layers can slip past each other and graphite can act as a lubricant. This lubricant never evaporates because the molecule is too big to fly off. Graphite lubricants do deteriorate as the pressure of the lubricated surfaces literally tears the graphite sp$^3$ sheets apart into dirty black elemental carbons. The conductivity is due to the electrons in the ring (Fig. 10.24b) being free to roam around the interplaner $\pi$ cloud structure.

Another material of great interest is Silica which is not a molecule but chains and networks of SiO$_2$ connected so that each Si connects to four oxygen as in Fig. 10.26. Depending up on how you heat and melt SiO$_2$ and then cool it to a solid you can get sand, glass or quartz. Different types of glasses (Pyrex, lens, glass etc.) come from adding different impurities to the molten silica. Table 10.5 shows this. Borosilicate glass is Pyrex and it does not expand, contract or crack as the temperature changes so you can cook with it. [Mention recycling sand is to cheap to do it.]

Note SiO$_2$ is very different from CO$_2$ because the two sideways bonds each due to the $\pi$ bond made out of parallel p orbits on Csp & Osp$^2$, cannot form and overlap and lower the energy in the case of Silicon, since Silicon is bigger and they cannot touch. Hence the structure we described above is the lower energy. Silicates are chains and networks of SiO$_4$ ions with metal atoms attached to neutralized the ions. Silicates form clays. Ceramics are crystals of silicates in sand—when heated the silicates become frozen in glass which act as cement.

Actually these materials, which also have various metal ions in the

\[
\begin{array}{c}
\text{O} - \text{Si} - \text{O} \\
\text{O} \\
\text{O} \\
\text{Si}
\end{array}
\]

Structure, form a 3D amorphous material which gets weathered and chopped into thin detached moldable layers by rain and sun. When it is wet, kneaded, shaped
Figure 10.26
The structure of quartz (empirical formula SiO$_2$). Quartz contains chains of SiO$_4$ tetrahedra that share oxygen atoms.

<table>
<thead>
<tr>
<th>Type of Glass</th>
<th>SiO$_2$</th>
<th>CaO</th>
<th>Na$_2$O</th>
<th>B$_2$O$_3$</th>
<th>Al$_2$O$_3$</th>
<th>K$_2$O</th>
<th>MgO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Window (soda-lime glass)</td>
<td>72</td>
<td>11</td>
<td>13</td>
<td>—</td>
<td>0.3</td>
<td>3.8</td>
<td>—</td>
</tr>
<tr>
<td>Cookware (aluminosilicate glass)</td>
<td>55</td>
<td>15</td>
<td>—</td>
<td>—</td>
<td>20</td>
<td>—</td>
<td>10</td>
</tr>
<tr>
<td>Heat-resistant (borosilicate glass)</td>
<td>76</td>
<td>3</td>
<td>5</td>
<td>13</td>
<td>2</td>
<td>0.5</td>
<td>—</td>
</tr>
<tr>
<td>Optical</td>
<td>69</td>
<td>12</td>
<td>6</td>
<td>0.3</td>
<td>—</td>
<td>12</td>
<td>—</td>
</tr>
</tbody>
</table>
and allowed to dry, the 3D structure reconstructs and now is the "pot". The advantage of the material is it is high temperature resistance and the ability to make desired shapes.

Semiconductors: The microelectronics Revolution. Pure Silicon is like diamond (i.e. tetrahedral and is an insulator). Now imagine a situation where a small fraction of Si atoms are replaced in the lattice by As or B. This is called doping. In the former the lattice would have extra electrons. In the latter electrons would be missing from valance band orbitals creating "holes" or orbitals with one electron. The former, are called n-semiconductors (for negative) and the latter p-semiconductors (for positive). Since both have unpaired electrons they conduct a little (only a small amount of impurity) and are semiconductors. Now put a wafer slice of the n next to the p. Electrons will naturally flow from n to p and the p side is now negative and the n side positive. Note as an electron moves it leaves a "hole". Now if an external current has its negative wire attached to the P side it is repelled and the current does not flow. On the other hand if the positive wire is put to the p-side current flows easily because electrons like to go to p. Hence a rectifier has been created to change AC to pulsed DC current. Formally this could only be done by vacuum tubes and now by a device which today is almost invisible to the eye. The AC current presents the P side with +, -, +, - etc. at 60 cycles per second and passes current in the n to p direction only when the connection is +. Hmwk: 57, 61, 63, 67
Figure 10.29
(a) A silicon crystal doped with arsenic, which has one more valence electron than silicon. (b) A silicon crystal doped with boron, which has one less electron than silicon.

