



OX

THE SOLID STATE

A. UNIT CELLS & CRYSTAL PACKING

METAL SOLIDS

Objective: *Understand the structure of pure metals*

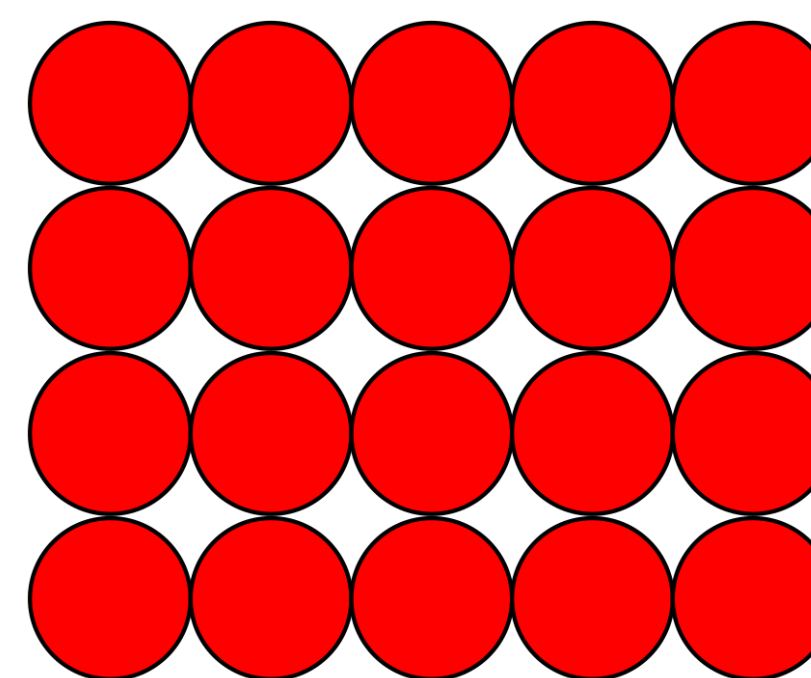


Most of the elements on the periodic table are metals. And, with the exception of mercury (Hg), which is a liquid, metals are solids in their standard state.

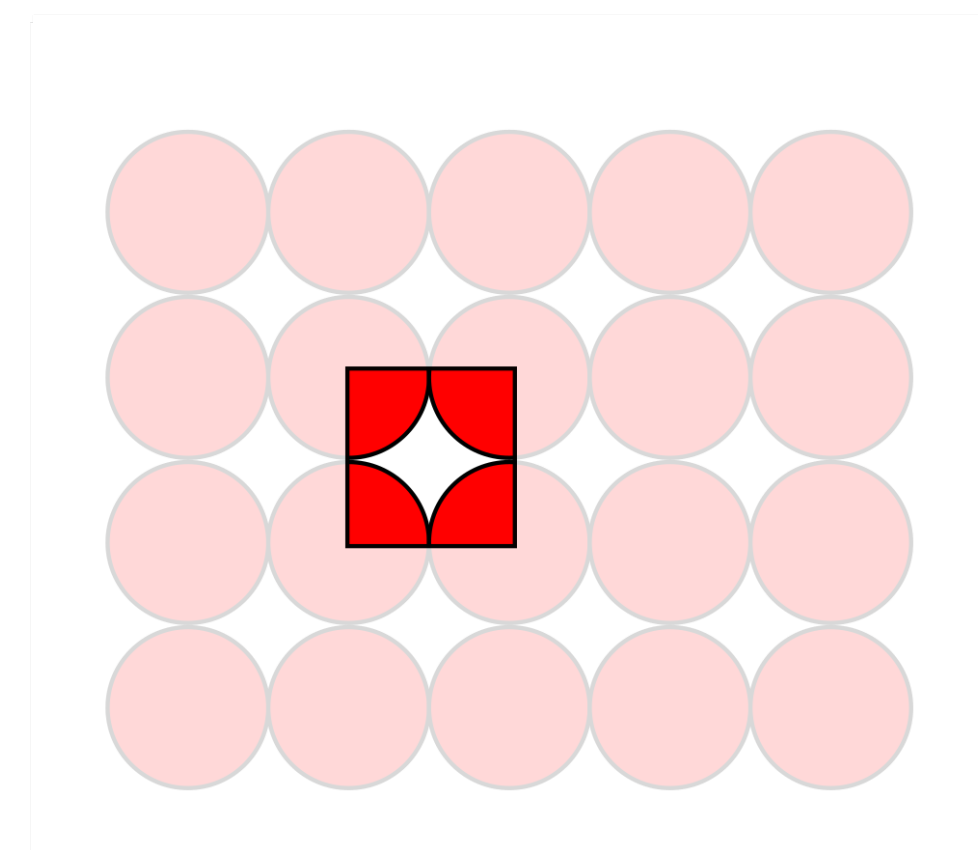
In chemical equations, we often denote metals, such iron, simply as Fe (s). Surely, though, we do not intend to consider just single atoms of metals.

While we can use Lewis structures and VSEPR theory to imagine how atoms in molecules are bonded and shaped, we need to think differently to understand the structures of metals. In fact, we need to consider the solid as a tightly-packed, crystalline, array of metal atoms.

If we represent metal atoms as hard spheres, our first inclination might be to simply arrange the metal atoms right next to and on top of each other, in all direction. Such a packing arrangement is referred to as simple cubic (sc).



