Chapter 15

Making Accommodations—Solubility and Molecular Recognition

Principles of bonding and thermodynamics are put to the test here and in the two chapters following. In each, a major area introduced in Chapter 3 is reopened and examined thoroughly, with full advantage taken of all that has gone before. In Chapter 16: acids and bases, first encountered in Section 3-2. In Chapter 17: redox reactions, treated briefly in Section 3-3. In the present chapter: the chemistry of weak bonds, as exemplified by dissolution–precipitation and host–guest interactions (originally, Section 3-4).

Useful resources in PoC *include Table C-16 (thermodynamic data, pages A85–A92), Table C-17 (qualitative solubilities, page A94), Table C-18 (quantitative solubilities, page A95), and Table C-19 (solubility-product constants, pages A96–A97). All systems are at 25°C, unless stated otherwise.*

1. In addition to the discussion of saturation on pages 531–535 and R15.2–R15.4 of *PoC*, see also pages 407–412 and 449–452 for related earlier material.

(a) Consider the heterogeneous equilibrium between the pure phase and solution phase of some solute A:

$$\text{A(undissolved)} \rightleftarrows \text{A(dissolved)}$$

$$K = \frac{[\text{A(dissolved)}]}{[\text{A(undissolved)}]}$$

When the reaction quotient is equal to K, the solution is said to be *saturated.* A dynamic equilibrium is maintained between the two phases, and no additional solute can be dissolved.

(b) A solution need not be saturated in order to sustain thermal equilibrium, whereby a uniform temperature is established throughout the phase. Saturation pertains to uniformity of concentration, not to uniformity of temperature.

See Section 14-9 in *PoC* for a summary treatment of thermal equilibrium.

2. The presence of undissolved solute certifies that *two* phases are in equilibrium—a dissolved phase (solute in solvent) and an undissolved phase (pure solute). Below the saturation point, additional solute will continue to dissolve until the reaction quotient Q matches the equilibrium constant K, whereupon heterogeneous (two-phase) equilibrium sets in.

3. The various categories of equilibrium are covered in Sections 11-4 and 11-6 (disorder–order), Chapter 12 (chemical), Section 14-9 (thermal), and pages 540–543 (osmotic). For a brief summary, see pages R15.2–R15.4.

In each instance, an ongoing exchange of matter or energy at the microscopic level produces an apparent stasis at the macroscopic level. Bulk properties of the system remain constant in time and uniform in space.

(a) *Disorder–order equilibrium* in a saturated solution arises when two opposing processes (dissolution and precipitation) come into balance:

$$\text{A(undissolved)} \rightleftarrows \text{A(dissolved)}$$

There is a continual exchange of matter and free energy between two distinct phases.

(b) *Chemical equilibrium* arises when dissolved ions and molecules undergo a reaction in solution:

$$\text{reactants} \rightleftarrows \text{products}$$

Two opposing processes (formation of products and regeneration of reactants) come into balance, and there is a continual exchange of matter and free energy between reactants and products.

(c) *Thermal equilibrium* arises when particles in solution establish a uniform temperature all throughout. The colliding particles continually exchange energy—some gain, some lose—and eventually a balance is struck. The average distribution of energy conforms to a Boltzmann distribution consistent with some temperature T. See pages 384–391 in *PoC*.

(d) *Osmotic equilibrium* arises when matter flows between regions of different concentration. Matter and free energy are exchanged continually as two opposing processes (transport back and forth) come into balance.

4. Thermodynamics predicts only the final concentrations when a system comes to equilibrium. It says nothing about either the time required to reach equilibrium or the microscopic mechanism by which equilibrium is eventually realized. A solution therefore can remain temporarily out of equilibrium (supersaturated) without violating the laws of thermodynamics. The *kinetics* of a process will determine when and how the system comes to its equilibrium state. See Chapter 18.

5. Thermodynamics versus kinetics.

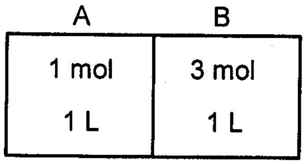
(a) The solution will not be fully equilibrated until concentrations are uniform throughout the entire phase. To be at equilibrium, a system must persist in a state where its macroscopic properties are constant in time and uniform in space.

(b) We know from experience that sugar dissolves in hot tea within a matter of seconds.

6. We assume that the system is ideal, with undifferentiated intermolecular interactions and with zero enthalpy of mixing. If so, then the driving force comes entirely from an increase in local entropy. See the solution to Exercise 46 in Chapter 14.

The argument for entropy is similar to what we advanced in Chapter 14 to explain the random mixing of particles in a gas. If a single particle is equally likely to be found in two places (left and right, say), then the probability that N particles will all be found together is $(\frac{1}{2})^N$. This number falls rapidly to zero even for modest N, leaving a uniform distribution as overwhelmingly most probable. See Section 14-2 and Example 14-4.

7. We begin with two solutions, equal in volume but having different concentrations:



Each subsystem contains a different amount of solute.

(a) Water will flow from the dilute solution in compartment A to the concentrated solution in compartment B until the two molarities are equal.

(b) The volume of solution A goes down, and the volume of solution B goes up—but the amount of solute in each compartment remains the same. We denote by ΔV the volume of H_2O (in liters) passing between compartments,

$$[\mathrm{A}]_{\mathrm{eq}} = [\mathrm{B}]_{\mathrm{eq}}$$

$$\frac{1\ \mathrm{mol}}{(1-\Delta V)\ \mathrm{L}} = \frac{3\ \mathrm{mol}}{(1+\Delta V)\ \mathrm{L}}$$

and we solve the resulting linear equation for ΔV:

$$1 + \Delta V = 3(1 - \Delta V)$$

$$1 + \Delta V = 3 - 3\Delta V$$

$$4\Delta V = 2$$

$$\Delta V = 0.5$$

The net flow is equal to 0.5 L.

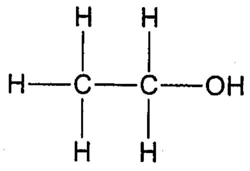
(c) The equilibrium concentrations are equal, 2 *M* for both A and B:

$$[\mathrm{A}]_{\mathrm{eq}} = \frac{1\ \mathrm{mol}}{(1-0.5)\ \mathrm{L}} = 2\ \mathrm{mol\ L^{-1}}$$

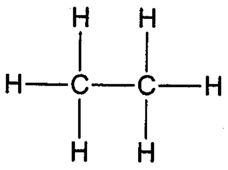
$$[\mathrm{B}]_{\mathrm{eq}} = \frac{3\ \mathrm{mol}}{(1+0.5)\ \mathrm{L}} = 2\ \mathrm{mol\ L^{-1}}$$

8. For a similar exercise, see Example 15-13 in *PoC* (beginning on page R15.18). The general question of solubility and structure, including hydrophilic and hydrophobic effects, is discussed on pages 546–555. Noncovalent interactions are treated in Section 9-3 and reviewed on pages R9.2–R9.4. See also pages 396–398.

(a) Ethanol, which forms hydrogen bonds (like H_2O), is more soluble in the polar solvent:



ethanol



ethane

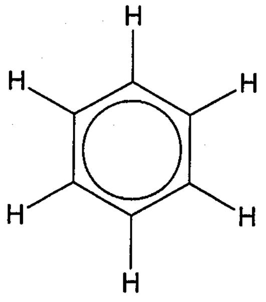
Ethane, a nonpolar hydrocarbon, is insoluble in water.

(b) Both propanol ($CH_3CH_2CH_2OH$) and butanol ($CH_3CH_2CH_2CH_2OH$) contain a polar OH group that enables them to form hydrogen bonds. The smaller molecule, however, carries its target on a shorter hydrophobic chain and thus interacts more effectively with water. Propanol is more soluble than butanol.

(c) Similar to (a): Serine, able to form hydrogen bonds, is more soluble in water than ethene, a nonpolar hydrocarbon.

(d) Similar to (b): Vitamin A, which contains only one polar OH group in a relatively large molecule, is nearly nonpolar. The smaller vitamin C molecule contains four OH groups and is soluble in water. Vitamin A is not.

9. The rule of "like dissolves like" is the same as in Exercise 8, but now the solvent is benzene—a nonpolar, hydrophobic molecule:



benzene

(a) Toluene, an aromatic hydrocarbon with a structure similar to benzene, interacts via London dispersion forces and is soluble in the nonpolar solvent. NaCl, an ionic solid, requires a polar solvent to break the strong ionic bonds. It dissolves in water, not benzene.

(b) Similar to (a): The nonpolar molecule, ethane, is soluble in the nonpolar solvent. By contrast, sulfuric acid is a polar species requiring a polar solvent (water, for example).

(c) Naphthalene, an aromatic hydrocarbon subject to London dispersion interactions, is soluble in benzene. Sucrose is a carbohydrate soluble in water. Its hydroxyl (OH) groups enable it to form hydrogen bonds with H_2O.

For related sample problems dealing with solution stoichiometry, see Examples 3-7 and 9-2. See also Exercises 24 through 30 in Chapter 3 and Exercises 23 through 29 in Chapter 9.

