Solutions II
Solid-Liquid Solutions

PROBLEMS AND SOLUTIONS

25–1. The density of a glycerol/water solution that is 40.0% glycerol by mass is 1.101 g·mL^{-1} at 20°C. Calculate the molality and the molarity of glycerol in the solution at 20°C. Calculate the molality at 0°C.

The mass of glycerol per millimeter of solution is

$$\text{g glycerol per mL} = (0.400)(1.101 \text{ g·mL}^{-1}) = 0.4404 \text{ g·mL}^{-1}$$

The number of moles of glycerol per liter of solution is

$$\text{molarity} = \frac{440.4 \text{ g·L}^{-1}}{92.093 \text{ g·mol}^{-1}} = 4.78 \text{ mol·L}^{-1}$$

The number of grams of water per 0.4404 grams of glycerol is given by

$$1.101 \text{ g} - 0.4404 \text{ g} = 0.6606 \text{ g H}_2\text{O}$$

or 0.4404 g glycerol per 0.6606 g H_2O, or 0.6666 g glycerol per g H_2O. Therefore,

$$\text{molality} = \frac{666.6 \text{ g·kg}^{-1}}{92.094 \text{ g·mol}^{-1}} = 7.24 \text{ mol·kg}^{-1}$$

25–2. Concentrated sulfuric acid is sold as a solution that is 98.0% sulfuric acid and 2.0% water by mass. Given that the density is 1.84 g·mL^{-1}, calculate the molarity of concentrated sulfuric acid.

$$\text{g H}_2\text{SO}_4 \text{ per mL solution} = (0.980)(1.84 \text{ g·mL}^{-1}) = 1.80 \text{ g·mL}^{-1})$$

$$\text{molarity} = \frac{1800 \text{ g·L}^{-1}}{98.08 \text{ g·mol}^{-1}} = 18.4 \text{ mol·L}^{-1}$$

25–3. Concentrated phosphoric acid is sold as a solution that is 85% phosphoric acid and 15% water by mass. Given that the molarity is 15 M, calculate the density of concentrated phosphoric acid.

A 15 molar solution implies that there are

$$(15 \text{ mol·L}^{-1})(97.998 \text{ g·mol}^{-1}) = 1470 \text{ g of phosphoric acid per liter of solution}$$

Therefore, the density of the solution is

$$\text{density} = \frac{1470 \text{ g·L}^{-1}}{0.85} = 1700 \text{ g·L}^{-1} = 1.7 \text{ g·mL}^{-1}$$

25–4. Calculate the mole fraction of glucose in an aqueous solution that is $0.500 \text{ mol·kg}^{-1}$ glucose.

There are 0.500 mol glucose per kg H_2O. so

$$x_2 = \frac{0.500 \text{ mol}}{0.500 \text{ mol} + \dfrac{1000 \text{ g } H_2O}{18.02 \text{ g·mol}^{-1} H_2O}} = 0.00893$$

25–5. Show that the relation between molarity and molality for a solution with a single solute is

$$c = \frac{(1000 \text{ mL·L}^{-1})\rho m}{1000 \text{ g·kg}^{-1} + m M_2}$$

where c is the molarity, m is the molality, ρ is the density of the solution in g·mL^{-1}, and M_2 is the molar mass (g·mol^{-1}) of the solute.

Consider a solution of a certain molality, m, containing 1000 g of solvent. The total mass of the solution is $1000 \text{ g·kg}^{-1} + m M_2$ and its volume (in mL) is $(1000 \text{ g·kg}^{-1} + m M_2)/\rho$, where ρ is the density of the the the solution in g·mL^{-1}. The volume of the solution in liters is $(1000 \text{ g·kg}^{-1} + m M_2)/\rho(1000 \text{ mL·L}^{-1})$ liters. There are m moles of solute per $(1000 \text{ g·kg}^{-1} + m M_2)/\rho(1000 \text{ mL·L}^{-1})$ liters, so the molarity is

$$c = \frac{(1000 \text{ mL·L}^{-1})\rho m}{1000 \text{ g·kg}^{-1} + m M_2}$$

25–6. The *CRC Handbook of Chemistry and Physics* has tables of "concentrative properties of aqueous solutions" for many solutions. Some entries for CsCl(s) are

$A/\%$	$\rho/\text{g·mL}^{-1}$	$c/\text{mol·L}^{-1}$
1.00	1.0058	0.060
5.00	1.0374	0.308
10.00	1.0798	0.641
20.00	1.1756	1.396
40.00	1.4226	3.380

where A is the mass percent of the solute, ρ is the density of the solution, and c is the molarity. Using these data, calculate the molality at each concentration.

Using the result of the previous problem,

$$m = \frac{(1000 \text{ g·kg}^{-1})c}{(1000 \text{ mL·L}^{-1})\rho - M_2 c}$$

We have then $(M_2 = 168.36 \text{ g·mol}^{-1})$

$c/\text{mol·L}^{-1}$	$m/\text{mol·kg}^{-1}$
0.060	0.060
0.308	0.313
0.641	0.660
1.396	1.484
3.380	3.960

25–7. Derive a relation between the mass percentage (A) of a solute in a solution and its molality (m). Calculate the molality of an aqueous sucrose solution that is 18% sucrose $(C_{12}H_{22}O_{11})$ by mass.

Mass percentage of solute, A_2, is given by

$$A_2 = \frac{\text{mass}_2}{\text{mass}_1 + \text{mass}_2} \times 100$$

If we take a solution containing 1000 g of solvent, then $\text{mass}_2 = m M_2$ and $\text{mass}_1 = 1000 \text{ g·kg}^{-1}$, so

$$A_2 = \frac{m M_2}{1000 \text{ g·kg}^{-1} + m M_2} \times 100$$

Solve for m to get

$$m = \frac{(1000 \text{ g·kg}^{-1})A_2}{(100 - A_2)M_2}$$

For an aqueous sucrose solution that is 18% sucrose by mass,

$$m = \frac{(1000 \text{ g·kg}^{-1})(18)}{(100 - 18)(342.3 \text{ g·mol}^{-1})} = 0.73 \text{ mol·kg}^{-1}$$

25–8. Derive a relation between the mole fraction of the solvent and the molality of a solution.

Start with

$$x_2 = \frac{n_2}{n_1 + n_2}$$

Now take a solution containing 1000 g of solvent, so that $n_2 = m$ and $n_1 = (1000 \text{ g})/M_1$, where M_1 is the molar mass of the solvent. Therefore,

$$x_2 = \frac{m}{\dfrac{1000 \text{ g·kg}^{-1}}{M_1} + m} = \frac{m M_1}{1000 \text{ g·kg}^{-1} + m M_1}$$

and

$$x_1 = 1 - x_2 = \frac{1000 \text{ g} \cdot \text{kg}^{-1}}{1000 \text{ g} \cdot \text{kg}^{-1} + mM_1}$$

25–9. The volume of an aqueous sodium chloride solution at 25°C can be expressed as

$$V/\text{mL} = 1001.70 + (17.298 \text{ kg} \cdot \text{mol}^{-1})m + (0.9777 \text{ kg}^2 \cdot \text{mol}^{-2})m^2$$

$$- (0.0569 \text{ kg}^3 \cdot \text{mol}^{-3})m^3$$

$$0 \le m \le 6 \text{ mol} \cdot \text{kg}^{-1}$$

where m is the molality. Calculate the molarity of a solution that is 3.00 molal in sodium chloride.

The volume of the solution at a 3.00 mol·kg⁻¹ concentration is

$$V/\text{mL} = 1060.86$$

The mass of a 3.00 mol·kg⁻¹ NaCl(aq) solution that contains 1000 g of solvent is

$$\text{mass} = 1000 \text{ g} \cdot \text{kg}^{-1} + (3.00 \text{ mol} \cdot \text{kg}^{-1})(58.444 \text{ g} \cdot \text{mol}^{-1})$$

$$= 1175.33 \text{ g}$$

The density of the solution is

$$\rho^{\text{sln}} = \frac{1175.33 \text{ g}}{1060.86 \text{ mL}} = 1.108 \text{ g} \cdot \text{mL}^{-1}$$

and so the molarity is (see Problem 25–5)

$$c = \frac{(1000 \text{ mL} \cdot \text{L}^{-1})\rho m}{1000 \text{ g} \cdot \text{kg}^{-1} + mM_2}$$

$$= \frac{(1000 \text{ mL} \cdot \text{L}^{-1})(1.108 \text{ g} \cdot \text{mL}^{-1})(3.00 \text{ mol} \cdot \text{kg}^{-1})}{1000 \text{ g} \cdot \text{kg}^{-1} + (3.00 \text{ mol} \cdot \text{kg}^{-1})(58.444 \text{ g} \cdot \text{mol}^{-1})}$$

$$= 2.83 \text{ mol} \cdot \text{L}^{-1}$$

25–10. If x_2^∞, m^∞, and c^∞ are the mole fraction, molality, and molarity, respectively, of a solute at infinite dilution, show that

$$x_2^\infty = \frac{m^\infty M_1}{1000 \text{ g} \cdot \text{kg}^{-1}} = \frac{c^\infty M_1}{(1000 \text{ mL} \cdot \text{L}^{-1})\rho_1}$$

where M_1 is the molar mass (g·mol⁻¹) and ρ_1 is the density (g·mL⁻¹) of the solvent. Note that mole fraction, molality, and molarity are all directly proportional to each other at low concentrations.

Start with $x_2 = n_2/(n_1 + n_2)$. At infinite dilution, $n_2 \to 0$, and so

$$x_2 = \frac{n_2}{n_1 + n_2} \longrightarrow \frac{n_2}{n_1} \quad \text{as} \quad n_2 \longrightarrow 0$$

Consider a solution containing 1000 g of solvent. In this case, $n_2 = m$ and $n_1 = (1000 \text{ g} \cdot \text{kg}^{-1})/M_1$, where M_1 is the molar mass of the solvent. Then

$$x_2^\infty = \frac{m^\infty}{\dfrac{1000 \text{ g} \cdot \text{kg}^{-1}}{M_1}} = \frac{m^\infty M_1}{1000 \text{ g} \cdot \text{kg}^{-1}}$$

According to Problem 25–5, $c^\infty \to (\text{mL} \cdot \text{L}^{-1})\rho m^\infty / (\text{g} \cdot \text{kg}^{-1})$, so

$$x_2^\infty = \frac{c^\infty}{\left(\dfrac{1000 \text{ mL} \cdot \text{L}^{-1}}{M_1}\right)\rho} = \frac{c^\infty M_1}{(1000 \text{ mL} \cdot \text{L}^{-1})\rho}$$

25–11. Consider two solutions whose solute activities are a_2' and a_2'', referred to the same standard state. Show that the difference in the chemical potentials of these two solutions is independent of the standard state and depends only upon the ratio a_2'/a_2''. Now choose one of these solutions to be at an arbitrary concentration and the other at a very dilute concentration (essentially infinitely dilute) and argue that

$$\frac{a_2'}{a_2''} = \frac{\gamma_{2x} x_2}{x_2^\infty} = \frac{\gamma_{2m} m}{m^\infty} = \frac{\gamma_{2c} c}{c^\infty}$$

Let

$$\mu_2' = (\mu_2^\circ)' + RT \ln a_2'$$
$$\mu_2'' = (\mu_2^\circ)'' + RT \ln a_2'' = (\mu_2^\circ)' + RT \ln a_2''$$

Therefore,

$$\Delta\mu = \mu_2' - \mu_2'' = RT \ln \frac{a_2'}{a_2''}$$

If the solution denoted by the double prime is very dilute, then $a_2'' = x_2^\infty$, m^∞, or c^∞. Therefore,

$$\frac{a_2'}{a_2''} = \frac{\gamma_{2x} x_2}{x_2^\infty} = \frac{\gamma_{2m} m}{m^\infty} = \frac{\gamma_{2c} c}{c^\infty}$$

25–12. Use Equations 25.4, 25.11, and the results of the previous two problems to show that

$$\gamma_{2x} = \gamma_{2m} \left(1 + \frac{mM_1}{1000 \text{ g} \cdot \text{kg}^{-1}}\right) = \gamma_{2c} \left(\frac{\rho}{\rho_1} + \frac{c[M_1 - M_2] \cdot}{\rho_1[1000 \text{ mL} \cdot \text{L}^{-1}]}\right)$$

where ρ is the density of the solution. Thus, we see that the three different activity coefficients are related to one another.