Simple cubic packing



Cutout of unit cell

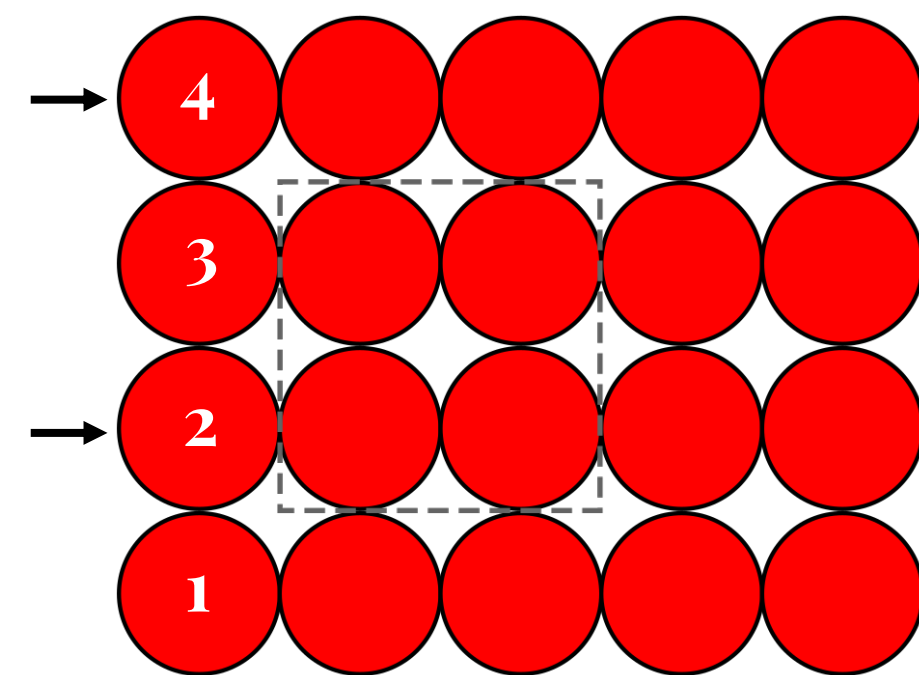
Unfortunately, this is rather *inefficient* packing, as evidenced by the many large empty voids (holes) in the diagrams above. Only one such metal, Polonium (Po), adopts the sc packing arrangement. For all other metals, we need to consider *more efficient* packing arrangements.

CUBIC-CLOSE PACKING

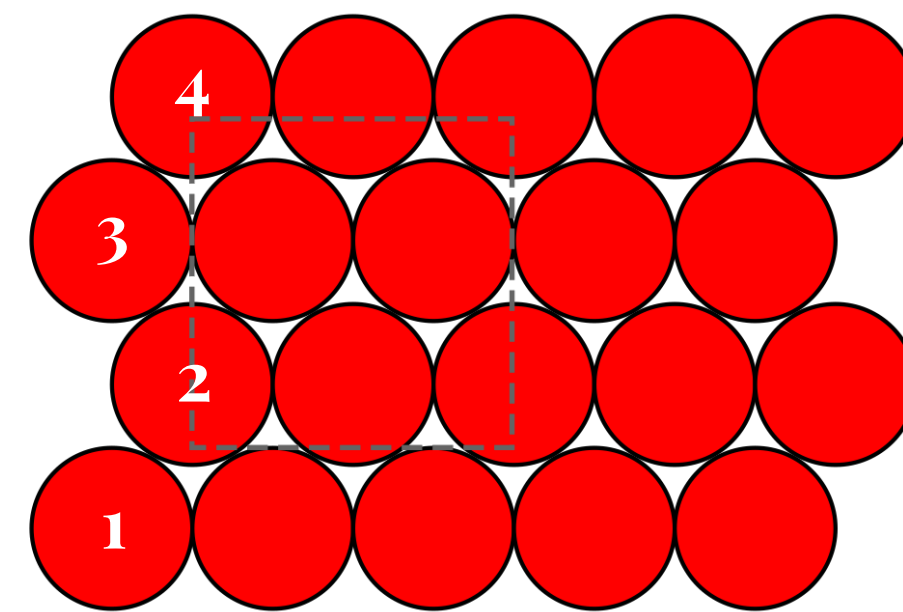
Objective: Define cubic-close packing (*ccp*)



It turns out we can significantly increase the packing efficiency with a fairly simple rearrangement. Instead of stacking the atoms right atop each other in the simple cubic arrangement, we can shift every *other* row of atoms (the even numbers below) over by a half-atom distance to fill part of the voids (holes).



