

Chapter 11

Disorder–Order and Phase Transitions

Condensation of a gas sets the stage for the upcoming treatment of equilibrium thermodynamics, a story to unfold fully in Chapters 12 through 17. The present discussion, focusing on liquid–vapor and solution–vapor systems, provides a first look at equilibrium as a dynamic balance struck between opposing forces.

Exercises in Chapter 11 proceed roughly in the following sequence: (1) Intermolecular interactions and real gases. (2) Critical phenomena and phase transitions. (3) Vapor pressure and dynamic equilibrium. (4) Colligative properties of ideal solutions. (5) Deviations from ideality in real solutions.

The opening questions dealing with gases and intermolecular interactions look back to Chapters 9 and 10; the subsequent problems on phase equilibrium (beginning with Exercise 13) look ahead to Chapter 12 and beyond.

1. For condensation to occur, particles in a gas must interact sufficiently to form cooperative structures that can withstand the prevailing thermal energy—structures such as dimers, trimers, and other clusters. Conditions of low temperature and high pressure favor condensation.
2. The interparticle potential for an ideal gas is zero at all separations r , except for $r = 0$ (where the particles are touching and where the potential energy $U(r)$ rises abruptly to infinity). See Figure 11-4 in *PoC*, page 400.
3. A *hypothetically* ideal gas will remain a gas down to 0 K (absolute zero), never liquefying. All atoms and molecules do, however, have the potential to interact, and any real gas will condense at suitably low temperature and high pressure. A phase transition is possible when the intermolecular potential becomes comparable to the existing thermal energy.

4. Both the $\text{N}\cdots\text{N}$ and $\text{N}_2\cdots\text{N}_2$ potential functions have similar shapes, but the curve for $\text{N}\cdots\text{N}$ is substantially deeper and its minimum occurs at a smaller separation.

The potential functions resemble those for $\text{H}\cdots\text{H}$ and $\text{H}_2\cdots\text{H}_2$ interactions. See Figure 11-1 in *PoC* (page 395).

(a) The $\text{N}\cdots\text{N}$ interatomic potential owes its depth to the formation of a strong covalent bond: a triple bond with a dissociation energy of 946 kJ mol^{-1} and average length of 1.1 \AA . (See Table C-13 in *PoC*, page A82.)

(b) The $\text{N}_2\cdots\text{N}_2$ intermolecular potential arises only from the very weak London dispersion interactions available to the two nonpolar molecules. Its minimum occurs at approximately $r_0 = 4.1 \text{ \AA}$, with a depth U_0 of about 0.8 kJ mol^{-1} . (See J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids*, Wiley, 1954.)

5. The various noncovalent interactions are summarized in the table below. See Sections 9-3 and 11-1 in *PoC* for details, together with the solution provided for Exercise 8 in Chapter 9. A brief discussion is also given on pages R9.2–R9.4.

TYPE	ENERGY AT 5 Å (kJ mol^{-1})	DISTANCE DEPENDENCE	SYSTEM
ion–ion	≈ 250	$1/r$	ions
hydrogen bonding	≈ 20	contact	N, O, or F linked by H
ion–dipole	≈ 15	$1/r^2$	ions and polar molecules
dipole–dipole	≈ 2	$1/r^3$	polar molecules (nonrotating)
London (dispersion)	≈ 2	$1/r^6$	all

The stronger the interaction, the more pronounced will be the deviation from ideality. The potential energy of two permanent dipoles falls off as $1/r^3$ in stationary systems, persisting over greater distances than an interaction between induced dipoles (dispersion), which falls off as $1/r^6$. Hydrogen bonding, where present, is typically the strongest interaction available to neutral closed-shell species.

6. A gas behaves ideally or nearly so at high temperature (where a large thermal energy destroys any incipient clusters) and low density (where particles are far apart and unable to interact effectively). Deviations from ideality become most pronounced at high pressures and at low temperatures—more and more so below the critical temperature. Note that density for an ideal gas is directly proportional to pressure and inversely proportional to temperature:

$$\rho = \frac{n}{V} = \frac{P}{RT}$$

See Section 11-2 plus Examples 11-1 and 11-2 in PoC for material relevant to the van der Waals equation. Parameters a and b for selected systems are listed in Table C-14 of Appendix C (page A83).

7. For convenience, define the molar density

$$\rho = \frac{n}{V}$$

so that $n = \rho V$. With this definition we then rewrite the van der Waals equation

$$P_{\text{vdw}} = \frac{nRT}{V - nb} - a \frac{n^2}{V^2}$$

in the form

$$P_{\text{vdw}} = \frac{\rho RT}{1 - \rho b} - a\rho^2$$

Given $\rho = 1.00 \text{ mol L}^{-1}$, we insert values for a , b , and T to compute the van der Waals pressure. Krypton at 300 K ($a = 2.33 \text{ atm L}^2 \text{ mol}^{-2}$, $b = 0.0396 \text{ L mol}^{-1}$) will serve as a typical example:

$$\begin{aligned} P_{\text{vdw}} &= \frac{\rho RT}{1 - \rho b} - a\rho^2 \\ &= \frac{(1.00 \text{ mol L}^{-1})(0.08206 \text{ atm L mol}^{-1} \text{ K}^{-1})(300 \text{ K})}{1 - (1.00 \text{ mol L}^{-1})(0.0396 \text{ L mol}^{-1})} \\ &\quad - (2.33 \text{ atm L}^2 \text{ mol}^{-2})(1.00 \text{ mol L}^{-1})^2 \\ &= 23.3 \text{ atm} \end{aligned}$$

The ideal pressure, derived from $PV = nRT$, depends only on density and temperature:

$$\begin{aligned} P_{\text{ideal}} &= \frac{nRT}{V} = \rho RT \\ &= (1.00 \text{ mol L}^{-1})(0.08206 \text{ atm L mol}^{-1} \text{ K}^{-1})(300 \text{ K}) \\ &= 24.6 \text{ atm} \end{aligned}$$

The remaining systems are all handled the same way, each with its own values of a and b .

(a) $\rho = 1.00 \text{ mol L}^{-1}$, $T = 300 \text{ K}$:

	$a \text{ (atm L}^2 \text{ mol}^{-2}\text{)}$	$b \text{ (L mol}^{-1}\text{)}$	$P_{\text{vdw}} \text{ (atm)}$	$P_{\text{ideal}} \text{ (atm)}$
Kr	2.33	0.0396	23.3	24.6
Ar	1.36	0.0320	24.1	24.6
H ₂	0.25	0.0265	25.0	24.6

(b) $\rho = 1.00 \text{ mol L}^{-1}$, $T = 1000 \text{ K}$:

	$a \text{ (atm L}^2 \text{ mol}^{-2}\text{)}$	$b \text{ (L mol}^{-1}\text{)}$	$P_{\text{vdw}} \text{ (atm)}$	$P_{\text{ideal}} \text{ (atm)}$
Kr	2.33	0.0396	83.1	82.1
Ar	1.36	0.0320	83.4	82.1
H ₂	0.25	0.0265	84.0	82.1

The relative deviations are mostly smaller at higher temperature.