Using the result of the previous problem,

$$\gamma_{2x} = \frac{x_2^\infty}{m^\infty} \frac{m}{x_2} \gamma_{2m}$$

Using the result of Equation 25.4 and Problem 25–10, we have

$$\gamma_{2x} = \gamma_{2m} \left(\frac{M_1}{1000 \text{ g} \cdot \text{kg}^{-1}}\right)\left(\frac{1000 \text{ g} \cdot \text{kg}^{-1}}{M_1} + m\right) = \gamma_{2m} \left(1 + \frac{mM_1}{1000 \text{ g} \cdot \text{kg}^{-1}}\right)$$

Similarly, Problem 25–11 gives us

$$\gamma_{2x} = \gamma_{2c} \frac{x_2^\infty}{c^\infty} \frac{c}{x_2}$$

Using Equation 25.11 and the result of Problem 25–11, we have

$$\gamma_{2x} = \gamma_{2c} \left[\frac{M_1}{(1000 \text{ mL}\cdot\text{L}^{-1})\rho_1} \right] \left[\frac{(1000 \text{ mL}\cdot\text{L}^{-1})\rho + c(M_1 - M_2)}{M_1} \right]$$

$$= \gamma_{2c} \left[\frac{\rho}{\rho_1} + \frac{c(M_1 - M_2)}{(1000 \text{ mL}\cdot\text{L}^{-1})\rho_1} \right]$$

25–13. Use Equations 25.4, 25.11, and the results of Problem 25–12 to derive

$$\gamma_{2m} = \gamma_{2c} \left(\frac{\rho}{\rho_1} - \frac{cM_2}{\rho_1[1000 \text{ mL}\cdot\text{L}^{-1}]} \right)$$

Given that the density of an aqueous citric acid ($M_2 = 192.12 \text{ g}\cdot\text{mol}^{-1}$) solution at 20°C is given by

$$\rho/\text{g}\cdot\text{mL}^{-1} = 0.99823 + (0.077102 \text{ L}\cdot\text{mol}^{-1})c$$

$$0 \le c < 1.772 \text{ mol}\cdot\text{L}^{-1}$$

plot γ_{2m}/γ_{2c} versus c. Up to what concentration do γ_{2m} and γ_{2c} differ by 2%?
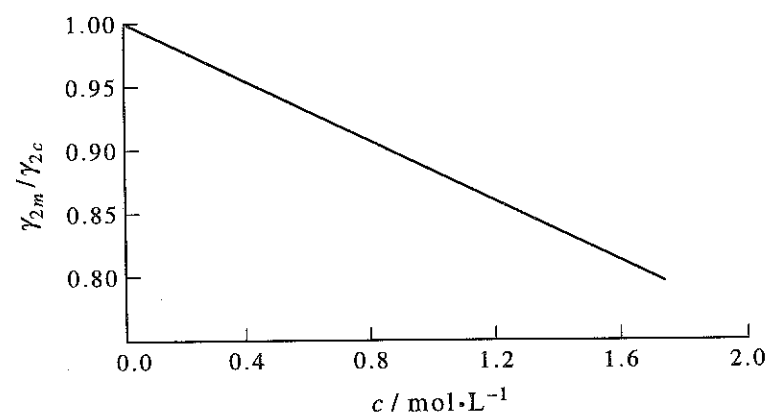
From Problem 25–11,

$$\gamma_{2m} = \gamma_{2c} \frac{m^\infty}{c^\infty} \frac{c}{m}$$

Using the results from Problems 25–5 and 25–10,

$$\gamma_{2m} = \gamma_{2c} \frac{1}{\rho_1} \left[\frac{(1000 \text{ mL}\cdot\text{L}^{-1})\rho - cM_2}{1000 \text{ mL}\cdot\text{L}^{-1}} \right] = \gamma_{2c} \left[\frac{\rho}{\rho_1} - \frac{cM_2}{\rho_1(1000 \text{ mL}\cdot\text{L}^{-1})} \right]$$

The ratio γ_{2m}/γ_{2c} is plotted below.

25–14. The *CRC Handbook of Chemistry and Physics* gives a table of mass percent of sucrose in an aqueous solution and its corresponding molarity at 25°C. Use these data to plot molality versus molarity for an aqueous sucrose solution.

Use the relation between mass percentage and molality that is derived in Problem 25–7 to calculate the molality at each mass percentage. Some representative values of A, c, and m and the plot of m against c are given below.

A	$c/\text{mol}\cdot\text{L}^{-1}$	$m/\text{mol}\cdot\text{kg}^{-1}$	A	$c/\text{mol}\cdot\text{L}^{-1}$	$m/\text{mol}\cdot\text{kg}^{-1}$
1.00	0.029	0.030	24.00	0.771	0.923
2.00	0.059	0.060	28.00	0.914	1.136
3.00	0.089	0.090	32.00	1.063	1.375
4.00	0.118	0.122	36.00	1.216	1.643
5.00	0.149	0.154	40.00	1.375	1.948
6.00	0.179	0.186	44.00	1.539	2.295
7.00	0.210	0.220	48.00	1.709	2.697
8.00	0.241	0.254	52.00	1.885	3.165
9.00	0.272	0.289	56.00	2.067	3.718
10.00	0.303	0.325	60.00	2.255	4.382
12.00	0.367	0.398	64.00	2.450	5.194
14.00	0.431	0.476	68.00	2.652	6.208
16.00	0.497	0.556	72.00	2.860	7.512
18.00	0.564	0.641	76.00	3.076	9.251
20.00	0.632	0.730	80.00	3.299	11.686
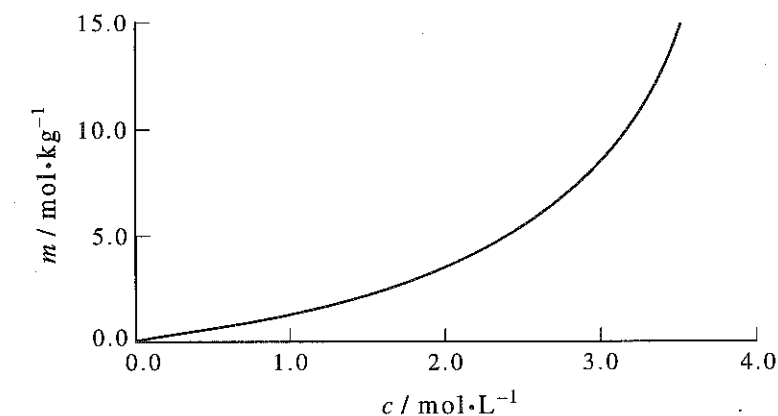
25–15. Using the data in Table 25.2, calculate the activity coefficient of water (on a mole fraction basis) at a sucrose concentration of 3.00 molal.

We use the equation $\gamma_1 = a_1/x_1$. The relation between molality and mole fraction is given by Equation 25.4:

$$x_1 = 1 - x_2 = \frac{1}{1 + \dfrac{mM_1}{1000 \text{ g}\cdot\text{kg}^{-1}}} = \frac{1000 \text{ g}\cdot\text{kg}^{-1}}{1000 \text{ g}\cdot\text{kg}^{-1} + mM_1}$$

At $m = 3.00 \text{ mol·kg}^{-1}$ (with $M_1 = 18.02 \text{ g·mol}^{-1}$), we have $x_1 = 0.9487$. Therefore,

$$\gamma_1 = \frac{0.93276}{0.9487} = 0.983$$

25–16. Using the data in Table 25.2, plot the activity coefficient of water (on a mole fraction basis) against the mole fraction of water.

Calculate the mole fraction from the molality according to Problem 25–15, use the relation $\gamma_{1x} = a_1/x_1$, and plot the results to get

Mole fraction
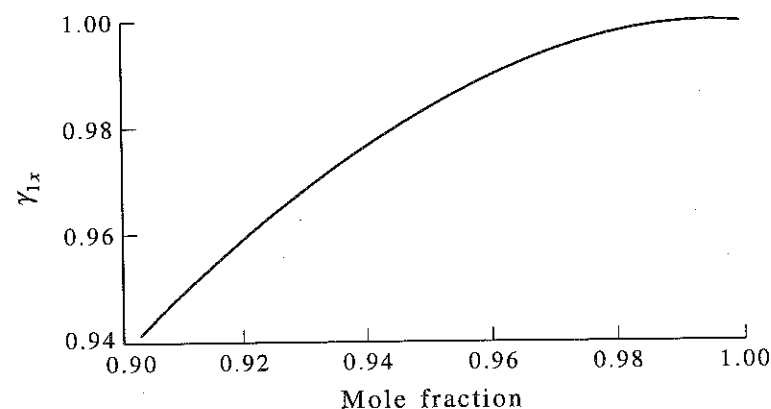
25–17. Using the data in Table 25.2, calculate ϕ at each value of m and reproduce Figure 25.2.

Use Equation 25.13,

$$\ln a_1 = -\frac{m\phi}{55.506 \text{ mol·kg}^{-1}}$$

25–18. Fit the data for the osmotic coefficient of sucrose in Table 25.2 to a fourth-degree polynomial and calculate γ_{2m} for a 1.00-molal solution. Compare your result with the one obtained in Example 25–5.

Suppressing the units of the coefficients, we get

$$\phi = 1 + 0.075329m + 0.016554m^2 - 0.0039647m^3 + 0.00024694m^4$$

Use Equation 25.15 to write

$$\ln \gamma_{2m} = \phi - 1 + \int_0^{1.00} \frac{\phi - 1}{m} dm = 0.08816 + 0.08235 = 0.1705$$

and so $\gamma_{2m} = 1.186$.

25–19. Using the data for sucrose given in Table 25.2, determine $\ln \gamma_{2m}$ at 3.00 molal by plotting $(\phi - 1)/m$ versus m and determining the area under the curve by numerical integration (Mathchapter G) rather than by curve fitting ϕ first. Compare your result with the value given in Table 25.2.

Using Kaleidagraph, we obtain

$$\int_0^{3.00} \frac{\phi - 1}{m} dm = 0.272$$

From Table 25.2, $\phi - 1 = 0.2879$, and so $\ln \gamma_{2m} = 0.560$, and $\gamma_{2m} = 1.75$.

25–20. Equation 25.18 can be used to determine the activity of the solvent at its freezing point. Assuming that ΔC_P^* is independent of temperature, show that

$$\Delta_{\text{fus}}\overline{H}(T) = \Delta_{\text{fus}}\overline{H}(T_{\text{fus}}^*) + \Delta\overline{C}_P^*(T - T_{\text{fus}}^*)$$

where $\Delta_{\text{fus}}\overline{H}(T_{\text{fus}}^*)$ is the molar enthalpy of fusion at the freezing point of the pure solvent (T_{fus}^*) and $\Delta\overline{C}_P^*$ is the difference in the molar heat capacities of liquid and solid solvent. Using Equation 25.18, show that

$$-\ln a_1 = \frac{\Delta_{\text{fus}}\overline{H}(T_{\text{fus}}^*)}{R(T_{\text{fus}}^*)^2}\theta + \frac{1}{R(T_{\text{fus}}^*)^2}\left(\frac{\Delta_{\text{fus}}\overline{H}(T_{\text{fus}}^*)}{T_{\text{fus}}^*} - \frac{\Delta\overline{C}_P}{2}\right)\theta^2 + \cdots$$

where $\theta = T_{\text{fus}}^* - T_{\text{fus}}$.