10. Note, in each case, that we apply the relationship connecting concentration, volume and amount:

$$\text{Concentration} \times \text{volume} = \text{amount}$$

$$\frac{\text{mol}}{\text{L}} \times \text{L} = \text{mol}$$

$$\frac{\text{g}}{\text{L}} \times \text{L} = \text{g}$$

(a) Dissolve 5.33 g Na_2SO_4 in a total volume of 100 mL:

$$\underbrace{\left(\frac{0.375 \text{ mol } Na_2SO_4}{\text{L}} \times \frac{142.043 \text{ g } Na_2SO_4}{\text{mol } Na_2SO_4}\right)}_{\text{CONCENTRATION}} \times \underbrace{\left(\frac{1 \text{ L}}{1000 \text{ mL}} \times 100 \text{ mL}\right)}_{\text{VOLUME}} = \underbrace{5.33 \text{ g } Na_2SO_4}_{\text{AMOUNT}}$$

(b) Dissolve 2.55 g $AgNO_3$ in a total volume of 100 mL:

$$\left(\frac{0.150 \text{ mol } AgNO_3}{\text{L}} \times \frac{169.873 \text{ g } AgNO_3}{\text{mol } AgNO_3}\right) \times \left(\frac{1 \text{ L}}{1000 \text{ mL}} \times 100 \text{ mL}\right) = 2.55 \text{ g } AgNO_3$$

(c) Dissolve 11.3 g $C_6H_{12}O_6$ in a total volume of 100 mL:

$$\left(\frac{0.625 \text{ mol } C_6H_{12}O_6}{\text{L}} \times \frac{180.158 \text{ g } C_6H_{12}O_6}{\text{mol } C_6H_{12}O_6}\right) \times \left(\frac{1 \text{ L}}{1000 \text{ mL}} \times 100 \text{ mL}\right) = 11.3 \text{ g } C_6H_{12}O_6$$

(d) Dissolve 3.65 g HCl in a total volume of 100 mL:

$$\left(\frac{1.00 \text{ mol HCl}}{\text{L}} \times \frac{36.461 \text{ g HCl}}{\text{mol HCl}}\right) \times \left(\frac{1 \text{ L}}{1000 \text{ mL}} \times 100 \text{ mL}\right) = 3.65 \text{ g HCl}$$

11. The amount of solute (n moles) remains constant, but the total volume of solution changes from V_1 to V_2:

Initial concentration: $c_1 = \frac{n}{V_1}$

Final concentration: $c_2 = \frac{n}{V_2}$

With each concentration inversely proportional to the volume, the final concentration is thus diluted by a factor of 0.8:

$$\frac{c_2}{c_1} = \frac{V_1}{V_2} = \frac{0.100 \text{ L}}{0.125 \text{ L}} = 0.800$$

Recognize, too, the general dilution equation that falls out of the calculation:

$$\text{moles} = \text{moles}$$

$$c_1V_1 = c_2V_2$$

A similar relationship governs the titration of acids and bases, as demonstrated in Example 16-8 (beginning on page R16.20 of *PoC*).

(a) The original 0.375 M solution contains 0.0375 mol dissolved in 0.100 L:

$$n = c_1V_1 = \frac{0.375 \text{ mol}}{\text{L}} \times 0.100 \text{ L} = 0.0375 \text{ mol}$$

If this same 0.0375 mol is now dissolved in 0.125 L, the concentration falls to 0.300 M:

$$c_2 = \frac{c_1V_1}{V_2} = \frac{(0.375 \text{ mol L}^{-1})(0.100 \text{ L})}{0.125 \text{ L}} = \frac{0.0375 \text{ mol}}{0.125 \text{ L}} = 0.300 \text{ mol L}^{-1}$$

The remaining calculations are all done in the same way.

(b) $\frac{0.0150 \text{ mol}}{0.125 \text{ L}} = 0.120 \text{ mol L}^{-1}$

(c) $\frac{0.0625 \text{ mol}}{0.125 \text{ L}} = 0.500 \text{ mol L}^{-1}$

(d) $\frac{0.100 \text{ mol}}{0.125 \text{ L}} = 0.800 \text{ mol L}^{-1}$

12. The original amount of solute, n =1.00 mol, remains the same throughout any change in total volume:

$$\begin{array}{ccc} \text{CONCENTRATION} & \text{VOLUME} & \text{AMOUNT} \\ (c_1) & (V_1) & (n) \end{array}$$

$$\frac{2.00 \text{ mol solute}}{\text{L}} \times \left(\frac{1 \text{ L}}{1000 \text{ mL}} \times 500 \text{ mL}\right) = 1.00 \text{ mol solute}$$

(a) Solve for the volume V_2 needed to produce a concentration c_2 of 1.00 M:

$$c_2 = \frac{c_1V_1}{V_2} = \frac{1.00 \text{ mol}}{V_2} = 1.00 \text{ mol L}^{-1}$$

$$V_2 = 1.00 \text{ L}$$

The remaining calculations are all done in the same way.

(b) $$\frac{1.00\text{ mol}}{V_2} = 0.50\text{ mol L}^{-1}$$

$$V_2 = 2.0\text{ L}$$

(c) $$\frac{1.00\text{ mol}}{V_2} = 0.25\text{ mol L}^{-1}$$

$$V_2 = 4.0\text{ L}$$

(d) $$\frac{1.00\text{ mol}}{V_2} = 0.10\text{ mol L}^{-1}$$

$$V_2 = 10.\text{ L}$$

13. Multiply the concentration (amount per unit volume) by the volume of solution to obtain the amount dissolved:

$$\text{Concentration} \times \text{volume} = \text{amount}$$

$$\frac{\text{mol}}{\text{L}} \times \text{L} = \text{mol}$$

Taking 50.0 mL of 0.750 M Na_2SO_4, for example, we calculate the molar amount of each ion as follows:

$$\left(\frac{0.750\text{ mol Na}_2\text{SO}_4}{\text{L}} \times \frac{2\text{ mol Na}^+}{\text{mol Na}_2\text{SO}_4}\right) \times \left(\frac{1\text{ L}}{1000\text{ mL}} \times 50.0\text{ mL}\right) = 0.0750\text{ mol Na}^+$$

$$\left(\frac{0.750\text{ mol Na}_2\text{SO}_4}{\text{L}} \times \frac{1\text{ mol SO}_4^{2-}}{\text{mol Na}_2\text{SO}_4}\right) \times \left(\frac{1\text{ L}}{1000\text{ mL}} \times 50.0\text{ mL}\right) = 0.0375\text{ mol SO}_4^{2-}$$

Note that one mole of SO_4^{2-} and two moles of Na^+ are produced per mole of Na_2SO_4 dissolved.

All the calculations are done in the same way. Results are summarized in the following table:

	CONCENTRATION (M)	n_{Na^+}	$n_{\text{SO}_4^{2-}}$
(a)	0.750	0.0750	0.0375
(b)	1.256	0.1256	0.0628
(c)	0.105	0.0105	0.00525
(d)	3.07×10^{-3}	3.07×10^{-4}	1.54×10^{-4}
(e)	4.92×10^{-5}	4.92×10^{-6}	2.46×10^{-6}

Having reviewed the arithmetic of molarity and moles, we turn to basic operations involving solubility and the solubility-product constant.

14. See Example 15-1 for a variant calculation of this type.

(a) Convert grams into moles and milliliters into liters, taking into account the 2:1 ionic stoichiometry of Na_2CO_3:

$$\frac{7.1\text{ g Na}_2\text{CO}_3}{100\text{ mL}} \times \frac{1\text{ mol Na}_2\text{CO}_3}{105.989\text{ g Na}_2\text{CO}_3} \times \frac{2\text{ mol Na}^+}{\text{mol Na}_2\text{CO}_3} \times \frac{1000\text{ mL}}{\text{L}} = 1.34\text{ mol Na}^+\text{ L}^{-1}$$

$$\frac{7.1\text{ g Na}_2\text{CO}_3}{100\text{ mL}} \times \frac{1\text{ mol Na}_2\text{CO}_3}{105.989\text{ g Na}_2\text{CO}_3} \times \frac{1\text{ mol CO}_3^{2-}}{\text{mol Na}_2\text{CO}_3} \times \frac{1000\text{ mL}}{\text{L}} = 0.67\text{ mol CO}_3^{2-}\text{ L}^{-1}$$

The final values, rounded to two significant figures, are as follows:

$$[\text{Na}^+] = 1.3\ M \qquad [\text{CO}_3^{2-}] = 0.67\ M$$

(b) Given the stoichiometry and one set of equilibrium concentrations,

$$\begin{array}{cccc} \text{Na}_2\text{CO}_3(s) \rightleftarrows & 2\text{Na}^+(aq) & + & \text{CO}_3^{2-}(aq) \\ & 1.34\ M & & 0.67\ M \end{array}$$

we can compute the equilibrium constant:

$$K_{\text{sp}} = [\text{Na}^+]^2[\text{CO}_3^{2-}] = (1.34)^2(0.67) = 1.2$$

15. We apply Le Châtelier's principle (but with caution, bearing in mind the warning on page R15.15 of *PoC*).

For quantitative problems involving solution thermodynamics, see Exercises 27 through 30.

(a) The decreased solubility in hot water suggests that the dissolution is exothermic:

$$\Delta H_{\text{soln}} < 0$$

Heat functions as a product, and the system relieves the stress of a higher temperature (more heat) by shifting to the left—toward precipitation of solid Li_2CO_3 (the reactant in the process):

$$\text{Li}_2\text{CO}_3(s) \leftarrow 2\text{Li}^+(aq) + \text{CO}_3^{2-}(aq) + \text{heat}$$

See pages 456–457 in *PoC*, along with Examples 12-15 and 15-9.