8. Use the same equation as in the preceding exercise,

$$P_{\text{vdw}} = \frac{\rho RT}{1 - \rho b} - a\rho^2$$

this time for hydrogen gas at a tenfold higher density:

$$a = 0.25 \text{ atm L}^2 \text{ mol}^{-2} \quad b = 0.0265 \text{ L mol}^{-1} \quad \rho = 10.0 \text{ mol L}^{-1}$$

The predicted real pressures are higher than the ideal pressures, and the relative deviations are consistently greater at this higher density. Compare the results below with those obtained for H₂ in Exercise 7:

	$T \text{ (K)}$	$P_{\text{vdw}} \text{ (atm)}$	$P_{\text{ideal}} \text{ (atm)}$
(a)	300	310.	246
(b)	1000	1.09×10^3	821

See pages 405–406, 412, 422–424, and R11.3 in PoC for an explanation of critical temperature and pressure.

Noncovalent interactions are discussed primarily in Section 9-3 and reviewed on pages R9.2–R9.4 and in Section 11-1. Examples 9-6, 9-7, 9-8, and 11-3, as well as Exercises 30 through 39 of Chapter 9, offer additional practice in using microscopic interactions to predict macroscopic properties. See also Exercise 8 of Chapter 9.

9. The critical temperature marks the highest temperature at which a gas can be liquefied under pressure. The critical pressure specifies the minimum pressure needed to liquefy a

gas at its critical temperature. Above the critical temperature, no amount of squeezing will force a condensation.

10. The normal boiling temperature is the temperature at which the vapor pressure of a liquid becomes equal to 1 atm. The critical temperature is the highest temperature at which a liquid can coexist in equilibrium with its vapor. Both the normal boiling temperature (T_b) and the critical temperature (T_c) are determined by intermolecular forces: T_b and T_c are generally higher in systems with strong interactions.

For details about boiling and boiling point, see pages 411–412 in *PoC* and also Example 9-7 (beginning on page R9.14). Boiling-point elevation is covered on page 418 and illustrated in Example 11-8.

11. The stronger the noncovalent interactions, the better the molecules are able to sustain clusters—even at relatively high thermal energies. Strong intermolecular interactions produce a high critical temperature.

Critical temperatures for selected systems are listed in Table C-14 of *PoC* (Appendix C, page A83)

(a) CH_3F is polar. CH_4 is nonpolar. The polar molecule has the stronger noncovalent interactions (dipole–dipole versus London dispersion force) and hence the higher critical temperature:

	T_c (K)
CH_3F	317.8
CH_4	190.53

(b) Both CH_4 and He are nonpolar and interact mainly by the weak London dispersion force. Methane, however, interacts more efficiently since it is more massive and thus offers a larger, more polarizable distribution of electrons:

	T_c (K)
CH_4	190.53
He	5.19

(c) Similar to the preceding pair: C_3H_8 and $\text{C}_{18}\text{H}_{38}$ are both nonpolar hydrocarbons that interact primarily through the dispersion force. Octadecane, the larger and more polarizable molecule, has a higher critical temperature:

	T_c (K)
$\text{C}_{18}\text{H}_{38}$	746
C_3H_8	369.82

(d) Same reasoning as for (b) and (c). Xenon, the heavier atom, has the higher critical temperature:

	T_c (K)
Xe	289.73
Ne	44.4

(e) Water can form *hydrogen bonds*, strongest of the noncovalent interactions between neutral species. By comparison, CO has only a weak dipole moment. The critical temperatures reflect the relative strength of interactions:

	T_c (K)
H ₂ O	647.14
CO	132.91

12. NH₃ can form hydrogen bonds and therefore boils at a higher temperature than PH₃. Only the atoms N, O, and F are considered sufficiently electronegative to engage in hydrogen bonding (although such interactions are also possible with certain anions, among them Cl⁻).

Fluids at supercritical temperatures are discussed on pages 422–424 of PoC.

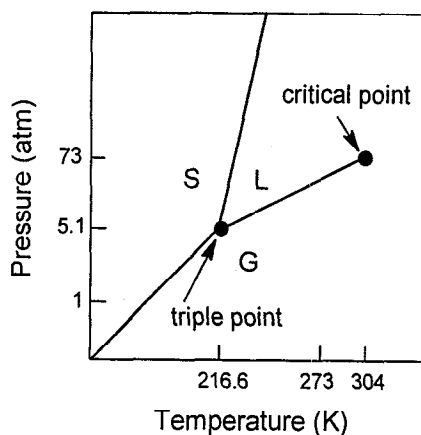
13. The stated temperature of 700°C is above the critical temperature for water. Regardless of pressure, H₂O can exist only as a single fluid phase (supercritical with respect to temperature) once T_c is exceeded. Vapor and liquid are unable to coexist at any pressure under these conditions.

- (a) Fluid at supercritical temperature.
- (b) Fluid at supercritical temperature.
- (c) Fluid at supercritical temperature.
- (d) Fluid at supercritical temperature and pressure.

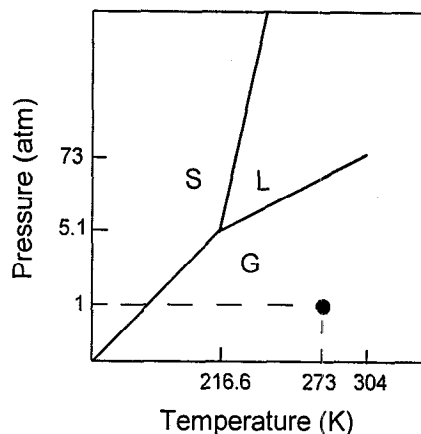
14. The phase diagrams shown in this exercise, like those in *PoC*, are purely schematic and are not drawn to scale.

See Section 11-5 and also Examples 11-9 and 11-10 for further discussion of phase diagrams.

(a) The solid–liquid line slopes upward from left to right, characteristic of a system for which the solid is more dense than the liquid:



(b) Only *gaseous* CO₂ exists at STP (1 atm, 273 K). The specified pressure and temperature lie below the triple point:



(c) We observe no “Dry Ice Cubes” at 1 atm, because liquid and solid do not coexist at pressures below the triple point. Carbon dioxide sublimates directly from solid to gas.