Figure 10.30
Energy-level diagrams for (a) an n-type semiconductor and (b) a p-type semiconductor.
Figure 10.31
The p-n junction involves the contact of a p-type and an n-type semiconductor. (a) The charge carriers of the p-type region are holes (O). In the n-type region the charge carriers are electrons (●). (b) No current flows (reverse bias). (c) Current readily flows (forward bias). Note that each electron that crosses the boundary leaves a hole behind. Thus the electrons and the holes move in opposite directions.
Omit sect 10.7 on ions solids as it is not clearly written in the book. How “vapor pressure and change of state”. We have already discussed vapor pressure, which is the pressure of a gas above liquid or solid in a closed container. We recall the discussion based on the rate at which molecules take off from the surface of the condensed phase (i.e. liquid or solid) at a fixed temperature. This is constant. On the other hand

The number of vapor molecules landing is proportional to the number in the vapor. Hence as more take off at a fixed temperature more will land and equilibrium will be reached. The pressure of the vapor at this point is called the equilibrium vapor pressure of the liquid or solid. Generally its value goes up with the temperature as the kinetic energy increases and hence the take off rate increases; the landing rate takes longer to catch up creasing the rate equality to be achieved at a higher pressure. On the other hand by similar reasoning if a substance has stronger intermolecular forces or is heavier it will have a lower vapor pressure. Fig. 10.39 shows that at a given temperature only the average kinetic energy is fixed and goes up with T. The molecules themselves have a distribution of velocities (like grades on an exam). The fraction at each kinetic energy (essentially at each velocity for a fixed molecular species and therefore fixed mass) is fixed by the value of T. The figure shows that higher T implies a higher fraction above the KE needed for take off (escape). This figure also
The dependence of vapor pressure on temperature.

Figure 10.39

The number of molecules in a liquid with a given energy versus kinetic energy at two temperatures. Part (a) shows a lower temperature than that in part (b). Note that the proportion of molecules with enough energy to escape the liquid to the vapor phase (indicated by shaded areas) increases dramatically with temperature. This causes vapor pressure to increase markedly with temperature.
explains evaporation (called sublimation of the solid vaporizes) at a fixed temperature the fraction stays fixed. If the hot molecules leave, the liquid absorbs heat from the atmosphere and restores the fraction. The T of the universe drops but not noticeably because the drop is too small to effect the universe. As such hot molecules always exist and can take off. Of course the volume of the liquid decreases and eventually disappears as the total number of molecules decrease but the fraction in the hot range does not change.

Empirically it has been found that if $P_{\text{vap}}$ is the vapor pressure and $\Delta H_{\text{vap}}$ the enthalpy or heat of vaporization for most liquids that $\ln P_{\text{vap}} = \frac{-\Delta H_{\text{vap}}}{R} \left( \frac{1}{T^oK} \right) + C$. C is a constant; R is the gas constant, now 8.3145 J/K - mole; $\Delta H_{\text{vap}}$ is in Joules per mole and C is constant that depends on the substance only. Comparing this to the straight line formula $y = mx + b$, we see that if we plot $\ln P_{\text{vap}}$ verses $\frac{1}{T^oK}$ the slop will give the value of $\frac{-\Delta H_{\text{vap}}}{R}$. Since R is known this gives $\Delta H_{\text{vap}}$ (see example 10.5). Also if we evaluate this formula twice, once at $T_1$ and once at $T_2$ and take the difference we get a formula that enables you to get the Vapor pressure at other temperatures if you know $\Delta H_{\text{vap}}$ and the $P_{\text{vap}}$ at one temperature

\[
\ln P_{\text{vap}}^{\left( T_1 \right)} - \ln P_{\text{vap}}^{\left( T_2 \right)} = \frac{-\Delta H_{\text{vap}}}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)
\]

See exercise 10.6. (Hmwk. 73, 75)
Sample Exercise 10.5 Determining Enthalpies of Vaporization

Using the plots in Fig. 10.40(b), determine whether water or diethyl ether has a larger enthalpy of vaporization.

Solution
When \( \ln(P_{\text{vap}}) \) is plotted versus \( 1/T \), the slope of the resulting straight line is

\[
-\frac{\Delta H_{\text{vap}}}{R}
\]

Note from Fig. 10.40(b) that the slopes of the lines for water and diethyl ether are both negative, as expected, and that the line for ether has the smaller slope. Ether has the smaller value of \( \Delta H_{\text{vap}} \). This makes sense because the hydrogen bonding in water causes it to have a relatively large enthalpy of vaporization.