Use

$$\left(\frac{\partial \Delta_{\text{fus}}\overline{H}}{\partial T}\right)_P = \Delta\overline{C}_P^*$$

to derive

$$\Delta_{\text{fus}}\overline{H}(T) - \Delta_{\text{fus}}\overline{H}(T^*) = \Delta\overline{C}_P^*(T - T^*)$$

Using Equation 25.18

$$\ln a_1 = \int_{T_{\text{fus}}^*}^{T_{\text{fus}}} \frac{\Delta_{\text{fus}}\overline{H}(T)}{RT^2} dT$$

$$= \frac{\Delta_{\text{fus}}\overline{H}(T_{\text{fus}}^*)}{R} \int_{T_{\text{fus}}^*}^{T_{\text{fus}}} \frac{dT}{T^2} + \frac{\Delta\overline{C}_P}{R} \int_{T_{\text{fus}}^*}^{T_{\text{fus}}} \frac{dT(T - T_{\text{fus}}^*)}{T^2}$$

$$= \frac{\Delta_{\text{fus}}\overline{H}(T_{\text{fus}}^*)}{R}\left(-\frac{1}{T_{\text{fus}}} + \frac{1}{T_{\text{fus}}^*}\right) + \frac{\Delta\overline{C}_P^*}{R}\left(\ln\frac{T_{\text{fus}}}{T_{\text{fus}}^*} + \frac{T_{\text{fus}}^*}{T_{\text{fus}}} - \frac{T_{\text{fus}}^*}{T_{\text{fus}}^*}\right)$$

$$= \frac{\Delta_{\text{fus}}\overline{H}(T_{\text{fus}}^*)}{RT_{\text{fus}}^*}\left(\frac{T_{\text{fus}} - T_{\text{fus}}^*}{T_{\text{fus}}}\right) + \frac{\Delta\overline{C}_P^*}{R}\left(\ln\frac{T_{\text{fus}}}{T_{\text{fus}}^*} + \frac{T_{\text{fus}}^* - T_{\text{fus}}}{T_{\text{fus}}}\right)$$

Now let $T_{\text{fus}} = T_{\text{fus}}^* - \theta$ and use $1/(1 - x) = 1 + x + x^2 + \cdots$ to get

$$\frac{1}{T_{\text{fus}}} = \frac{1}{T_{\text{fus}}^* - \theta} = \frac{1}{T_{\text{fus}}^*}\left[1 + \frac{\theta}{T_{\text{fus}}^*} + \frac{\theta^2}{(T_{\text{fus}}^*)^2} + \cdots\right]$$

and use $\ln(1-x) = -x - x^2/2 + \cdots$ to get

$$\ln\frac{T_{\text{fus}}}{T^*_{\text{fus}}} = \ln\left(1 - \frac{\theta}{T^*_{\text{fus}}}\right) = -\frac{\theta}{T^*_{\text{fus}}} - \frac{1}{2}\frac{\theta^2}{(T^*_{\text{fus}})^2} + \cdots$$

Finally, then

$$-\ln a_1 = -\frac{\Delta_{\text{fus}}\overline{H}(T^*_{\text{fus}})}{R(T^*_{\text{fus}})^2}\left(-\theta - \frac{\theta^2}{T^*_{\text{fus}}} + \cdots\right)$$

$$-\frac{\Delta\overline{C}^*_P}{RT^*_{\text{fus}}}\left[-\theta - \frac{\theta^2}{2T^*_{\text{fus}}} + \cdots + \theta\left(1 + \frac{\theta}{T^*_{\text{fus}}} + \cdots\right)\right]$$

$$= \frac{\Delta_{\text{fus}}\overline{H}(T^*_{\text{fus}})}{R(T^*_{\text{fus}})^2}\theta + \frac{1}{R(T^*_{\text{fus}})^2}\left(\frac{\Delta_{\text{fus}}\overline{H}(T^*_{\text{fus}})}{T^*_{\text{fus}}} - \frac{\Delta\overline{C}^*_P}{2}\right)\theta^2 + \cdots$$

25–21. Take $\Delta_{\text{fus}}\overline{H}(T^*_{\text{fus}}) = 6.01\text{ kJ·mol}^{-1}$, $\overline{C}^l_P = 75.2\text{ J·K}^{-1}\text{·mol}^{-1}$, and $\overline{C}^s_P = 37.6\text{ J·K}^{-1}\text{·mol}^{-1}$ to show that the equation for $-\ln a_1$ in the previous problem becomes

$$-\ln a_1 = (0.00969\text{ K}^{-1})\theta + (5.2 \times 10^{-6}\text{ K}^{-2})\theta^2 + \cdots$$

for an aqueous solution. The freezing point depression of a 1.95-molal aqueous sucrose solution is 4.45°C. Calculate the value of a_1 at this concentration. Compare your result with the value in Table 25.2. The value you calculated in this problem is for 0°C, whereas the value in Table 25.2 is for 25°C, but the difference is fairly small because a_1 does not vary greatly with temperature (Problem 25–61).

Using the final equation in Problem 25–20, we have

$$-\ln a_1 = \frac{(6.01\text{ kJ·mol}^{-1})\theta}{(8.314\text{ J·mol}^{-1}\text{·K}^{-1})(273.2\text{ K})^2}$$

$$+ \frac{1}{(8.314\text{ J·mol}^{-1}\text{·K}^{-1})(273.2\text{ K})^2}\left(\frac{6.01\text{ kJ·mol}^{-1}}{273.2\text{ K}} - 18.8\text{ J·mol}^{-1}\text{·K}^{-1}\right)$$

$$= (0.00969\text{ K}^{-1})\theta + (5.2 \times 10^{-6}\text{ K}^{-2})\theta^2 + \cdots$$

If $\theta = 4.45\text{ K}$, then

$$\ln a_1 = -(0.00969\text{ K}^{-1})(4.45\text{ K}) - (5.2 \times 10^{-6}\text{ K}^{-2})(4.45\text{ K})^2$$

$$= -0.0432$$

and so $a_1 = 0.958$.

25–22. The freezing point of a 5.0-molal aqueous glycerol (1,2,3-propanetriol) solution is -10.6°C. Calculate the activity of water at 0°C in this solution. (See Problems 25–20 and 25–21.)

Use the equation derived in Problem 25–21

$$\ln a_1 = -(0.00969\text{ K}^{-1})\theta - (5.2 \times 10^{-6}\text{ K}^{-2})\theta^2$$

with $\theta = 10.6\text{ K}$ to get

$$\ln a_1 = -(0.00969\text{ K}^{-1})(10.6\text{ K}) - (5.2 \times 10^{-6}\text{ K}^{-2})(10.6\text{ K})^2$$

$$= -0.103$$

and so $a_1 = 0.902$.

25–23. Show that replacing T_{fus} by T^*_{fus} in the denominator of $(T_{\text{fus}} - T^*_{\text{fus}})/T^*_{\text{fus}}T_{\text{fus}}$ (see Equation 25.20) gives $-\theta/(T^*_{\text{fus}})^2 - \theta^2/(T^*_{\text{fus}})^3 + \cdots$ where $\theta = T^*_{\text{fus}} - T_{\text{fus}}$.

$$\frac{T_{\text{fus}} - T^*_{\text{fus}}}{T_{\text{fus}}T^*_{\text{fus}}} = \frac{-\theta}{T^*_{\text{fus}}(T^*_{\text{fus}} - \theta)} = -\frac{\theta}{(T^*_{\text{fus}})^2\left(1 - \dfrac{\theta}{T^*_{\text{fus}}}\right)}$$

Now use the expansion $1/(1-x) = x + x^2 + \cdots$ to write

$$\frac{T_{\text{fus}} - T^*_{\text{fus}}}{T_{\text{fus}}T^*_{\text{fus}}} = -\frac{\theta}{(T^*_{\text{fus}})^2}\left[1 + \frac{\theta}{T^*_{\text{fus}}} + \frac{\theta^2}{(T^*_{\text{fus}})^2} + \cdots\right]$$

$$= -\frac{\theta}{(T^*_{\text{fus}})^2} - \frac{\theta^2}{(T^*_{\text{fus}})^3} + \cdots$$

25–24. Calculate the value of the freezing point depression constant for nitrobenzene, whose freezing point is 5.7°C and whose molar enthalpy of fusion is 11.59 kJ·mol^{-1}.

Using Equation 25.23, we write

$$K_f = \left(\frac{M_1}{1000\text{ g·kg}^{-1}}\right)\frac{R(T^*_{\text{fus}})^2}{\Delta_{\text{fus}}\overline{H}}$$

$$= \left(\frac{123.11\text{ g·mol}^{-1}}{1000\text{ g·kg}^{-1}}\right)\left[\frac{(8.314\text{ J·mol}^{-1}\text{·K}^{-1})(278.9\text{ K})^2}{11.59 \times 10^3\text{ J·mol}^{-1}}\right]$$

$$= 6.87\text{ K·kg·mol}^{-1}$$

25–25. Use an argument similar to the one we used to derive Equations 25.22 and 25.23 to derive Equations 25.24 and 25.25.

The condition for equilibrium at a temperature T is

$$\mu^g_1(T, P) = \mu^{\text{sln}}_1(T, P) = \mu^*_1(T, P) + RT\ln a_1 = \mu^l + RT\ln a_1$$

Solving for $\ln a_1$ gives

$$\ln a_1 = \frac{\mu^g_1 - \mu^l_1}{RT}$$

Use the Gibbs-Helmholtz equation (Example 24–1) to get

$$\left(\frac{\partial \ln a_1}{\partial T}\right)_{P,x_1} = \frac{\overline{H}^l_1 - \overline{H}^g_1}{RT^2} = -\frac{\Delta_{\text{vap}}\overline{H}}{RT^2}$$

This equation is similar to Equation 25.17 except for the negative sign, which occurs because boiling points of solutions are elevated whereas freezing points are lowered. The rest of the derivation follows Equations 25.18 through 25.23.

25–26. Calculate the boiling point elevation constant for cyclohexane given that $T_{vap} = 354$ K and that $\Delta_{vap}\overline{H} = 29.97$ kJ·mol^{-1}.

Using the analog of Equation 25.23, we have

$$K_b = \frac{(84.161 \text{ g·mol}^{-1})(8.314 \text{ J·mol}^{-1}\text{·K}^{-1})(354 \text{ K})^2}{(1000 \text{ g·kg}^{-1})(29.97 \times 10^3 \text{ J·mol}^{-1})}$$

$$= 2.93 \text{ K·kg·mol}^{-1}$$

25–27. A solution containing 1.470 g of dichlorobenzene in 50.00 g of benzene boils at 80.60°C at a pressure of 1.00 bar. The boiling point of pure benzene is 80.09°C and the molar enthalpy of vaporization of pure benzene is 32.0 kJ·mol^{-1}. Determine the molecular mass of dichlorobenzene from these data.