Moreover, even if a solid–liquid equilibrium were to exist, the solid would still not float since it is denser than the liquid.

15. Consider, for example, the equilibrium between liquid and vapor phases. A state of dynamic equilibrium develops when the rates of the opposing processes (evaporation and condensation) become equal. Once equilibrium is reached, the vapor pressure stays constant as long as enough liquid is present to maintain the balance between evaporation and condensation. A change in temperature will disrupt the equilibrium.

Full treatment of equilibrium begins in Chapter 12, and various aspects of the subject figure prominently throughout the remainder of *PoC*. A thermodynamic–kinetic reconciliation of dynamic equilibrium is offered at the end of Chapter 18.

Exercises 16 through 24 form an extended series designed to illustrate the meaning of equilibrium vapor pressure. See pages 409–412 plus Examples 11-4 and 11-5 in PoC.

16. Liquid water and water vapor can coexist in dynamic equilibrium under defined conditions, with the vapor maintaining a constant pressure at a fixed temperature. At 15°C, in particular, the partial pressure of water vapor above a reservoir of liquid remains 12.8 torr regardless of the volume occupied by the gas. Molecules of H₂O evaporate and condense at equal rates, and so the density of the vapor ($\rho = n/V$) holds constant. Pressure is fixed accordingly:

$$P = \rho RT$$

17. A liquid boils when its vapor pressure becomes equal to the prevailing atmospheric pressure.

(a) For water to boil at 15°C, the external pressure must fall to 12.8 torr—as might happen at very high altitudes, for example, or in a partially evacuated vessel.

(b) Water vapor at 15°C may indeed exert a pressure less than 12.8 torr, provided that the vapor is not in equilibrium with a liquid phase. Such a condition arises when there are too few molecules both to populate the vapor phase and to maintain a reservoir of liquid. See the next several problems, especially Exercises 21 through 23.

In addition, the partial pressure of water at 15°C will drop below 12.8 torr if the vapor is in equilibrium not with pure liquid but rather with an aqueous solution (in which the mole fraction of H₂O is less than 1). See Exercise 26.

18. Equilibrium between liquid and vapor can be established only if enough molecules are on hand to populate the volume available to the gas. The partial pressure will then become equal to the equilibrium vapor pressure, and there will be a reservoir of unevaporated liquid to support a balanced traffic across the interface. Larger volumes overhead will hold more molecules in the vapor, but the density and pressure will always be the same.

If, however, there is insufficient liquid to maintain a dynamic equilibrium with gas-phase molecules in the space above, then all of the liquid will evaporate. When it does, there is no equilibrium and therefore no vapor pressure.

19. Once dynamic equilibrium between liquid and vapor is established, the partial pressure of water vapor stabilizes at 12.8 torr at 15°C (288 K).

(a) We begin with 10.0 mL of liquid and ask if this quantity is sufficient to sustain equilibrium after evaporation. The first step is to calculate the total number of moles initially present, assuming a density of 1.00 g mL⁻¹:

$$10.0 \text{ mL H}_2\text{O}(\ell) \times \frac{1.00 \text{ g}}{\text{mL}} \times \frac{1 \text{ mol}}{18.015 \text{ g}} = 0.55509 \text{ mol H}_2\text{O}(\ell) \quad (\text{before round-off})$$

Next, we determine the number of moles needed to generate 12.8 torr in a gaseous volume of 5.00 L at 288 K:

$$n = \frac{PV}{RT} = \frac{\left(12.8 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}}\right)(5.00 \text{ L})}{(0.08206 \text{ atm L mol}^{-1} \text{ K}^{-1})(288 \text{ K})} = 0.00356 \text{ mol}$$

This amount (0.00356 mole of vapor) is less than the original 0.555 mole of liquid. There is enough liquid present to establish and maintain dynamic equilibrium.

The final partial pressure is the equilibrium vapor pressure of water at the stated temperature: 12.8 torr.

(b) Subtract the molar amount of vapor from the original molar amount of liquid to obtain the volume of unevaporated liquid:

$$\left[0.55509 \text{ mol H}_2\text{O}(\ell) - 0.00356 \text{ mol H}_2\text{O}(\text{g})\right] \times \frac{18.015 \text{ g}}{\text{mol}} \times \frac{1.00 \text{ mL}}{\text{g}} = 9.94 \text{ mL H}_2\text{O}(\ell)$$

Note that nonsignificant figures are retained for intermediate results to avoid round-off error. The final answer is limited to three significant figures.

20. From the preceding exercise we know that 0.555 mole of H₂O is present in 10.0 mL of liquid. Is this amount sufficient to permit equilibrium between liquid and vapor?

Ask, as before, how many moles of H₂O must go into the vapor phase—but this time to fill a volume of 100 L:

$$P = 12.8 \text{ torr} \quad V = 100.0 \text{ L} \quad T = 288 \text{ K}$$

$$n = \frac{PV}{RT} = \frac{\left(12.8 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}}\right)(100.0 \text{ L})}{(0.08206 \text{ atm L mol}^{-1} \text{ K}^{-1})(288 \text{ K})} = 0.0713 \text{ mol}$$

The amount is exactly what we expect: 20 times greater than the value found in a 5-liter container (see Exercise 19).

Of the original 0.555 mol H₂O(ℓ), a total of 0.0713 mol is lost to produce the equilibrium vapor pressure of 12.8 torr (the same pressure as before). The unevaporated liquid amounts to 8.72 mL:

$$\left[0.55509 \text{ mol H}_2\text{O}(\ell) - 0.07126 \text{ mol H}_2\text{O}(\text{g})\right] \times \frac{18.015 \text{ g}}{\text{mol}} \times \frac{1.00 \text{ mL}}{\text{g}} = 8.72 \text{ mL H}_2\text{O}(\ell)$$

To avoid round-off error, we retain extra digits in the intermediate stages of the calculation.

21. Use the same method as in Exercise 19, beginning with the amount of gaseous water needed to produce a pressure of 12.8 torr in a volume of 1000 L:

$$n = \frac{PV}{RT} = \frac{\left(12.8 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}}\right)(1000.0 \text{ L})}{(0.08206 \text{ atm L mol}^{-1} \text{ K}^{-1})(288 \text{ K})} = 0.713 \text{ mol}$$

(a) Since the quantity n exceeds the 0.555 mole of liquid initially present (see Exercise 19), a liquid–vapor equilibrium cannot be established.

(b) All of the liquid evaporates, filling the 1000-L volume with 0.555 mol vapor at a pressure of 9.97 torr:

$$P = \frac{nRT}{V} = \frac{(0.555 \text{ mol})(0.08206 \text{ atm L mol}^{-1} \text{ K}^{-1})(288 \text{ K})}{1000.0 \text{ L}} \times \frac{760 \text{ torr}}{\text{atm}} = 9.97 \text{ torr}$$

(c) No liquid remains.