(b) Use Hess's law (Section 13-4 and Examples 13-9 through 13-11) to calculate the heat of solution:

$$\mathrm{Li_2CO_3(s)} \rightleftarrows 2\mathrm{Li^+(aq)} + \mathrm{CO_3^{2-}(aq)}$$

$$\begin{aligned}\Delta H^\circ &= 2\,\Delta H_\mathrm{f}^\circ\left[\mathrm{Li^+(aq)}\right] + \Delta H_\mathrm{f}^\circ\left[\mathrm{CO_3^{2-}(aq)}\right] - \Delta H_\mathrm{f}^\circ\left[\mathrm{Li_2CO_3(s)}\right] \\ &= \left(-\frac{278.5\ \mathrm{kJ}}{\mathrm{mol}} \times 2\ \mathrm{mol}\right) + \left(-\frac{677.1\ \mathrm{kJ}}{\mathrm{mol}} \times 1\ \mathrm{mol}\right) - \left(-\frac{1215.9\ \mathrm{kJ}}{\mathrm{mol}} \times 1\ \mathrm{mol}\right) \\ &= -18.2\ \mathrm{kJ} \quad (\text{per mole } \mathrm{Li_2CO_3} \text{ at } 25^\circ\mathrm{C})\end{aligned}$$

See also Example 15-10, beginning on page R15.15.

16. Similar to the preceding exercise. See pages 512–513 and 543–546 in *PoC*, as well as Examples 14-7 and 15-10, for the interrelationship of enthalpy, entropy, temperature, and free energy.

(a) An increased solubility at high temperature suggests that the dissolution is endothermic:

$$\Delta H_\mathrm{soln} > 0$$

The increased stress imposed by more heat (a reactant) is dissipated by a shift to the right, toward the dissolution of more sodium nitrate:

$$\text{heat} + \mathrm{NaNO_3(s)} \rightarrow \mathrm{Na^+(aq)} + \mathrm{NO_3^-(aq)}$$

(b) The unfavorable rise in enthalpy ($\Delta H_\mathrm{soln} > 0$) is presumably compensated for by a favorable increase in entropy ($\Delta S_\mathrm{soln} > 0$):

$$\Delta G_\mathrm{soln} = \Delta H_\mathrm{soln} - T\,\Delta S_\mathrm{soln} < 0 \qquad \text{if} \qquad T > \frac{\Delta H_\mathrm{soln}}{\Delta S_\mathrm{soln}}$$

$$(\Delta H_\mathrm{soln} > 0, \quad \Delta S_\mathrm{soln} > 0)$$

Beginning with straightforward calculations of solubility and solubility product (Exercises 17, 18, 19, and 21), we work our way through problems involving simple precipitation (Exercises 20 and 22), the common-ion effect (Exercises 23 and 24), and selective precipitation (Exercises 25 and 26).

17. Denote the equilibrium concentrations of Hg_2^{2+} and Cl^- by x and $2x$, respectively:

$$\begin{array}{cccc} Hg_2Cl_2(s) \rightleftarrows & Hg_2^{2+}(aq) & + & 2Cl^-(aq) \\ & x & & 2x \end{array}$$

The mass-action equation is solved as a simple cube root:

$$[Hg_2^{2+}][Cl^-]^2 = K_{sp}$$

$$x(2x)^2 = 1.5 \times 10^{-18}$$

$$4x^3 = 1.5 \times 10^{-18}$$

$$x = \left(\frac{1.5 \times 10^{-18}}{4}\right)^{1/3} = 7.2 \times 10^{-7}\ M = [Hg_2^{2+}]$$

$$2x = 1.44 \times 10^{-6}\ M = 1.4 \times 10^{-6}\ M = [Cl^-] \quad \text{(2 sig fig)}$$

See pages 535–537 and Example 15-2 in *PoC*.

18. The 1:3 ionic stoichiometry of the reaction

$$\begin{array}{cccc} Al(OH)_3(s) \rightleftarrows & Al^{3+}(aq) & + & 3OH^-(aq) \\ & x & & 3x \end{array}$$

produces a quartic (fourth-degree) equilibrium expression:

$$[Al^{3+}][OH^-]^3 = K_{sp}$$

$$x(3x)^3 = 1.9 \times 10^{-33}$$

$$27x^4 = 1.9 \times 10^{-33}$$

$$x = [Al(OH)_3(aq)] = 2.9 \times 10^{-9}\ M$$

From the equilibrium concentration of $Al(OH)_3$, we then calculate the mass that will dissolve in a volume of 50 mL:

$$\frac{2.9 \times 10^{-9}\text{ mol Al(OH)}_3}{\text{L}} \times \frac{78.004\text{ g Al(OH)}_3}{\text{mol Al(OH)}_3} \times \frac{1\text{ L}}{1000\text{ mL}} \times 50.0\text{ mL}$$

$$= 1.1 \times 10^{-8}\text{ g Al(OH)}_3$$

19. Given equilibrium concentrations of barium and sulfate ions,

$$\begin{array}{cccc} BaSO_4(s) & \rightleftarrows & Ba^{2+}(aq) & + & SO_4^{2-}(aq) \\ & & 1.05 \times 10^{-5}\,M & & 1.05 \times 10^{-5}\,M \end{array}$$

we obtain a numerical value for the solubility-product constant:

$$K_{sp} = [Ba^{2+}][SO_4^{2-}] = (1.05 \times 10^{-5})^2 = 1.10 \times 10^{-10}$$

See also pages 535–537 and Example 15-1 in *PoC* (beginning on page R15.5).

20. Compute the value of the reaction quotient, Q, for the process

$$PbCl_2(s) \rightleftarrows Pb^{2+}(aq) + 2Cl^-(aq)$$

$$K_{sp} = [Pb^{2+}][Cl^-]^2 = 1.6 \times 10^{-5}$$

and compare it with the equilibrium constant, K_{sp}. Systems for which $Q > K_{sp}$ should eventually yield a precipitate. See Section 12-4 and Examples 12-8, 12-12, 14-9, and 15-2 for illustrations of nonequilibrium conditions.

The first step is to calculate the molar amounts of Pb^{2+} and Cl^- in their respective solutions before mixing:

$$\text{Concentration} \times \text{volume} = \text{amount}$$

$$\frac{\text{mol}}{\text{L}} \times \text{L} = \text{mol}$$

Taking the data given in part (a), for example, we proceed as follows:

$$\frac{0.025 \text{ mol Pb(NO}_3)_2}{\text{L}} \times \frac{1 \text{ mol Pb}^{2+}}{\text{mol Pb(NO}_3)_2} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times 50.0 \text{ mL} = 1.25 \times 10^{-3} \text{ mol Pb}^{2+}$$

$$\frac{0.025 \text{ mol NaCl}}{\text{L}} \times \frac{1 \text{ mol Cl}^-}{\text{mol NaCl}} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times 50.0 \text{ mL} = 1.25 \times 10^{-3} \text{ mol Cl}^-$$

We assume next (for simplicity) that the individual volumes add without change,

$$50.0 \text{ mL} + 50.0 \text{ mL} = 100.0 \text{ mL}$$

and we go on to determine the initial concentrations of Pb^{2+} and Cl^- in the combined solution:

$$[\text{Pb}^{2+}]_0 = \frac{1.25\times10^{-3}\text{ mol Pb}^{2+}}{0.1000\text{ L}} = 1.25\times10^{-2}\ M$$

$$[\text{Cl}^-]_0 = \frac{1.25\times10^{-3}\text{ mol Cl}^-}{0.1000\text{ L}} = 1.25\times10^{-2}\ M$$

The solution is unsaturated, since $Q < K_{\text{sp}}$:

$$Q = [\text{Pb}^{2+}]_0[\text{Cl}^-]_0^2 = \left(1.25\times10^{-2}\right)\left(1.25\times10^{-2}\right)^2 = 1.95\times10^{-6} < K_{\text{sp}}$$

No precipitate forms.

The remaining calculations are done in exactly the same way. Results are summarized below:

	$[\text{Pb}^{2+}]_0$ (M)	$[\text{Cl}^-]_0$ (M)	Q		COMMENT
(a)	1.25×10^{-2}	1.25×10^{-2}	1.95×10^{-6}	$Q < K_{\text{sp}}$	unsaturated: no precipitate
(b)	2.50×10^{-2}	1.25×10^{-2}	3.91×10^{-6}	$Q < K_{\text{sp}}$	unsaturated: no precipitate
(c)	1.25×10^{-2}	2.50×10^{-2}	7.81×10^{-6}	$Q < K_{\text{sp}}$	unsaturated: no precipitate
(d)	2.50×10^{-2}	2.50×10^{-2}	1.56×10^{-5}	$Q \approx K_{\text{sp}}$	near precipitation threshold
(e)	2.50×10^{-4}	5.00×10^{-1}	6.25×10^{-5}	$Q > K_{\text{sp}}$	precipitate will form

The numbers are all shown with three digits, both for ease of comparison and (in part d) to highlight the small difference between Q and K_{sp}.

