

Chapter 9

States of Matter

In Chapter 9 we embark on a new course, moving away from a picture of atoms and molecules acting alone to one of atoms and molecules acting collectively. We begin to consider the aggregated states of matter: gases, liquids, solids, and some of the phases in between. The present chapter, important in itself, also serves as prelude to the main work of transformation and equilibrium, a theme that begins in Chapter 10 and builds continuously after that.

At first, the shift in focus appears little more than another step up the organizational hierarchy of matter. From electrons and intact nuclei, we built atoms. From atoms, we built molecules. And now—from those same atoms and molecules, governed by the same laws—we build phases. In some ways, it seems more a difference in degree than in kind.

But we also find that the whole is not simply the sum of its parts. Two particles are different from one. Six particles are different from two. Six hundred particles are different from six, and 6.02×10^{23} particles are different still. Microscopic adjustments in structure and energy, invisible to the eye, lead to macroscopic consequences plain to see.

With macroscopic aggregates, too, we come upon the notions of disorder, chance, and statistical inevitability—ideas that will accompany us from this point forward as we drive to equilibrium, trying to understand why matter always seems to take the course it does.

The first 13 exercises provide a brief review of essential issues such as order and disorder, noncovalent interactions, and the microscopic–macroscopic determination of structure and properties.

1. *Solid*—a form of matter in which noncovalent interactions express themselves to the strongest extent possible, lending both short-range order and long-range order to the microscopic arrangement. Individual molecules, influenced strongly by their neighbors, are allowed only minimal freedom of motion. Molecular energies and speeds are low, intermolecular distances are short, and densities are high. The aggregate structure typically displays considerable symmetry.

Liquid—strongly governed, like a solid, by intermolecular interactions; but, unlike a solid, possessing just short-range order. The interacting particles hold together only over short distances and only for short times before breaking up and reassembling elsewhere. Molecules in a liquid are more energetic than molecules in a solid. They move faster. They collide. They change positions. There is no rule of symmetry by which the particles occupy set positions in some regular framework, as otherwise they would in a crystalline lattice.

Gas—a phase free from both long-range order and short-range order, chaotic and unpredictable at the level of the individual molecule. Intermolecular interactions are either absent or expressed only weakly. The particles move fast and independently, separated from one another by distances large on a molecular scale.

See Section 9-4 and also Chapters 10 and 11.

2. A system is *ordered* if it displays a certain regularity of organization—if its particles maintain relatively fixed positions in space and time. The particles in an ordered structure assume their positions in a predictable way; there is a rule and pattern to the microscopic arrangement.

Where the pattern persists over long distances, as in a crystalline solid, the assembly exhibits *long-range* order. Each individual component has a fixed, permanent address. Every location is known beforehand, predetermined by a particular rule of symmetry.

For assemblies having just *short-range* order, the organization is strictly local. Here and there we find pockets of regularity where order prevails. Small groups form in which each member is constrained by its neighbors—groups such as the clusters that hold together briefly and over short distances in a liquid. Inside each group we discern a pattern, whereas from group to group we see only random variation.

When regularity breaks down even within each group, then there is randomness everywhere: no long-range order, no short-range order. A gas.

3. The uncertainty principle (Section 4-6) imposes limits on our simultaneous knowledge of position and momentum. If we measure exactly *where* a particle is, we must accept a proportionally large indeterminacy in its momentum and velocity. If we measure exactly how fast and in what direction a particle is heading, we can say little about its position at the same time.

One consequence is this: Nothing can stand completely still, for then both the position and velocity (zero) would be known to unlimited accuracy. No particle—especially no small particle—can have a truly fixed address. The location of an atom in a

lattice is limited ultimately by the uncertainty principle, although usually the indeterminacy does not seriously distort our picture of crystalline symmetry.

See also the discussion of *zero-point energy* on page 737 of *PoC*.

4. A crystal possesses both long-range order and translational symmetry. Every unit cell is related to every other unit cell by a regular pattern of displacement throughout the crystal, like squares on a chessboard.

A quasicrystal, too, possesses long-range order, and its atoms also occupy positions according to a rule—but not the rule of a chessboard, where every square is reached by so many steps in one direction and so many in the other. Lacking translational symmetry, the pattern of a quasicrystal (Section 9-5) has no periodicity. It never repeats itself.

5. Pulling together anywhere from a few particles to a few thousand, a nanocrystal has properties intermediate between those of a molecule and those of a bulk phase. Among small clusters in particular, atoms or molecules near the surface face an environment substantially different from particles in the interior. Chemical, electric, and magnetic behavior all depend strongly on the interplay of the interior and exterior structure. See Section 9-7.

6. A liquid crystal (Section 9-8) falls between the extremes of liquid and solid in its organization and symmetry. It possesses the rotational order of a crystal, but not the translational order. Similar to a liquid, the molecules flow from point to point; *unlike* a liquid, however, the molecules do not tumble randomly along all axes while they flow. They maintain, to some extent, fixed orientations throughout their drift, thereby preserving a measure of rotational order.

7. Noncovalent interactions such as ion–ion forces, ion–dipole forces, dipole–dipole forces, hydrogen bonds, and London dispersion forces hold together the phases of matter in a balance of attraction and repulsion. Despite the different names, all of the forces derive from the same origin: the electromagnetic interaction, governed by the laws of quantum mechanics for microscopic particles. Nuclei attract electrons. Electrons repel electrons. Nuclei repel nuclei.

The ability to interact is built into the structure of every particle, and this ability remains present in whatever phase of matter the atoms, molecules, and ions might be assembled. Whether the particles actually do interact, however, is determined by circumstances: by speed and internal energy, by external pressure, by temperature, and so forth. A gas is a gas, for example, not because its particles are intrinsically unable to interact, but rather because conditions are unfavorable for such interactions. The temperature is too high and the pressure is too low; and, as a result, the particles move too fast and are too far apart. Change the conditions, and the interactions will be expressed. The gas will become a liquid.