The value of $\Delta_{vap}T$ is

$$\Delta_{vap}T = 80.60°\text{C} - 80.09°\text{C} = 0.51°\text{C} = 0.51 \text{ K}$$
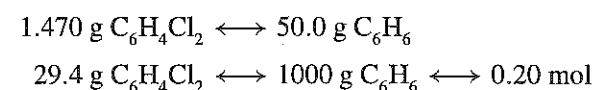
Using the analog of Equation 25.23, we have

$$K_b = \frac{(78.108 \text{ g·mol}^{-1})(8.314 \text{ J·mol}^{-1}\text{·K}^{-1})(353.2 \text{ K})^2}{(1000 \text{ g·kg}^{-1})(32.0 \times 10^3 \text{ J·mol}^{-1})}$$

$$= 2.53 \text{ K·kg·mol}^{-1}$$

The molality is given by

$$m = \frac{\Delta_{vap}T}{K_b} = \frac{0.51 \text{ K}}{2.53 \text{ K·kg}^{-1}\text{·mol}^{-1}} = 0.20 \text{ mol·kg}^{-1}$$

Therefore,

$$1.470 \text{ g } C_6H_4Cl_2 \longleftrightarrow 50.0 \text{ g } C_6H_6$$

$$29.4 \text{ g } C_6H_4Cl_2 \longleftrightarrow 1000 \text{ g } C_6H_6 \longleftrightarrow 0.20 \text{ mol}$$

and so the molecular mass is 147.

25–28. Consider the following phase diagram for a typical pure substance. Label the region corresponding to each phase. Illustrate how this diagram changes for a dilute solution of a nonvolatile solute.
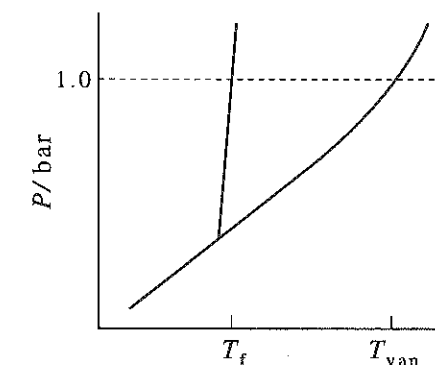
Now demonstrate that the boiling point increases and the freezing point decreases as a result of the dissolution of the solute.

Use the following figure for water, which is self-explanatory

$T_f^o - T_f$ = freezing point depression $T_b - T_b^o$ = boiling point elevation

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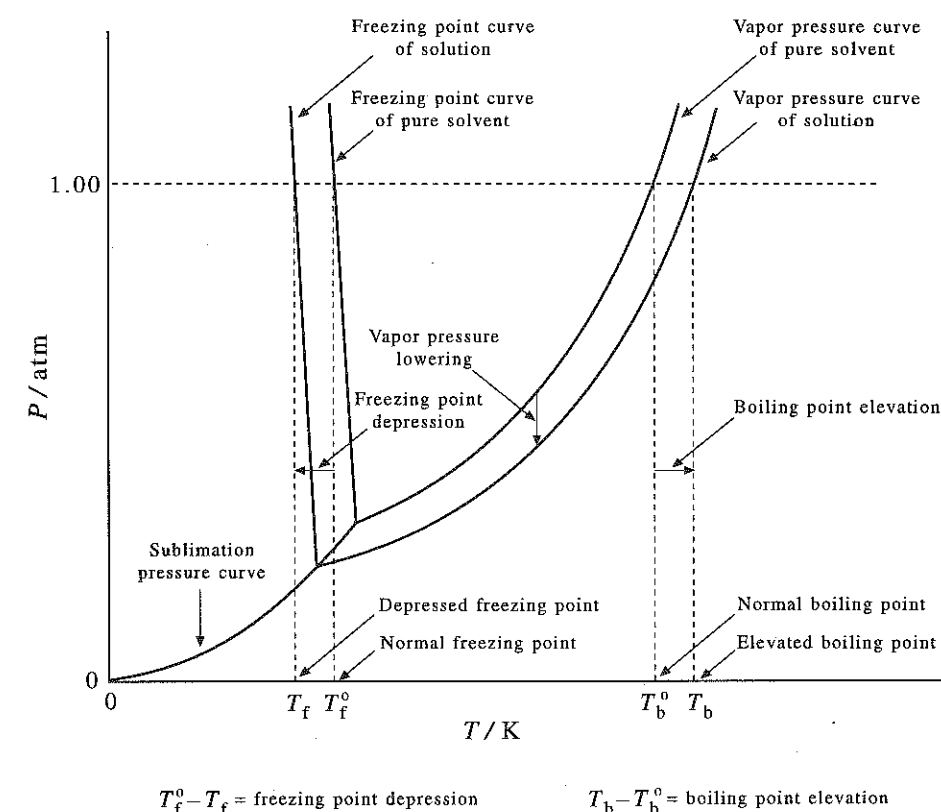
25–29. A solution containing 0.80 grams of a protein in 100 mL of a solution has an osmotic pressure of 2.06 torr at 25.0°C. What is the molecular mass of the protein?

We use Equation 25.31,

$$c = \frac{\Pi}{RT} = \frac{(2.06 \text{ torr})/(760 \text{ torr·atm}^{-1})}{(0.08206 \text{ L·atm·mol}^{-1}\text{·K}^{-1})(298.2 \text{ K})}$$

$$= 1.11 \times 10^{-4} \text{ mol·L}^{-1} = 1.11 \times 10^{-5} \text{ mol/100 mL}$$

Therefore, 1.11×10^{-5} mol corresponds to 0.80 g protein, and so the molecular mass of the protein is 72 000.

25–30. Show that the osmotic pressure of an aqueous solution can be written as

$$\Pi = \frac{RT}{V^*}\left(\frac{m}{55.506 \text{ mol·kg}^{-1}}\right)\phi$$

Simply substitute Equation 25.13 into Equation 25.30.

25–31. According to Table 25.2, the activity of the water in a 2.00 molal sucrose solution is 0.95807. What external pressure must be applied to the solution at 25.0°C to make the activity of the water in the solution the same as that in pure water at 25.0°C and 1 atm? Take the density of water to be 0.997 g·mL^{-1}.

Using Equation 25.30, we have

$$\Pi = -\frac{RT \ln a_1}{V_1^*} = -\frac{(0.08206 \text{ L·atm·mol}^{-1}\cdot\text{K}^{-1})(298.2 \text{ K})(\ln 0.95807)}{0.01807 \text{ L·mol}^{-1}}$$

$$= 58.0 \text{ atm}$$

25–32. Show that $a_2 = a_\pm^2 = m^2\gamma_\pm^2$ for a 2–2 salt such as $CuSO_4$ and that $a_2 = a_\pm^4 = 27m^4\gamma_\pm^4$ for a 1–3 salt such as $LaCl_3$.

Equation 25.40 gives us $a_2 = a_\pm^\nu = m_\pm^\nu \gamma_\pm^\nu$. For a 2–2 salt, such as $MgSO_4$, $\nu_+ = 1$, $\nu_- = 1$, $m_+ = m$, and $m_- = m$, and so $a_2 = a_\pm^2 = m^2\gamma_\pm^2$, or $a_\pm = m\gamma_\pm$.

For a 1–3 salt, such as $LaCl_3$, $\nu_+ = 1$, $\nu_- = 3$, $m_+ = m$, and $m_- = 3m$, and so $a_2 = a_\pm^4 = [m^1(3m)^3]\gamma_\pm^4$, or $a_\pm = 27^{1/4}m\gamma_\pm$.

25–33. Verify the following table:

Type of salt	Example	I_m
1 – 1	KCl	m
1 – 2	$CaCl_2$	$3m$
2 – 1	K_2SO_4	$3m$
2 – 2	$MgSO_4$	$4m$
1 – 3	$LaCl_3$	$6m$
3 – 1	Na_3PO_4	$6m$

Show that the general result for I_m is $|z_+z_-|(\nu_1 + \nu_2)m/2$.

We use Equation 25.52 in terms of molality.

$$I_m = \frac{1}{2}\sum_{j=1}^{s} z_j^2 m_j = \frac{1}{2}(z_+^2 m_+ + z_-^2 m_-) \tag{1}$$

for a binary salt. Therefore, we have the following table.

type	I_m
1–1	$\frac{1}{2}(1m_+ + 1m_-) = \frac{1}{2}(2m) = m$
1–2	$\frac{1}{2}(4m_+ + 1m_-) = \frac{1}{2}(4m + 2m) = 3m$
2–1	$\frac{1}{2}(m_+ + 4m_-) = \frac{1}{2}(2m + 4m) = 3m$
2–2	$\frac{1}{2}(4m_+ + 4m_-) = \frac{1}{2}(8m) = 4m$
1–3	$\frac{1}{2}(9m_+ + 1m_-) = \frac{1}{2}(9m + 3m) = 6m$
3–1	$\frac{1}{2}(m_+ + 9m_-) = \frac{1}{2}(3m + 9m) = 6m$

To prove the general result, substitute $m_+ = \nu_+ m$ and $m_- = \nu_- m$ into Equation 1 to get

$$I_m = \frac{1}{2}(z_+^2\nu_+ + z_-^2\nu_-)m$$

Now use the electroneutrality condition $z_+\nu_+ = |z_-|\nu_-$ to get

$$I_m = \frac{1}{2}(z_+|z_-|\nu_- + |z_-|^2\nu_-)m$$

$$= \frac{z_+|z_-|}{2}\left(\nu_- + \frac{|z_-|\nu_-}{z_+}\right)m = \frac{|z_-z_+|}{2}(\nu_+ + \nu_-)m$$

25–34. Show that the inclusion of the factor ν in Equation 25.41 allows $\phi \to 1$ as $m \to 0$ for solutions of electrolytes as well as nonelectrolytes. *Hint:* Realize that x_2 involves the total number of moles of solute particles (see Equation 25.44).

For a nonelectrolyte, $\ln a_1 \to \ln x_1 \to \ln(1 - x_2) \to -x_2$ as $x_2 \to 0$. According to Equation 25.21, $x_2 \to M_1 m/(1000 \text{ g·kg}^{-1})$ as $m \to 0$, so ϕ defined by $\ln a_1 = -M_1 m\phi/(1000 \text{ g·kg}^{-1})$ (Equation 25.13) becomes $\phi = (\ln a_1)/x_2 = 1$ as $x_2 \to 0$ or $m \to 0$. For an electrolyte, $x_2 \to \nu M_1 m/(1000 \text{ g·kg}^{-1})$ as $x_2 \to 0$ or $m \to 0$. Therefore, ϕ defined by $\ln a_1 = -\nu M_1 m/(1000 \text{ g·kg}^{-1})$ (Equation 25.41) becomes $\phi = (\ln a_1)/x_2 = 1$ as $x_2 \to 0$ or $m \to 0$.

25–35. Use Equation 25.41 and the Gibbs-Duhem equation to derive Equation 25.42.

Consider an aqueous solution consisting of 1000 g of water. The Gibbs-Duhem equation is

$$n_1 d\ln a_1 + n_2 \ln a_2 = 0$$

or

$$(55.506 \text{ mol·kg}^{-1})d\ln a_1 + md\ln a_2 = 0$$

Use Equation 25.41 to obtain

$$-\nu d(m\phi) + md\ln a_2 = 0$$

Equation 25.37 gives $a_2 = a_\pm^\nu = m_\pm^\nu \gamma_\pm^\nu$, and so we have

$$-\nu d(m\phi) + m\nu d\ln m_\pm\gamma_\pm = 0$$

But generally $m_{\pm} = cm$, where c is a constant whose value depends upon the type of electrolyte (see Table 25.3), and so

$$vd(m\phi) = mvd \ln(cm\gamma_{\pm})$$
$$= mvd \ln(m\gamma_{\pm})$$

Thus

$$d(m\phi) = md \ln(m\gamma_{\pm})$$

or

$$md\phi + \phi dm = m(d \ln \gamma_{\pm} + d \ln m)$$

Division by m gives

$$d\phi + \phi \frac{dm}{m} = d \ln \gamma_{\pm} + \frac{dm}{m}$$

or

$$d \ln \gamma_{\pm} = d\phi + \frac{\phi - 1}{m} dm$$

Now integrate from $m = 0$ (where $\gamma_{\pm} = \phi = 1$) to m to obtain Equation 25.42.