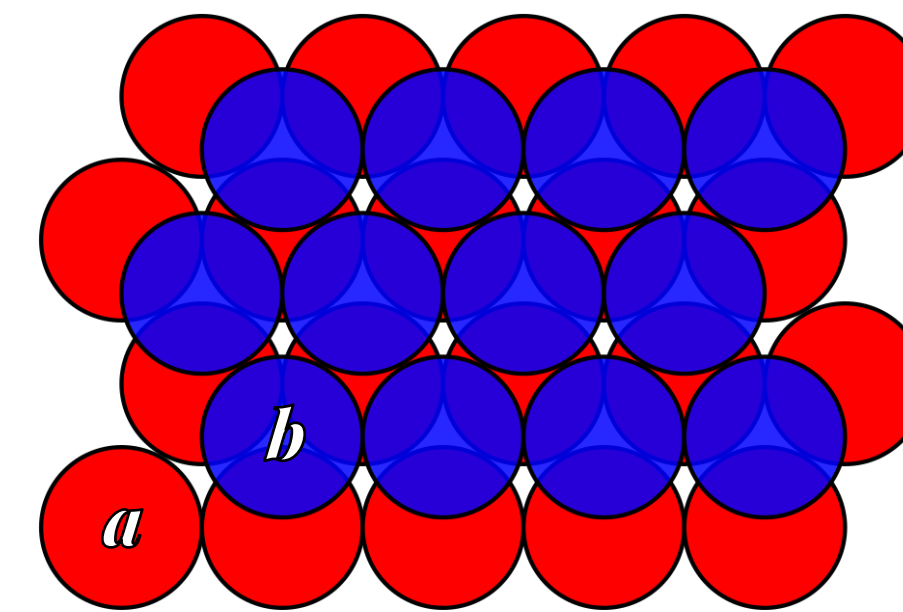
Simple cubic packing



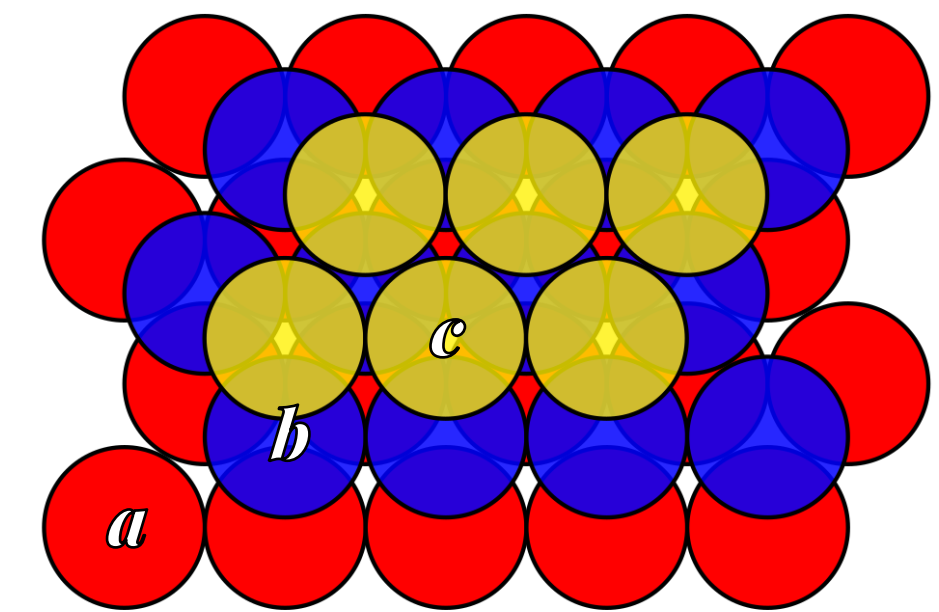
Cubic-close packing

This more efficient, and preferred, arrangement is called cubic-close packing (*ccp*). In the diagram, a gray-dashed outline shows that (i) the sizes of the holes are now smaller and (ii) more atoms fit per unit area in the *ccp* arrangement.

A second layer of atoms (blue) will sit on top of the red layer, but atop the holes. A third layer of atoms (yellow) will then sit atop the holes of the blue layer. Note, so far, *none* of the layers are directly on top of each other. However, a fourth layer, sitting atop the holes of the yellow layer, would be identical to the red layer. We call this an *abcabc* pattern.



ccp with 2 layers



ccp with 3 layers

THE UNIT CELLS

Objective: *Understand the sc, bcc, and fcc unit cells*



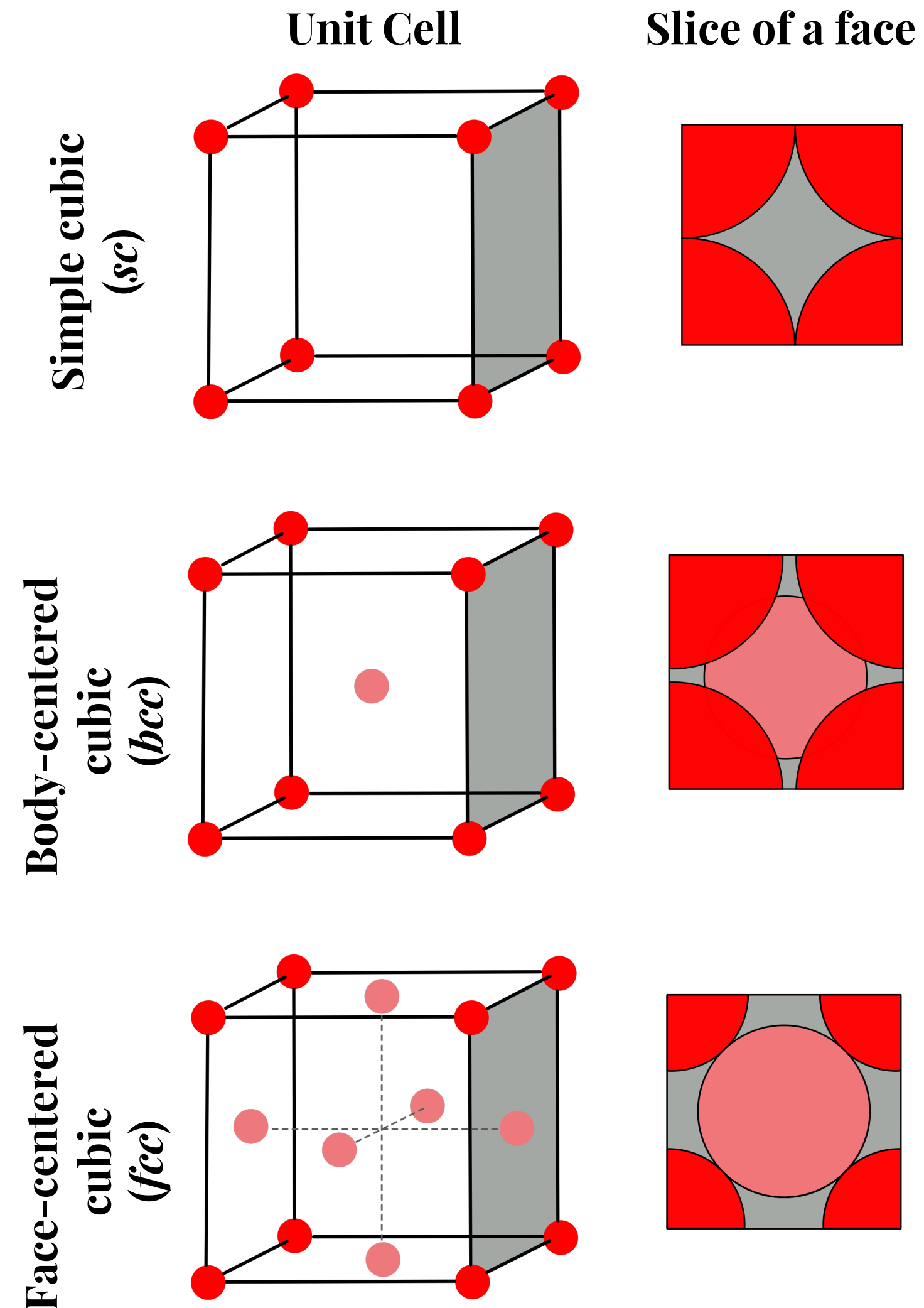
Rather than envisioning infinite layers of atoms, we can simplify our understanding of solid-state structures by considering just the smallest repeating pattern, the unit cell, which is represented by a cube.

