Emmerich Wilhelm, *J. Phys. Chem.*, **85**, 3230–3237, 1981). Table 12.6 lists values of $\ln(k_{\text{H,B}}/p^\circ)$ at eleven temperatures in the range 275 K–328 K and at pressures close to 1 bar. Use these data to evaluate $\Delta_{\text{sol,B}}H^\circ$ and $\Delta_{\text{sol,B}}C_p^\circ$ at $T = 298.15$ K. This can be done by a graphical method. Better precision will be obtained by making a least-squares fit of the data to the three-term polynomial

$$\ln(k_{\text{H,B}}/p^\circ) = a + b(1/T) + c(1/T)^2$$

and using the values of the coefficients a , b , and c for the evaluations.

12.15

Liquid water and liquid benzene have very small mutual solubilities. Equilibria in the binary water–benzene system were investigated by Tucker, Lane, and Christian (*J. Solution Chem.*, **10**, 1–20, 1981) as follows. A known amount of distilled water was admitted to an evacuated, thermostatted vessel. Part of the water vaporized to form a vapor phase. Small, precisely measured volumes of liquid benzene were then added incrementally from the sample loop of a liquid-chromatography valve. The benzene distributed itself between the liquid and gaseous phases in the vessel. After each addition, the pressure was read with a precision pressure gauge. From the known amounts of water and benzene and the total pressure, the liquid composition and the partial pressure of the benzene were calculated. The fugacity of the benzene in the vapor phase was calculated from its partial pressure and the second virial coefficient.

At a fixed temperature, for mole fractions x_{B} of benzene in the liquid phase up to about 3×10^{-4} (less than the solubility of benzene in water), the fugacity of the benzene in the equilibrated gas phase was found to have the following dependence on x_{B} :

$$\frac{f_{\text{B}}}{x_{\text{B}}} = k_{\text{H,B}} - Ax_{\text{B}} \quad (12.11.1)$$

Here $k_{\text{H,B}}$ is the Henry's law constant and A is a constant related to deviations from Henry's law. At 30°C , the measured values were $k_{\text{H,B}} = 385.5$ bar and $A = 2.24 \times 10^4$ bar.

(a) Treat benzene (B) as the solute and find its activity coefficient on a mole fraction basis, $\gamma_{x,\text{B}}$, at 30°C in the solution of composition $x_{\text{B}} = 3.00 \times 10^{-4}$.

(b) The fugacity of benzene vapor in equilibrium with pure liquid benzene at 30°C is $f_{\text{B}}^* = 0.1576$ bar. Estimate the mole fraction solubility of liquid benzene in water at this temperature.

(c) The calculation of $\gamma_{x,\text{B}}$ in part (a) treated the benzene as a single solute species with deviations from infinite-dilution behavior. Tucker et al suggested a dimerization model to explain the observed negative deviations from Henry's law. (Classical thermodynamics, of course, cannot prove such a molecular interpretation of observed macroscopic behavior.) The model assumes that there are two solute species, a monomer (M) and a dimer (D), in reaction equilibrium: $2\text{M} \rightleftharpoons \text{D}$. Let n_{B} be the total amount of C_6H_6 present in solution, and define the mole fractions

$$x_{\text{B}} \stackrel{\text{def}}{=} \frac{n_{\text{B}}}{n_{\text{A}} + n_{\text{B}}} \approx \frac{n_{\text{B}}}{n_{\text{A}}} \quad (12.11.2)$$

$$x_{\text{M}} \stackrel{\text{def}}{=} \frac{n_{\text{M}}}{n_{\text{A}} + n_{\text{M}} + n_{\text{D}}} \approx \frac{n_{\text{M}}}{n_{\text{A}}} \quad x_{\text{D}} \stackrel{\text{def}}{=} \frac{n_{\text{D}}}{n_{\text{A}} + n_{\text{M}} + n_{\text{D}}} \approx \frac{n_{\text{D}}}{n_{\text{A}}} \quad (12.11.3)$$