25–36. The osmotic coefficient of $CaCl_2(aq)$ solutions can be expressed as

$$\phi = 1.0000 - (1.2083 \text{ kg}^{1/2} \cdot \text{mol}^{-1/2}) m^{1/2} + (3.2215 \text{ kg} \cdot \text{mol}^{-1}) m$$
$$- (3.6991 \text{ kg}^{3/2} \cdot \text{mol}^{-3/2}) m^{3/2} + (2.3355 \text{ kg}^2 \cdot \text{mol}^{-2}) m^2$$
$$- (0.67218 \text{ kg}^{5/2} \cdot \text{mol}^{-5/2}) m^{5/2} + (0.069749 \text{ kg}^3 \cdot \text{mol}^{-3}) m^3$$

$$0 \leq m \leq 5.00 \text{ mol} \cdot \text{kg}^{-1}$$

Use this expression to calculate and plot $\ln \gamma_{\pm}$ as a function of $m^{1/2}$.

Substitute the expression for ϕ given in the problem into Equation 25.42. The result is shown in the following figure.
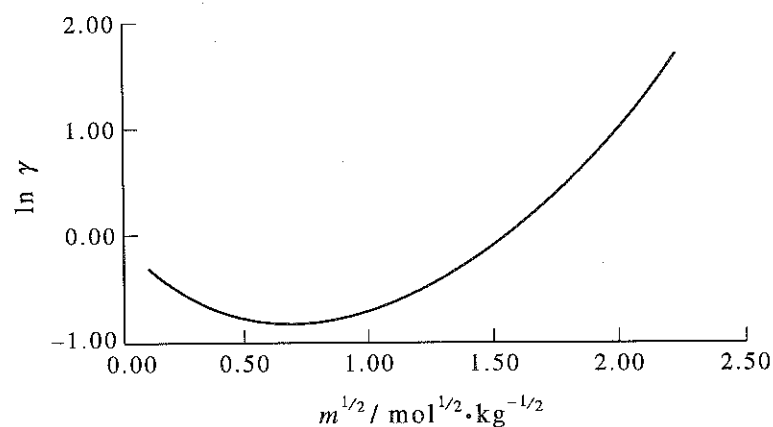
25–37. Use Equation 25.43 to calculate $\ln \gamma_{\pm}$ for $NaCl(aq)$ at 25°C as a function of molality and plot it versus $m^{1/2}$. Compare your results with those in Table 25.4.

Substitute Equation 25.43 into Equation 25.42. The result is shown in the following figure. The calculated and experimental values are indistinguishable on the graph.
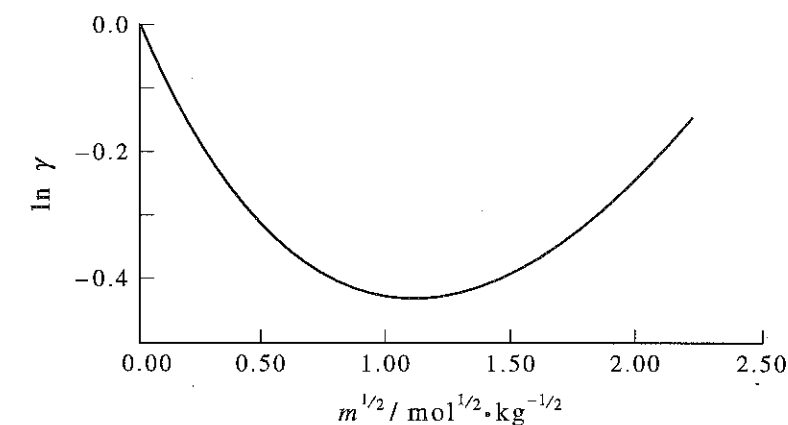
25–38. In Problem 25–19, you determined $\ln \gamma_{2m}$ for sucrose by calculating the area under the curve of $\phi - 1$ versus m. When dealing with solutions of electrolytes, it is better numerically to plot $(\phi - 1)/m^{1/2}$ versus $m^{1/2}$ because of the natural dependence of ϕ on $m^{1/2}$. Show that

$$\ln \gamma_{\pm} = \phi - 1 + 2 \int_0^{m^{1/2}} \frac{\phi - 1}{m^{1/2}} dm^{1/2}$$

Start with Equation 25.42, and let $x = m^{1/2}$ and $dx = dm/2m^{1/2} = dm/2x$ to obtain

$$\int_0^m \frac{\phi - 1}{m'} dm' = \int_0^x \frac{\phi - 1}{x'^2} 2x' dx'$$
$$= 2 \int_0^{m^{1/2}} \frac{\phi - 1}{m^{1/2}} dm^{1/2}$$

The full expression for $\ln \gamma_{\pm}$ is

$$\ln \gamma_{\pm} = \phi - 1 + 2 \int_0^{m^{1/2}} \frac{\phi - 1}{m^{1/2}} dm^{1/2}$$

25–39. Use the data in Table 25.4 to calculate $\ln \gamma_{\pm}$ for $NaCl(aq)$ at 25°C by plotting $(\phi - 1)/m^{1/2}$ against $m^{1/2}$ and determine the area under the curve by numerical integration (Mathchapter G). Compare your values of $\ln \gamma_{\pm}$ with those you obtained in Problem 25–37, where you calculate $\ln \gamma_{\pm}$ from a curve-fit expression of ϕ as a polynomial in $m^{1/2}$.

The plot is essentially identical to the one obtained in Problem 25–37.

25–40. Don Juan Pond in the Wright Valley of Antarctica freezes at $-57°C$. The major solute in the pond is $CaCl_2$. Estimate the concentration of $CaCl_2$ in the pond water.

We say "estimate" because the concentration will be too large for Equation 25.45 to be quantitative. Nevertheless, we can "estimate" the molality to be

$$m \approx \frac{57 \text{ K}}{(3)(1.84 \text{ K·kg·mol}^{-1})} = 10 \text{ mol·kg}^{-1}$$

where the factor of 3 in the denominator results because $\nu = 3$ for $CaCl_2$.

25–41. A solution of mercury(II) chloride is a poor conductor of electricity. A 40.7-g sample of $HgCl_2$ is dissolved in 100.0 g of water, and the freezing point of the solution is found to be $-2.83°C$. Explain why $HgCl_2$ in solution is a poor conductor of electricity.


Because 40.7 g $HgCl_2$ corresponds to 0.150 mol $HgCl_2$, the molality of the solution is 1.50 mol·kg^{-1}. Using Equation 25.45, we find ν to be

$$\nu = \frac{\Delta T_{fus}}{K_f m} = \frac{2.83 \text{ K}}{(1.84 \text{ K·kg·mol}^{-1})(1.50 \text{ mol·kg}^{-1})} = 1.02$$

This result indicates that $HgCl_2$ is not dissociated under these conditions, and so is a poor conductor of electricity.

25–42. The freezing point of a 0.25-molal aqueous solution of Mayer's reagent, K_2HgI_4, is found to be $-1.41°C$. Suggest a possible dissociation reaction that takes place when K_2HgI_4 is dissolved in water.

Use Equation 25.45 to obtain $\nu = 3$. The equation for the dissociation reaction is

$$K_2HgI_4(aq) \longrightarrow 2 K^+(aq) + HgI_4^{2-}(aq)$$
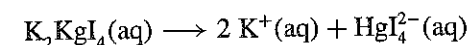
25–43. Given the following freezing-point depression data, determine the number of ions produced per formula unit when the indicated substance is dissolved in water to produce a 1.00-molal solution.

Formula	$\Delta T/K$
$PtCl_2·4NH_3$	5.58
$PtCl_2·3NH_3$	3.72
$PtCl_2·2NH_3$	1.86
$KPtCl_3·NH_3$	3.72
K_2PtCl_4	5.58

Interpret your results.

Use Equation 25.45 to obtain

formula	ν	ions	
$PtCl_2·4NH_3$	3	$Pt(NH_3)_4^{2+}$	$2 Cl^-$
$PtCl_2·3NH_3$	2	$Pt(NH_3)_3Cl^+$	Cl^-
$PtCl_2·2NH_3$	1	$Pt(NH_3)_2Cl_2$	
$KPtCl_3·NH_3$	2	K^+	$Pt(NH_3)Cl_3^-$
K_2PtCl_4	3	$2 K^+$	$PtCl_4^{2-}$

25–44. An aqueous solution of NaCl has an ionic strength of 0.315 mol·L^{-1}. At what concentration will an aqueous solution of K_2SO_4 have the same ionic strength?

The ionic strength, I_c, equals c for a 1–1 electrolyte and $3c$ for a 2–1 electrolyte. Therefore, a solution of $K_2SO_4(aq)$ would have an ionic strength of 0.315 mol·L^{-1} when its molarity is 0.105 mol·L^{-1}.

25–45. Derive the "practical" formula for κ^2 given by Equation 25.53.

Start with

$$\kappa^2 = \frac{1}{\varepsilon_0 \varepsilon_r k_B T} \sum_{j=1}^{s} q_j^2 \frac{N_j}{V} = \frac{N_A e^2}{\varepsilon_0 \varepsilon_r k_B T} \sum_{j=1}^{s} z_j^2 \frac{n_j}{V}$$

Now

$$\frac{n_j}{V} = (1000 \text{ L·m}^{-3}) c_j$$

because V, being in SI units, has units of m^3. Therefore,

$$\kappa^2 = \frac{2e^2 N_A (1000 \text{ L·m}^{-3})}{\varepsilon_0 \varepsilon_r k_B T} (I_c/\text{mol·L}^{-1})$$

25–46. Some authors define ionic strength in terms of molality rather than molarity, in which case

$$I_m = \frac{1}{2} \sum_{j=1}^{s} z_j^2 m_j$$

Show that this definition modifies Equation 25.53 for dilute solutions to be

$$\kappa^2 = \frac{2e^2 N_A (1000 \text{ L·m}^{-3}) \rho}{\varepsilon_0 \varepsilon_r kT} (I_m/\text{mol·kg}^{-1})$$

where ρ is the density of the solvent (in $g·mL^{-1}$).

For dilute solutions, $c = \rho m$ (see Problem 25–5), and so $I_c = \rho I_m$. Therefore,

$$\kappa^2 = \frac{2e^2 N_A (1000 \text{ L·m}^{-3}) \rho}{\varepsilon_0 \varepsilon_r kT} (I_m/\text{mol·kg}^{-1})$$

25–47. Show that

$$\ln \gamma_{\pm} = -1.171 |z_+ z_-| (I_m / \text{mol} \cdot \text{kg}^{-1})^{1/2}$$

for an aqueous solution at 25.0°C, where I_m is the ionic strength expressed in terms of molality. Take ε_r to be 78.54 and the density of water to be 0.99707 g·mL^{-1}.