There are *three* major unit cells (lattices) to consider:

- Simple cubic (*sc*)
- Body-centered cubic (*bcc*)
- Face-centered cubic (*fcc*)

We have already explored the *sc* unit cell. The *bcc* unit cell is like the *sc* lattice but with an atom in the center. And the *fcc* unit cell is actually the same as the *ccp* structure!

The three unit cells are shown below, along with a cross-section (or slice) of the right-side face.



PACKING DENSITY

Objective: *Understand the sc, bcc, and fcc unit cells*



If we consider a single sc unit cell, there are eight atoms total, one occupying each corner of the cube. But these eight atoms are fractional, as only $\frac{1}{8}$ of each corner-atom is actually *inside* the unit cell. So, for a sc unit cell, there is only 1 atom per unit cell.

$$\text{Atoms per sc cell} = \frac{1}{8} \times 8 \text{ atoms} = 1 \text{ atom}$$

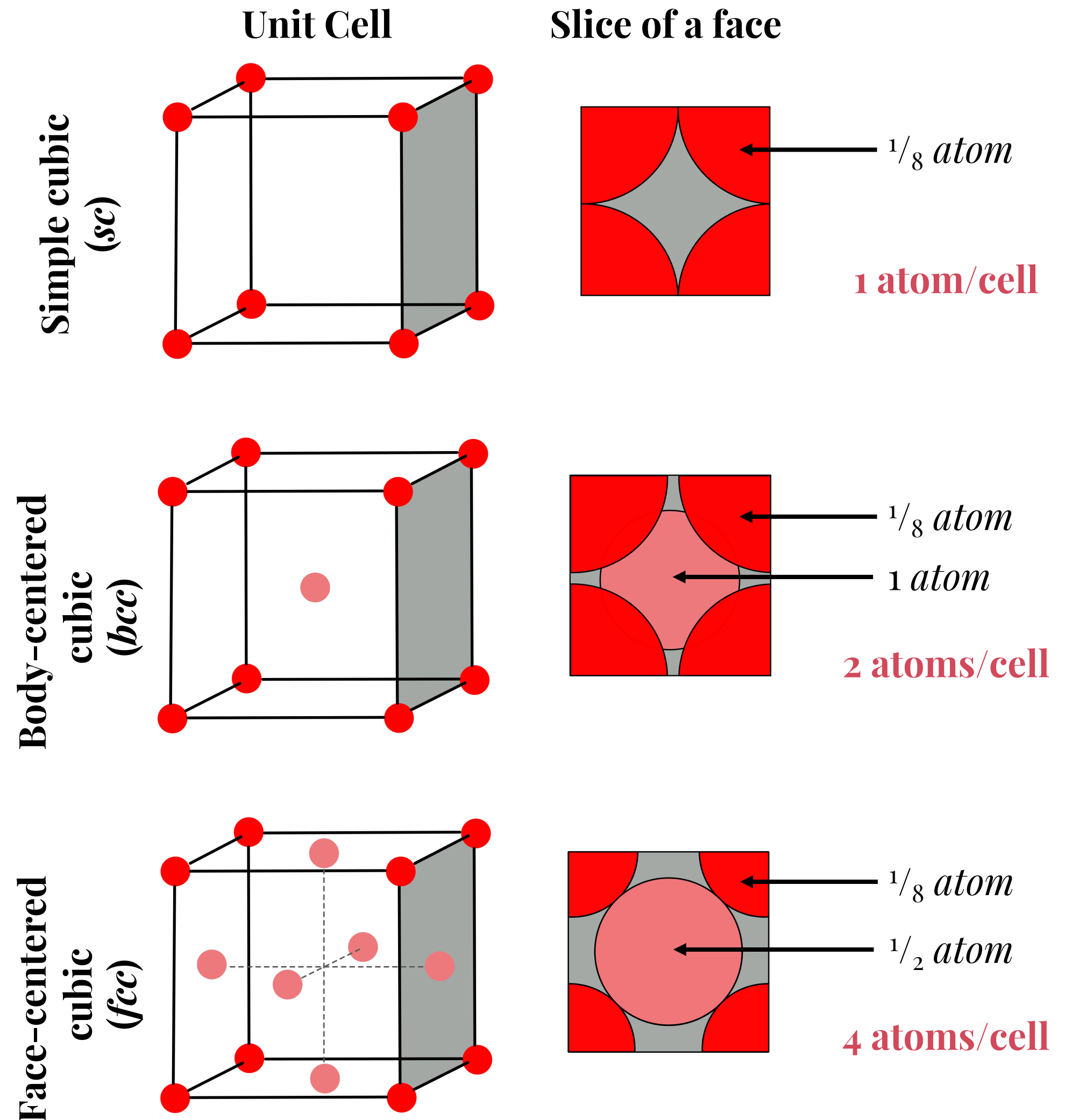
For a bcc unit cell, there are the eight corner atoms and one entire atom in the body-center.