See Chapter 10 for an extended treatment of the gaseous state. Chapter 11 takes up the subject of phase transitions.

8. Noncovalent interactions are discussed in Section 9-3 of *PoC* and recapitulated on pages R9.2–R9.4.

(a) *Ion-ion* interactions are ordinary Coulomb attractions and repulsions between charged particles, of the kind found especially in ionic crystals and electrolytic solutions. Coulomb forces involving point charges are the strongest and most far-reaching of the noncovalent interactions. The potential energy falls off as $1/r$.

(b) An *ion-dipole* coupling arises when an ion (treated as a point charge) interacts with a dipole (a two-point charge), such as occurs between the ions and solvent molecules in an aqueous electrolytic solution. One point of the dipole attracts the ion; the other repels it. The potential energy varies as $1/r^2$.

(c) A *dipole-dipole* interaction comes about from the mutual attraction of two permanent dipole moments: Dipole A lines up relative to dipole B in such a way as to bring the positive end of one dipole closest to the negative end of the other. The potential energy goes as $1/r^3$ for stationary molecules.

(d) *Hydrogen bonds* represent a special case of the electrostatic interaction, manifested most often by the strongly electronegative atoms N, O, and F. Covalently bonded to one of these electron-withdrawing species, an H atom loses some of its electron density and thus presents a positively charged target for a lone pair on N, O, or F somewhere else. The small, partially positive hydrogen atom serves as the bridge between two nonbonded atoms in an unusually strong (and linear) connection of the type $A-H \cdots B$. Hydrogen bonding is generally operative only on contact, where the atoms effectively touch.

(e) The *London dispersion interaction* is a transient attraction between *induced* dipoles, arising from a momentary skewing of the charge in an electron cloud. Requiring no permanent dipole moment, the London interaction permits even atoms and nonpolar molecules to associate. Example: Ar and Ar. Distance dependence: $1/r^6$.

9. The polar Y molecules stick together by attractions between permanent dipole moments, an interaction stronger than the dispersion forces available to the nonpolar X molecules. The molecules of substance Y, cohering more tightly than those of substance X, hold together as a liquid. Substance X is a gas.

10. The more the molecules stick together, the greater is the energy needed to tear them apart. Liquids in which the molecules are strongly attracted have a correspondingly high boiling point.

Since species X and Y are both nonpolar, their only mechanism of interaction is through the attraction of induced dipoles (London dispersion forces). The larger and heavier molecule (Y) has the larger and more polarizable electron cloud—a charge distribution more easily distorted and therefore better able to develop a transient dipole moment. The momentary separation of charge extends over a greater distance.

Liquid Y is knitted together more tightly and presumably has the higher boiling point.

11. Imagine that the unbranched hydrocarbon molecules (X) nestle together from one end to the other, like spoons in a drawer, whereas the spherical hydrocarbons (Y) touch only at one point. With more points of attachment, the chains in X interact along their entire length and hence cohere more strongly than the spheres. Liquid X boils at the higher temperature.

See the example of pentane and neopentane, discussed on pages 269–270 and 398–399 of *PoC*.

12. The effects of temperature and pressure on gases, liquids, and solids will be treated extensively in Chapters 10 and 11.

(a) High pressures and low temperatures favor the formation of solids, where molecules are squeezed closest together and have the lowest energies.

(b) Low pressures and high temperatures are favorable for gases, where the particles are spaced far apart and have large velocities.

13. Gases are easiest to compress, because the widely separated particles have considerable space in which to squeeze together. Solids, where the particles are already close packed, are hardest to compress. There is barely room to spare.

Liquids are nearer in this aspect to solids than to gases. Like solids, liquids are dense phases with scant extra space for compression. They differ from solids more in the absence of long-range order than in any expansion of interparticle spacing.

Exercises 14 through 19, based in part on Examples 9-1, 9-4, and 9-5, deal mostly with packing and density in crystals.

14. The face-centered cubic unit cell contains four ions of each type,

$$\frac{0.25 \text{ Na}^+}{\text{edge}} \times 12 \text{ edges} + \frac{1 \text{ Na}^+}{\text{center}} \times 1 \text{ center} = 4 \text{ Na}^+$$

$$\frac{0.125 \text{ F}^-}{\text{corner}} \times 8 \text{ corners} + \frac{0.5 \text{ F}^-}{\text{face}} \times 6 \text{ faces} = 4 \text{ F}^-$$

giving us a total mass of 2.7889×10^{-22} g in a volume of 9.9523×10^{-23} cm³:

$$\text{Mass} = 4m_{\text{Na}} + 4m_{\text{F}} = 4(22.9898 + 18.9984) \text{ u} \times \frac{1.0000 \text{ g}}{6.0221 \times 10^{23} \text{ u}} = 2.7889 \times 10^{-22} \text{ g}$$

$$\text{Volume} = a^3 = \left(4.6342 \overset{\circ}{\text{A}} \times \frac{10^{-8} \text{ cm}}{\overset{\circ}{\text{A}}} \right)^3 = 9.9523 \times 10^{-23} \text{ cm}^3$$

Note that the mass of each ion differs only negligibly from the mass of its parent atom. Furthermore, the combined mass of cation plus anion is equal to the combined mass of both atoms.

Putting together mass and volume (and avoiding round-off until the end, as usual), we obtain a density of 2.8023 g cm^{-3} :

$$\text{Density} = \frac{\text{mass}}{\text{volume}} = \frac{2.7889 \times 10^{-22} \text{ g}}{(4.6342 \times 10^{-8} \text{ cm})^3} = 2.8023 \text{ g cm}^{-3}$$

For a drawing of the unit cell, qualitatively the same as for NaCl, see Figure R9-1 in *PoC* (page R9.11). A similar calculation for NaCl is undertaken in Example 9-4.