See Exercise 10.71.

Sample Exercise 10.6 Calculating Vapor Pressure

The vapor pressure of water at 25°C is 23.8 torr, and the heat of vaporization of water at 25°C is 43.9 kJ/mol. Calculate the vapor pressure of water at 50°C.

Solution
We will use Equation (10.5):

\[
\ln\left(\frac{P_{\text{vap}}^{T_1}}{P_{\text{vap}}^{T_2}}\right) = \frac{\Delta H_{\text{vap}}}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)
\]

For water we have

\[
P_{\text{vap}}^{T_1} = 23.8 \text{ torr}
\]

\[
T_1 = 25 + 273 = 298 \text{ K}
\]

\[
T_2 = 50. + 273 = 323 \text{ K}
\]

\[
\Delta H_{\text{vap}} = 43.9 \text{ kJ/mol} = 43,900 \text{ J/mol}
\]

\[
R = 8.3145 \text{ J/K mol}
\]

Thus

\[
\ln\left(\frac{23.8 \text{ torr}}{P_{\text{vap}}^{T_2} \text{ (torr)}}\right) = \frac{43,900 \text{ J/mol}}{8.3145 \text{ J/K mol}} \left( \frac{1}{323 \text{ K}} - \frac{1}{298 \text{ K}} \right)
\]

\[
\ln\left(\frac{23.8}{P_{\text{vap}}^{T_2} \text{ (torr)}\right) = -1.37
\]

Taking the antilog (see Appendix 1.2) of both sides gives

\[
\frac{23.8}{P_{\text{vap}}^{T_2}} = 0.254
\]

\[
P_{\text{vap}}^{T_2} = 93.7 \text{ torr}
\]

See Exercises 10.73 through 10.76.
Recall as discussed earlier that boiling occurs only when the temperature, T is such that the $P_{\text{vap}}$ at that T equals the atmospheric pressure. The “bubble” of boiling formed in the liquid body by the separating molecules takes up space and lifts the surface of the liquid which in turn lifts the atmosphere. Hence $P_{\text{vap}}$ and therefore the T which it depends on must be higher (lower) if the atmospheric P is higher (lower). Hence water boils at lower temperatures up in the mountains. Now it is clear that the $P_{\text{vap}}$ as a function of T determines liquid boiling but it may sound strange to say that the T melting point (= T fusion) is the T at which the liquids $P_{\text{vap}}$ and solid $P_{\text{vap}}$ are equal. This is seen in Fig. 10.44. If the T is such that $P_{\text{vap}}$ (solid) $>$ $P_{\text{vap}}$ (liquid), more molecules will take off from the solid than the liquid. Since the “skies” have more molecules from the solid and since landing depends only on the total number of molecules in the gas which is the same for the liquid and solids point of view, we get a net transfer of molecules from solid to liquid and the solid disappears. A similar argument would say that only the solid exists at a higher T at which $P_{\text{vap}}$ (liquid) $>$ $P_{\text{vap}}$ (solid). At the T at which
Apparatus allows solid + liquid to interact only via the vapor state.

**Figure 10.44**
**Solid and liquid phases in equilibrium with the vapor phase**

$P_{\text{vap (liquid)}} = P_{\text{vap (solid)}}$ they are both existing and this is the $T_{\text{melting}} = T_{\text{fusion}}$. It takes time for liquids to freeze or to boil, the molecules need to organize or gain kinetic energy respectively. If you cool or heat too rapidly for a short time you can have supercooled ($T < T_{\text{fusion}}$) liquid or superheated liquid ($T > T_{\text{BP}}$). Any small disturbance (e.g. dirt, dust, a glass rod) can cause a sudden change back to the solid or gas (respectively). In the boiling case the sudden formation of vapor and release of heat causes the liquid to “bump” and usually the result is a violent and dangerous “boiling over”. Putting porous beads in the pots prevents this by giving forth bubbles of trapped air caught in its pores. The bubbles “condition” the liquid for its own bubble formation and boiling starts more quickly and bumping does not occur. **Phase diagrams** — a summary of information on what phase (gas, liquid, solid) the material of interest is in at a $P$ and $T$. So make a $P$ vs $T$ plot as in Fig. 10.47 ($\text{H}_2\text{O}$) or Fig. 10.52 ($\text{CO}_2$).