$$\text{Atoms per bcc cell} = \frac{1}{8} \times 8 \text{ atoms} + 1 \text{ atom} = 2 \text{ atoms}$$

For a fcc unit cell, there are the eight corner atoms and six facial atoms that are only $\frac{1}{2}$ inside the unit cell.

$$\text{Atoms per fcc cell} = \frac{1}{8} \times 8 \text{ atoms} + \frac{1}{2} \times 6 \text{ atoms} = 4 \text{ atoms}$$

Based on the number of atoms per unit cell, it is clear that sc is the least dense and fcc the **most dense** type of packing.



HEXAGONAL-CLOSE PACKING (HCP)

Objective: Define hexagonal-close packing (*hcp*)

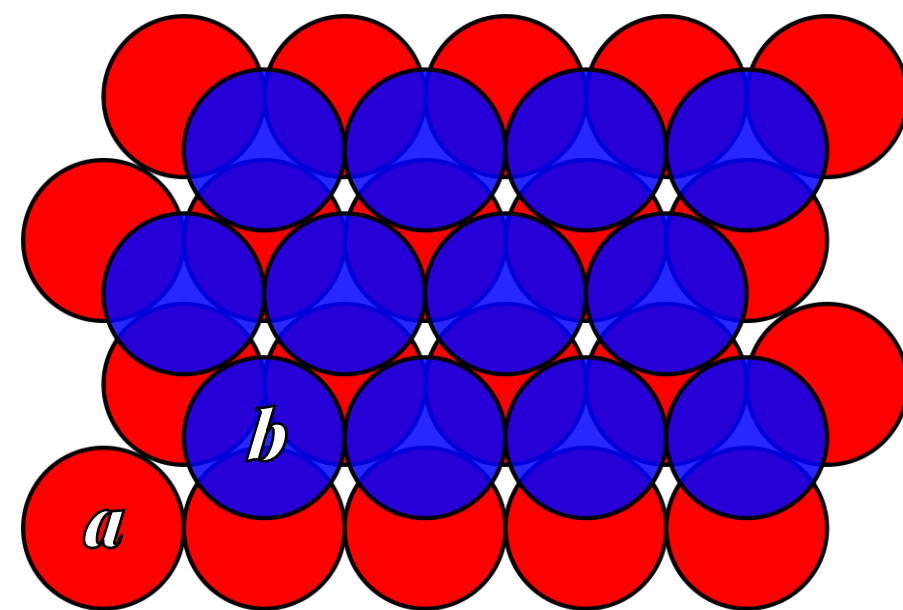


There is an even-more dense packing arrangement than *ccp*. This densest packing arrangement is called **hexagonal-close packing (*hcp*)** and will give rise to unit cells that are not cubic.

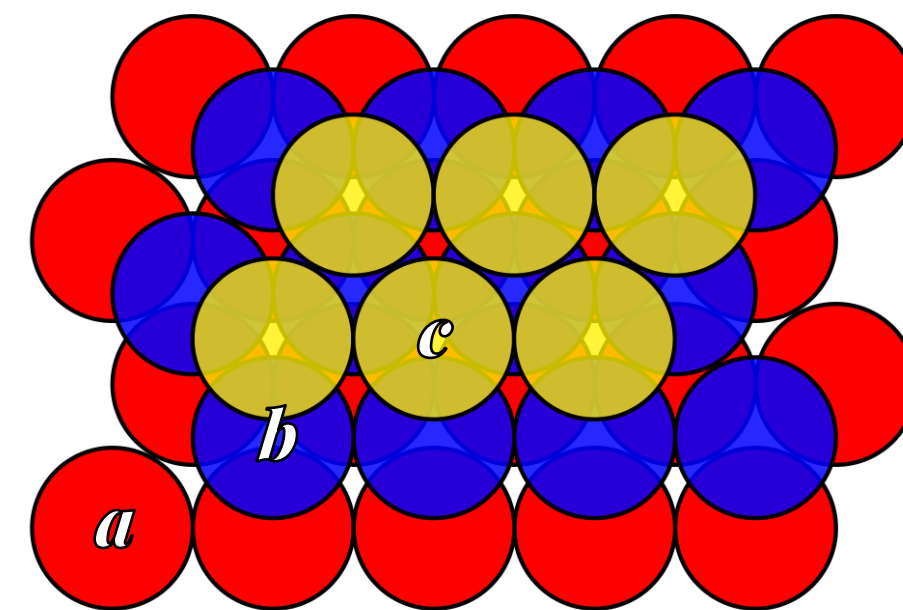
The difference between *hcp* and *ccp* arises from the position of the third layer. For *ccp*, the third layer (*c*) is distinct from the lower two layers (*a* and *b*).

Let us start again with the layering of atoms in *ccp*, where the pattern was *abcabc*.