15. Given the density and total mass,

$$\text{Density} = \frac{\text{mass}}{\text{volume}} = 5.5710 \text{ g cm}^{-3}$$

$$\text{Mass} = 4m_{\text{Ag}} + 4m_{\text{Cl}} = 4(107.8682 + 35.453) \text{ u} \times \frac{1.0000 \text{ g}}{6.0221 \times 10^{23} \text{ u}} = 9.5197 \times 10^{-22} \text{ g}$$

we solve for the volume and thence the edge (a) of the face-centered cubic unit cell:

$$\text{Volume} = \frac{\text{mass}}{\text{density}} = a^3$$

$$a = \left(\frac{\text{mass}}{\text{density}} \right)^{1/3} = \left(\frac{9.5197 \times 10^{-22} \text{ g}}{5.5710 \text{ g cm}^{-3}} \right)^{1/3} = 5.5492 \times 10^{-8} \text{ cm} = 5.5492 \text{ \AA}$$

The procedure is similar to that followed in Exercise 14.

16. A variation on Exercise 14. Given the density and volume,

$$\text{Density} = 6.4772 \text{ g cm}^{-3}$$

$$\text{Volume} = a^3 = \left(5.7745 \overset{\circ}{\text{A}} \times \frac{10^{-8} \text{ cm}}{\overset{\circ}{\text{A}}} \right)^3 = 1.9255 \times 10^{-22} \text{ cm}^3$$

we first solve for the total mass:

$$\text{Mass} = \text{density} \times \text{volume}$$

$$= (6.4772 \text{ g cm}^{-3}) (1.9255 \times 10^{-22} \text{ cm}^3) \times \frac{6.0221 \times 10^{23} \text{ u}}{1.0000 \text{ g}} = 751.07 \text{ u}$$

But since the unit cell is a face-centered cube (see Example 9-4 in *PoC*), this total mass must be distributed among four Ag atoms and four X atoms:

$$4m_{\text{Ag}} + 4m_{\text{X}} = 751.07 \text{ u}$$

$$4(107.8682 \text{ u}) + 4m_{\text{X}} = 751.07 \text{ u}$$

$$m_{\text{X}} = \frac{1}{4} \times 751.07 \text{ u} - 107.8682 \text{ u} = 79.90 \text{ u}$$

The unspecified atom X is therefore Br, which has a standard atomic mass of 79.904 u (equivalently, 79.904 g mol⁻¹).

17. See Example 9-5, beginning on page R9.12 of *PoC*.

(a) The body-centered cubic unit cell contains a total of two atoms:

$$\frac{1 \text{ Na}}{\text{center}} \times 1 \text{ center} + \frac{0.125 \text{ Na}}{\text{corner}} \times 8 \text{ corners} = 2 \text{ Na}$$

(b) Knowing the mass and volume of a unit cell,

$$\text{Mass} = 2m_{\text{Na}} = 2(22.9898 \text{ u}) \times \frac{1.0000 \text{ g}}{6.0221 \times 10^{23} \text{ u}} = 7.6351 \times 10^{-23} \text{ g}$$

$$\text{Volume} = a^3 = \left(4.2856 \overset{\circ}{\text{A}} \times \frac{10^{-8} \text{ cm}}{\overset{\circ}{\text{A}}} \right)^3$$

we calculate the density:

$$\text{Density} = \frac{\text{mass}}{\text{volume}} = \frac{\text{mass}}{a^3} = \frac{7.6351 \times 10^{-23} \text{ g}}{(4.2856 \times 10^{-8} \text{ cm})^3} = 0.97002 \text{ g cm}^{-3}$$

For a drawing of the body-centered cubic cell, see Figure R9.2(b) in *PoC* (page R9.13).

18. Use the density and volume (a^3) to compute the total mass of the *two* atoms X in each body-centered cubic unit cell:

$$\text{Mass} = \text{density} \times \text{volume}$$

$$2m_{\text{X}} = (7.86 \text{ g cm}^{-3})(2.8664 \times 10^{-8} \text{ cm})^3 \times \frac{6.0221 \times 10^{23} \text{ u}}{1.0000 \text{ g}} = 111.48 \text{ u}$$

The mass of a single atom X,

$$m_X = \frac{1}{2} \times 111.48 \text{ u} = 55.7 \text{ u} \quad (3 \text{ sig fig})$$

then suggests that the unknown atom is Fe (iron).

See Example 9-5 in *PoC* (beginning on page R9.12) and also Exercise 17 for a description of the body-centered cubic unit cell.

19. To count the number of atoms in a given volume, we first multiply density and volume to determine the total mass:

$$\text{Density} = \frac{\text{mass}}{\text{volume}}$$

$$\text{Mass} = \text{density} \times \text{volume}$$

Next, we convert mass into moles and moles into atoms in the usual way. The procedure, similar to that used in Example 9-1, is illustrated below for Ag (density = 10.50 g mL⁻¹):

DENSITY	VOLUME OF A 1 mm ³ CUBE	MOLAR MASS	AVOGADRO'S NUMBER
$\frac{10.50 \text{ g Ag}}{\text{mL}}$	$\times \frac{1 \text{ mL}}{\text{cm}^3} \times \left(1 \text{ mm} \times \frac{1 \text{ cm}}{10 \text{ mm}}\right)^3$	$\times \frac{1 \text{ mol}}{107.8682 \text{ g Ag}}$	$\times \frac{6.0221 \times 10^{23} \text{ atoms Ag}}{\text{mol}}$
			$= 5.862 \times 10^{19} \text{ atoms Ag}$

