Problems

Concentration Units

7.1 How many grams of water must be added to 20.0 g of urea to prepare a 5.00% aqueous urea solution by weight?

7.2 What is the molarity of a 2.12 mol kg^{-1} aqueous sulfuric acid solution? The density of this solution is 1.30 g cm^{-3}.

7.3 Calculate the molality of a 1.50 M aqueous ethanol solution. The density of the solution is 0.980 g cm^{-3}.

7.4 The concentrated sulfuric acid we use in the laboratory is 98.0% sulfuric acid by weight. Calculate the molality and molarity of concentrated sulfuric acid if the density of the solution is 1.83 g cm^{-3}.

7.5 Convert a 0.25 mol kg^{-1} sucrose solution into percent by weight. The density of the solution is 1.2 g cm^{-3}.

7.6 For dilute aqueous solutions in which the density of the solution is roughly equal to that of the pure solvent, the molarity of the solution is equal to its molality. Show that this statement is correct for a 0.010 M aqueous urea $[(NH_2)_2CO]$ solution.

7.7 The blood sugar (glucose) level of a diabetic patient is approximately 0.140 g of glucose/100 mL of blood. Every time the patient ingests 40 g of glucose, her blood glucose level rises to approximately 0.240 g/100 mL of blood. Calculate the number of moles of glucose per milliliter of blood and the total number of moles and grams of glucose in the blood before and after consumption of glucose. (Assume that the total volume of blood in her body is 5.0 L.)

7.8 The strength of alcoholic beverages is usually described in terms of "proof," which is defined as twice the percentage by volume of ethanol. Calculate the number of grams of alcohol in 2 quarts of 75-proof gin. What is the molality of the gin? (The density of ethanol is 0.80 g cm^{-3}; 1 quart = 0.946 L.)

Thermodynamics of Mixing

7.9 Liquids A and B form a nonideal solution. Provide a molecular interpretation for each of the following situations: $\Delta_{\text{mix}}H > 0$, $\Delta_{\text{mix}}H < 0$, $\Delta_{\text{mix}}V > 0$, $\Delta_{\text{mix}}V < 0$.

7.10 Calculate the changes in entropy for the following processes: **(a)** mixing of 1 mole of nitrogen and 1 mole of oxygen, and **(b)** mixing of 2 moles of argon, 1 mole of helium, and 3 moles of hydrogen. Both **(a)** and **(b)** are carried out under conditions of constant temperature (298 K) and constant pressure. Assume ideal behavior.

7.11 At 25 °C and 1 atm pressure, the absolute third-law entropies of methane and ethane are 186.19 J K^{-1} mol^{-1} and 229.49 J K^{-1} mol^{-1}, respectively, in the gas phase. Calculate the absolute third-law entropy of a "solution" containing 1 mole of each gas. Assume ideal behavior.

Henry's Law

7.12 Prove the statement that an alternative way to express Henry's law of gas solubility is to say that the volume of gas that dissolves in a fixed volume of solution is independent of pressure at a given temperature.

7.13 A miner working 900 ft below the surface had a soft drink beverage during the lunch break. To his surprise, the drink seemed very flat (that is, not much effervescence was observed upon removing the cap). Shortly after lunch, he took the elevator up to the surface. During the trip up, he felt a great urge to belch. Explain.

7.14 The Henry's law constant of oxygen in water at 25 °C is 773 atm mol^{-1} kg of water. Calculate the molality of oxygen in water under a partial pressure of 0.20 atm. Assuming that the solubility of oxygen in blood at 37 °C is roughly the same as that in water at 25 °C, comment on the prospect for our survival without hemoglobin molecules. (The total volume of blood in the human body is about 5 L.)

7.15 The solubility of N_2 in blood at 37 °C and a partial pressure of 0.80 atm is 5.6×10^{-4} mol L^{-1}. A deep-sea diver breathes compressed air with a partial pressure of N_2 equal to 4.0 atm. Assume that the total volume of blood in the body is 5.0 L. Calculate the amount of N_2 gas released (in liters) when the diver returns to the surface of water, where the partial pressure of N_2 is 0.80 atm.

