

16.20: Problems

- At 100 C, the enthalpy of vaporization of water is $40.657 \text{ kJ mol}^{-1}$. Calculate the boiling-point elevation constant for water when the solute concentration is expressed in molality units.
- At 0 C, the enthalpy of fusion of water is $6.009 \text{ kJ mol}^{-1}$. Calculate the freezing-point depression constant for water when the solute concentration is expressed in molality units.
- A solution is prepared by dissolving 20.0 g of ethylene glycol (1,2-ethanediol) in 1 kg of water. Estimate the boiling point and the freezing point of this solution.
- A biopolymer has a molecular weight of 250,000 dalton. At 300 K, estimate the osmotic pressure of a solution that contains 1 g of this substance in 10 mL of water.
- Cyclohexanol melts at 25.46 C; the enthalpy of fusion is 1.76 kJ mol^{-1} . Estimate the freezing-point depression constant when the solute concentration is expressed as a mole fraction and when it is expressed in molality units. A solution is prepared by mixing 1 g of ethylene glycol with 50 g of liquid cyclohexanol. How much is the freezing point of this solution depressed relative to the freezing point of pure cyclohexanol?
- Freezing-point depression data for numerous solutes in aqueous solution³ are reproduced below. Calculate the freezing-point depression, $-\Delta T_{fp}/m$, for each of these solutes. Compare these values to the freezing-point depression constant that you calculated in problem 2. Explain any differences.

Solute	molality	$-\Delta T_{fp}, K$
Acetone	0.087	0.16
ethanol	0.109	0.20
ethylene glycol	0.081	0.15
ammonia	0.295	0.55
glycerol	0.110	0.18
lithium chloride	0.119	0.42
nitric acid	0.080	0.28
potassium bromide	0.042	0.15
barium chloride	0.024	0.12

- In a binary solution of solute A in solvent B , the mole fractions in the pure solvent are $y_A = 0$ and $y_B = 1$. We let the pure solvent be the solvent standard state; when $y_A = 0$, $y_B = \tilde{a}_B = 1$, and $\ln \tilde{a}_B = 0$. What happens to the value of $\ln \tilde{a}_B$ as $y_A \rightarrow 1$? Sketch the graph of $(1 - y_A)/y_A$ versus $\ln \tilde{a}_B$. For $(0 < y_A^* < 1)$, shade the area on this graph that represents the integral

$$\int_{y_A}^{y_A^*} \left(\frac{1 - y_A}{y_A} \right) d \ln \gamma_A$$

Is this area greater or less than zero?

- In a binary solution of solute A in solvent B , the activity coefficient of the solvent can be modeled by the equation $\ln \gamma_B(y_A) = cy_A^p$, where the constants c and p are found by using least squares to fit experimental data to the equation. Find an equation for $\ln \gamma_A(y_A)$. For $c = 8.4$ and $p = 2.12$, plot $\ln \gamma_B(y_A)$ and $\ln \gamma_A(y_A)$ versus y_A .
- A series of solutions contains a non-volatile solute, A , dissolved in a solvent, B . At a fixed temperature, the vapor pressure of solvent B is measured for these solutions and for pure B ($y_A = 0$). At low solute concentrations, the vapor pressure varies with the solute mole fraction according to $P = P^*(1 - y_A) \exp(-\alpha y_A^\beta)$.

- (a) If the pure solvent at one bar is taken as the standard state for liquid A , and gaseous B behaves as an ideal gas, how does the activity of solvent B vary with y_A ?
- (b) How does $\ln \gamma_B$ vary with y_A ?
- (c) Find $\ln \gamma_A (y_A)$.