The molar volume, obtainable also from the density and molar mass, is the volume occupied by one mole of substance:

$$\frac{1 \text{ mL}}{10.50 \text{ g Ag}} \times \frac{107.8682 \text{ g Ag}}{\text{mol}} = 10.27 \text{ mL mol}^{-1}$$

Values for all five elements, calculated in the same way, are listed in the following table:

SUBSTANCE	DENSITY (g mL ⁻¹)	MOLAR VOLUME (mL mol ⁻¹)	N mm ⁻³
(a) Ag	10.50	10.27	5.862×10^{19}
(b) B	2.34	4.62	1.30×10^{20}
(c) Bi	9.80	21.3	2.82×10^{19}
(d) K	0.86	45	1.3×10^{19}
(e) Ne	0.00090	2.2×10^4	2.7×10^{16}

With Exercises 20 through 22, we begin to move from solids to liquids and gases. See also Example 9-1 for a foreshadowing of the ideal gas.

20. Each of the halogens is a nonpolar molecule, able to interact primarily through dispersion forces between induced dipoles. Remember the rule of thumb: the more electrons, the more polarizable is the electron cloud. Heavier atoms and molecules experience correspondingly stronger dispersion interactions.

Heaviest and “stickiest” among the specified halogens is iodine, which exists as a solid at room temperature. Bromine, with a lower mass, is a liquid. Chlorine, lighter still, is a gas.

21. We obtain the density directly from the molar volume and molar mass:

$$(a) \frac{1 \text{ mol Cl}_2}{22.06 \text{ L}} \times \frac{70.906 \text{ g Cl}_2}{\text{mol Cl}_2} \times \frac{1 \text{ L}}{1000 \text{ mL}} = 3.214 \times 10^{-3} \text{ g Cl}_2 \text{ mL}^{-1}$$

$$(b) \frac{1 \text{ mol Br}_2}{0.0512 \text{ L}} \times \frac{159.808 \text{ g Br}_2}{\text{mol Br}_2} \times \frac{1 \text{ L}}{1000 \text{ mL}} = 3.12 \text{ g Br}_2 \text{ mL}^{-1}$$

$$(c) \frac{1 \text{ mol I}_2}{0.0515 \text{ L}} \times \frac{253.808 \text{ g I}_2}{\text{mol I}_2} \times \frac{1 \text{ L}}{1000 \text{ mL}} = 4.93 \text{ g I}_2 \text{ mL}^{-1}$$

Solids and liquids, the condensed phases, usually differ much less in density than do liquids and gases. Think, for instance, of the small change in volume that accompanies the melting of an ice cube, compared with the huge expansion evident when water boils away as steam. The condensed phases are, after all, *dense*. Particles in liquids and solids are packed together with little free space remaining.

So it is with Br₂ and I₂. One is a liquid and one is a solid, yet each occupies almost the same molar volume. One mole of each condensed halogen takes up approximately the same amount of space.

The gaseous species, Cl₂, is different. Largely uncontained by intermolecular forces, the molecules fly apart and occupy a volume far greater than either liquid or solid.

22. Here we touch on the *ideal gas*, a model to be explored at length in the next chapter.

(a) Since Cl₂ is already a gas, we expect the even lighter F₂ molecules also to exist as a gas at room temperature (they do). Moreover, since intermolecular interactions are mostly suppressed in a gas, there should be little difference in molar volume relative to chlorine. If the particles do not interact, then their structural idiosyncrasies are presumably irrelevant—but see below, part b.

(b) To a first approximation, we expect that fluorine gas will have nearly the same molar volume as chlorine gas.

That said, F₂ (38.0 g mol⁻¹) is less massive than Cl₂ (70.9 g mol⁻¹) and consequently its intermolecular interactions will be even weaker. Refining our

expectations, then, we predict that the molar volume of F_2 will be close to but perhaps slightly greater than that of Cl_2 (22.06 L mol^{-1}). The density, inversely proportional to molar volume, is bounded in the other direction:

$$\text{Molar volume} = \frac{\text{molar mass}}{\text{density}} \geq 22.06 \text{ L mol}^{-1}$$

$$\text{Density} = \frac{\text{molar mass}}{\text{molar volume}} \leq \frac{37.997 \text{ g } F_2 \text{ mol}^{-1}}{22.06 \text{ L mol}^{-1}} = 1.72 \text{ g L}^{-1}$$

Experimental values for the molar volume and density of F_2 at 15°C are 22.40 L mol^{-1} and 1.696 g L^{-1} , respectively, a difference of less than 2% from the estimates made above.

Exercises 23 through 29 provide practice in manipulating molarity and mole fraction—key descriptors of the solution state. For sample problems, see Examples 3-7 and 9-2. See also Exercises 24 through 30 of Chapter 3.

23. Convert grams per milliliter into moles per liter:

$$\begin{aligned} \frac{36.4 \text{ g Na}_2\text{SO}_4}{463 \text{ mL}} \times \frac{1 \text{ mol Na}_2\text{SO}_4}{142.043 \text{ g Na}_2\text{SO}_4} \times \frac{1000 \text{ mL}}{\text{L}} \times \frac{2 \text{ mol Na}^+}{\text{mol Na}_2\text{SO}_4} \\ = 1.11 \text{ mol Na}^+ \text{ L}^{-1} = 1.11 \text{ M} \end{aligned}$$

24. Multiply concentration (moles per unit volume) by volume to obtain the number of moles, and then use Avogadro's number to convert between moles and particles:

$$\begin{array}{ccc} \text{CONCENTRATION} & \text{VOLUME} & \text{AVOGADRO'S NUMBER} \\ \left(\frac{0.553 \text{ mol Na}_2\text{SO}_4}{\text{L}} \times \frac{1 \text{ mol SO}_4^{2-}}{\text{mol Na}_2\text{SO}_4} \right) & (1.00 \times 10^{-3} \text{ L}) & \times \frac{6.022 \times 10^{23} \text{ ions SO}_4^{2-}}{\text{mol SO}_4^{2-}} \\ & & = 3.33 \times 10^{20} \text{ ions SO}_4^{2-} \end{array}$$

The concentration of Na_2SO_4 , 0.553 M , is implicit in the calculation made in Exercise 23.