22. Similar to the preceding exercise, but here we force a condensation by lowering the temperature.

(a) No liquid is present. If liquid and vapor were in equilibrium, then the partial pressure of water vapor at 288 K would be 12.8 torr—not 6.1 torr.

(b) Vapor pressures for water are collected in Table C-15 of *PoC* (page A84), where we find that 6.1 torr corresponds to a temperature of 4°C.

Condensation therefore becomes possible in this system at temperatures of 4°C (277 K) and below.

(c) First, we compute the molar amount of gas initially present at 288 K:

$$P = 6.1 \text{ torr} \quad V = 1000.0 \text{ L} \quad T = 288 \text{ K}$$

$$n_{\text{initial}} = \frac{PV}{RT} = \frac{\left(6.1 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}}\right)(1000.0 \text{ L})}{(0.08206 \text{ atm L mol}^{-1} \text{ K}^{-1})(288 \text{ K})} = 0.34 \text{ mol} \quad (\text{at } 288 \text{ K})$$

Second, we note from Table C-15 that the vapor pressure at 0°C (273 K) is only 4.6 torr. **We then recalculate** the number of moles that can be supported at this lower temperature:

$$P = 4.6 \text{ torr} \quad V = 1000.0 \text{ L} \quad T = 273 \text{ K}$$

$$n_{\text{equil}} = \frac{PV}{RT} = \frac{\left(4.6 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}}\right)(1000.0 \text{ L})}{(0.08206 \text{ atm L mol}^{-1} \text{ K}^{-1})(273 \text{ K})} = 0.27 \text{ mol (at 273 K)}$$

The difference gives us the amount and volume of liquid water condensed:

$$\left[0.34 \text{ mol H}_2\text{O(g)} - 0.27 \text{ mol H}_2\text{O(g)}\right] \times \frac{18.015 \text{ g}}{\text{mol}} \times \frac{1.00 \text{ mL}}{\text{g}} = 1.3 \text{ mL H}_2\text{O(l)}$$

23. A wrap-up of Exercises 19 through 22.

(a) There is 0.555 mol H₂O(l) initially present in 10.0 mL:

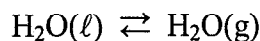
$$10.0 \text{ mL H}_2\text{O(l)} \times \frac{1.00 \text{ g}}{\text{mL}} \times \frac{1 \text{ mol}}{18.015 \text{ g}} = 0.555 \text{ mol H}_2\text{O(l)}$$

Imagine now that all but one tiny droplet evaporates, leaving just enough liquid to maintain equilibrium with the vapor. If so, then we simply compute the volume needed to support 0.555 mole of gas at a temperature of 288 K and a partial pressure of 12.8 torr (the equilibrium vapor pressure):

$$V = \frac{nRT}{P} = \frac{(0.555 \text{ mol})(0.08206 \text{ atm L mol}^{-1} \text{ K}^{-1})(288 \text{ K})}{\left(12.8 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}}\right)} = 779 \text{ L}$$

A liquid–vapor equilibrium can be sustained in any volume less than 779 L.

(b) Vapor pressure depends only on the two species participating in the equilibrium, liquid water and gaseous water:



Partial pressures arising from any other gases are irrelevant.

24. There is no inconsistency. If insufficient liquid is on hand to support a dynamic equilibrium in the volume above, then all of the liquid will evaporate. When it does, there is no equilibrium and hence no “vapor pressure”—a term that implies the coexistence of two phases. If, instead, enough liquid is present both to populate the vapor phase and to maintain a reservoir of unevaporated liquid, then the equilibrium pressure of the vapor will be the same regardless of the volume occupied.

We turn now to the equilibrium vapor pressure and other colligative properties of an ideal solution (discussed on pages 412–420 of PoC and illustrated in Examples 11-6 through 11-8).

25. A solution is said to be ideal if solute–solvent, solvent–solvent, and solute–solute interactions are effectively all the same. Ideality is approached most closely at low concentrations of solute. See pages 412–413 and R11.4.

26. Use Raoult's law

$$P_i = X_i P_i^\circ$$

to solve for the partial pressure P_i of some volatile component i , present in the solution with mole fraction X_i :

$$X_i = \frac{n_i}{n_{\text{tot}}}$$

The symbols n_i and n_{tot} indicate, respectively, the molar amount of i and the combined molar amount of all species present. P_i° denotes the vapor pressure of component i in its pure phase. See pages 413–418, page R11.4, and Example 11-6.

Our convention throughout will be to treat the solvent as component 1 and the solute as component 2.

(a) Glucose, a molecular solute, produces one mole of particles per mole dissolved:

$$n_1 = 100.0 \text{ g H}_2\text{O} \times \frac{1 \text{ mol H}_2\text{O}}{18.015 \text{ g H}_2\text{O}} = 5.551 \text{ mol H}_2\text{O}$$

$$n_2 = 10.0 \text{ g C}_6\text{H}_{12}\text{O}_6 \times \frac{1 \text{ mol C}_6\text{H}_{12}\text{O}_6}{180.158 \text{ g C}_6\text{H}_{12}\text{O}_6} = 0.0555 \text{ mol C}_6\text{H}_{12}\text{O}_6$$

$$P_1 = X_1 P_1^\circ = \frac{n_1}{n_1 + n_2} P_1^\circ = \frac{5.551 \text{ mol}}{(5.551 + 0.0555) \text{ mol}} \times 12.8 \text{ torr} = 12.7 \text{ torr} \quad (3 \text{ sig fig})$$

The mole fraction of H_2O is reduced from 1.0000 in the pure solvent to 0.9901 in the solution. Vapor pressure falls from 12.8 torr to 12.67 torr, which we round off to the tenths' place. See Table C-15 and also the preceding exercises for data concerning the vapor pressure of pure water.