10. In [Section 14.14](#), we find for liquid solvent B ,

$$\bar{L}_B^o = H_B^o - \bar{H}_B^{ref} = \lim_{T \rightarrow 0} \left(- \frac{\partial \Delta_{mix} \bar{H}}{\partial n_B} \right)_{P, T, n_A}$$

Since \bar{H}_B^* is the molar enthalpy of pure liquid B , we have

$$\left(\frac{\partial \bar{H}_B^*}{\partial T} \right)_P = C_P (B, \text{liquid}, T)$$

In [Section 16.15](#), we set

$$\left(\frac{\partial \bar{H}_B^{ref}}{\partial T} \right)_P = C_P (B, \text{liquid}, T)$$

Show that this is equivalent to the condition

$$\left(\frac{\partial \bar{L}_B^o}{\partial T} \right)_P \ll C_P (B, \text{liquid}, T)$$

11. If $p z_A = -q z_B$, prove that

$$\frac{p z_A^2 + q z_B^2}{p + q} = -z_A z_B$$

12. At temperatures of 5 °C, 25 °C, and 45 °C, evaluate Debye-Hückel parameter κ for aqueous sodium chloride solutions at concentrations of 10^{-3} m , 10^{-2} m , and 10^{-1} m .

13. Introducing the approximation $1 + \kappa a_c \approx 1$ produces the Debye-Hückel limiting law, which is strictly applicable only in the limiting case of an infinitely dilute solution. Introducing the approximation avoids the problem of choosing an appropriate value for a_c . If $a_c = 0.2 \text{ nm}$, calculate $1 + \kappa a_c$ for aqueous solutions in which the ionic strength, I , is 10^{-3} m , 10^{-2} m , and 10^{-1} m . What does the result suggest about the ionic-strength range over which the limiting law is a good approximation?

14. The solubility product for barium sulfate, $K_{sp} = \tilde{a}_{Ba^{2+}} \tilde{a}_{SO_4^{2-}}$, is 1.08×10^{-10} . Estimate the solubility of barium sulfate in pure water and in 10^{-2} m potassium perchlorate.

15. The enthalpy of vaporization³ of n-butane at its normal boiling point, 272.65 K, is $22.44 \text{ kJ mol}^{-1}$. In the temperature range (273.15, 348.15), the solubility³ of n-butane in water is given by

$$\ln y_A = A + \frac{100 B}{T} + C \ln \left(\frac{T}{100} \right)$$

where $A = -102.029$, $B = 146.040 \text{ K}^{-1}$, and $C = 38.7599$. From the result we develop in [Section 16.14](#), calculate $\Delta_{\text{vap}} \bar{H}_{A, \text{solution}}$ for n-butane at its normal boiling point. (Note that the normal boiling temperature is slightly below the temperature range to which the equation for $\ln y_A$ is valid.) Comment.

16. The enthalpy of vaporization³ of molecular oxygen at its normal boiling point, 90.02 K, is 6.82 kJ mol^{-1} . In the temperature range (273.15, 348.15), the solubility³ of oxygen in water is given by

$$\ln y_A = A + \frac{100 B}{T} + C \ln \left(\frac{T}{100} \right)$$

where $A = -66.7354$, $B = 87.4755 \text{ K}^{-1}$, and $C = 24.4526$. From the result we develop in [Section 16.14](#), calculate $\Delta_{\text{vap}} \overline{H}_{A,\text{solution}}$ for oxygen at 273.25 K and at its normal boiling point, 90.02 K. Comment.

Notes

¹ Raoult's law and ideal solutions can be defined using fugacities in place of partial pressures. The result is more general but—for those whose intuition has not yet embraced fugacity—less transparent.

² For a discussion of the concentration range in which the Debye-Huckel model is valid and of various supplemental models that allow for the effects of forces that are specific to the chemical characteristics of the interacting ions, see Lewis and Randall, Pitzer and Brewer, *Thermodynamics*, 2nd Edition, McGraw Hill Book Company, New York, 1961, Chapter 23.

³ Data from *CRC Handbook of Chemistry and Physics*, 79th Edition, David R. Lide, Ed., CRC Press, 1998-1999.

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