Chemical Potential and Activity

7.16 Which of the following has a higher chemical potential? If neither, answer "same." **(a)** $H_2O(s)$ or $H_2O(l)$ at water's normal melting point, **(b)** $H_2O(s)$ at −5 °C and 1 bar or $H_2O(l)$ at −5 °C and 1 bar, **(c)** benzene at 25 °C and 1 bar or benzene in a 0.1 *M* toluene solution in benzene at 25 °C and 1 bar.

7.17 A solution of ethanol and *n*-propanol behaves ideally. Calculate the chemical potential of ethanol in solution relative to that of pure ethanol when its mole fraction is 0.40 at its boiling point (78.3 °C).

7.18 Derive the phase rule (Equation 6.23) in terms of chemical potentials.

7.19 The following data give the pressures for carbon disulfide–acetone solutions at 35.2 °C. Calculate the activity coefficients of both components based on deviations from Raoult's law and Henry's law. (*Hint:* First determine Henry's law constants graphically.)

x_{CS_2}	0	0.20	0.45	0.67	0.83	1.00
P_{CS_2}/torr	0	272	390	438	465	512
$P_{C_3H_6O}$/torr	344	291	250	217	180	0

7.20 A solution is made up by dissolving 73 g of glucose ($C_6H_{12}O_6$; molar mass 180.2 g) in 966 g of water. Calculate the activity coefficient of glucose in this solution if the solution freezes at −0.66 °C.

7.21 A certain dilute solution has an osmotic pressure of 12.2 atm at 20 °C. Calculate the difference between the chemical potential of the solvent in the solution and that of pure water. Assume that the density is the same as that of water. (*Hint:* Express the chemical potential in terms of mole fraction, x_1, and rewrite the osmotic pressure equation as $\pi V = n_2 RT$, where n_2 is the number of moles of the solute and $V = 1$ L.)

7.22 At 45 °C, the vapor pressure of water for a glucose solution in which the mole fraction of glucose is 0.080 is 65.76 mmHg. Calculate the activity and activity coefficient of the water in the solution. The vapor pressure of pure water at 45 °C is 71.88 mmHg.

7.23 Consider a binary liquid mixture A and B, where A is volatile and B is nonvolatile. The composition of the solution in terms of mole fraction is $x_A = 0.045$ and $x_B = 0.955$. The vapor pressure of A from the mixture is 5.60 mmHg, and that of pure A is 196.4 mmHg at the same temperature. Calculate the activity coefficient of A at this concentration.

Colligative Properties

7.24 List the important assumptions in the derivation of Equation 7.39.

7.25 Liquids A (bp = T_A°) and B (bp = T_B°) form an ideal solution. Predict the range of boiling points of solutions formed by mixing different amounts of A and B.

7.26 A mixture of ethanol and *n*-propanol behaves ideally at 36.4 °C. **(a)** Determine graphically the mole fraction of *n*-propanol in a mixture of ethanol and *n*-propanol that boils at 36.4 °C and 72 mmHg. **(b)** What is the total vapor pressure over the mixture at 36.4 °C when the mole fraction of *n*-propanol is 0.60? **(c)** Calculate the composition of the vapor in **(b)**. (The equilibrium vapor pressures of ethanol and *n*-propanol at 36.4 °C are 108 mmHg and 40.0 mmHg, respectively.)

7.27 Two beakers, 1 and 2, containing 50 mL of 0.10 *M* urea and 50 mL of 0.20 *M* urea, respectively, are placed under a tightly sealed bell jar at 298 K. Calculate the mole fraction of urea in the solutions at equilibrium. Assume ideal behavior. (*Hint:* Use Raoult's law and note that at equilibrium, the mole fraction of urea is the same in both solutions.)

7.28 At 298 K, the vapor pressure of pure water is 23.76 mmHg and that of seawater is 22.98 mmHg. Assuming that seawater contains only NaCl, estimate its concentration. (*Hint:* Sodium chloride is a strong electrolyte.)

7.29 Trees in cold climates may be subjected to temperatures as low as −60 °C. Estimate the concentration of an aqueous solution in the body of the tree that would remain unfrozen at this temperature. Is this a reasonable concentration? Comment on your result.