21. We consider the dissolution–precipitation equilibrium of calcium fluoride:

$$\begin{array}{ccccc} \text{CaF}_2(s) & \rightleftarrows & \text{Ca}^{2+}(aq) & + & 2\text{F}^-(aq) \\ & & x & & 2x \end{array}$$

(a) The equilibrium expression yields a simple cubic equation:

$$[\text{Ca}^{2+}][\text{F}^-]^2 = K_{\text{sp}}$$

$$x(2x)^2 = 3.9\times10^{-11}$$

$$4x^3 = 3.9\times10^{-11}$$

$$x = [\text{Ca}^{2+}] = 2.14\times10^{-4}$$

$[\text{Ca}^{2+}] = 2.1\times10^{-4}\ M$ $\quad$ $[\text{F}^-] = 2[\text{Ca}^{2+}] = 4.3\times10^{-4}\ M$ (2 sig fig)

(b) Convert moles into grams, rounding off the final result to two significant figures:

$$\frac{2.14 \times 10^{-4} \text{ mol CaF}_2}{\text{L}} \times \frac{78.075 \text{ g CaF}_2}{\text{mol CaF}_2} = \frac{0.017 \text{ g CaF}_2}{\text{L}}$$

(c) Multiply concentration by volume to obtain the amount dissolved:

$$\begin{array}{ccc} \text{CONCENTRATION} & \text{VOLUME} & \text{AMOUNT} \\ \left(\dfrac{2.14 \times 10^{-4} \text{ mol Ca}^{2+}}{\text{L}} \times \dfrac{1 \text{ L}}{1000 \text{ mL}}\right) & \times 100 \text{ mL} & = 2.14 \times 10^{-5} \text{ mol Ca}^{2+} \end{array}$$

The values below are rounded to two significant figures:

$$n_{\text{Ca}^{2+}} = 2.1 \times 10^{-5} \text{ mol} \qquad n_{\text{F}^-} = 2n_{\text{Ca}^{2+}} = 4.3 \times 10^{-5} \text{ mol}$$

22. We continue with the heterogeneous equilibrium between solid calcium fluoride and its dissolved ions:

$$\text{CaF}_2(s) \rightleftarrows \text{Ca}^{2+}(aq) + 2\text{F}^-(aq)$$

$$K_{\text{sp}} = [\text{Ca}^{2+}][\text{F}^-]^2 = 3.9 \times 10^{-11}$$

Dissolution of CaF_2 at 25°C (see Exercise 21) produces the following ionic concentrations in a saturated solution:

$$[\text{Ca}^{2+}]_{\text{eq}} = 2.14 \times 10^{-4}\ M = c$$

$$[\text{F}^-]_{\text{eq}} = 2[\text{Ca}^{2+}]_{\text{eq}} = 2c$$

To avoid round-off errors, we shall temporarily retain a third (nonsignificant) digit in the computations that follow.

See Example 15-2 in *PoC* (beginning on page R15.6) for a similar calculation involving a change in volume.

(a) At equilibrium, the reaction quotient is equal to the solubility-product constant:

$$Q = c(2c)^2 = 4c^3 = K_{\text{sp}} \qquad \text{(equilibrium)}$$

Halving the volume instantly doubles both concentrations, creating an out-of-equilibrium system with a reaction quotient greater than K_{sp}:

$$[\mathrm{Ca}^{2+}]_{\mathrm{noneq}} = 2(2.14 \times 10^{-4}\ M) = 2c$$

$$[\mathrm{F}^{-}]_{\mathrm{noneq}} = 2[\mathrm{Ca}^{2+}]_{\mathrm{noneq}} = 4c$$

$$Q = (2c)(4c)^2 = 8\left(4c^3\right) = 8K_{\mathrm{sp}} = 3.1 \times 10^{-10}$$

(b) Whereas before we had 2.14 × 10^{-5} mol in 100 mL,

$$c = \frac{2.14 \times 10^{-5}\ \text{mol CaF}_2}{0.100\ \text{L}} = 2.14 \times 10^{-4}\ M$$

we must now have half the amount in half the volume if equilibrium is to be restored:

half the amount   same concentration

$$c = \frac{\frac{1}{2}\left(2.14 \times 10^{-5}\right)\ \text{mol CaF}_2}{\frac{1}{2}\left(0.100\ \text{L}\right)} = \frac{1.07 \times 10^{-5}\ \text{mol CaF}_2}{0.050\ \text{L}} = 2.14 \times 10^{-4}\ M$$

half the volume

Thus 1.07 × 10^{-5} mol $\mathrm{CaF_2}$ will precipitate from solution, and 1.07 × 10^{-5} mol will remain dissolved in the reduced volume of 50 mL. To two significant figures, the amounts in moles and grams are 1.1 × 10^{-5} mol and 8.4 × 10^{-4} g:

$$1.07 \times 10^{-5}\ \text{mol CaF}_2 \times \frac{78.075\ \text{g CaF}_2}{\text{mol CaF}_2} = 8.4 \times 10^{-4}\ \text{g CaF}_2$$

(c) With equilibrium reestablished, the concentration of $\mathrm{CaF_2}$ is once again $c = 2.14 \times 10^{-4}\ M$. The original amounts and volumes are both cut in half, thereby preserving the ratio n/V:

$$\frac{2.14 \times 10^{-4}\ \text{mol CaF}_2}{\text{L}} \times \frac{1\ \text{mol Ca}^{2+}}{\text{mol CaF}_2} \times 0.050\ \text{L} = 1.1 \times 10^{-5}\ \text{mol Ca}^{2+}$$

$$\frac{2.14 \times 10^{-4}\ \text{mol CaF}_2}{\text{L}} \times \frac{2\ \text{mol F}^{-}}{\text{mol CaF}_2} \times 0.050\ \text{L} = 2.1 \times 10^{-5}\ \text{mol F}^{-}$$

23. The common-ion effect is covered on page 537 and illustrated in Example 15-3 of *PoC* (beginning on page R15.8). Le Châtelier's principle is treated in Section 12-6.

(a) Adding CaF_2 to a solution of $AgNO_3$ makes possible two additional precipitates:

$$\text{AgF} \qquad\qquad \text{Ca(NO}_3)_2$$

Looking up the solubilities of these compounds, however, we find that both calcium nitrate and silver fluoride are strongly soluble in water (> 1000 g L^{-1}; see Tables C-17 and C-18 in *PoC,* pages A94–A95). Neither Ag^+ nor NO_3^- competes effectively for F^- or Ca^{2+}, and consequently the dissolution–precipitation equilibrium of calcium fluoride remains unaffected:

$$\begin{array}{ccccc} \text{CaF}_2(s) & \rightleftarrows & \text{Ca}^{2+}(aq) & + & 2\text{F}^-(aq) \\ & & x & & 2x \end{array}$$

There is no common-ion effect. The molar solubility, already calculated in Exercise 21, stays fixed at 2.1×10^{-4} *M*:

$$[\text{Ca}^{2+}][\text{F}^-]^2 = K_{\text{sp}}$$

$$x(2x)^2 = 3.9 \times 10^{-11}$$

$$4x^3 = 3.9 \times 10^{-11}$$

$$x = [\text{CaF}_2(aq)] = 2.14 \times 10^{-4}\ M = 2.1 \times 10^{-4}\ M \quad \text{(2 sig fig)}$$

Expressed in units of mass, the equivalent value is 0.017 g L^{-1}:

$$\frac{2.14 \times 10^{-4}\ \text{mol CaF}_2}{\text{L}} \times \frac{78.075\ \text{g CaF}_2}{\text{mol CaF}_2} = \frac{0.017\ \text{g CaF}_2}{\text{L}}$$

(b) The reasoning is the same as in (a). A concentration of 0.100 *M* $AgNO_3$ has no effect on the solubility of CaF_2, which holds at 0.017 g L^{-1}.

(c) The fluoride ion, F^-, is a dissolution product of CaF_2:

$$\text{CaF}_2(s) \rightleftarrows \text{Ca}^{2+}(aq) + 2\text{F}^-(aq)$$

An existing 0.050 *M* concentration of NaF therefore will depress the solubility of CaF_2, because this initial amount of F^- (acting as a *common ion*) puts a leftward stress on any subsequent equilibrium. The final concentration x of dissolved CaF_2 will be less than its value in pure water, dwarfed by the large quantity of F^- already present:

$$\begin{array}{cccc} CaF_2(s) \rightleftarrows & Ca^{2+}(aq) & + & 2F^-(aq) \\ & x & & 0.050 + 2x \end{array}$$

The resulting mass-action expression gives us a cubic equation to solve,

$$K_{sp} = [Ca^{2+}][F^-]^2$$

$$3.9 \times 10^{-11} = x(0.050 + 2x)^2$$

which we simplify by assuming that $2x$ is small relative to 0.050:

$$0.050 + 2x \approx 0.050$$

This assumption, predicated on the small magnitude of K_{sp}, yields an approximate linear equation

$$x(0.050)^2 \approx 3.9 \times 10^{-11}$$

with the solution

$$x \approx \frac{3.9 \times 10^{-11}}{(0.050)^2} = 1.56 \times 10^{-8}$$

Substituting $x = 1.56 \times 10^{-8}$ into the full cubic equation,

$$(1.56 \times 10^{-8})[0.050 + 2(1.56 \times 10^{-8})]^2 = 3.900004 \times 10^{-11}$$

we quickly establish the validity of the approximation. The solubility, to two significant figures, is 1.2×10^{-6} g L^{-1}:

$$\frac{1.56 \times 10^{-8} \text{ mol CaF}_2}{\text{L}} \times \frac{78.075 \text{ g CaF}_2}{\text{mol CaF}_2} = 1.2 \times 10^{-6} \text{ g CaF}_2 \text{ L}^{-1}$$

(d) Use the same approach as in (c), this time beginning with an initial fluoride concentration of 0.100 *M*:

$$[F^-]_0 = 0.100\ M$$

The cubic mass-action equation

$$x(0.100 + 2x)^2 = 3.9 \times 10^{-11}$$

simplifies to the approximate linear form

$$x(0.100)^2 \approx 3.9 \times 10^{-11}$$

with the assumption that $2x << 0.100$. Its root, $x = 3.9 \times 10^{-9}$ M, yields 3.0×10^{-7} g L^{-1}:

$$\frac{3.9 \times 10^{-9} \text{ mol CaF}_2}{\text{L}} \times \frac{78.075 \text{ g CaF}_2}{\text{mol CaF}_2} = 3.0 \times 10^{-7} \text{ g CaF}_2 \text{ L}^{-1}$$