We use the equation for κ^2 that is derived in Problem 25–46.

$$\kappa^2 = \frac{(2)(1.6022 \times 10^{-19} \text{ C})^2 (6.0221 \times 10^{23} \text{ mol}^{-1})(1000 \text{ L} \cdot \text{m}^{-3})(0.99707 \text{ g} \cdot \text{mL}^{-1})}{(8.8542 \times 10^{-12} \text{ C}^2 \cdot \text{s}^2 \cdot \text{kg}^{-1} \cdot \text{m}^{-3})(78.54)(1.3806 \times 10^{-23} \text{ J} \cdot \text{K}^{-1})(298.2 \text{ K})}$$
$$\times (I_m / \text{mol} \cdot \text{kg}^{-1})$$
$$= (1.077 \times 10^{19} \text{ g} \cdot \text{L} \cdot \text{mL}^{-1} \cdot \text{J}^{-1} \cdot \text{s}^{-2})(I_m / \text{mol} \cdot \text{kg}^{-1})$$
$$= (1.077 \times 10^{19} \text{ g} \cdot \text{L} \cdot \text{mL}^{-1}) \frac{1 \text{ kg}}{1000 \text{ g}} \frac{1000 \text{ mL}}{1 \text{ L}} (\text{J}^{-1} \cdot \text{s}^{-2})(I_m / \text{mol} \cdot \text{kg}^{-1})$$
$$= (1.077 \times 10^{19} \text{ m}^{-2})(I_m / \text{mol} \cdot \text{kg}^{-1})$$

The expression for $\ln \gamma_{\pm}$ is

$$\ln \gamma_{\pm} = -|z_+ z_-| \frac{e^2 \kappa}{8\pi \varepsilon_0 \varepsilon_r kT}$$
$$= -|z_+ z_-| \frac{(1.6022 \times 10^{-19} \text{ C})^2 (1.077 \times 10^{19} \text{ m}^{-2})^{1/2} (I_m / \text{mol} \cdot \text{kg}^{-1})^{1/2}}{8\pi (8.8542 \times 10^{-12} \text{ C}^2 \cdot \text{s}^2 \cdot \text{kg}^{-1} \cdot \text{m}^{-3})(78.54)(1.3806 \times 10^{-23} \text{ J} \cdot \text{K}^{-1})(298.2 \text{ K})}$$
$$= -1.171 |z_+ z_-| (I_m / \text{mol} \cdot \text{kg}^{-1})^{1/2}$$

25–48. Use the Debye-Hückel theory to calculate $\ln \gamma_{\pm}$ for a 0.010-molar NaCl(aq) solution at 25.0°C. Take $\varepsilon_r = 78.54$ for H_2O(l) at 25.0°C. The experimental value of $\ln \gamma_{\pm}$ is -0.103.

We can use Equation 25.56 directly.

$$\ln \gamma_{\pm} = -1.173(0.010)^{1/2} = -0.1173$$

and so $\gamma_{\pm} = 0.889$.

25–49. Derive the general equation

$$\phi = 1 + \frac{1}{m} \int_0^m m' d \ln \gamma_{\pm}$$

(*Hint*: See the derivation in Problem 25–35.) Use this result to show that

$$\phi = 1 + \frac{\ln \gamma_{\pm}}{3}$$

for the Debye-Hückel theory.

Start with (see Problem 25–35)

$$d(m\phi) = md \ln(m\gamma_{\pm}) = m(d \ln m + d \ln \gamma_{\pm})$$
$$= dm + md \ln \gamma_{\pm}$$

---

and integrate from $m = 0$ to arbitrary m to obtain

$$m\phi = m + \int_0^m m' d \ln \gamma_{\pm}$$

or

$$\phi = 1 + \frac{1}{m} \int_0^m m' d \ln \gamma_{\pm} \qquad (1)$$

Now use Equation 25.49 to write $\ln \gamma_{\pm}$ as

$$\ln \gamma_{\pm} = -|q_+ q_-| \frac{(\kappa / m^{1/2})}{8\pi \varepsilon_0 \varepsilon_r k_B T} m^{1/2}$$

where $\kappa / m^{1/2}$ is *independent of m*. Then

$$d \ln \gamma_{\pm} = -|q_+ q_-| \frac{(\kappa / m^{1/2})}{8\pi \varepsilon_0 \varepsilon_r k_B T} \frac{dm}{2m^{1/2}} = \frac{\ln \gamma_{\pm}}{2m} dm$$

and

$$md \ln \gamma_{\pm} = -\frac{1}{2}|q_+ q_-| \frac{(\kappa / m^{1/2})}{8\pi \varepsilon_0 \varepsilon_r k_B T} m^{1/2} dm = \frac{\ln \gamma_{\pm}}{2} dm$$

Substitute these results into Equation 1 to obtain

$$\phi - 1 = \frac{1}{m} \int_0^m m' d \ln \gamma_{\pm}$$
$$= -\frac{1}{2}|q_+ q_-| \frac{(\kappa / m^{1/2})}{8\pi \varepsilon_0 \varepsilon_r k_B T} \frac{1}{m} \int_0^m m'^{1/2} dm'$$
$$= \frac{\ln \gamma_{\pm}}{3}$$

25–50. In the Debye-Hückel theory, the ions are modeled as point ions and the solvent is modeled as a continuous medium (no structure) with a relative permittivity ε_r. Consider an ion of type i ($i = $ a cation or an anion) situated at the origin of a spherical coordinate system. The presence of this ion at the origin will attract ions of opposite charge and repel ions of the same charge. Let $N_{ij}(r)$ be the number of ions of type j ($j = $ a cation or an anion) situated at a distance r from the central ion of type i (a cation or anion). We can use a Boltzmann factor to say that

$$N_{ij}(r) = N_j e^{-w_{ij}(r)/k_B T}$$

where N_j / V is the bulk number density of j ions and $w_{ij}(r)$ is the interaction energy of an i ion with a j ion. This interaction energy will be electrostatic in origin, so let $w_{ij}(r) = q_j \psi_i(r)$, where q_j is the charge on the j ion and $\psi_i(r)$ is the electrostatic potential due to the central i ion.

A fundamental equation from physics that relates a spherically symmetric electrostatic potential $\psi_i(r)$ to a spherically symmetric charge density $\rho_i(r)$ is Poisson's equation

$$\frac{1}{r^2} \frac{d}{dr} \left[r^2 \frac{d\psi_i(r)}{dr} \right] = -\frac{\rho_i(r)}{\varepsilon_0 \varepsilon_r} \qquad (1)$$

where ε_r is the relative permittivity of the solvent. In our case, $\rho_i(r)$ is the charge density around the central ion (of type i). First, show that

$$\rho_i(r) = \frac{1}{V} \sum_j q_j N_{ij}(r) = \sum_j q_j C_j e^{-q_j \psi_i(r)/k_B T}$$

where C_j is the bulk number density of species j ($C_j = N_j/V$). Linearize the exponential term and use the condition of electroneutrality to show that

$$\rho_i(r) = -\psi_i(r) \sum_j \frac{q_j^2 C_j}{k_B T} \tag{2}$$

Now substitute $\rho_i(r)$ into Poisson's equation to get

$$\frac{1}{r^2} \frac{d}{dr}\left[r^2 \frac{d\psi_i(r)}{dr} \right] = \kappa^2 \psi_i(r) \tag{3}$$

where

$$\kappa^2 = \sum_j \frac{q_j^2 C_j}{\varepsilon_0 \varepsilon_r k_B T} = \sum_j \frac{q_j^2}{\varepsilon_0 \varepsilon_r k_B T}\left(\frac{N_j}{V}\right) \tag{4}$$

Show that Equation 3 can be written as

$$\frac{d^2}{dr^2}[r\psi_i(r)] = \kappa^2[r\psi_i(r)]$$

Now show that the only solution for $\psi_i(r)$ that is finite for large values of r is

$$\psi_i(r) = \frac{Ae^{-\kappa r}}{r} \tag{5}$$

where A is a constant. Use the fact that if the concentration is very small, then $\psi_i(r)$ is just Coulomb's law and so $A = q_i/4\pi\varepsilon_0\varepsilon_r$ and

$$\psi_i(r) = \frac{q_i e^{-\kappa r}}{4\pi\varepsilon_0\varepsilon_r r} \tag{6}$$

Equation 6 is a central result of the Debye-Hückel theory. The factor of $e^{-\kappa r}$ modulates the resulting Coulombic potential, so Equation 6 is called a *screened Coulombic potential.*

The number of ions of type j situated at a distance r from the central ion of type i is given by

$$N_{ij}(r) = N_j e^{-q_j \psi_i(r)/k_B T}$$

The charge about a central ion of type i due to ions of type j is given by $q_j N_{ij}(r)$ and the net charge is given by $\sum_j q_j N_{ij}(r)$. The charge density at a distance r from the central ion of type i is given by

$$\rho_i(r) = \frac{1}{V}\sum_j q_j N_{ij}(r) = \sum_j q_j C_j e^{-q_j \psi_i(r)/k_B T}$$

Now expand the exponential using the expansion $e^{-x} = 1 - x + \cdots$ to obtain

$$\rho_i(r) = \sum_j q_j C_j - \frac{\psi_i(r)}{k_B T}\sum_j q_j^2 C_j + \cdots$$

$$= 0 \text{ (by electroneutrality)} - \frac{\psi_i(r)}{k_B T}\sum_j q_j^2 C_j^2 + \cdots$$

Now substitute $\rho_i(r)$ into Poisson's equation to get

$$\frac{1}{r^2}\frac{d}{dr}\left[r^2 \frac{d\psi_i(r)}{dr}\right] = \kappa^2 \psi_i(r) \tag{3}$$

where

$$\kappa^2 = \frac{1}{\varepsilon_0\varepsilon_r k_B T}\sum_j q_j^2 C_j$$

Now

$$\frac{1}{r^2}\frac{d}{dr}\left[r^2\frac{d\psi_i(r)}{dr}\right] = \frac{d^2\psi_i(r)}{dr^2} + \frac{2}{r}\frac{d\psi_i(r)}{dr}$$

and

$$\frac{d^2[r\psi_i(r)]}{dr^2} = r\frac{d^2\psi_i(r)}{dr^2} + 2\frac{d\psi_i(r)}{dr}$$

so

$$\frac{1}{r^2}\frac{d}{dr}\left[r^2\frac{d\psi_i(r)}{dr}\right] = \frac{1}{r}\frac{d^2[r\psi_i(r)]}{dr^2}$$

Therefore, Equation 3 can be written as

$$\frac{d^2[r\psi_i(r)]}{dr^2} = \kappa^2[r\psi(r)]$$

This differential equation has the general solution

$$r\psi_i(r) = Be^{\kappa r} + Ae^{-\kappa r}$$

or

$$\psi_i(r) = \frac{B}{r}e^{\kappa r} + \frac{A}{r}e^{-\kappa r}$$

But B must be zero for $\psi_i(r)$ to be finite as $r \to \infty$. Therefore, we have simply

$$\psi_i(r) = \frac{A}{r}e^{-\kappa r}$$

If the concentration is very small, then $\kappa \to 0$ and $\psi_i(r) \to q_i/4\pi\varepsilon_0\varepsilon_r r$. Therefore,

$$\psi_i(r) \longrightarrow \frac{A}{r} = \frac{q_i}{4\pi\varepsilon_0\varepsilon_r r}$$

and we see that $A = q_i/4\pi\varepsilon_0\varepsilon_r$. Finally then, we have

$$\psi_i(r) = \frac{q_i e^{-\kappa r}}{4\pi\varepsilon_0\varepsilon_r r}$$

25–51. Use Equations 2 and 6 of the previous problem to show that the net charge in a spherical shell of radius r surrounding a central ion of type i is

$$p_i(r)dr = \rho_i(r)4\pi r^2 dr = -q_i \kappa^2 r e^{-\kappa r}dr$$

as in Equation 25.54. Why is

$$\int_0^\infty p_i(r)dr = -q_i$$

Start with

$$p_i(r)dr = \rho_i(r)4\pi r^2 dr$$

Equations 2 and 4 of Problem 25–50 show that

$$-\frac{\rho_i(r)}{\varepsilon_0 \varepsilon_r} = \kappa^2 \psi_i(r)$$

so that

$$p_i(r)dr = -\varepsilon_0 \varepsilon_r \kappa^2 \psi_i(r)4\pi r^2 dr$$

Using Equation 6 of Problem 25–50, we have

$$p_i(r)dr = -q_i \kappa^2 r e^{-\kappa r} dr$$

Therefore,

$$\int_0^\infty p_i(r)dr = -q_i \kappa^2 \int_0^\infty r e^{-\kappa r} dr = -q_i$$

which it must be because of electroneutrality.