7.30 Explain why jams can be stored under atmospheric conditions for long periods of time without spoilage.

7.31 Provide a molecular interpretation for the positive and negative deviations in the boiling-point curves and the formation of azeotropes.

7.32 The freezing-point-depression measurement of benzoic acid in acetone yields a molar mass of 122 g; the same measurement in benzene gives a value of 242 g. Account for this discrepancy. (*Hint:* Consider solvent–solute and solute–solute interactions.)

7.33 A common antifreeze for car radiators is ethylene glycol, $CH_2(OH)CH_2(OH)$. How many milliliters of this substance would you add to 6.5 L of water in the radiator if the coldest day in winter is −20 °C? Would you keep this substance in the radiator in the summer to prevent the water from boiling? (The density and boiling point of ethylene glycol are 1.11 g cm^{-3} and 470 K, respectively.)

7.34 For intravenous injections, great care is taken to ensure that the concentration of solutions to be injected is comparable to that of blood plasma. Why?

7.35 The tallest trees known are the redwoods in California. Assuming the height of a redwood to be 105 m (about 350 ft), estimate the osmotic pressure required to push water up from the roots to the treetop.

7.36 A mixture of liquids A and B exhibits ideal behavior. At 84 °C, the total vapor pressure of a solution containing 1.2 moles of A and 2.3 moles of B is 331 mmHg. Upon the addition of another mole of B to the solution, the vapor pressure increases to 347 mmHg. Calculate the vapor pressures of pure A and B at 84 °C.

7.37 Fish breathe the dissolved air in water through their gills. Assuming the partial pressures of oxygen and nitrogen in air to be 0.20 atm and 0.80 atm, respectively, calculate the mole fractions of oxygen and nitrogen in water at 298 K. Comment on your results.

7.38 Liquids A (molar mass 100 g mol^{-1}) and B (molar mass 110 g mol^{-1}) form an ideal solution. At 55 °C, A has a vapor pressure of 95 mmHg and B a vapor pressure of 42 mmHg. A solution is prepared by mixing equal weights of A and B. **(a)** Calculate the mole fraction of each component in the solution. **(b)** Calculate the partial pressures of A and B over the solution at 55 °C. **(c)** Suppose that some of the vapor described in **(b)** is condensed to a liquid. Calculate the mole fraction of each component in this liquid and the vapor pressure of each component above this liquid at 55 °C.

7.39 Lysozyme extracted from chicken egg white has a molar mass of 13,930 g mol^{-1}. Exactly 0.1 g of this protein is dissolved in 50 g of water at 298 K. Calculate the vapor pressure lowering, the depression in freezing point, the elevation of boiling point, and the osmotic pressure of this solution. The vapor pressure of pure water at 298 K is 23.76 mmHg.