The effect, we see, depends on the square of the initial fluoride concentration. Doubling $[\text{F}^-]_0$ relative to its value in (c) depresses the solubility of CaF_2 by an additional factor of 4:

$$x \approx \frac{K_{\text{sp}}}{[\text{F}^-]_0^2}$$

$$\frac{\dfrac{K_{\text{sp}}}{(0.100)^2}}{\dfrac{K_{\text{sp}}}{(0.050)^2}} = \frac{(0.050)^2}{(0.100)^2} = \left(\frac{1}{2}\right)^2 = \frac{1}{4}$$

24. With its solubility-product constant equal to 1.8×10^{-10}, a solution of silver chloride in pure water reaches saturation when $[\text{Ag}^+] = [\text{Cl}^-] = 1.34 \times 10^{-5}$ M:

$$\begin{array}{ccccc} \text{AgCl(s)} & \rightleftarrows & \text{Ag}^+\text{(aq)} & + & \text{Cl}^-\text{(aq)} \\ & & x & & x \end{array}$$

$$[\text{Ag}^+][\text{Cl}^-] = K_{\text{sp}}$$

$$x^2 = 1.8 \times 10^{-10}$$

$$x = 1.34 \times 10^{-5} = 1.3 \times 10^{-5} \ M \quad \text{(2 sig fig)}$$

Depressed, however, by a preexisting 0.100 M concentration of Ag^+,

$$\begin{array}{ccccc} \text{AgCl(s)} & \rightleftarrows & \text{Ag}^+\text{(aq)} & + & \text{Cl}^-\text{(aq)} \\ & & 0.100 + x & & x \end{array}$$

the solubility of AgCl in 0.100 M AgNO_3 falls by four orders of magnitude:

$$[\mathrm{Ag^+}][\mathrm{Cl^-}] = K_{\mathrm{sp}}$$

$$(0.100 + x)x = 1.8 \times 10^{-10}$$

$$(0.100)x \approx 1.8 \times 10^{-10} \quad \text{(assume that } x << 0.100)$$

$$x = [\mathrm{AgCl(aq)}] = 1.8 \times 10^{-9}\ M$$

The corresponding mass in 0.100 L is only 2.6×10^{-8} g:

$$\frac{1.8 \times 10^{-9}\ \text{mol AgCl}}{\text{L}} \times \frac{143.321\ \text{g AgCl}}{\text{mol AgCl}} \times 0.100\ \text{L} = 2.6 \times 10^{-8}\ \text{g AgCl}$$

See pages 537–540 and Example 15-4 in PoC *for illustrations of selective precipitation.*

25. Start with the unmixed solutions of NaCl and Na_2CrO_4,

$$\frac{0.100\ \text{mol NaCl}}{\text{L}} \times \frac{1\ \text{mol Cl}^-}{\text{mol NaCl}} \times \frac{1\ \text{L}}{1000\ \text{mL}} \times 50.0\ \text{mL} = 5.00 \times 10^{-3}\ \text{mol Cl}^-$$

$$\frac{0.050\ \text{mol Na}_2\text{CrO}_4}{\text{L}} \times \frac{1\ \text{mol CrO}_4^{2-}}{\text{mol Na}_2\text{CrO}_4} \times \frac{1\ \text{L}}{1000\ \text{mL}} \times 50.0\ \text{mL} = 2.5 \times 10^{-3}\ \text{mol CrO}_4^{2-}$$

and assume that the total volume is 0.1000 L (100.0 mL) after the two are combined. Since the amount of each anion remains unchanged, we have the following initial concentrations:

$$[\mathrm{Cl^-}]_0 = \frac{5.00 \times 10^{-3}\ \text{mol Cl}^-}{0.1000\ \text{L}} = 5.00 \times 10^{-2}\ M$$

$$[\mathrm{CrO_4^{2-}}]_0 = \frac{2.5 \times 10^{-3}\ \text{mol CrO}_4^{2-}}{0.1000\ \text{L}} = 2.5 \times 10^{-2}\ M$$

Now add incremental amounts of Ag^+ to the 100-mL mixture, and calculate the threshold for precipitation of both AgCl and Ag_2CrO_4.

(a) Since $[\mathrm{Cl^-}]_0$ is already set at 5.00×10^{-2} M, solid AgCl will precipitate when $[\mathrm{Ag^+}]$ reaches 3.6×10^{-9} M:

$$\mathrm{AgCl(s)} \rightleftarrows \mathrm{Ag^+(aq)} + \mathrm{Cl^-(aq)}$$

$$K_{\mathrm{sp}} = [\mathrm{Ag^+}][\mathrm{Cl^-}] = 1.8 \times 10^{-10}$$

$$[\mathrm{Ag^+}] = \frac{K_{\mathrm{sp}}}{[\mathrm{Cl^-}]} = \frac{1.8 \times 10^{-10}}{5.00 \times 10^{-2}} = 3.6 \times 10^{-9}\ M$$

Going through the same calculation for silver chromate, we find that Ag_2CrO_4 begins to precipitate at a silver concentration of 6.6×10^{-6} *M* (a value over 1800 times greater than for AgCl):

$$\mathrm{Ag_2CrO_4(s)} \rightleftarrows 2\mathrm{Ag^+(aq)} + \mathrm{CrO_4^{2-}(aq)}$$

$$K_{\mathrm{sp}} = [\mathrm{Ag^+}]^2[\mathrm{CrO_4^{2-}}] = 1.1 \times 10^{-12}$$

$$[\mathrm{Ag^+}]^2 = \frac{K_{\mathrm{sp}}}{[\mathrm{CrO_4^{2-}}]}$$

$$[\mathrm{Ag^+}] = \sqrt{\frac{K_{\mathrm{sp}}}{[\mathrm{CrO_4^{2-}}]}} = \sqrt{\frac{1.1 \times 10^{-12}}{2.5 \times 10^{-2}}} = 6.6 \times 10^{-6}\ M$$

Silver chloride therefore precipitates first, despite having the larger value of K_{sp}. Equilibrium among Ag_2CrO_4(s), Ag^+(aq), and CrO_4^{2-}(aq) depends on $[Ag^+]^2$, not simply $[Ag^+]$.

(b) Precipitation of AgCl begins when $[Ag^+] = 3.6 \times 10^{-9}$ *M*. To obtain the required amount, we multiply concentration by volume:

$$\frac{3.6 \times 10^{-9}\ \text{mol Ag}^+}{\text{L}} \times 0.1000\ \text{L} = 3.6 \times 10^{-10}\ \text{mol Ag}^+$$

(c) Similar. Precipitation of Ag_2CrO_4 begins when $[Ag^+] = 6.6 \times 10^{-6}$ *M*:

$$\frac{6.6 \times 10^{-6}\ \text{mol Ag}^+}{\text{L}} \times 0.1000\ \text{L} = 6.6 \times 10^{-7}\ \text{mol Ag}^+$$

26. A continuation of the preceding exercise.

(a) We know from Exercise 25 that Ag_2CrO_4 begins to precipitate when $[Ag^+] = 6.6 \times 10^{-6}$ *M*. If so, then the competing concentration of Cl^- must have been reduced to 2.7×10^{-5} *M*:

$$\mathrm{AgCl(s)} \rightleftarrows \mathrm{Ag^+(aq)} + \mathrm{Cl^-(aq)}$$

$$K_{sp} = [\mathrm{Ag^+}][\mathrm{Cl^-}] = 1.8 \times 10^{-10}$$

$$[\mathrm{Cl^-}] = \frac{K_{sp}}{[\mathrm{Ag^+}]} = \frac{1.8 \times 10^{-10}}{6.6 \times 10^{-6}} = 2.7 \times 10^{-5}\ M$$

Meanwhile, the concentration of Na^+ (a spectator ion) remains unchanged from its original value. We start with 5.00×10^{-3} mol Na^+ from solution A and combine this amount with 5.0×10^{-3} mol Na^+ from solution B, producing a 0.100 *M* solution (0.0100 mol in 0.1000 L):

$$\text{A:}\quad \frac{0.100\ \text{mol NaCl}}{\text{L}} \times \frac{1\ \text{mol Na}^+}{\text{mol NaCl}} \times 0.0500\ \text{L} = 5.00 \times 10^{-3}\ \text{mol Na}^+$$

$$\text{B:}\quad \frac{0.050\ \text{mol Na}_2\text{CrO}_4}{\text{L}} \times \frac{2\ \text{mol Na}^+}{\text{mol Na}_2\text{CrO}_4} \times 0.0500\ \text{L} = 5.0 \times 10^{-3}\ \text{mol Na}^+$$

$$\text{A + B:}\quad \frac{0.00500\ \text{mol Na}^+ + 0.0050\ \text{mol Na}^+}{0.1000\ \text{L}} = \frac{0.0100\ \text{mol Na}^+}{0.1000\ \text{L}} = 0.100\ M\ \text{Na}^+$$

(b) Before the addition of $AgNO_3$, the solution contains 5.00×10^{-3} mol Cl^- (see Exercise 25). At the point where Ag_2CrO_4 begins to precipitate, the concentration of Cl^- has been reduced to 2.7×10^{-5} *M* (see above, part a).