25. Assume that the density of the solution is 1.000 g mL^{-1} , a reasonable estimate for water between 0°C and 25°C (see Table C-15 in *PoC*, page A84). For any 1.00 M solution, we then have

$$1.00 \text{ M} = \frac{1.00 \text{ mol solute}}{1.00 \text{ L solution}}$$

and we can determine the number of moles of some arbitrary molecular solute (n_{solute}) and water (n_{solvent}) in, say, 1.000 L :

$$n_{\text{solute}} = \frac{1.00 \text{ mol solute}}{1.00 \text{ L solution}} \times 1.000 \text{ L} = 1.00 \text{ mol solute}$$

$$n_{\text{solvent}} = \frac{1.000 \text{ g H}_2\text{O}}{\text{mL H}_2\text{O}} \times \frac{1000 \text{ mL}}{\text{L}} \times \frac{1 \text{ mol H}_2\text{O}}{18.015 \text{ g H}_2\text{O}} \times 1.000 \text{ L} = 55.51 \text{ mol solvent}$$

The mole fractions follow directly from the definition:

$$X_{\text{solute}} = \frac{n_{\text{solute}}}{n_{\text{solute}} + n_{\text{solvent}}} = \frac{1.00 \text{ mol}}{1.00 \text{ mol} + 55.51 \text{ mol}} = 0.0177$$

$$X_{\text{solvent}} = \frac{n_{\text{solvent}}}{n_{\text{solute}} + n_{\text{solvent}}} = \frac{55.51 \text{ mol}}{1.00 \text{ mol} + 55.51 \text{ mol}} = 0.9823$$

Note that X_{solute} and X_{solvent} always sum to 1.

26. For convenience, first convert the densities from g mL^{-1} into mol mL^{-1} :

$$\frac{0.7914 \text{ g CH}_3\text{OH}}{\text{mL}} \times \frac{1 \text{ mol CH}_3\text{OH}}{32.042 \text{ g CH}_3\text{OH}} = \frac{0.02470 \text{ mol CH}_3\text{OH}}{\text{mL}}$$

$$\frac{0.7893 \text{ g CH}_3\text{CH}_2\text{OH}}{\text{mL}} \times \frac{1 \text{ mol CH}_3\text{CH}_2\text{OH}}{46.069 \text{ g CH}_3\text{CH}_2\text{OH}} = \frac{0.01713 \text{ mol CH}_3\text{CH}_2\text{OH}}{\text{mL}}$$

$$\frac{0.9982 \text{ g H}_2\text{O}}{\text{mL}} \times \frac{1 \text{ mol H}_2\text{O}}{18.015 \text{ g H}_2\text{O}} = \frac{0.05541 \text{ mol H}_2\text{O}}{\text{mL}}$$

Next, calculate the number of moles of each component. The mixture specified in (a) will serve as an example for all the rest:

$$n_{\text{CH}_3\text{OH}} = \frac{0.02470 \text{ mol CH}_3\text{OH}}{\text{mL}} \times 10.0 \text{ mL} = 0.2470 \text{ mol CH}_3\text{OH}$$

$$n_{\text{CH}_3\text{CH}_2\text{OH}} = \frac{0.01713 \text{ mol CH}_3\text{CH}_2\text{OH}}{\text{mL}} \times 10.0 \text{ mL} = 0.1713 \text{ mol CH}_3\text{CH}_2\text{OH}$$

Finally, calculate the mole fractions to three significant figures (reflecting the precision of each separate volume, 10.0 mL):

$$X_{\text{CH}_3\text{OH}} = \frac{n_{\text{CH}_3\text{OH}}}{n_{\text{CH}_3\text{OH}} + n_{\text{CH}_3\text{CH}_2\text{OH}}} = \frac{0.2470 \text{ mol}}{0.2470 \text{ mol} + 0.1713 \text{ mol}} = 0.590 \quad (3 \text{ sig fig})$$

$$X_{\text{CH}_3\text{CH}_2\text{OH}} = \frac{n_{\text{CH}_3\text{CH}_2\text{OH}}}{n_{\text{CH}_3\text{OH}} + n_{\text{CH}_3\text{CH}_2\text{OH}}} = \frac{0.1713 \text{ mol}}{0.2470 \text{ mol} + 0.1713 \text{ mol}} = 0.410 \quad (3 \text{ sig fig})$$

Check the results. The sum of the mole fractions must equal 1, and indeed it does:

$$X_{\text{CH}_3\text{OH}} + X_{\text{CH}_3\text{CH}_2\text{OH}} = 0.590 + 0.410 = 1.000$$

Mole fractions for each mixture are tabulated below:

	$X_{\text{CH}_3\text{OH}}$	$X_{\text{CH}_3\text{CH}_2\text{OH}}$	$X_{\text{H}_2\text{O}}$
(a)	0.590	0.410	—
(b)	0.308	—	0.692
(c)	—	0.236	0.764
(d)	0.254	0.176	0.570
(e)	0.0417	0.422	0.5365

27. Making use of the data provided in Exercise 26, we shall assume a temperature of 20°C and a density of 0.9982 g mL⁻¹. The mole fractions calculated in (b) scarcely differ for densities slightly more or slightly less than this value.