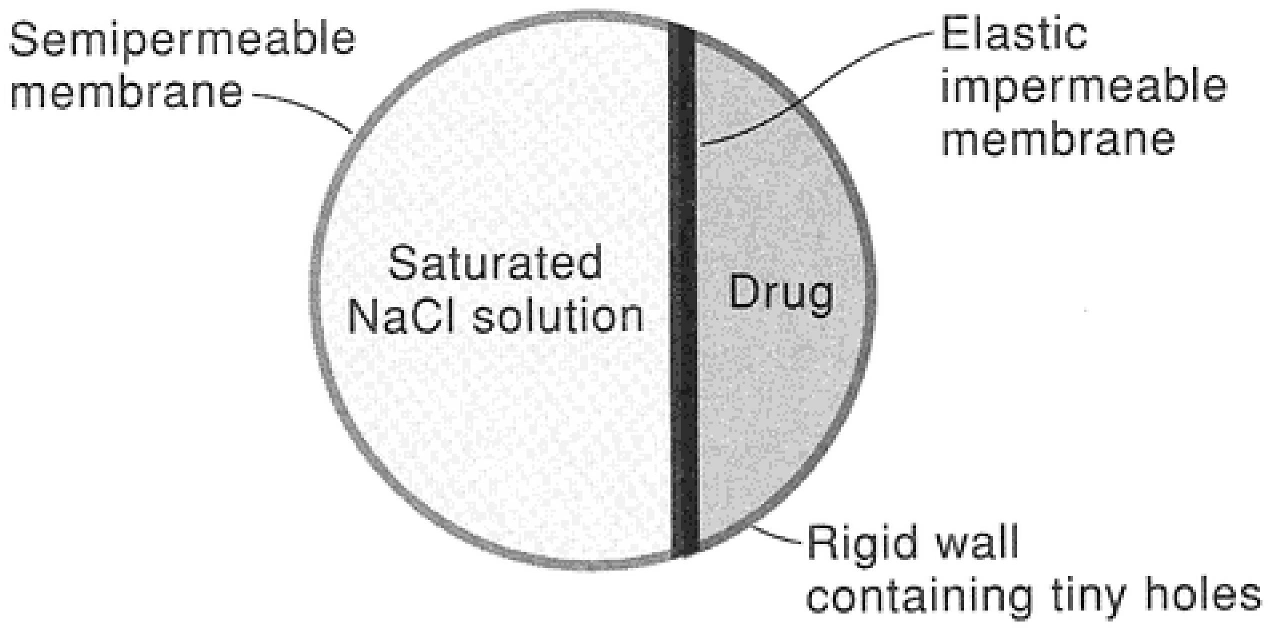
7.40 The following argument is frequently used to explain the fact that the vapor pressure of the solvent is lower over a solution than over the pure solvent and that lowering is proportional to the concentration. A dynamic equilibrium exists in both cases, so that the rate at which molecules of solvent evaporate from the liquid is always equal to that at which they condense. The rate of condensation is proportional to the partial pressure of the vapor, whereas that of evaporation is unimpaired in the pure solvent but is impaired by solute molecules in the surface of the solution. Hence the rate of escape is reduced in proportion to the concentration of the solute, and maintenance of equilibrium requires a corresponding lowering of the rate of condensation and therefore of the partial pressure of the vapor phase. Explain why this argument is incorrect. [*Source:* K. J. Mysels, *J. Chem. Educ.* **32**, 179 (1955).]

7.41 A compound weighing 0.458 g is dissolved in 30.0 g of acetic acid. The freezing point of the solution is found to be 1.50 K below that of the pure solvent. Calculate the molar mass of the compound.

7.42 Two aqueous urea solutions have osmotic pressures of 2.4 atm and 4.6 atm, respectively, at a certain temperature. What is the osmotic pressure of a solution prepared by mixing equal volumes of these two solutions at the same temperature?

7.43 A forensic chemist is given a white powder for analysis. She dissolves 0.50 g of the substance in 8.0 g of benzene. The solution freezes at 3.9 °C. Can the chemist conclude that the compound is cocaine ($C_{17}H_{21}NO_4$)? What assumptions are made in the analysis? The freezing point of benzene is 5.5 °C.

7.44 "Time-release" drugs have the advantage of releasing the drug to the body at a constant rate so that the drug concentration at any time is not high enough to have harmful side effects or so low as to be ineffective. A schematic diagram of a pill that works on this basis is shown below. Explain how it works.



7.45 A nonvolatile organic compound, Z, was used to make up two solutions. Solution A contains 5.00 g of Z dissolved in 100 g of water, and solution B contains 2.31 g of Z dissolved in 100 g of benzene. Solution A has a vapor pressure of 754.5 mmHg at the normal boiling point of water, and solution B has the same vapor pressure at the normal boiling point of benzene. Calculate the molar mass of Z in solutions A and B, and account for the difference.

7.46 Acetic acid is a polar molecule that can form hydrogen bonds with water molecules. Therefore, it has a high solubility in water. Yet acetic acid is also soluble in benzene (C_6H_6), a nonpolar solvent that lacks the ability to form hydrogen bonds. A solution of 3.8 g of CH_3COOH in 80 g C_6H_6 has a freezing point of 3.5 °C. Calculate the molar mass of the solute, and suggest what its structure might be. (*Hint:* Acetic acid molecules can form hydrogen bonds among themselves.)

7.47 At 85 °C, the vapor pressure of A is 566 torr and that of B is 250 torr. Calculate the composition of a mixture of A and B that boils at 85 °C when the pressure is 0.60 atm. Also, calculate the composition of the vapor mixture. Assume ideal behavior.