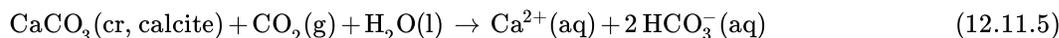
where the approximations are for dilute solution. In the model, the individual monomer and dimer particles behave as solutes in an ideal-dilute solution, with activity coefficients of unity. The monomer is in transfer equilibrium with the gas phase: $x_{\text{M}} = f_{\text{B}}/k_{\text{H,B}}$. The equilibrium constant expression (using a mole fraction basis for the solute standard states and setting pressure factors equal to 1) is $K = x_{\text{D}}/x_{\text{M}}^2$. From the relation $n_{\text{B}} = n_{\text{M}} + 2n_{\text{D}}$, and because the solution is very dilute, the expression becomes

$$K = \frac{x_B - x_M}{2x_M^2} \quad (12.11.4)$$

Make individual calculations of K from the values of f_B measured at $x_B = 1.00 \times 10^{-4}$, $x_B = 2.00 \times 10^{-4}$, and $x_B = 3.00 \times 10^{-4}$. Extrapolate the calculated values of K to $x_B = 0$ in order to eliminate nonideal effects such as higher aggregates. Finally, find the fraction of the benzene molecules present in the dimer form at $x_B = 3.00 \times 10^{-4}$ if this model is correct.

12.16

Use data in Appendix H to evaluate the thermodynamic equilibrium constant at 298.15 K for the limestone reaction



12.17

For the dissociation equilibrium of formic acid, $\text{HCO}_2\text{H}(\text{aq}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{HCO}_2^-(\text{aq})$, the acid dissociation constant at 298.15 K has the value $K_a = 1.77 \times 10^{-4}$.

(a) Use Eq. 12.9.7 to find the degree of dissociation and the hydrogen ion molality in a 0.01000 molal formic acid solution. You can safely set Γ_{\pm} and $\gamma_{m,\text{HA}}$ equal to 1, and use the Debye–Hückel limiting law (Eq. 10.4.8) to calculate γ_{\pm} . You can do this calculation by iteration: Start with an initial estimate of the ionic strength (in this case 0), calculate γ_{\pm} and α , and repeat these steps until the value of α no longer changes.

(b) Estimate the degree of dissociation of formic acid in a solution that is 0.01000 molal in both formic acid and sodium nitrate, again using the Debye–Hückel limiting law for γ_{\pm} . Compare with the value in part (a).

12.18

Use the following experimental information to evaluate the standard molar enthalpy of formation and the standard molar entropy of the aqueous chloride ion at 298.15 K, based on the conventions $\Delta_f H^\circ(\text{H}^+, \text{aq}) = 0$ and $S_m^\circ(\text{H}^+, \text{aq}) = 0$ (Secs. 11.3.2 and 11.8.4). (Your calculated values will be close to, but not exactly the same as, those listed in Appendix H, which are based on the same data combined with data of other workers.)

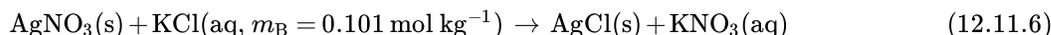
• 12.19

The solubility of crystalline AgCl in ultrapure water has been determined from the electrical conductivity of the saturated solution (J. A. Gledhill and G. McP. Malan, *Trans. Faraday Soc.*, **48**, 258–262, 1952). The average of five measurements at 298.15 K is $s_B = 1.337 \times 10^{-5} \text{ mol dm}^{-3}$. The density of water at this temperature is $\rho_A^* = 0.9970 \text{ kg dm}^{-3}$.

(a) From these data and the Debye–Hückel limiting law, calculate the solubility product K_s of AgCl at 298.15 K

12.20

The following reaction was carried out in an adiabatic solution calorimeter by Wagman and Kilday (*J. Res. Natl. Bur. Stand. (U.S.)*, **77A**, 569–579, 1973):



The reaction can be assumed to go to completion, and the amount of KCl was in slight excess, so the amount of AgCl formed was equal to the initial amount of AgNO₃. After correction for the enthalpies of diluting the solutes in the initial and final solutions to infinite dilution, the standard molar reaction enthalpy at 298.15 K was found to be $\Delta_r H^\circ = -43.042 \text{ kJ mol}^{-1}$. The same workers used solution calorimetry to obtain the molar enthalpy of solution at infinite dilution of crystalline AgNO₃ at 298.15 K: $\Delta_{\text{sol,B}} H^\infty = 22.727 \text{ kJ mol}^{-1}$.

(a) Show that the difference of these two values is the standard molar reaction enthalpy for the precipitation reaction



and evaluate this quantity.

(b) Evaluate the standard molar enthalpy of formation of aqueous Ag⁺ ion at 298.15 K, using the results of part (a) and the values $\Delta_f H^\circ(\text{Cl}^-, \text{aq}) = -167.08 \text{ kJ mol}^{-1}$ and $\Delta_f H^\circ(\text{AgCl, s}) = -127.01 \text{ kJ mol}^{-1}$ from Appendix H. (These values come from calculations similar to those in Probs. 12.18 and 14.4.) The calculated value will be close to, but not exactly the same as, the value listed in Appendix H, which is based on the same data combined with data of other workers.

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