(b) NaCl produces two moles of dissolved ions ($\text{Na}^+ + \text{Cl}^-$) per mole of compound:

$$n_1 = 100.0 \text{ g H}_2\text{O} \times \frac{1 \text{ mol H}_2\text{O}}{18.015 \text{ g H}_2\text{O}} = 5.551 \text{ mol H}_2\text{O}$$

$$n_2 = 10.0 \text{ g NaCl} \times \frac{1 \text{ mol NaCl}}{58.443 \text{ g NaCl}} \times \frac{2 \text{ mol particles}}{\text{mol NaCl}} = 0.342 \text{ mol particles}$$

$$P_1 = X_1 P_1^\circ = \frac{n_1}{n_1 + n_2} P_1^\circ = \frac{5.551 \text{ mol}}{(5.551 + 0.342) \text{ mol}} \times 12.8 \text{ torr} = 12.1 \text{ torr}$$

(c) NaNO_3 yields two moles of dissolved ions ($\text{Na}^+ + \text{NO}_3^-$) per mole of compound:

$$n_1 = 100.0 \text{ g H}_2\text{O} \times \frac{1 \text{ mol H}_2\text{O}}{18.015 \text{ g H}_2\text{O}} = 5.551 \text{ mol H}_2\text{O}$$

$$n_2 = 10.0 \text{ g NaNO}_3 \times \frac{1 \text{ mol NaNO}_3}{84.995 \text{ g NaNO}_3} \times \frac{2 \text{ mol particles}}{\text{mol NaNO}_3} = 0.235 \text{ mol particles}$$

$$P_1 = X_1 P_1^\circ = \frac{n_1}{n_1 + n_2} P_1^\circ = \frac{5.551 \text{ mol}}{(5.551 + 0.235) \text{ mol}} \times 12.8 \text{ torr} = 12.3 \text{ torr}$$

(d) Na_2SO_4 yields three moles of dissolved ions ($2\text{Na}^+ + \text{SO}_4^{2-}$) per mole of compound:

$$n_1 = 100.0 \text{ g H}_2\text{O} \times \frac{1 \text{ mol H}_2\text{O}}{18.015 \text{ g H}_2\text{O}} = 5.551 \text{ mol H}_2\text{O}$$

$$n_2 = 10.0 \text{ g Na}_2\text{SO}_4 \times \frac{1 \text{ mol Na}_2\text{SO}_4}{142.043 \text{ g Na}_2\text{SO}_4} \times \frac{3 \text{ mol particles}}{\text{mol Na}_2\text{SO}_4} = 0.211 \text{ mol particles}$$

$$P_1 = X_1 P_1^\circ = \frac{n_1}{n_1 + n_2} P_1^\circ = \frac{5.551 \text{ mol}}{(5.551 + 0.211) \text{ mol}} \times 12.8 \text{ torr} = 12.3 \text{ torr}$$

There is no pattern to the results, since equal numbers of *grams*—not moles—are mixed with the same amount of solvent. Each solution contains a different concentration of dissolved particles.

27. Use the method developed in the preceding exercise, working in each case with the same amount of water:

$$n_1 = 5.551 \text{ mol H}_2\text{O} \quad P_1^\circ = 12.8 \text{ torr at } 15^\circ\text{C}$$

The vapor pressure is lowered by 1.77% in all of the systems considered. See the detailed calculations that follow.

(a) We dissolve 0.100 mole of a molecular solute, glucose, thereby lowering the mole fraction of water to 0.9823:

$$n_2 = 18.0 \text{ g C}_6\text{H}_{12}\text{O}_6 \times \frac{1 \text{ mol C}_6\text{H}_{12}\text{O}_6}{180.158 \text{ g C}_6\text{H}_{12}\text{O}_6} = 0.100 \text{ mol C}_6\text{H}_{12}\text{O}_6$$

$$P_1 = X_1 P_1^\circ = \frac{n_1}{n_1 + n_2} P_1^\circ = \frac{5.551 \text{ mol}}{(5.551 + 0.100) \text{ mol}} \times 12.8 \text{ torr}$$

$$= 0.9823 \times 12.8 \text{ torr} = 12.6 \text{ torr}$$

The percent decrease in vapor pressure follows directly from the mole fraction:

$$\frac{P_1^\circ - P_1}{P_1^\circ} \times 100\% = \frac{(1 - X_1)P_1^\circ}{P_1^\circ} \times 100\% = 1.77\%$$

(b) Similar, but here we dissolve an ionic solute that produces two moles of particles per mole of compound:

$$n_2 = 2.92 \text{ g NaCl} \times \frac{1 \text{ mol NaCl}}{58.443 \text{ g NaCl}} \times \frac{2 \text{ mol particles}}{\text{mol NaCl}} = 0.100 \text{ mol particles}$$

$$P_1 = X_1 P_1^\circ = \frac{n_1}{n_1 + n_2} P_1^\circ = \frac{5.551 \text{ mol}}{(5.551 + 0.100) \text{ mol}} \times 12.8 \text{ torr} = 12.6 \text{ torr}$$

The reduced mole fraction, $X_1 = 0.9823$, lowers the vapor pressure of water by 1.77%.

(c) Again, we dissolve 0.100 mole of particles and realize a vapor-pressure lowering of 1.77%. Each mole of NaNO_3 releases two moles of ions:

$$n_2 = 4.25 \text{ g NaNO}_3 \times \frac{1 \text{ mol NaNO}_3}{84.995 \text{ g NaNO}_3} \times \frac{2 \text{ mol particles}}{\text{mol NaNO}_3} = 0.100 \text{ mol particles}$$

$$P_1 = X_1 P_1^\circ = \frac{n_1}{n_1 + n_2} P_1^\circ = \frac{5.551 \text{ mol}}{(5.551 + 0.100) \text{ mol}} \times 12.8 \text{ torr} = 12.6 \text{ torr}$$

The mole fraction of water, X_1 , falls to 0.9823.

(d) We achieve the same lowering of 1.77% by dissolving the appropriate gram-amount of Na_2SO_4 , a solute that yields three moles of ions per mole of compound:

$$n_2 = 4.73 \text{ g Na}_2\text{SO}_4 \times \frac{1 \text{ mol Na}_2\text{SO}_4}{142.043 \text{ g Na}_2\text{SO}_4} \times \frac{3 \text{ mol particles}}{\text{mol Na}_2\text{SO}_4} = 0.100 \text{ mol particles}$$

$$P_1 = X_1 P_1^\circ = \frac{n_1}{n_1 + n_2} P_1^\circ = \frac{5.551 \text{ mol}}{(5.551 + 0.100) \text{ mol}} \times 12.8 \text{ torr} = 12.6 \text{ torr}$$

Vapor pressures in (a) through (d) are identical because each solution contains the same number of dissolved particles in the same volume. The mole fraction of H_2O is unchanged:

$$X_1 = \frac{5.551}{5.551 + 0.100} = 0.9823$$

28. The procedure is similar to that used in the preceding two exercises:

$$P_1 = X_1 P_1^\circ$$

$$X_1 = \frac{P_1}{P_1^\circ} = \frac{n_1}{n_1 + n_2}$$

Given the mole fraction and amount of solvent,

$$X_1 = \frac{P_1}{P_1^\circ} = \frac{49.0 \text{ torr}}{50.0 \text{ torr}} = 0.980$$

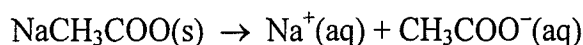
$$n_1 = 500. \text{ g H}_2\text{O} \times \frac{1 \text{ mol H}_2\text{O}}{18.015 \text{ g H}_2\text{O}} = 27.75 \text{ mol H}_2\text{O}$$

we solve for the amount of solute:

$$n_2 = \frac{n_1(1 - X_1)}{X_1} = \frac{(27.75 \text{ mol})(1 - 0.980)}{0.980} = 0.566 \text{ mol}$$

Each solute therefore must yield 0.566 mole of dissolved particles.