(a) Convert grams per milliliter into moles per liter:

$$\frac{2.00 \text{ g Li}_2\text{SO}_4}{50.0 \text{ mL}} \times \frac{1 \text{ mol Li}_2\text{SO}_4}{109.946 \text{ g Li}_2\text{SO}_4} \times \frac{1000 \text{ mL}}{\text{L}} = \frac{0.364 \text{ mol Li}_2\text{SO}_4}{\text{L}} = 0.364 \text{ M}$$

(b) Calculate the molar amounts and then the corresponding mole fractions as shown.

Moles:

$$n_{\text{Li}^+} = 2.00 \text{ g Li}_2\text{SO}_4 \times \frac{1 \text{ mol Li}_2\text{SO}_4}{109.946 \text{ g Li}_2\text{SO}_4} \times \frac{2 \text{ mol Li}^+}{\text{mol Li}_2\text{SO}_4} = 0.0364 \text{ mol Li}^+$$

$$n_{\text{SO}_4^{2-}} = 2.00 \text{ g Li}_2\text{SO}_4 \times \frac{1 \text{ mol Li}_2\text{SO}_4}{109.946 \text{ g Li}_2\text{SO}_4} \times \frac{1 \text{ mol SO}_4^{2-}}{\text{mol Li}_2\text{SO}_4} = 0.0182 \text{ mol SO}_4^{2-}$$

$$n_{\text{H}_2\text{O}} = 50.0 \text{ mL H}_2\text{O} \times \frac{0.9982 \text{ g H}_2\text{O}}{\text{mL H}_2\text{O}} \times \frac{1 \text{ mol H}_2\text{O}}{18.015 \text{ g H}_2\text{O}} = 2.77 \text{ mol H}_2\text{O}$$

Mole fractions:

$$X_{\text{Li}^+} = \frac{n_{\text{Li}^+}}{n_{\text{Li}^+} + n_{\text{SO}_4^{2-}} + n_{\text{H}_2\text{O}}} = \frac{0.0364 \text{ mol}}{0.0364 \text{ mol} + 0.0182 \text{ mol} + 2.77 \text{ mol}} = 0.0129$$

$$X_{\text{SO}_4^{2-}} = \frac{n_{\text{SO}_4^{2-}}}{n_{\text{Li}^+} + n_{\text{SO}_4^{2-}} + n_{\text{H}_2\text{O}}} = \frac{0.0182 \text{ mol}}{0.0364 \text{ mol} + 0.0182 \text{ mol} + 2.77 \text{ mol}} = 0.00644$$

$$X_{\text{H}_2\text{O}} = \frac{n_{\text{H}_2\text{O}}}{n_{\text{Li}^+} + n_{\text{SO}_4^{2-}} + n_{\text{H}_2\text{O}}} = \frac{2.77 \text{ mol}}{0.0364 \text{ mol} + 0.0182 \text{ mol} + 2.77 \text{ mol}} = 0.981$$

28. We have the same molar amount of Li_2SO_4 as in Exercise 27 ($2.00 \text{ g} = 0.0182 \text{ mol}$), but now a larger volume: 1000 mL rather than 50 mL.

(a) *Molarity.* The 20-fold increase in volume necessarily dilutes the original concentration (0.364 M) by the same factor:

$$\frac{0.364 \text{ M (in 50 mL)}}{20} = 0.0182 \text{ M (in 1000 mL)}$$

We arrive at the same answer, of course, by explicitly converting 2.00 g L^{-1} into its equivalent value in moles per liter:

$$\frac{2.00 \text{ g Li}_2\text{SO}_4}{1.00 \text{ L}} \times \frac{1 \text{ mol Li}_2\text{SO}_4}{109.946 \text{ g Li}_2\text{SO}_4} = 0.0182 \text{ M}$$

See also Exercise 28 of Chapter 3 for additional discussion of the dilution problem.

(b) *Mole fraction.* Since the amount of Li_2SO_4 is unchanged from Exercise 27, we carry over the earlier values of n_{Li^+} and $n_{\text{SO}_4^{2-}}$ while recalculating $n_{\text{H}_2\text{O}}$:

$$n_{\text{Li}^+} = 0.0364 \text{ mol Li}^+$$

$$n_{\text{SO}_4^{2-}} = 0.0182 \text{ mol SO}_4^{2-}$$

$$n_{\text{H}_2\text{O}} = 1.00 \text{ L} \times \frac{0.9982 \text{ g H}_2\text{O}}{\text{mL}} \times \frac{1000 \text{ mL}}{\text{L}} \times \frac{1 \text{ mol H}_2\text{O}}{18.015 \text{ g H}_2\text{O}} = 55.41 \text{ mol H}_2\text{O}$$

Reported to three significant figures, the corresponding mole fractions are as follows:

$$X_{\text{Li}^+} = \frac{n_{\text{Li}^+}}{n_{\text{Li}^+} + n_{\text{SO}_4^{2-}} + n_{\text{H}_2\text{O}}} = \frac{0.0364 \text{ mol}}{0.0364 \text{ mol} + 0.0182 \text{ mol} + 55.41 \text{ mol}} = 0.000656$$

$$X_{\text{SO}_4^{2-}} = \frac{n_{\text{SO}_4^{2-}}}{n_{\text{Li}^+} + n_{\text{SO}_4^{2-}} + n_{\text{H}_2\text{O}}} = \frac{0.0182 \text{ mol}}{0.0364 \text{ mol} + 0.0182 \text{ mol} + 55.41 \text{ mol}} = 0.000328$$

$$X_{\text{H}_2\text{O}} = \frac{n_{\text{H}_2\text{O}}}{n_{\text{Li}^+} + n_{\text{SO}_4^{2-}} + n_{\text{H}_2\text{O}}} = \frac{55.41 \text{ mol}}{0.0364 \text{ mol} + 0.0182 \text{ mol} + 55.41 \text{ mol}} = 0.999$$