25–52. Use the result of the previous problem to show that the most probable value of r is $1/\kappa$.

Problem 25–51 shows that $p_i(r) \approx r e^{-\kappa r}$. Therefore, the most probable value of r is given by

$$\frac{dp_i}{dr} \approx e^{-\kappa r} - \kappa r e^{-\kappa r} = 0$$

or $r_{mp} = 1/\kappa$.

25–53. Show that

$$r_{mp} = \frac{1}{\kappa} = \frac{304 \text{ pm}}{(c/\text{mol·L}^{-1})^{1/2}}$$

where c is the molarity of an aqueous solution of a 1–1 electrolyte at 25°C. Take $\varepsilon_r = 78.54$ for $H_2O(l)$ at 25°C.

Use Equation 25.53

$$\kappa^2 = \frac{2(1.602 \times 10^{-19} \text{ C})^2(6.022 \times 10^{23} \text{ mol}^{-1})(1000 \text{ L·m}^{-3})(I_c/\text{mol·L}^{-1})}{(8.8542 \times 10^{-12} \text{ C·s}^2 \cdot \text{kg}^{-1} \cdot \text{m}^{-3})(78.54)(1.3806 \times 10^{-23} \text{ J·K}^{-1})(298.15 \text{ K})}$$

$$= (1.080 \times 10^{19} \text{ g·L·mL}^{-1} \cdot \text{s}^{-2} \cdot \text{J}^{-1})(I_c/\text{mol·L}^{-1})$$

$$= (1.080 \times 10^{19} \text{ g·L·mL}^{-1})\frac{1 \text{ kg}}{1000 \text{ g}} \cdot \frac{1000 \text{ mL}}{1 \text{ L}}(\text{s}^{-2} \cdot \text{J}^{-1})(I_c/\text{mol·L}^{-1})$$

$$= (1.080 \times 10^{19} \text{ m}^{-2})(I_c/\text{mol·L}^{-1})$$

$$\kappa = (3.29 \times 10^9 \text{ m}^{-1})(I_c/\text{mol·L}^{-1})^{1/2}$$

For a 1–1 electrolyte, $I_c = c$, and so

$$\frac{1}{\kappa} = \frac{3.04 \times 10^{-10} \text{ m}}{(c/\text{mol·L}^{-1})^{1/2}} = \frac{304 \text{ pm}}{(c/\text{mol·L}^{-1})^{1/2}}$$

25–54. Show that

$$r_{mp} = \frac{1}{\kappa} = 430 \text{ pm}$$

for a 0.50-molar aqueous solution of a 1–1 electrolyte at 25°C. Take $\varepsilon_r = 78.54$ for $H_2O(l)$ at 25°C.

Use Equation 25.55 and the result of Problem 25–52:

$$r_{mp} = \frac{1}{\kappa} = \frac{304 \text{ pm}}{(c/\text{mol·L}^{-1})^{1/2}} = \frac{304 \text{ pm}}{(0.50)^{1/2}} = 430 \text{ pm}$$

25–55. How does the thickness of the ionic atmosphere compare for a 1–1 electrolyte and a 2–2 electrolyte?

Equation 25.50 shows that $\kappa_{2-2}^2 = 4\kappa_{1-1}^2$, or that $\kappa_{2-2} = 2\kappa_{1-1}$. Because $1/\kappa$ is a measure of the thickness of an ionic atmosphere, we see that the thickness of the ionic atmosphere of a 2–2 electrolyte is one half that of a 1–1 electrolyte.

25–56. In this problem, we will calculate the total electrostatic energy of an electrolyte solution in the Debye-Hückel theory. Use the equations in Problem 25–50 to show that the number of ions of type j in a spherical shell of radii r and $r + dr$ about a central ion of type i is

$$\left(\frac{N_{ij}(r)}{V}\right)4\pi r^2 dr = C_j e^{-q_j \psi_i(r)/k_B T}4\pi r^2 dr \approx C_j\left(1 - \frac{q_j \psi_i(r)}{k_B T}\right)4\pi r^2 dr \tag{1}$$

The total Coulombic interaction between the central ion of type i and the ions of type j in the spherical shell is $N_{ij}(r)u_{ij}(r)4\pi r^2 dr/V$ where $u_{ij}(r) = q_i q_j/4\pi \varepsilon_0 \varepsilon_r r$. To determine the electrostatic interaction energy of all the ions in the solution with the central ion (of type i), U_i^{el}, sum $N_{ij}(r)u_{ij}(r)/V$ over all types of ions in a spherical shell and then integrate over all spherical shells to get

$$U_i^{el} = \int_0^\infty \left(\sum_j \frac{N_{ij}(r)u_{ij}(r)}{V}\right)4\pi r^2 dr$$

$$= \sum_j \frac{C_j q_i q_j}{\varepsilon_0 \varepsilon_r}\int_0^\infty\left(1 - \frac{q_j \psi_i(r)}{k_B T}\right)r dr$$

Use electroneutrality to show that

$$U_i^{el} = -q_i \kappa^2 \int_0^\infty \psi_i(r)r dr$$

Now, using Equation 6 of Problem 25–50, show that the interaction of all ions with the central ion (of type i) is given by

$$U_i^{el} = -\frac{q_i^2 \kappa^2}{4\pi \varepsilon_0 \varepsilon_r}\int_0^\infty e^{-\kappa r}dr = -\frac{q_i^2 \kappa}{4\pi \varepsilon_0 \varepsilon_r}$$

Now argue that the total electrostatic energy is

$$U^{el} = \frac{1}{2}\sum_i N_i U_i^{el} = -\frac{V k_B T \kappa^3}{8\pi}$$

Why is there a factor of 1/2 in this equation? Wouldn't you be overcounting the energy otherwise?

According to Problem 25–50, the number of ions of type j in a spherical shell of radii r and $r + dr$ about a central ion of type i is given by

$$\frac{N_{ij}(r)4\pi r^2 dr}{V} = C_j e^{-q_j \psi_i(r)/k_B T} 4\pi r^2 dr$$

Linearize the exponential term to obtain

$$\frac{N_{ij}(r)4\pi r^2 dr}{V} = C_j \left(1 - \frac{q_j \psi_i(r)}{k_B T}\right) 4\pi r^2 dr$$

The Coulombic interaction between the ions in the spherical shell and the central ion (of type i) is $u_{ij}(r)N_{ij}(r)4\pi r^2 dr/V$, where $u_{ij}(r) = q_i q_j/4\pi\varepsilon_0\varepsilon_r r$. The interaction of all ions with the central ion is given by

$$U_i^{el} = \int_0^\infty \sum_j \frac{u_{ij}(r)N_{ij}(r)4\pi r^2 dr}{V} = \sum_j \int_0^\infty \left(\frac{q_i q_j}{4\pi\varepsilon_0\varepsilon_r r}\right) C_j \left(1 - \frac{q_j \psi_i(r)}{k_B T}\right) 4\pi r^2 dr$$

$$= \frac{q_i}{4\pi\varepsilon_0\varepsilon_r} \sum_j \int_0^\infty q_j C_j 4\pi r dr - \frac{q_i}{4\pi\varepsilon_0\varepsilon_r k_B T} \sum_j q_j^2 C_j \int_0^\infty \psi_i(r)4\pi r dr$$

$$= 0 \text{ (by electroneutrality)} - q_i \left(\sum_j \frac{q_j^2 C_j}{\varepsilon_0\varepsilon_r k_B T}\right)\int_0^\infty \psi_i(r)r dr$$

$$= -q_i \kappa^2 \int_0^\infty \psi_i(r)r dr$$

Using Equation 6 of Problem 25–50,

$$U_i^{el} = -\frac{q_i^2 \kappa^2}{4\pi\varepsilon_0\varepsilon_r} \int_0^\infty e^{-\kappa r} dr = -\frac{q_i^2 \kappa}{4\pi\varepsilon_0\varepsilon_r}$$

The total electrostatic energy is given by

$$U^{el} = \frac{1}{2}\sum_i N_i U_i^{el} = -\frac{V k_B T \kappa}{8\pi} \sum_i \frac{q_i^2 C_i}{\varepsilon_0\varepsilon_r k_B T} = -\frac{V k_B T \kappa^3}{8\pi}$$

The factor of 1/2 is needed in the second term in the above equation because in the summation over i, each ion occurs both as a central ion and as an ion in the spherical shell.

25–57. We derived an expression for U^{el} in the previous problem. Use the Gibbs-Helmholtz equation for A (Problem 22–23) to show that

$$A^{el} = -\frac{V k_B T \kappa^3}{12\pi}$$

Use the Gibbs-Helmholtz equation for A written in the form

$$\left(\frac{\partial\beta A^{el}}{\partial\beta}\right) = U^{el}$$

with (see Problem 25–56)

$$U^{el} = -\frac{V k_B T \kappa^3}{8\pi} = -\frac{V}{8\pi(k_B T)^{1/2}}\left(\sum_j \frac{q_j^2}{\varepsilon_0\varepsilon_r}C_j\right)^{3/2}$$

$$= -\frac{V\beta^{1/2}}{8\pi}\left(\sum_j \frac{q_j^2 C_j}{\varepsilon_0\varepsilon_r}\right)^{3/2}$$

Substitute this result into the Gibbs-Helmholtz equation and integrate from 0 to β to obtain

$$\beta A^{el} = -\frac{V\beta^{3/2}}{12\pi}\left(\sum_j \frac{q_j^2 C_j}{\varepsilon_0\varepsilon_r}\right)^{3/2} = -\frac{V\kappa^3}{12\pi}$$

or

$$A^{el} = -\frac{V k_B T \kappa^3}{12\pi}$$

25–58. If we assume that the electrostatic interactions are the sole cause of the nonideality of an electrolyte solution, then we can say that

$$\mu_j^{el} = \left(\frac{\partial A^{el}}{\partial n_j}\right)_{T,V} = RT \ln\gamma_j^{el}$$

or that

$$\mu_j^{el} = \left(\frac{\partial A^{el}}{\partial N_j}\right)_{T,V} = k_B T \ln\gamma_j^{el}$$

Use the result you got for A^{el} in the previous problem to show that

$$k_B T \ln\gamma_j^{el} = -\frac{\kappa q_j^2}{8\pi\varepsilon_0\varepsilon_r}$$

Use the formula

$$\gamma_\pm^\nu = \gamma_+^{\nu_+}\gamma_-^{\nu_-}$$

to show that

$$\ln\gamma_\pm = -\left(\frac{\nu_+ q_+^2 + \nu_- q_-^2}{\nu_+ + \nu_-}\right)\frac{\kappa}{8\pi\varepsilon_0\varepsilon_r k_B T}$$

Use the electroneutrality condition $\nu_+ q_+ + \nu_- q_- = 0$ to rewrite $\ln\gamma_\pm$ as

$$\ln\gamma_\pm = -|q_+ q_-|\frac{\kappa}{8\pi\varepsilon_0\varepsilon_r k_B T}$$

in agreement with Equation 25.49.