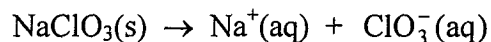
(a) Sodium acetate dissociates into the sodium cation and acetate anion:



We need 23.2 g:

$$0.566 \text{ mol particles} \times \frac{1 \text{ mol NaCH}_3\text{COO}}{2 \text{ mol particles}} \times \frac{82.034 \text{ g NaCH}_3\text{COO}}{\text{mol NaCH}_3\text{COO}} = 23.2 \text{ g NaCH}_3\text{COO}$$

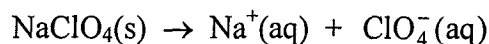
(b) Similar. Two moles of ions are produced per mole of dissolved compound,



and the required mass is 30.1 g:

$$0.566 \text{ mol particles} \times \frac{1 \text{ mol NaClO}_3}{2 \text{ mol particles}} \times \frac{106.441 \text{ g NaClO}_3}{\text{mol NaClO}_3} = 30.1 \text{ g NaClO}_3$$

(c) Again, two moles of dissolved ions—but with an even larger molar mass:



$$0.566 \text{ mol particles} \times \frac{1 \text{ mol NaClO}_4}{2 \text{ mol particles}} \times \frac{122.440 \text{ g NaClO}_4}{\text{mol NaClO}_4} = 34.7 \text{ g NaClO}_4$$

(d) Here we have a molecular solute with a molar mass of 342.300 g:

$$0.566 \text{ mol particles} \times \frac{1 \text{ mol C}_{12}\text{H}_{22}\text{O}_{11}}{\text{mol particles}} \times \frac{342.300 \text{ g C}_{12}\text{H}_{22}\text{O}_{11}}{\text{mol C}_{12}\text{H}_{22}\text{O}_{11}} = 194 \text{ g C}_{12}\text{H}_{22}\text{O}_{11}$$

(e) Similar:

$$0.566 \text{ mol particles} \times \frac{1 \text{ mol C}_6\text{H}_{12}\text{O}_6}{\text{mol particles}} \times \frac{180.158 \text{ g C}_6\text{H}_{12}\text{O}_6}{\text{mol C}_6\text{H}_{12}\text{O}_6} = 102 \text{ g C}_6\text{H}_{12}\text{O}_6$$

29. We continue to use Raoult's law to calculate vapor-pressure lowering in an ideal solution. See pages 413–417, page R11.4, and Example 11-6 in *PoC*.

(a) Start with the known amount and vapor pressure of ethanol, the solvent:

VOLUME DENSITY MOLAR MASS MOLES

$$n_1 = (125.0 \text{ mL C}_2\text{H}_5\text{OH})(0.7873 \text{ g mL}^{-1}) \times \frac{1 \text{ mol}}{46.069 \text{ g}} = 2.136 \text{ mol C}_2\text{H}_5\text{OH}$$

$$P_1^\circ = 59.3 \text{ torr (pure ethanol)}$$

$$P_1 = 57.15 \text{ torr (ethanol with dissolved compound Y)}$$

With the mole fraction of ethanol given by Raoult's law,

$$X_1 = \frac{P_1}{P_1^\circ} = \frac{57.15 \text{ torr}}{59.3 \text{ torr}} = \frac{n_1}{n_1 + n_2}$$

we then solve for the amount of compound Y:

$$n_2 = \frac{n_1(1 - X_1)}{X_1} = \frac{(2.136 \text{ mol})\left(1 - \frac{57.15}{59.3}\right)}{\left(\frac{57.15}{59.3}\right)} = 0.08036 \text{ mol Y}$$

Since we are told that 5.00 grams of this compound were dissolved, we now know the molar mass:

$$m = \frac{5.00 \text{ g}}{0.08036 \text{ mol}} = 62.2 \text{ g mol}^{-1}$$

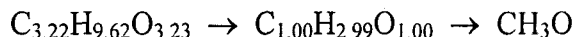
(b) First, determine the empirical formula from the elemental composition. Assume 100 g:

$$38.7 \text{ g C} \times \frac{1 \text{ mol C}}{12.011 \text{ g C}} = 3.22 \text{ mol C}$$

$$9.7 \text{ g H} \times \frac{1 \text{ mol H}}{1.00794 \text{ g H}} = 9.62 \text{ mol H}$$

$$51.6 \text{ g O} \times \frac{1 \text{ mol O}}{15.9994 \text{ g O}} = 3.23 \text{ mol O}$$

Reducing the molar proportions to lowest terms,



we obtain an empirical formula of CH_3O . The formula weight is 31.034, effectively half the molar mass of 62.2 g mol^{-1} calculated in (a). Hence the molecular formula is $\text{C}_2\text{H}_6\text{O}_2$.

30. In contrast to the exercises immediately preceding, here we have a volatile solute as well as a volatile solvent. Each component establishes its own vapor pressure in proportion to its own mole fraction.

Knowing that the mixture contains equal volumes of H_2O and $\text{C}_2\text{H}_5\text{OH}$, we shall

assume arbitrarily that 1.000 mL of each liquid is present. The first step is to calculate the two molar amounts:

$$n_1 = 1.000 \text{ mL H}_2\text{O} \times \frac{0.9971 \text{ g}}{\text{mL}} \times \frac{1 \text{ mol}}{18.015 \text{ g}} = 0.05535 \text{ mol H}_2\text{O}$$

$$n_2 = 1.000 \text{ mL C}_2\text{H}_5\text{OH} \times \frac{0.7873 \text{ g}}{\text{mL}} \times \frac{1 \text{ mol}}{46.069 \text{ g}} = 0.01709 \text{ mol C}_2\text{H}_5\text{OH}$$

Next, we calculate the mole fractions:

$$X_1 = \frac{n_1}{n_1 + n_2} = \frac{0.05535 \text{ mol}}{(0.05535 + 0.01709) \text{ mol}} = 0.7641$$

$$X_2 = \frac{n_2}{n_1 + n_2} = \frac{0.01709 \text{ mol}}{(0.05535 + 0.01709) \text{ mol}} = 0.2359$$