Thus only 2.7×10^{-6} mol Cl^- remains in a total volume of 0.1000 L:

$$\frac{2.7 \times 10^{-5}\ \text{mol Cl}^-}{\text{L}} \times 0.1000\ \text{L} = 2.7 \times 10^{-6}\ \text{mol Cl}^-$$

The difference,

$$(5.00 \times 10^{-3}\ \text{mol}) - (2.7 \times 10^{-6}\ \text{mol}) = 0.0049973\ \text{mol} \approx 5.00 \times 10^{-3}\ \text{mol}$$

has precipitated from solution in the form of solid AgCl:

$$\left(5.00 \times 10^{-3} - 2.7 \times 10^{-6}\right)\ \text{mol AgCl} \times \frac{143.321\ \text{g AgCl}}{\text{mol AgCl}} = 0.716\ \text{g AgCl}$$

Nearly all of the original Cl^- is gone.

Thermodynamic aspects of dissolution–precipitation and host–guest equilibria are treated on pages 543–550 and 564–567 of PoC. *Relevant sample problems include Examples 15-8 through 15-12.*

27. We examine the role played by enthalpy, entropy, and free energy in three different dissolution–precipitation reactions. For similar calculations, see Example 14-7 (beginning on page R14.15 of *PoC*) and also Exercises 33 through 44 in Chapter 14. All formation data are taken from Table C-16 in *PoC* (Appendix C, pages A85–A92).

Of the three solutes considered, potassium chloride is the only one that has a negative free energy of solution. As a result, KCl is considerably more soluble than either AgCl or $Ca(OH)_2$. See the detailed calculations that follow.

(a) For potassium chloride in water,

$$\mathrm{KCl(s)} \rightleftarrows \mathrm{K^+(aq)} + \mathrm{Cl^-(aq)}$$

the attendant increase in entropy is favorable for dissolution but the increase in enthalpy is not:

$$\begin{aligned}\Delta H^\circ &= \Delta H_f^\circ\left[\mathrm{K^+(aq)}\right] + \Delta H_f^\circ\left[\mathrm{Cl^-(aq)}\right] - \Delta H_f^\circ\left[\mathrm{KCl(s)}\right]\\ &= \left(-252.4\ \mathrm{kJ\ mol^{-1}}\right) + \left(-167.2\ \mathrm{kJ\ mol^{-1}}\right) - \left(-436.5\ \mathrm{kJ\ mol^{-1}}\right)\\ &= 16.9\ \mathrm{kJ\ mol^{-1}} \quad \text{(endothermic)}\end{aligned}$$

$$\begin{aligned}\Delta S^\circ &= S^\circ\left[\mathrm{K^+(aq)}\right] + S^\circ\left[\mathrm{Cl^-(aq)}\right] - S^\circ\left[\mathrm{KCl(s)}\right]\\ &= \left(102.5\ \mathrm{J\ mol^{-1}\ K^{-1}}\right) + \left(56.5\ \mathrm{J\ mol^{-1}\ K^{-1}}\right) - \left(82.6\ \mathrm{J\ mol^{-1}\ K^{-1}}\right)\\ &= 76.4\ \mathrm{J\ mol^{-1}\ K^{-1}} \quad \text{(entropy increases)}\end{aligned}$$

This combination of ΔH° and ΔS° results in a spontaneous reaction at 25°C. The standard change in free energy is negative:

$$\begin{aligned}\Delta G^\circ &= \Delta G_f^\circ\left[\mathrm{K^+(aq)}\right] + \Delta G_f^\circ\left[\mathrm{Cl^-(aq)}\right] - \Delta G_f^\circ\left[\mathrm{KCl(s)}\right]\\ &= \left(-283.3\ \mathrm{kJ\ mol^{-1}}\right) + \left(-131.2\ \mathrm{kJ\ mol^{-1}}\right) - \left(-408.5\ \mathrm{kJ\ mol^{-1}}\right)\\ &= -6.0\ \mathrm{kJ\ mol^{-1}} \quad (\text{spontaneous}, K > 1)\end{aligned}$$

Since ΔG° is a negative number, the equilibrium constant is greater than 1:

$$K = \exp\left(-\frac{\Delta G^\circ}{RT}\right) = \exp\left(\frac{\left|\Delta G^\circ\right|}{RT}\right) > 1 \qquad \text{if} \qquad \Delta G^\circ < 0$$

(b) Similar to the dissolution of KCl, the reaction

$$\mathrm{AgCl(s)} \rightleftarrows \mathrm{Ag^+(aq)} + \mathrm{Cl^-(aq)}$$

is favored by an increase in entropy but hindered by an increase in enthalpy:

$$\begin{aligned}\Delta H^\circ &= \Delta H_\mathrm{f}^\circ\left[\mathrm{Ag^+(aq)}\right] + \Delta H_\mathrm{f}^\circ\left[\mathrm{Cl^-(aq)}\right] - \Delta H_\mathrm{f}^\circ\left[\mathrm{AgCl(s)}\right]\\ &= \left(105.6\ \mathrm{kJ\ mol^{-1}}\right) + \left(-167.2\ \mathrm{kJ\ mol^{-1}}\right) - \left(-127.1\ \mathrm{kJ\ mol^{-1}}\right)\\ &= 65.5\ \mathrm{kJ\ mol^{-1}} \quad \text{(endothermic)}\end{aligned}$$

$$\begin{aligned}\Delta S^\circ &= S^\circ\left[\mathrm{Ag^+(aq)}\right] + S^\circ\left[\mathrm{Cl^-(aq)}\right] - S^\circ\left[\mathrm{AgCl(s)}\right]\\ &= \left(72.7\ \mathrm{J\ mol^{-1}\ K^{-1}}\right) + \left(56.5\ \mathrm{J\ mol^{-1}\ K^{-1}}\right) - \left(96.2\ \mathrm{J\ mol^{-1}\ K^{-1}}\right)\\ &= 33.0\ \mathrm{J\ mol^{-1}\ K^{-1}} \quad \text{(entropy increases)}\end{aligned}$$

Unlike the outcome for KCl, though, the net effect is to create an *increase* in free energy and thereby render the reaction nonspontaneous at 25°C:

$$\begin{aligned}\Delta G^\circ &= \Delta G_\mathrm{f}^\circ\left[\mathrm{Ag^+(aq)}\right] + \Delta G_\mathrm{f}^\circ\left[\mathrm{Cl^-(aq)}\right] - \Delta G_\mathrm{f}^\circ\left[\mathrm{AgCl(s)}\right]\\ &= \left(77.1\ \mathrm{kJ\ mol^{-1}}\right) + \left(-131.2\ \mathrm{kJ\ mol^{-1}}\right) - \left(-109.8\ \mathrm{kJ\ mol^{-1}}\right)\\ &= 55.7\ \mathrm{kJ\ mol^{-1}} \quad (\text{nonspontaneous, } K \ll 1)\end{aligned}$$

The enthalpy term dominates the expression

$$\Delta G^\circ = \Delta H^\circ - T\,\Delta S^\circ$$

at room temperature, and its influence is reflected in the tabulated values of $\Delta G_\mathrm{f}^\circ$ (25° C). See Exercise 28 for an explicit calculation of K.

(c) When calcium hydroxide dissolves in water,

$$\mathrm{Ca(OH)_2(s)} \rightleftarrows \mathrm{Ca^{2+}(aq)} + \mathrm{2OH^{-}(aq)}$$

the decrease in enthalpy is favorable but the decrease in entropy is not:

$$\begin{aligned}\Delta H^\circ &= \Delta H_\mathrm{f}^\circ\left[\mathrm{Ca^{2+}(aq)}\right] + 2\,\Delta H_\mathrm{f}^\circ\left[\mathrm{OH^-(aq)}\right] - \Delta H_\mathrm{f}^\circ\left[\mathrm{Ca(OH)_2(s)}\right]\\ &= \left(-\frac{542.8\ \mathrm{kJ}}{\mathrm{mol}}\times 1\ \mathrm{mol}\right) + \left(-\frac{230.0\ \mathrm{kJ}}{\mathrm{mol}}\times 2\ \mathrm{mol}\right) - \left(-\frac{985.2\ \mathrm{kJ}}{\mathrm{mol}}\times 1\ \mathrm{mol}\right)\\ &= -17.6\ \text{kJ per mole of } \mathrm{Ca(OH)_2} \quad \text{(exothermic)}\end{aligned}$$

$$\begin{aligned}\Delta S^\circ &= S^\circ\left[\mathrm{Ca^{2+}(aq)}\right] + 2\,S^\circ\left[\mathrm{OH^-(aq)}\right] - S^\circ\left[\mathrm{Ca(OH)_2(s)}\right]\\ &= \left(-\frac{53.1\ \mathrm{J}}{\mathrm{mol\ K}}\times 1\ \mathrm{mol}\right) + \left(-\frac{10.8\ \mathrm{J}}{\mathrm{mol\ K}}\times 2\ \mathrm{mol}\right) - \left(\frac{83.4\ \mathrm{J}}{\mathrm{mol\ K}}\times 1\ \mathrm{mol}\right)\\ &= -158.1\ \mathrm{J\ K^{-1}}\ \text{per mole of } \mathrm{Ca(OH)_2} \quad \text{(entropy decreases)}\end{aligned}$$

Since the net change in free energy, 29.5 kJ, is positive, the reaction is nonspontaneous at 25°C:

$$\begin{aligned}\Delta G^\circ &= \Delta G_\mathrm{f}^\circ\left[\mathrm{Ca^{2+}(aq)}\right] + 2\,\Delta G_\mathrm{f}^\circ\left[\mathrm{OH^-(aq)}\right] - \Delta G_\mathrm{f}^\circ\left[\mathrm{Ca(OH)_2(s)}\right]\\ &= \left(-\frac{553.6\ \mathrm{kJ}}{\mathrm{mol}}\times 1\ \mathrm{mol}\right) + \left(-\frac{157.2\ \mathrm{kJ}}{\mathrm{mol}}\times 2\ \mathrm{mol}\right) - \left(-\frac{897.5\ \mathrm{kJ}}{\mathrm{mol}}\times 1\ \mathrm{mol}\right)\\ &= 29.5\ \text{kJ per mole of } \mathrm{Ca(OH)_2} \quad (\text{nonspontaneous, } K \ll 1)\end{aligned}$$

The equilibrium constant, calculated in Exercise 28, is less than 1.