Using the final result from Problem 25–57,

$$\mu_j^{\text{el}} = \left(\frac{\partial A^{\text{el}}}{\partial N_j}\right)_{\beta,V}$$

$$= -\frac{V\beta^{1/2}}{12\pi}\frac{\partial}{\partial N_j}\left(\sum_j \frac{q_j^2 C_j}{\varepsilon_0 \varepsilon_r V}\right)^{3/2} = -\frac{V\beta^{1/2}}{12\pi}\cdot\frac{3}{2}\left(\sum_j \frac{q_j^2 C_j}{\varepsilon_0 \varepsilon_r}\right)^{1/2}\frac{q_j^2}{\varepsilon_0 \varepsilon_r V}$$

$$= -\frac{\kappa q_j^2}{8\pi\varepsilon_0\varepsilon_r} = k_{\text{B}}T\ln\gamma_j^{\text{el}}$$

Now, take the logarithm of the equation $\gamma_\pm^\nu = \gamma_+^{\nu_+}\gamma_-^{\nu_-}$ and the previous result to obtain

$$\ln\gamma_\pm = \frac{\nu_+\ln\gamma_+ + \nu_-\ln\gamma_-}{\nu_+ + \nu_-} = -\left(\frac{\kappa}{8\pi\varepsilon_0\varepsilon_r k_{\text{B}}T}\right)\left(\frac{\nu_+ q_+^2 + \nu_- q_-^2}{\nu_+ + \nu_-}\right)$$

But

$$\nu_+ q_+^2 + \nu_- q_-^2 = q_+(\nu_+ q_+) + \nu_- q_-^2 = q_+(|\nu_- q_-|) + \nu_-|q_-|^2$$

$$= q_+|q_-|\left(\nu_- + \nu_-\frac{|q_-|}{q_+}\right) = |q_+ q_-|(\nu_- + \nu_+)$$

where we have used the electroneutrality condition, $\nu_+ q_+ = \nu_-|q_-|$, and so finally

$$\ln\gamma_\pm = -|q_+ q_-|\frac{\kappa}{8\pi\varepsilon_0\varepsilon_r k_{\text{B}}T}$$

25–59. Derive Equation 25.56 from Equation 25.49.

See the solution to Problem 25–47, but do not include the factor $\rho = 0.99707$ g·mL^{-1}.

25–60. Show that Equation 25.59 reduces to Equation 25.49 for small concentrations.

We want to show that Equation 25.59 reduces to Equation 25.49 as $\rho \to 0$ or as $\kappa \to 0$. Let's consider $\ln\gamma_\pm^{\text{el}}$ first. Use the fact that $(1+x)^{1/2} = 1 + x/2 - x^2/8 + x^3/16 + \cdots$ to write

$$x(1+2x)^{1/2} - x - x^2 = x\left[1 + x - \frac{(2x)^2}{8} + \frac{(2x)^3}{16} + O(x^4)\right] - x - x^2$$

$$= -\frac{x^3}{2}$$

Using the fact that $x = \kappa d$, Equation 25.60 becomes

$$\ln\gamma_\pm^{\text{el}} = -\frac{\kappa^3}{8\pi\rho}$$

For a 1–1 electrolyte, $\kappa^2 = \rho/\varepsilon_0\varepsilon_r k_{\text{B}}T$, so we have

$$\ln\gamma_\pm^{\text{el}} = -\frac{\kappa}{8\pi\varepsilon_0\varepsilon_r k_{\text{B}}T}$$

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in agreement with Equation 25.49 for a 1–1 electrolyte. The $\ln\gamma^{\text{HS}}$ contribution to Equation 25.59 is negligible when $\rho \to 0$ because $y = \pi\rho d^3/6$.

25–61. In this problem, we will investigate the temperature dependence of activities. Starting with the equation $\mu_1 = \mu_1^* + RT\ln a_1$, show that

$$\left(\frac{\partial\ln a_1}{\partial T}\right)_{P,x_1} = \frac{\overline{H}_1^* - \overline{H}_1}{RT^2}$$

where $\overline{H}_1^*$ is the molar enthalpy of the pure solvent (at one bar) and $\overline{H}_1$ is its partial molar enthalpy in the solution. The difference between $\overline{H}_1^*$ and $\overline{H}_1$ is small for dilute solutions, so a_1 is fairly independent of temperature.

Starting with $\mu_1 = \mu_1^* + RT\ln a_1$, differentiate μ_1/T with respect to T to obtain

$$\left(\frac{\partial\mu_1/T}{\partial T}\right)_{P,x_1} - \left(\frac{\partial\mu_1^*/T}{\partial T}\right)_P = R\left(\frac{\partial\ln a_1}{\partial T}\right)_{P,x_1}$$

Now use the equation (see Example 24–1)

$$\left(\frac{\partial\mu_j/T}{\partial T}\right)_{P,x_1} = -\frac{\overline{H}_j}{T^2}$$

to write

$$\left(\frac{\partial\ln a_1}{\partial T}\right)_{P,x_1} = \frac{\overline{H}_1^* - \overline{H}_1}{RT^2}$$

25–62. Henry's law says that the pressure of a gas in equilibrium with a non-electrolyte solution of the gas in a liquid is proportional to the molality of the gas in the solution for sufficiently dilute solutions. What form do you think Henry's law takes on for a gas such as HCl(g) dissolved in water? Use the following data for HCl(g) at 25°C to test your prediction.

$P_{\text{HCl}}/10^{-11}$ atm	$m_{\text{HCl}}/10^{-3}$ mol·kg^{-1}
0.147	1.81
0.238	2.32
0.443	3.19
0.663	3.93
0.851	4.47
1.080	5.06
1.622	6.25
1.929	6.84
2.083	7.12

A plot of pressure against molality is not a straight line, but a plot of pressure against molality squared is almost a straight line. This is due to the fact that HCl(aq) dissociates into H$^+$(aq) and Cl$^-$(aq).

25-63. When the pressures in Problem 25-62 are plotted against molality squared, the result is almost a straight line. Curve fit the data to polynomials of the form

$$P = k_K m^2 (1 + c_1 m^{1/2} + c_2 m + c_3 m^{3/2} + \cdots)$$

of increasing degree and evaluate k_H.

If the data are fitted to $P = k_H m^2$, k_H turns out to be (in units of $atm \cdot kg^2 \cdot mol^{-2}$) 4.15×10^{-7}. The subsequent fits are (suppressing the units)

k_H	c_1	c_2	c_3	c_4
4.83×10^{-7}	-1.77			
4.92×10^{-7}	-2.24	3.48		
4.93×10^{-7}	-2.33	4.75	-6.21	
4.93×10^{-7}	-2.34	5.07	-9.45	10.3

Thus we see that $k_H = 4.93 \times 10^{-7}$ $atm \cdot kg^2 \cdot mol^{-2}$.

25-64. When the data in Problem 25-62 are plotted in the form of P/m^2 against $m^{1/2}$, the result is essentially a straight line with a negative slope. Why is this so? Use Debye-Hückel theory to calculate the slope of this line and compare your result with the final value of c_1 in Problem 25-63.

The activity of the HCl(aq) is given by $a_{HCl} = P/k_H$. Using the fact that $a_{HCl} = a_\pm^2 = m^2 \gamma_\pm^2$, we have

$$P = k_H m^2 \gamma_\pm^2$$

Note that as $m \to 0$, $\gamma_\pm \to 1$, and $P \to k_H m^2$, as expected. The Debye-Hückel expression for $\gamma_\pm$ in this case is

$$\ln \gamma_\pm = -1.171 m^{1/2}$$

Substitute this expression for $\gamma_\pm$ into $P = k_H m^2 \gamma_\pm^2$ and linearize the exponential according to $e^{-x} = 1 - x + \cdots$ to obtain
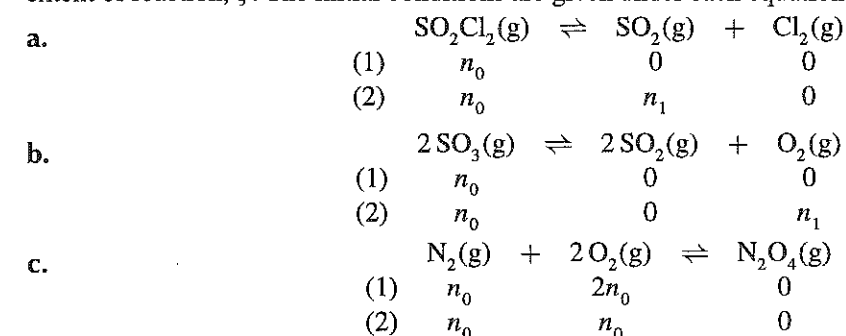
$$P = k_H m^2 (1 - 2.342 m^{1/2} + \cdots)$$

Thus, we predict that c_1 in Problem 25-63 is equal to -2.34, in excellent agreement.
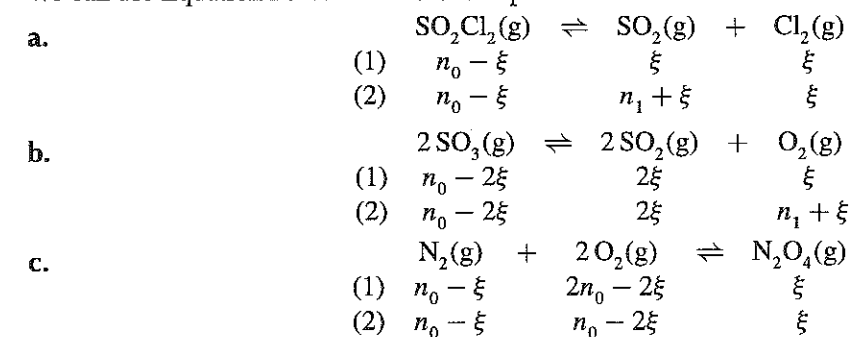


Chemical Equilibrium

PROBLEMS AND SOLUTIONS

26-1. Express the concentrations of each species in the following chemical equations in terms of the extent of reaction, ξ. The initial conditions are given under each equation.

a.

	$SO_2Cl_2(g)$	$\rightleftharpoons$	$SO_2(g)$	$+$	$Cl_2(g)$
(1)	n_0		0		0
(2)	n_0		n_1		0

b.

	$2\,SO_3(g)$	$\rightleftharpoons$	$2\,SO_2(g)$	$+$	$O_2(g)$
(1)	n_0		0		0
(2)	n_0		0		n_1

c.

	$N_2(g)$	$+$	$2\,O_2(g)$	$\rightleftharpoons$	$N_2O_4(g)$
(1)	n_0		$2n_0$		0
(2)	n_0		n_0		0

We can use Equation 26.1 in all cases to express the concentrations of each species.

a.

	$SO_2Cl_2(g)$	$\rightleftharpoons$	$SO_2(g)$	$+$	$Cl_2(g)$
(1)	$n_0 - \xi$		ξ		ξ
(2)	$n_0 - \xi$		$n_1 + \xi$		ξ

b.

	$2\,SO_3(g)$	$\rightleftharpoons$	$2\,SO_2(g)$	$+$	$O_2(g)$
(1)	$n_0 - 2\xi$		2ξ		ξ
(2)	$n_0 - 2\xi$		2ξ		$n_1 + \xi$

c.

	$N_2(g)$	$+$	$2\,O_2(g)$	$\rightleftharpoons$	$N_2O_4(g)$
(1)	$n_0 - \xi$		$2n_0 - 2\xi$		ξ
(2)	$n_0 - \xi$		$n_0 - 2\xi$		ξ

26-2. Write out the equilibrium-constant expression for the reaction that is described by the equation

$$2\,SO_2(g) + O_2(g) \rightleftharpoons 2\,SO_3(g)$$
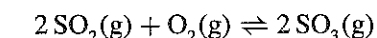
Compare your result to what you get if the reaction is represented by

$$SO_2(g) + \frac{1}{2} O_2(g) \rightleftharpoons SO_3(g)$$
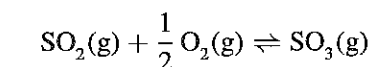
Using Equation 26.12, we write K_P for the first chemical equation as

$$K_P(T) = \frac{P_{SO_3}^2}{P_{O_2} P_{SO_2}^2}$$