Finally, we apply Raoult's law:

$$P_1 = X_1 P_1^\circ = (0.7641)(23.8 \text{ torr}) = 18.2 \text{ torr} \quad (\text{H}_2\text{O})$$

$$P_2 = X_2 P_2^\circ = (0.2359)(59.3 \text{ torr}) = 14.0 \text{ torr} \quad (\text{C}_2\text{H}_5\text{OH})$$

31. Start by calculating the concentration of dissolved particles, expressing the value as a *molality* (m): moles of solute particles per kilogram of solvent. Then use the total molality to compute the changes in freezing and boiling points:

$$\Delta T_f = K_f m \quad (\text{decrease})$$

$$\Delta T_b = K_b m \quad (\text{increase})$$

The KCl solution specified in (a),

$$\frac{3.52 \text{ g KCl}}{100.0 \text{ g H}_2\text{O}}$$

will serve as a sufficiently general example:

$$m = \frac{3.52 \text{ g KCl}}{100.0 \text{ g H}_2\text{O}} \times \frac{1 \text{ mol KCl}}{74.551 \text{ g KCl}} \times \frac{2 \text{ mol particles}}{\text{mol KCl}} \times \frac{1000 \text{ g H}_2\text{O}}{\text{kg H}_2\text{O}} = 0.944 \text{ mol kg}^{-1}$$

$$\Delta T_f = K_f m = (1.86^\circ \text{C kg mol}^{-1})(0.944 \text{ mol kg}^{-1}) = 1.76^\circ \text{C}$$

$$\Delta T_b = K_b m = (0.51^\circ \text{C kg mol}^{-1})(0.944 \text{ mol kg}^{-1}) = 0.48^\circ \text{C}$$

The solution freezes at -1.76°C and boils at 100.48°C :

$$T_f = 0.00^\circ\text{C} - 1.76^\circ\text{C} = -1.76^\circ\text{C}$$

$$T_b = 100.00^\circ\text{C} + 0.48^\circ\text{C} = 100.48^\circ\text{C}$$

All of the other systems are treated in the same way. See pages 418–420 and R11.4–R11.5 of *PoC*, together with Examples 11-7 and 11-8.

	MOLAR MASS (kg mol^{-1})	NO. MOLES PARTICLES	TOTAL MOLALITY (mol kg^{-1})	T_f ($^\circ\text{C}$)	T_b ($^\circ\text{C}$)
(a) KCl	74.551	2	0.944	-1.76	100.48
(b) $\text{Ce}_2(\text{SO}_4)_3$	568.423	5	0.503	-0.936	100.26
(c) NaCH_3COO	82.034	2	2.73	-5.08	101.4
(d) $\text{C}_{12}\text{H}_{22}\text{O}_{11}$	342.300	1	0.876	-1.63	100.45

32. Calculate the total molality, inclusive of all dissolved particles. The more concentrated solution has the lower freezing point and the higher boiling point.

(a) $\text{Pb}(\text{NO}_3)_2$ releases three moles of ions; KCl releases two:

$$\frac{0.010 \text{ mol Pb}(\text{NO}_3)_2}{\text{kg H}_2\text{O}} \times \frac{3 \text{ mol particles}}{\text{mol Pb}(\text{NO}_3)_2} = 0.030 \text{ mol kg}^{-1}$$

$$\frac{0.012 \text{ mol KCl}}{\text{kg H}_2\text{O}} \times \frac{2 \text{ mol particles}}{\text{mol KCl}} = 0.024 \text{ mol kg}^{-1}$$

The $\text{Pb}(\text{NO}_3)_2$ solution contains the larger concentration of dissolved particles and consequently shows the stronger colligative effects. It boils at a higher temperature and freezes at a lower temperature.

(b) Glucose is a molecular solute, whereas sodium nitrate dissociates into Na^+ and NO_3^- :

$$\frac{0.050 \text{ mol C}_6\text{H}_{12}\text{O}_6}{\text{kg H}_2\text{O}} \times \frac{1 \text{ mol particles}}{\text{mol C}_6\text{H}_{12}\text{O}_6} = 0.050 \text{ mol kg}^{-1}$$

$$\frac{0.020 \text{ mol NaNO}_3}{\text{kg H}_2\text{O}} \times \frac{2 \text{ mol particles}}{\text{mol NaNO}_3} = 0.040 \text{ mol kg}^{-1}$$

The solution of glucose freezes at the lower temperature and boils at the higher temperature.

(c) Both compounds are molecules (nonelectrolytes) and thus produce only one mole of particles per mole dissolved. A 0.040 *m* solution of $\text{C}_2\text{H}_6\text{O}_2$ has a lower freezing point and higher boiling point than a 0.030 *m* solution of $\text{C}_3\text{H}_8\text{O}_3$.

(d) Lithium sulfate dissociates into 2Li^+ and SO_4^{2-} ; magnesium sulfate dissociates into Mg^{2+} and SO_4^{2-} :

$$\frac{0.010 \text{ mol Li}_2\text{SO}_4}{\text{kg H}_2\text{O}} \times \frac{3 \text{ mol particles}}{\text{mol Li}_2\text{SO}_4} = 0.030 \text{ mol kg}^{-1}$$

$$\frac{0.010 \text{ mol MgSO}_4}{\text{kg H}_2\text{O}} \times \frac{2 \text{ mol particles}}{\text{mol MgSO}_4} = 0.020 \text{ mol kg}^{-1}$$

The Li_2SO_4 solution has the lower freezing point and higher boiling point.

33. Freezing-point depression and boiling-point elevation are both controlled by the total molality of solution:

$$\text{Total molality} = \frac{\text{moles particles}}{\text{kg solvent}}$$

See also Example 11-8 in *PoC* (page R11.16).

(a) We determine the total molality, *m*, from the extent of the boiling-point elevation:

$$\Delta T_b = K_b m$$

$$m = \frac{\Delta T_b}{K_b} = \frac{(101.70 - 100.00)^\circ\text{C}}{0.51^\circ\text{C kg mol}^{-1}} = 3.33 \text{ mol kg}^{-1}$$

Knowing m , we then compute the corresponding freezing-point depression and the resulting value of T_f :

$$\Delta T_f = K_f m = (1.86^\circ \text{C kg mol}^{-1})(3.33 \text{ mol kg}^{-1}) = 6.2^\circ \text{C}$$

$$T_f = 0.0^\circ \text{C} - 6.2^\circ \text{C} = -6.2^\circ \text{C}$$

(b) Convert moles of solute into grams of solute:

$$\frac{3.33 \text{ mol C}_2\text{H}_6\text{O}_2}{1000 \text{ g H}_2\text{O}} \times \frac{62.068 \text{ g C}_2\text{H}_6\text{O}_2}{\text{mol C}_2\text{H}_6\text{O}_2} \times 100 \text{ g H}_2\text{O} = 20.7 \text{ g C}_2\text{H}_6\text{O}_2$$