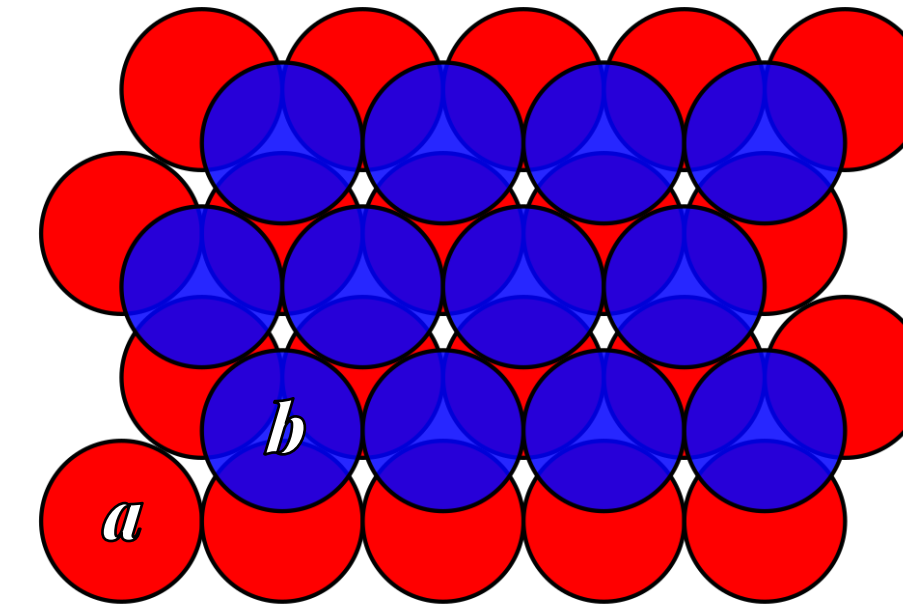
In contrast, for *hcp*, the third layer is actually the *same* as the first layer and we get an *abab* pattern instead.