28. The logarithmic relationship between free energy and the equilibrium constant is discussed in Section 14-8 of *PoC* and demonstrated in Example 14-8:

$$\Delta G^\circ = -RT\ln K \qquad\qquad K = \exp\left(-\frac{\Delta G^\circ}{RT}\right)$$

See also Exercises 38 through 43 in Chapter 14.

We use the values of ΔG° determined in the preceding exercise.

For AgCl (where $\Delta G^\circ = 55.7 \text{ kJ mol}^{-1} = 55{,}700 \text{ J mol}^{-1}$):

$$K_{\text{sp}} = \exp\left[-\frac{55{,}700 \text{ J mol}^{-1}}{(8.3145 \text{ J mol}^{-1} \text{ K}^{-1})(298.15 \text{ K})}\right] = 1.7 \times 10^{-10}$$

For $Ca(OH)_2$ (where $\Delta G^\circ = 29.5 \text{ kJ mol}^{-1} = 29{,}500 \text{ J mol}^{-1}$):

$$K_{\text{sp}} = \exp\left[-\frac{29{,}500 \text{ J mol}^{-1}}{(8.3145 \text{ J mol}^{-1} \text{ K}^{-1})(298.15 \text{ K})}\right] = 6.8 \times 10^{-6}$$

29. The procedure is identical to that used in Exercise 27.

(a) The dissolution of magnesium chloride,

$$MgCl_2(s) \rightleftarrows Mg^{2+}(aq) + 2Cl^-(aq)$$

is favored by a large drop in enthalpy but hindered by a decrease in entropy:

$$\begin{aligned}\Delta H^\circ &= \Delta H_f^\circ\left[Mg^{2+}(aq)\right] + 2\,\Delta H_f^\circ\left[Cl^-(aq)\right] - \Delta H_f^\circ\left[MgCl_2(s)\right] \\ &= \left(-\frac{466.9 \text{ kJ}}{\text{mol}} \times 1 \text{ mol}\right) + \left(-\frac{167.2 \text{ kJ}}{\text{mol}} \times 2 \text{ mol}\right) - \left(-\frac{641.3 \text{ kJ}}{\text{mol}} \times 1 \text{ mol}\right) \\ &= -160.0 \text{ kJ per mole of } MgCl_2 \quad \text{(exothermic)}\end{aligned}$$

$$\begin{aligned}\Delta S^\circ &= S^\circ\left[Mg^{2+}(aq)\right] + 2\,S^\circ\left[Cl^-(aq)\right] - S^\circ\left[MgCl_2(s)\right] \\ &= \left(-\frac{138.1 \text{ J}}{\text{mol K}} \times 1 \text{ mol}\right) + \left(\frac{56.5 \text{ J}}{\text{mol K}} \times 2 \text{ mol}\right) - \left(\frac{89.6 \text{ J}}{\text{mol K}} \times 1 \text{ mol}\right) \\ &= -114.7 \text{ J K}^{-1} \text{ per mole of } MgCl_2 \quad \text{(entropy decreases)}\end{aligned}$$

A considerable quantity of free energy is released at 25°C. The reaction is spontaneous, its equilibrium constant much greater than 1:

$$\begin{aligned}\Delta G^\circ &= \Delta G_f^\circ\left[Mg^{2+}(aq)\right] + 2\,\Delta G_f^\circ\left[Cl^-(aq)\right] - \Delta G_f^\circ\left[MgCl_2(s)\right] \\ &= \left(-\frac{454.8 \text{ kJ}}{\text{mol}} \times 1 \text{ mol}\right) + \left(-\frac{131.2 \text{ kJ}}{\text{mol}} \times 2 \text{ mol}\right) - \left(-\frac{591.8 \text{ kJ}}{\text{mol}} \times 1 \text{ mol}\right) \\ &= -125.4 \text{ kJ per mole of } MgCl_2 \quad (\text{spontaneous, } K >> 1)\end{aligned}$$

Note that $MgCl_2$, the only compound in this set with a negative free energy of solution, is the most soluble of the three. See (b) and (c) below.

(b) Changes in enthalpy and entropy are both unfavorable for the dissolution of barium sulfate:

$$BaSO_4(s) \rightleftarrows Ba^{2+}(aq) + SO_4^{2-}(aq)$$

Enthalpy goes up:

$$\begin{aligned}\Delta H^\circ &= \Delta H_f^\circ\left[Ba^{2+}(aq)\right] + \Delta H_f^\circ\left[SO_4^{2-}(aq)\right] - \Delta H_f^\circ\left[BaSO_4(s)\right]\\ &= \left(-537.6\text{ kJ mol}^{-1}\right) + \left(-909.3\text{ kJ mol}^{-1}\right) - \left(-1473.2\text{ kJ mol}^{-1}\right)\\ &= 26.3\text{ kJ mol}^{-1} \quad \text{(endothermic)}\end{aligned}$$

Entropy goes down:

$$\begin{aligned}\Delta S^\circ &= S^\circ\left[Ba^{2+}(aq)\right] + S^\circ\left[SO_4^{2-}(aq)\right] - S^\circ\left[BaSO_4(s)\right]\\ &= \left(9.6\text{ J mol}^{-1}\text{ K}^{-1}\right) + \left(20.1\text{ J mol}^{-1}\text{ K}^{-1}\right) - \left(132.2\text{ J mol}^{-1}\text{ K}^{-1}\right)\\ &= -102.5\text{ J mol}^{-1}\text{ K}^{-1} \quad \text{(entropy decreases)}\end{aligned}$$

Free energy goes up:

$$\begin{aligned}\Delta G^\circ &= \Delta G_f^\circ\left[Ba^{2+}(aq)\right] + \Delta G_f^\circ\left[SO_4^{2-}(aq)\right] - \Delta G_f^\circ\left[BaSO_4(s)\right]\\ &= \left(-560.8\text{ kJ mol}^{-1}\right) + \left(-744.5\text{ kJ mol}^{-1}\right) - \left(-1362.2\text{ kJ mol}^{-1}\right)\\ &= 56.9\text{ kJ mol}^{-1} \quad (\text{nonspontaneous, } K \ll 1)\end{aligned}$$

The reaction is not spontaneous at 25°C. Free energy is greater for the products than for the reactants, and the equilibrium constant is much less than 1.

(c) The dissolution of calcium sulfate,

$$CaSO_4(s) \rightleftarrows Ca^{2+}(aq) + SO_4^{2-}(aq)$$

is aided by a decrease in enthalpy but hindered by a decrease in entropy:

$$\begin{aligned}\Delta H^\circ &= \Delta H_f^\circ\left[\mathrm{Ca}^{2+}(\mathrm{aq})\right]+\Delta H_f^\circ\left[\mathrm{SO}_4^{2-}(\mathrm{aq})\right]-\Delta H_f^\circ\left[\mathrm{CaSO}_4(\mathrm{s})\right]\\ &=\left(-542.8\ \mathrm{kJ\ mol^{-1}}\right)+\left(-909.3\ \mathrm{kJ\ mol^{-1}}\right)-\left(-1434.5\ \mathrm{kJ\ mol^{-1}}\right)\\ &=-17.6\ \mathrm{kJ\ mol^{-1}}\quad \text{(exothermic)}\end{aligned}$$

$$\begin{aligned}\Delta S^\circ &= S^\circ\left[\mathrm{Ca}^{2+}(\mathrm{aq})\right]+S^\circ\left[\mathrm{SO}_4^{2-}(\mathrm{aq})\right]-S^\circ\left[\mathrm{CaSO}_4(\mathrm{s})\right]\\ &=\left(-53.1\ \mathrm{J\ mol^{-1}\ K^{-1}}\right)+\left(20.1\ \mathrm{J\ mol^{-1}\ K^{-1}}\right)-\left(106.5\ \mathrm{J\ mol^{-1}\ K^{-1}}\right)\\ &=-139.5\ \mathrm{J\ mol^{-1}\ K^{-1}}\quad \text{(entropy decreases)}\end{aligned}$$

The change in free energy at 25°C is positive, making the reaction nonspontaneous:

$$\begin{aligned}\Delta G^\circ &= \Delta G_f^\circ\left[\mathrm{Ca}^{2+}(\mathrm{aq})\right]+\Delta G_f^\circ\left[\mathrm{SO}_4^{2-}(\mathrm{aq})\right]-\Delta G_f^\circ\left[\mathrm{CaSO}_4(\mathrm{s})\right]\\ &=\left(-553.6\ \mathrm{kJ\ mol^{-1}}\right)+\left(-744.5\ \mathrm{kJ\ mol^{-1}}\right)-\left(-1322.0\ \mathrm{kJ\ mol^{-1}}\right)\\ &=23.9\ \mathrm{kJ\ mol^{-1}}\quad (\text{nonspontaneous, } K \ll 1)\end{aligned}$$