29. First, calculate the molar amount of Li_2SO_4 in each beaker separately:

$$n_{\text{A}} = \frac{0.500 \text{ mol Li}_2\text{SO}_4}{\text{L}} \times \left(50.0 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} \right) = 0.0250 \text{ mol Li}_2\text{SO}_4 \quad (\text{Beaker A})$$

$$n_{\text{B}} = \frac{0.250 \text{ mol Li}_2\text{SO}_4}{\text{L}} \times \left(100.0 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} \right) = 0.0250 \text{ mol Li}_2\text{SO}_4 \quad (\text{Beaker B})$$

Second, add the amounts and recalculate the concentration. Since both solutions contain the same solute, we may add the original volumes directly to obtain a total volume of 150.0 mL (0.1500 L) and a new concentration of 0.333 M:

$$\frac{0.0250 \text{ mol} + 0.0250 \text{ mol}}{0.0500 \text{ L} + 0.1000 \text{ L}} = 0.333 \text{ mol L}^{-1}$$

We conclude with a run of exercises dealing with noncovalent interactions and their macroscopic consequences. The material is drawn mostly from Sections 9-3, 9-6, and 9-9, as well as Examples 9-6 through 9-8.

30. The Coulomb force between charges q_1 and q_2 is proportional to q_1q_2/r^2 , where r is the distance separating the charges. The corresponding potential energy varies as $1/r$. See pages 303–304 and R9.2–R9.3 in *PoC*.

Recall also (from Section 6-3) that atomic and ionic radii of main-group elements typically increase going down a column. Rubidium is larger than lithium. Iodine is larger than fluorine. Calcium is larger than magnesium.

For sample problems dealing with lattice energies, see Examples 9-8 and 15-8 in *PoC* (beginning on pages R9.15 and R15.12, respectively).

(a) Smaller cations permit a closer packing and thus produce a stronger Coulomb attraction. Lattice energies increase as the ionic radii decrease from Rb^+ to Li^+ :

$$E(\text{RbCl}) < E(\text{KCl}) < E(\text{NaCl}) < E(\text{LiCl})$$

(b) Similar. The smaller anions are bound more tightly into the lattice:

$$E(\text{AgI}) < E(\text{AgBr}) < E(\text{AgCl}) < E(\text{AgF})$$

(c) Since the pairwise attraction is proportional to the product of the charges, Na^+Cl^- is the most weakly bound of the three. Both its anion and cation bear only a single unit of charge, whereas $\text{Ca}^{2+}\text{S}^{2-}$ and $\text{Mg}^{2+}\text{S}^{2-}$ each contain doubly charged ions. MgS , with the smaller cation, has a higher lattice energy than CaS :

$$E(\text{NaCl}) < E(\text{CaS}) < E(\text{MgS})$$

Published lattice energies for the compounds in (a), (b), and (c) are tabulated below. All values are in kJ mol^{-1} :

	F	Cl	Br	I	S
Li	1036	853	807	757	Mg 3406
Na	923	788	747	704	Ca 3119
K	821	717	682	649	
Rb	785	689	660	630	
Ag	969	912	900	886	

31. See Section 9-3, pages R9.2–R9.4, and Examples 9-6 and 9-7 (beginning on page R9.13) for a survey of noncovalent interactions.

(a) Calcium carbonate, $\text{CaCO}_3(\text{s})$: ionic bonds (Coulomb interactions) between Ca^{2+} and CO_3^{2-} .

(b) Elemental platinum, $\text{Pt}(\text{s})$: metallic bonds. The mobile valence electrons, delocalized throughout the crystal, are attracted to the ionized cores of the metal atoms.

(c) Frozen nitrogen, $\text{N}_2(\text{s})$: London dispersion interactions between nonpolar molecules.

(d) Ice, $\text{H}_2\text{O}(\text{s})$: hydrogen bonds between OH groups.

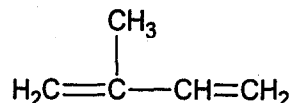
32. An example of how microscopic structure can determine macroscopic function: the polymer Kevlar.

(a) The extended chains in Kevlar are held together laterally by noncovalent hydrogen bonds between amide groups. An N–H linkage on one chain is connected by a hydrogen bond to a C=O group on another chain.

(b) Two important structural characteristics contribute to the extraordinary strength of Kevlar. First, each of the covalently bonded macromolecules is long and rigid. Extended chains run the length of the crystal, in contrast to the folded chains of polyethylene. Second, the macromolecules are further connected by hydrogen bonds. Both the long, stiff chains and the hydrogen bonds must be broken to sever a Kevlar fiber. Neither of these features is present in low-density polyethylene. See pages 344–349.

33. The difference between natural and vulcanized rubber: another example of how microscopic structure translates to macroscopic properties.

(a) The monomer is 2-methyl-1,3-butadiene (isoprene):



(b) Only the weak London dispersion interactions are present to connect one molecule of natural rubber to another.

(c) The cross-links, shown schematically in the exercise, arise from covalent bonds.

(d) The sulfur linkages transform the individual macromolecules into a three-dimensional elastic network—a single giant molecule that can pull back into its former configuration once a deforming stress is removed. Without cross-links, the chains would slip past one another under stress and never recover.

34. Polystyrene, encumbered by the bulky aromatic rings, forms an amorphous rather than crystalline solid. The entangled chains cannot extricate themselves sufficiently fast to organize into a crystal. In addition, intermolecular interactions are limited to the weak London dispersion force.