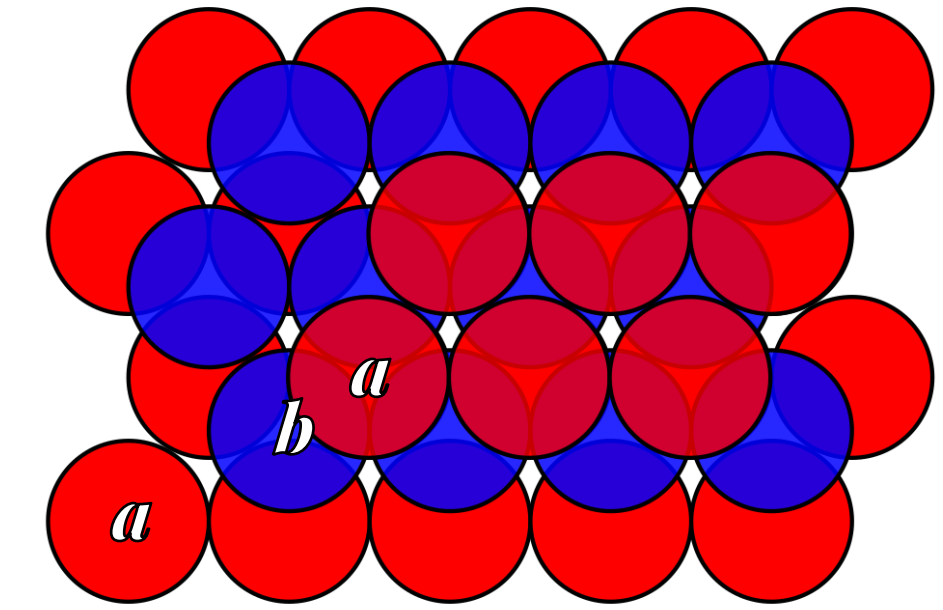
ccp with 2 layers



ccp with 3 layers



hcp with 2 layers



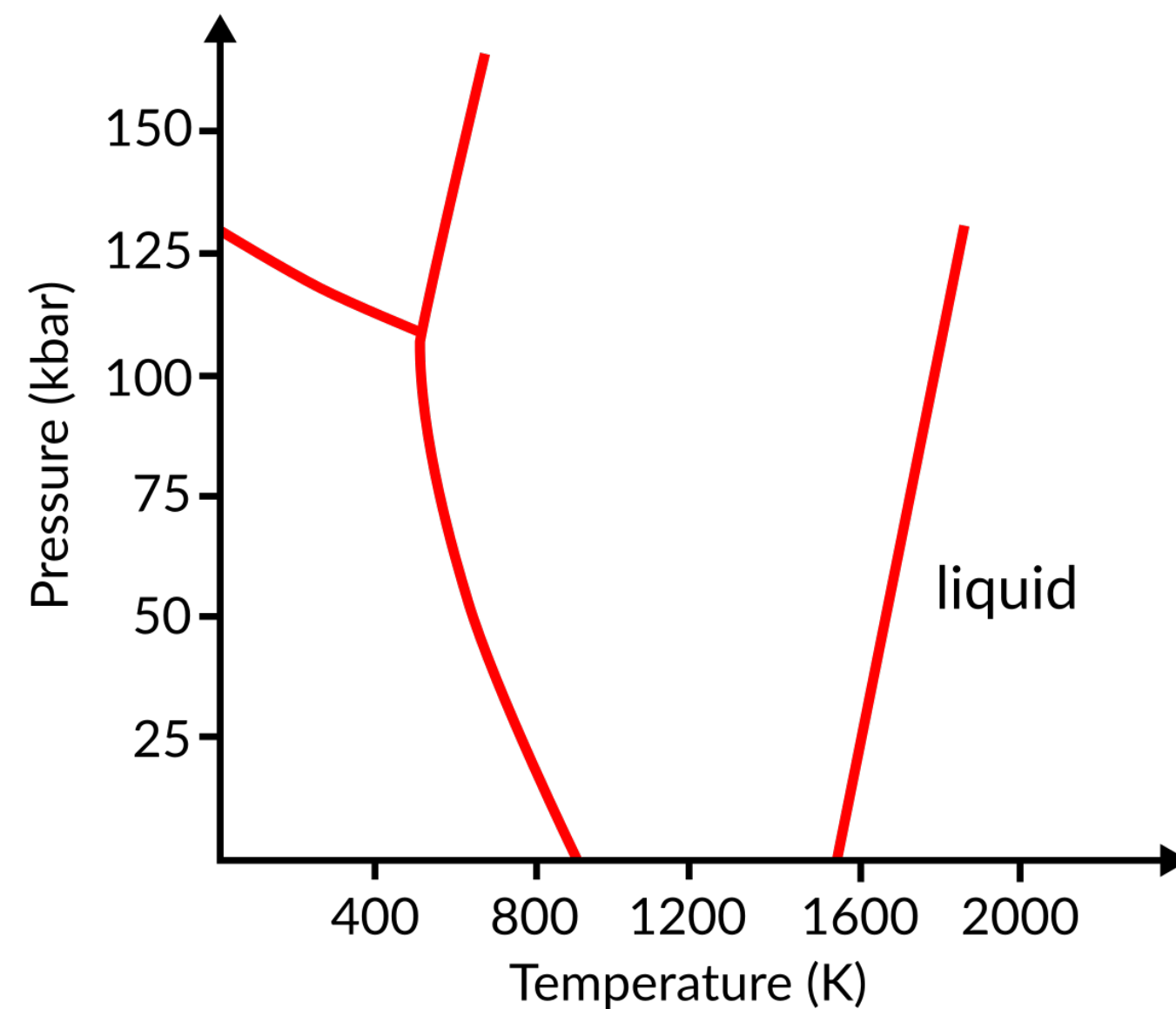
hcp with 3 layers

PRACTICE PROBLEMS



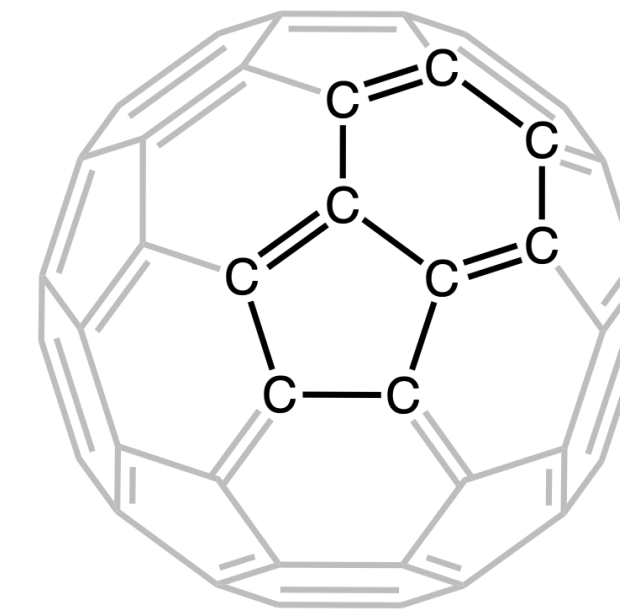
Practice Problem 1

Pure iron metal can exist in three different solid phases: body-centered cubic (*bcc*), face-centered cubic (*fcc*), hexagonal-close packing (*hcp*). The phase diagram for pure iron is shown below. In the diagram, label the *bcc*, *fcc*, and *hcp* phases for iron.



Practice Problem 2

Carbon exists in three allotropes: diamond, graphene, and fullerenes. Fullerenes are composed of 60 sp^2 -hybridized carbon atoms in five- and six-membered rings (C_{60}), as shown below.