34. Given the molality, freezing-point depression, and boiling-point elevation of the solution,

$$m = \frac{10.0 \text{ g C}_{14}\text{H}_{10}}{500. \text{ g C}_6\text{H}_6} \times \frac{1 \text{ mol C}_{14}\text{H}_{10}}{178.233 \text{ g C}_{14}\text{H}_{10}} \times \frac{1000 \text{ g C}_6\text{H}_6}{\text{kg C}_6\text{H}_6} = \frac{0.112 \text{ mol C}_{14}\text{H}_{10}}{\text{kg C}_6\text{H}_6}$$

$$\Delta T_f = K_f m = \text{normal f.p.} - \text{depressed f.p.} = 5.5^\circ \text{C} - 4.95^\circ \text{C} = 0.55^\circ \text{C}$$

$$\Delta T_b = K_b m = \text{elevated b.p.} - \text{normal b.p.} = 80.38^\circ \text{C} - 80.1^\circ \text{C} = 0.28^\circ \text{C}$$

we have sufficient data to determine both K_f and K_b :

$$K_f = \frac{\Delta T_f}{m} = \frac{0.55^\circ \text{C}}{0.112 \text{ mol kg}^{-1}} = 4.9^\circ \text{C kg mol}^{-1}$$

$$K_b = \frac{\Delta T_b}{m} = \frac{0.28^\circ \text{C}}{0.112 \text{ mol kg}^{-1}} = 2.5^\circ \text{C kg mol}^{-1}$$

The remaining exercises deal with colligative properties in real solutions. See pages 417–418 and Example 11-7 in PoC.

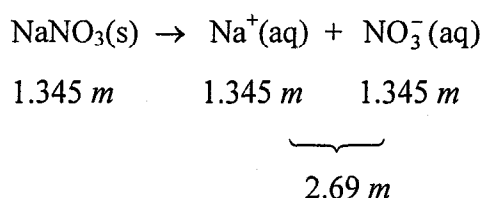
35. Colligative properties depend, in principle, only on the numerical concentration (and not the chemical type) of dissolved particles. Nevertheless, the effective molality of a real solution will often differ from the nominal molality of an ideal solution.

(a) First we calculate the nominal molality:

$$\Delta T_f = K_f m$$

$$m = \frac{\Delta T_f}{K_f} = \frac{5.00^\circ \text{C}}{1.86^\circ \text{C kg mol}^{-1}} = 2.69 \text{ mol kg}^{-1} \quad (\text{ideal})$$

(b) Dissolving 1.345 moles of NaNO_3 in 1.00 kilogram of water will produce a nominal ion concentration of 2.69 mol kg^{-1} , sufficient to depress the freezing point of an ideal solution by 5.00°C :



The effective molality of dissolved particles, however, is likely to be less than expected. Electrostatic attractions between Na^+ and NO_3^- will create *ion pairs*, thus reducing the number of independent particles in a nonideal solution. More than 1.345 moles of NaNO_3 will need to be dissolved in order to lower the freezing point by 5.00°C .

(c) A solution of ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$) will produce a more nearly ideal system. Molecules of $\text{C}_2\text{H}_6\text{O}_2$ do not dissociate into ions when dissolved.

36. Nonideal solutions are discussed and classified on pages 417–418 of *PoC*. See also Example 11-7, beginning on page R11.14.

(a) NaHCO_3 dissociates into Na^+ and HCO_3^- ions, and consequently a solution of sodium bicarbonate is susceptible to ion pairing. The electrolytic solution that results is more likely to deviate from ideality than a solution of $\text{C}_6\text{H}_{12}\text{O}_6$, in which no ions are formed.

(b) Both LiF and Li_2SO_4 produce ions in solution, but Li_2SO_4 is likely to deviate more from ideality. The SO_4^{2-} ions, with a larger charge than F^- , generate stronger electric fields and hence stronger attractions.

(c) KCl dissociates into the singly charged ions K^+ and Cl^- , whereas $\text{Ce}_2(\text{SO}_4)_3$ dissociates into two triply charged Ce^{3+} cations and three doubly charged SO_4^{2-} anions. A solution of cerium sulfate is more susceptible to ion pairing and less likely to be ideal.

37. Deviations from solution ideality are discussed on pages 417–418 of *PoC*. For a demonstration problem, see Example 11-7 in *PoC* (beginning on page R11.14).

(a) Both 1.5 *m* KCl and 1.0 *m* K₂SO₄ produce solutions with nominal concentrations of 3.0 *m*:

$$\frac{1.5 \text{ mol KCl}}{\text{kg H}_2\text{O}} \times \frac{2 \text{ mol particles}}{\text{mol KCl}} = \frac{3.0 \text{ mol particles}}{\text{kg H}_2\text{O}} \quad (\text{ideal})$$

$$\frac{1.0 \text{ mol K}_2\text{SO}_4}{\text{kg H}_2\text{O}} \times \frac{3 \text{ mol particles}}{\text{mol K}_2\text{SO}_4} = \frac{3.0 \text{ mol particles}}{\text{kg H}_2\text{O}} \quad (\text{ideal})$$

In *real* solutions, though, the effective concentration of independent particles is expected to be lower for K₂SO₄(aq) than for KCl(aq). The larger charge of the SO₄²⁻ ion enhances its electrostatic attraction to K⁺ ions, and therefore more ion pairs are able to form. A real solution of KCl, by contrast, will have a greater number of independent, unpaired ions able to lower the freezing point and raise the boiling point.

The 1.5 *m* KCl system has the higher effective molality, the lower freezing point, and the higher boiling point.

(b) Again, both systems yield solutions with the same nominal (ideal) molality—in this case, 1.0 *m*:

$$\frac{0.5 \text{ mol KCl}}{\text{kg H}_2\text{O}} \times \frac{2 \text{ mol particles}}{\text{mol KCl}} = \frac{1.0 \text{ mol particles}}{\text{kg H}_2\text{O}} \quad (\text{ideal})$$

$$\frac{1.0 \text{ mol C}_{12}\text{H}_{22}\text{O}_{11}}{\text{kg H}_2\text{O}} \times \frac{1 \text{ mol particles}}{\text{mol C}_{12}\text{H}_{22}\text{O}_{11}} = \frac{1.0 \text{ mol particles}}{\text{kg H}_2\text{O}} \quad (\text{ideal})$$

Nevertheless, the molecular solute (C₁₂H₂₂O₁₁) will have the higher effective molality since there is no opportunity to form ion pairs. A 1.0 *m* solution of sucrose is expected to have a lower freezing point and higher boiling point than a 0.5 *m* solution of potassium chloride.