The black lines are a plot of the melting, boiling and sublimation points (temperatures) at a given $P$. You create, in the lab such a plot, horizontal line by horizontal line, in which at fixed $P$ one starts at low $T$ and raises $T$ looking to see at which $T$’s a phase change.
Figure 10.47
Phase diagram for water

Steven S. Zumdahl, Chemistry, © Houghton Mifflin Company. All Rights Reserved.
Figure 10.52
Phase diagram for carbon dioxide

occurs. These transition temperatures (the flat parts of the heating curve on Fig. 10.42) become points on the horizontal line; connecting them gives the black lines. The phase itself is obvious, you see it. the experiment must be done in a chamber where P and T can be varied and where no vapor initially exists. Once you have the diagram you can read off what exists at a (P,T) point and how the material changes as P or T or as both P and T change. Most notable is that at low P liquids and even solids do not exist and that you go from solid directly to gas. Note the triple point i.e. the (P,T) point where all three phases exist at once.

Most fascinating is that the liquid gas line ends at some high T and P (usually high) called the critical point. (Its T and P are the critical T and Critical P respectively). If you are above this T<sub>crit</sub>, you cannot form a liquid no matter how high the P. Also, at P<sub>crit</sub> or above, as you increase T past T<sub>crit</sub> no phase change occurs in the sense that “heat” is added and T does not change till the phase change has occurred. Instead at T<sub>crit</sub> a fluid appears (super critical fluid) and remains over a T range at the end of which the vapor reoccurs. This fluid has wild properties. Light sent through it “sparkles” and the fluid dissolves many solids that nothing else dissolves. On the H<sub>2</sub>O phase diagram, Fig. 10.49 we see that the solid liquid line has a negative slope. All other materials have a positive slope. As such as P increases for fixed T we change to a liquid. But higher P implies higher density for water (liquid H<sub>2</sub>O) than ice solid H<sub>2</sub>O. This phenomena causes ice to float and to cover the oceans keeping them warm. If ice was heavier than water it would sink and the oceans would freeze solid killing all marine life. This also explains “ice skating”. The blade puts a high P on the ice (Fig. 10.49) and it changes to liquid lubricating the motion of the blades push forward.
Figure 10.42
**Heating curve for water**

Figure 10.47
The phase diagram for water. $T_m$ represents the normal melting point; $T_3$ and $P_3$ denote the triple point; $T_b$ represents the normal boiling point; $T_c$ represents the critical temperature; $P_c$ represents the critical pressure. The negative slope of the solid/liquid line reflects the fact that the density of ice is less than that of liquid water.

Figure 10.48
Diagrams of various heating experiments on samples of water in a closed system.

Figure 10.49
The phase diagram for water. At point $x$ on the phase diagram, water is a solid. However, as the external pressure is increased while the temperature remains constant (indicated by the vertical dotted line), the solid/liquid line is crossed and the ice melts.
Note CO₂ at P = 1 atm no liquid exist—so we get dry ice- dry ice is nice because it is not messy as it sublimes (no melting). Also consider a fire extinguisher—it always exists say on the T = 25°C (room temperature) line but it holds CO₂ at high P and therefore its a liquid. As you open the valve the P drops (comes down the T = 25°C line) and the phase changes to heavier than air CO₂ gas that squirts out and smothers the fire by blocking O₂.

The transistor (Fig. 10.50) a device that amplifies the voltage (electron push) i.e. it takes a low input voltage and changes it (amplifies it) to a high output voltage. Circuit 1 has variable input “low voltage” attached to it in away that the negative is at the left of the Ω doped silicon slice. The positive part of circuit is attached to the P semiconductor layer. This is just Fig. 10.31c. A current now flows through P in circuit 1. Recall P just has holes and only has electrons that came from the n which in circuit 1 is attached to the “-” of circuit 1. Now normally circuit 2 would not have a current because p is attached negatively in circuit 2 (Fig. 10.31b) i.e. P would have no electron to conduct - the few it had gotten from the n are pushed back to n. But when the circuits share a P, it has electrons due to the flow in current 1. So, circuit 2 sees in P a circuit 1 current, I₁ = V₁,low/R₁,Low that changes with time. Now applying V=IR to circuit 2 we get I₁ = V₁/R₂, and therefore V₂ must be a high number (as I₁ is fixed by circuit 1) and R₂ is made to be high). The voltage has been increased and the current outside circuit 2 (to the right) will then be big if R outside is not too big. This device which can be made on the head of a pin today replaces big vacuum tubes. Linked together it makes circuits. As such a radio that needed a big box to hold its electronics can now be put in a tiny ear phone plug; A big computer in 1960 fits in hand held box today. etc....
Figure 10.50
A schematic of two circuits connected by a transistor. The signal in circuit 1 is amplified in circuit 2.