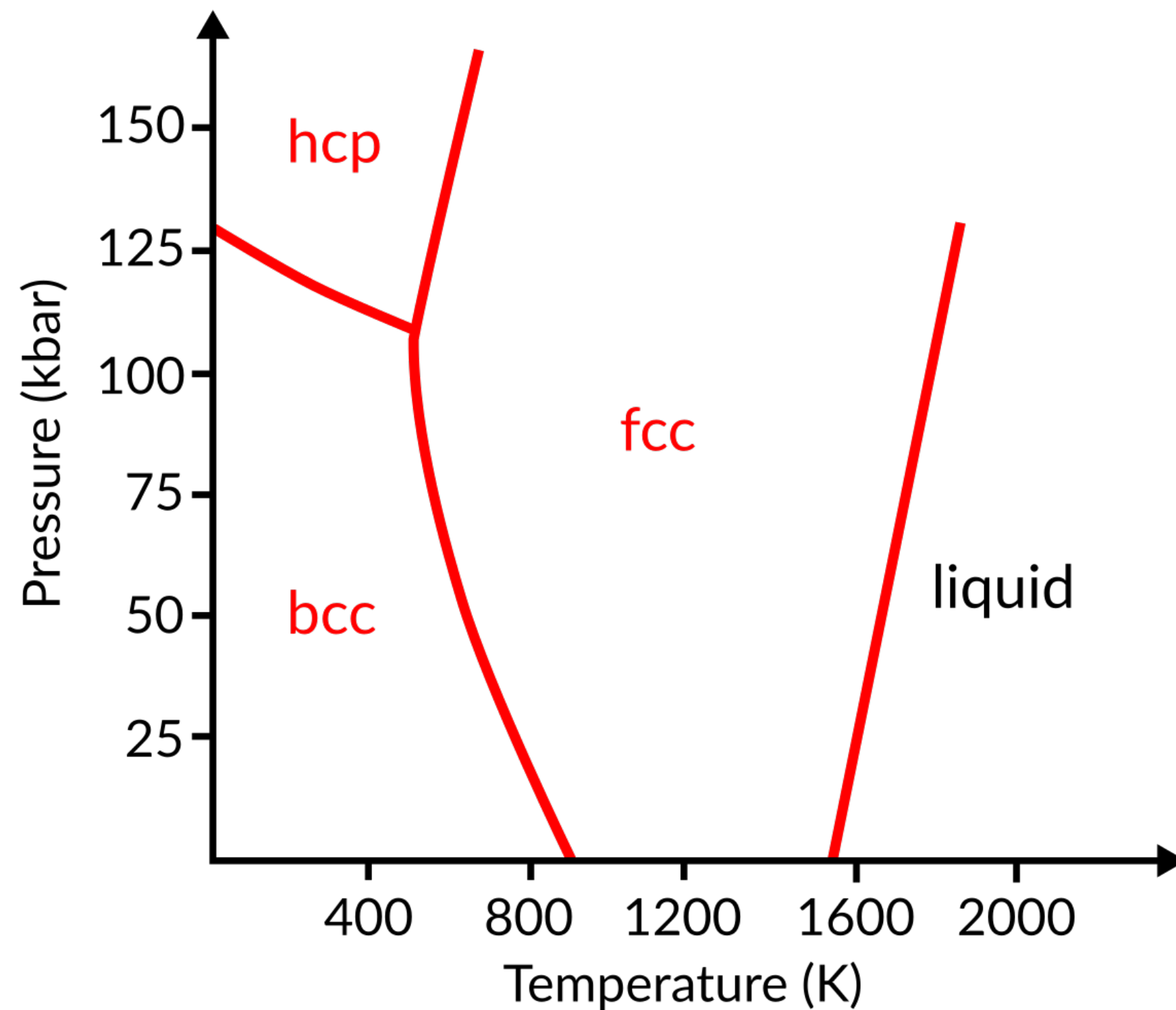


Molecules of C_{60} can also pack into cubic unit cells. Determine the number of carbon atoms inside a simple cubic (*sc*) and face-centered cubic (*fcc*) unit cell of fullerene.

PRACTICE PROBLEM 1

Pure iron metal can exist in three different solid phases: body-centered cubic (bcc), face-centered cubic (fcc), hexagonal-close packing (hcp). The phase diagram for pure iron is shown below. In the diagram, label the bcc, fcc, and hcp phases for iron.

— *answer* —



Recall that phase diagrams can inform us which phases are most dense. To do so, we need to compare the coexistence (equilibrium) line separating any two phases to determine which phase exists at the higher pressure (i.e. is more dense).

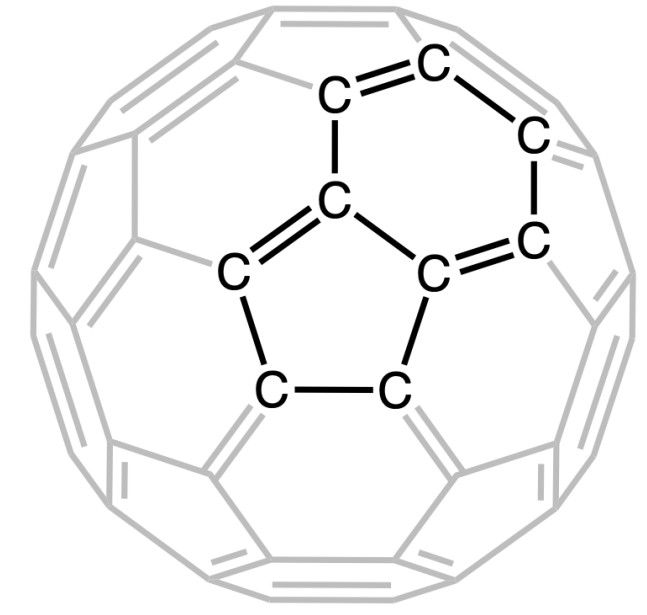
In terms of crystal packing, hcp is the densest form of packing, so *hcp* is the most dense solid phase of iron. Between *fcc* and *bcc*, *fcc* is more dense than *bcc* because there are 4 atoms per *fcc* unit cell vs. 2 atoms per *bcc* unit cell.

As *hcp* is the most dense, we can assign the region in the top-left as the *hcp* phase. To determine which region corresponds to the *bcc* phase and which to the *fcc* phase, we need to look at the line separating the two phases. In order for *fcc* to be more dense than *bcc*, the *fcc* phase must exist to the right of the line (i.e. at higher pressures).

Note: We could also compare the slopes of the lines. The *hcp-fcc* line slopes to the right, so the phase on the left is more dense. The *hcp-bcc* line slopes to the left, so the phase on the right is more dense. The *bcc-fcc* line slopes to the left, so the phase on the right is more dense.

PRACTICE PROBLEM 2

Carbon exists in three allotropes: diamond, graphene, and fullerenes. Fullerenes are composed of 60 sp^2 -hybridized carbon atoms in five- and six-membered rings (C_{60}), as shown to the right.



Molecules of C_{60} can also pack into cubic unit cells. Determine the number of carbon atoms inside a simple cubic (sc) and face-centered cubic (fcc) unit cell of fullerene.

— *answer* —

In this problem, we are treating a molecule of C_{60} as the hard sphere inside the unit cell.

In a sc unit cell, there is only 1 sphere inside the unit cell. This means there is 1 C_{60} molecule and **60 carbon atoms** inside a sc fullerene cell.

In a fcc unit cell, there are 4 spheres inside the unit cell. This means there are 4 C_{60} molecules and **240 carbon atoms** inside a fcc fullerene cell.