30. Use the same method as in Exercise 28, substituting the values of ΔG° obtained in Exercise 29.

For $BaSO_4$ (where $\Delta G^\circ = 56.9\ \mathrm{kJ\ mol^{-1}} = 56{,}900\ \mathrm{J\ mol^{-1}}$):

$$K_{\mathrm{sp}} = \exp\left(-\frac{\Delta G^\circ}{RT}\right)=\exp\left[-\frac{56{,}900\ \mathrm{J\ mol^{-1}}}{\left(8.3145\ \mathrm{J\ mol^{-1}\ K^{-1}}\right)\left(298.15\ \mathrm{K}\right)}\right]=1.1\times10^{-10}$$

For $CaSO_4$ (where $\Delta G^\circ = 23.9\ \mathrm{kJ\ mol^{-1}} = 23{,}900\ \mathrm{J\ mol^{-1}}$):

$$K_{\mathrm{sp}} = \exp\left(-\frac{\Delta G^\circ}{RT}\right)=\exp\left[-\frac{23{,}900\ \mathrm{J\ mol^{-1}}}{\left(8.3145\ \mathrm{J\ mol^{-1}\ K^{-1}}\right)\left(298.15\ \mathrm{K}\right)}\right]=6.5\times10^{-5}$$

Henry's law and the analogy to disorder–order equilibria are presented on pages 534–535 and in Example 15-7 of PoC.

31. Start with the atmospheric mole fractions of nitrogen and oxygen, implicit in the text of the problem:

Mole fraction of N_2 in air: $X_{N_2} = 0.78$

Mole fraction of O_2 in air: $X_{O_2} = 0.21$

Then use Dalton's law (*PoC*, pages 368–369 and Example 10-7) to establish the corresponding partial pressures:

Partial pressure of N_2: $P_{N_2} = X_{N_2} P_{\text{total}} = 0.78 \times 1.0 \text{ atm} = 0.78 \text{ atm}$

Partial pressure of O_2: $P_{O_2} = X_{O_2} P_{\text{total}} = 0.21 \times 1.0 \text{ atm} = 0.21 \text{ atm}$

Henry's law states that

$$P_A = K[\text{A(aq)}]$$

for the equilibrium

$$\text{A(aq)} \rightleftarrows \text{A(g)}$$

The aqueous concentrations follow directly:

$$[N_2(aq)] = \frac{P_{N_2}}{K_{N_2}} = \frac{0.78 \text{ atm}}{1.4 \times 10^3 \text{ atm L mol}^{-1}} = 5.6 \times 10^{-4}\ M$$

$$[O_2(aq)] = \frac{P_{O_2}}{K_{O_2}} = \frac{0.21 \text{ atm}}{7.2 \times 10^2 \text{ atm L mol}^{-1}} = 2.9 \times 10^{-4}\ M$$

32. The relevant Henry's law constants are provided in Exercise 31:

$N_2(aq) \rightleftarrows N_2(g)$ $\quad K_{N_2}(20°C) = 1.4 \times 10^3 \text{ atm L mol}^{-1}$

$O_2(aq) \rightleftarrows O_2(g)$ $\quad K_{O_2}(20°C) = 7.2 \times 10^2 \text{ atm L mol}^{-1}$

In each system, an increase in gas pressure shifts the equilibrium

$$\mathrm{A(aq)} \rightleftarrows \mathrm{A(g)}$$

to the left. More gas particles dissolve in the liquid.

(a) Nitrogen, under a partial pressure of 100 atm:

$$[\mathrm{N_2(aq)}] = \frac{P_{\mathrm{N_2}}}{K_{\mathrm{N_2}}} = \frac{100 \text{ atm}}{1.4 \times 10^3 \text{ atm L mol}^{-1}} = 0.071\ M$$

(b) Oxygen, under a partial pressure of 100 atm:

$$[\mathrm{O_2(aq)}] = \frac{P_{\mathrm{O_2}}}{K_{\mathrm{O_2}}} = \frac{100 \text{ atm}}{7.2 \times 10^2 \text{ atm L mol}^{-1}} = 0.14\ M$$

33. Subjected to high pressure inside a sealed bottle, the solution–vapor equilibrium

$$\mathrm{CO_2(aq)} \rightleftarrows \mathrm{CO_2(g)}$$

$$K = \frac{P_{\mathrm{CO_2}}}{[\mathrm{CO_2(aq)}]}$$

is initially biased toward the solution phase. The partial pressure of gaseous CO_2 is high, and the concentration of dissolved CO_2 is high as well:

$$\overset{\text{high}}{\searrow}\;[\mathrm{CO_2(aq)}] = \frac{P_{\mathrm{CO_2}}}{\underset{\nwarrow\,\text{fixed}}{K}} \longleftarrow \text{high}$$

A sudden reduction of CO_2 pressure then depresses the reaction quotient and drives the equilibrium to the right, in accordance with Le Châtelier's principle:

$$Q = \frac{P_{\mathrm{CO_2}}}{[\mathrm{CO_2(aq)}]} < K$$

Carbon dioxide gas bubbles out of the solution as the system adjusts to the loss of its gaseous product. When equilibrium is reestablished, the reduced values of both [CO_2(aq)] and P_{CO_2} will conform to the fixed value of K:

$$\overset{\text{low}\ \searrow}{[\mathrm{CO_2(aq)}]} = \underset{\nwarrow\ \text{fixed}}{\frac{P_{\mathrm{CO_2}}}{K}} \longleftarrow \text{low}$$

Osmosis and osmotic pressure are discussed on pages 540–543 and R15.4–R15.5 of PoC, *with accompanying sample problems in Examples 15-5 and 15-6. For treatment of other colligative properties, see pages 412–420 and Examples 11-6 through 11-8.*

34. See Example 15-5 (page R15.11) for the straightforward calculation of osmotic pressure. Note that we use the symbol c to denote the *total* concentration of dissolved ions or other particles.

(a) Knowing the temperature ($T = 298$ K) and concentration of dissolved particles,

$$c = \frac{0.10 \text{ mol AgNO}_3}{\text{L}} \times \frac{2 \text{ mol particles}}{\text{mol AgNO}_3} = 0.20\ M \text{ particles}$$

we also know the osmotic pressure:

$$\Pi = cRT = \left(0.20 \text{ mol L}^{-1}\right)\left(0.08206 \text{ atm L mol}^{-1}\text{ K}^{-1}\right)\left(298 \text{ K}\right) = 4.9 \text{ atm}$$

(b) Osmotic pressure, a colligative property, depends only on the total concentration of dissolved particles. A 0.067 M solution of Na_2SO_4 produces the same total concentration ($c = 0.20\ M$) and hence the same effect as a 0.10 M solution of $AgNO_3$:

$$\frac{0.20 \text{ mol particles}}{\text{L}} \times \frac{1 \text{ mol Na}_2\text{SO}_4}{3 \text{ mol particles}} = 0.067\ M \text{ Na}_2\text{SO}_4$$

(c) Glucose is a molecular solute, yielding one mole of undissociated molecules per mole of dissolved compound:

$$\frac{0.20 \text{ mol particles}}{\text{L}} \times \frac{1 \text{ mol C}_6\text{H}_{12}\text{O}_6}{\text{mol particles}} = 0.20\ M \text{ C}_6\text{H}_{12}\text{O}_6$$

35. See Examples 15-5 and 15-6, taking note of the relationship between concentration (*c*) and osmotic pressure (Π):

$$c = \frac{n}{V} = \frac{\Pi}{RT} \qquad\qquad n = \frac{m}{\mathcal{M}}$$

The symbols *m* and $\mathcal{M}$ denote the gram mass and molar mass, respectively. To obtain the requisite mass in grams, we substitute the number of moles (*n*) into the expression for concentration and solve for *m*:

$$m = \frac{\mathcal{M}\Pi V}{RT} = \frac{(180.158\text{ g }C_6H_{12}O_6\text{ mol}^{-1})(2.00\text{ atm})(0.100\text{ L})}{(0.08206\text{ atm L mol}^{-1}\text{ K}^{-1})(293.2\text{ K})} = 1.50\text{ g }C_6H_{12}O_6$$

Glucose, a molecular solute, produces one mole of dissolved particles per mole of dissolved material.

See Example 10-6 for an equation of similar *appearance* pertinent to an ideal gas. The determination of molar mass by boiling-point elevation, another colligative property, is demonstrated in Example 11-8.

36. A variation on the preceding exercise. Starting with the formula for osmotic pressure,

$$\Pi = cRT$$

we express the molar concentration ($c = n/V$) in terms of the gram mass (*m*) and molar mass ($\mathcal{M}$) of the solute:

$$n = \frac{m}{\mathcal{M}}$$

$$c = \frac{n}{V} = \frac{m}{\mathcal{M}V}$$

$$\Pi = cRT = \frac{mRT}{\mathcal{M}V}$$

Given values for *m*, *T*, Π, and *V*, we then solve for $\mathcal{M}$:

$$\mathcal{M} = \frac{mRT}{\Pi V} = \frac{(7.6\text{ g})(0.08206\text{ atm L mol}^{-1}\text{ K}^{-1})(310.2\text{ K})}{(8.4\text{ atm})(0.500\text{ L})} = 46\text{ g mol}^{-1}$$