Nylon 66 lacks the bulky side chains and is better able to crystallize into a (relatively) ordered phase. Strong hydrogen bonds between amide groups help hold the chains in place.

35. He, Ne, and CO₂ are nonpolar species, able to interact primarily through London dispersion forces. The strength of the interaction increases with mass:



Melting points follow the same trend.

Next comes H₂O, interacting much more strongly by means of hydrogen bonds. Strongest of all, finally, is the metallic solid Ag:

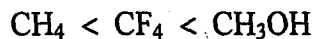


36. See also Examples 9-6 and 9-7 (beginning on page R9.13 of *PoC*).

- (a) Methanol, CH₃OH: hydrogen bonds between OH groups.
- (b) Iodine, I₂: London dispersion interactions between nonpolar molecules.
- (c) Tetrachloromethane, CCl₄: London dispersion interactions between nonpolar molecules. Although each C–Cl bond is polar, there is no net dipole moment in the symmetric tetrahedron.
- (d) Trichloriodomethane, CCl₃I: dipole–dipole interactions between polar molecules. The lone C–I bond leaves the molecule with a net dipole moment.
- (e) Water, H₂O: hydrogen bonds between OH groups.

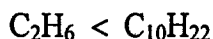
37. Nonpolar CH₄ and CF₄ can avail themselves only of the dispersion force, the weakest of the intermolecular interactions. Methane, the less massive molecule of the two, has the lower boiling point.

Methanol, however, boils at a considerably higher temperature owing to the strong hydrogen bonds it forms in the liquid state:

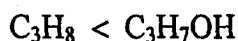


38. Similar: the relationship between intermolecular interactions and boiling point.

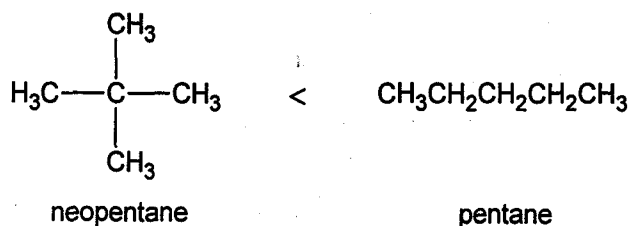
(a) The strength of dispersion interactions increases with molecular mass. The larger, heavier hydrocarbon has the higher boiling point:



(b) The OH group in propanol allows it to form hydrogen bonds, thereby raising the boiling point relative to propane:



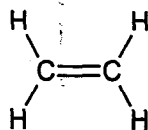
(c) The unbranched chain in normal pentane offers more points of contact—and thus more opportunities for intermolecular attraction—than the nearly spherical neopentane molecule:



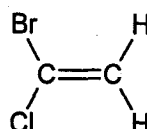
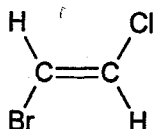
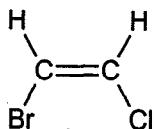
Normal pentane has the higher boiling point. See pages 269–270 and 398–399 in *PoC*.

39. Strong intermolecular interactions favor the liquid; weak intermolecular interactions favor the gas.

(a) Consider the structures of ethylene and three conceivable forms of bromochloroethylene:



ethylene

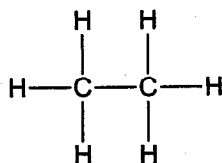


bromochloroethylene

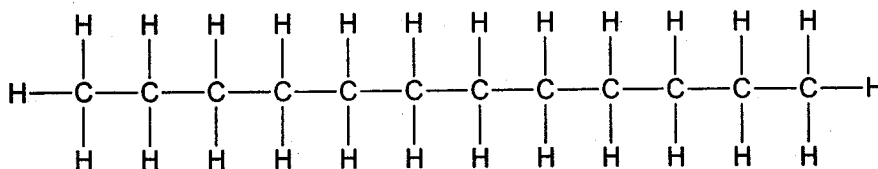
Ethylene is nonpolar and therefore can interact only by way of the London dispersion force—the weakest of the noncovalent interactions. C_2H_4 exists as a gas at room temperature.

Bromochloroethylene, by contrast, will have a net molecular dipole moment regardless of the placement of Br and Cl (which is left unspecified in the empirical formula). The residual dipole–dipole interactions, arising from the electronegativity difference between bromine and chlorine, allow $\text{C}_2\text{H}_2\text{BrCl}$ to exist as a liquid.

(b) Neither molecule has a net dipole moment, and both interact only via the weak London dispersion force. The larger, more massive structure, however, possesses the more polarizable electron cloud and allows induced dipoles to extend over greater distances:



ethane



dodecane

Dodecane (shown here in unbranched form, with a large surface area) interacts more strongly than ethane. C_2H_6 is normally a gas; $\text{C}_{12}\text{H}_{26}$ is normally a liquid.

(c) Ammonium chloride (NH_4Cl) is an ionic solid, bound tightly by ion-ion interactions between NH_4^+ and Cl^- . Molecules of ammonia (NH_3), although hydrogen bonded, are interconnected far more loosely and exist in the gaseous state.

40. A polymer is unlikely to be a gas under normal conditions. The molecules are too large, too massive, too complicated, too prone to interact.

Some polymers, like natural rubber, do have an odor, but this effect is attributable to the loss of *monomers* to the gas phase when covalent linkages are broken—as during heating.

41. Like particles in a gas, the electrons of a metal are free to range over large territories—here, a fixed lattice of positively charged sites. The valence electrons swarm through the metal with a freedom that suggests, at least, the chaotic motion of a gas.

42. The low density, fast motion, and high energy of a gas all tend to rob molecules of their individuality. Far apart and moving too fast for sustained interaction, the molecules of a gas are reduced largely to generic particles. Little more than indistinguishable lumps with mass and velocity, one kind of molecule has effectively the same properties as any other in the gas phase.