7.48 Comment on whether each of the following statements is true or false, and briefly explain your answer: **(a)** If one component of a solution obeys Raoult's law, then the other component must also obey the same law. **(b)** Intermolecular forces are small in ideal solutions. **(c)** When 15.0 mL of an aqueous 3.0 *M* ethanol solution is mixed with 55.0 mL of an aqueous 3.0 *M* ethanol solution, the total volume is 70.0 mL.

7.49 Liquids A and B form an ideal solution at a certain temperature. The vapor pressures of pure A and B are 450 torr and 732 torr, respectively, at this temperature. **(a)** A sample of the solution's vapor is condensed. Given that the original solution contains 3.3 moles of A and 8.7 moles of B, calculate the composition of the condensate in mole fractions. **(b)** Suggest a method for measuring the partial pressures of A and B at equilibrium.

7.50 Nonideal solutions are the result of unequal intermolecular forces between components. Based on this knowledge, comment on whether a racemic mixture of a liquid compound would behave as an ideal solution.

7.51 Calculate the molal boiling-point elevation constant (K_b) for water. The molar enthalpy of vaporization of water is 40.79 kJ mol^{-1} at 100 °C.

7.52 Explain the following phenomena. **(a)** A cucumber placed in concentrated brine (saltwater) shrivels into a pickle. **(b)** A carrot placed in fresh water swells in volume.

Additional Problems

7.53 Calculate the change in the Gibbs energy at 37 °C when the human kidneys secrete 0.275 mole of urea per kilogram of water from blood plasma to urine if the concentrations of urea in blood plasma and urine are 0.005 mol kg^{-1} and 0.326 mol kg^{-1}, respectively.

7.54 **(a)** Which of the following expressions is incorrect as a representation of the partial molar volume of component A in a two-component solution? Why? How would you correct it?

$$\left(\frac{\partial V_m}{\partial n_A}\right)_{T,P,n_B} \qquad \left(\frac{\partial V_m}{\partial x_A}\right)_{T,P,x_B}$$

(b) Given that the molar volume of this mixture (V_m) is given by

$$V_m = 0.34 + 3.6x_A x_B + 0.4x_B(1 - x_A)\ \text{L mol}^{-1}$$

derive an expression for the partial molar volume for A at $x_A = 0.20$.

7.55 The partial molar volumes for a benzene–carbon tetrachloride solution at 25 °C at a mole fraction of 0.5 are: $\overline{V}_b = 0.106$ L mol^{-1} and $\overline{V}_c = 0.100$ L mol^{-1}, respectively, where the subscripts b and c denote C_6H_6 and CCl_4. **(a)** What is the volume of a solution made up of one mole of each? **(b)** Given that the molar volumes are: $C_6H_6 = 0.089$ L mol^{-1} and $CCl_4 =$ 0.097 L mol^{-1}, what is the change in volume on mixing 1 mole each of C_6H_6 and CCl_4? **(c)** What can you deduce about the nature of intermolecular forces between C_6H_6 and CCl_4?

7.56 The osmotic pressure of poly(methyl methacrylate) in toluene has been measured at a series of concentrations at 298 K. Determine graphically the molar mass of the polymer.

π/atm	8.40×10^{-4}	1.72×10^{-3}	2.52×10^{-3}	3.23×10^{-3}	7.75×10^{-3}
$c/\text{g} \cdot \text{L}^{-1}$	8.10	12.31	15.00	18.17	28.05

7.57 Benzene and toluene form an ideal solution. Prove that to achieve the maximum entropy of mixing, the mole fraction of each component must be 0.5.

7.58 Suppose 2.6 moles of He at 0.80 atm and 25 °C are mixed with 4.1 moles of Ne at 2.7 atm and 25 °C. Calculate the Gibbs energy change for the process. Assume ideal behavior.

7.59 Two beakers are placed in a closed container. Beaker A initially contains 0.15 mole of naphthalene ($C_{10}H_8$) in 100 g of benzene (C_6H_6) and beaker B initially contains 31 g of an unknown compound dissolved in 100 g of benzene. At equilibrium, beaker A is found to have lost 7.0 g. Assuming ideal behavior, calculate the molar mass of the unknown compound. State any assumptions made.