1a. Describe the structure of Mg$_2$SiO$_4$. Describe the compound’s bonding.

The SiO$_4^{4-}$ anion has 4 oxygen atoms bonded to each Si atom. Therefore, there are no bridging O atoms and this compound is a simple ionic compound composed of two Mg$^{2+}$ cations bonded ionically to each SiO$_4^{4-}$ ion.

\[ \text{Mg}^{2+} \text{O-Si-O}^{2-} \text{Mg}^{2+} \]

1b. A mineral has the empirical formula MgSiO$_3$. The silicon-oxygen portion of the compound exists as long chains. Draw a portion of the structure and describe the bonding.

The SiO$_3^{2-}$ chain is an extended ionic structure with repeating SiO$_3$ units, each of which carries a 2- charge. The chain has a repeating -O-Si-O-Si- backbone and each Si is also bonded to two terminal O atoms.

One Mg$^{2+}$ ion is ionically bonded to the chain for each SiO$_3^{2-}$ unit.

1c. What is the general trend in silicate structures as the ratio of O to Si in the formula decreases?

As the O/Si ratio decreases, more O atoms are bridging and the silicate structures become more interconnected and complex. SiO$_4$ has a simple polyatomic structure (one Si per anion). Si$_2$O$_7$ is a dimeric anion with a single Si-O-Si bridge. SiO$_3$ makes chains or rings where each Si atom is bonded to two bridging O atoms and two terminal O atoms. Structures with even lower O/Si ratios adopt double chain, sheet, and 3-D network structures.
2. Describe how semiconductor chips are made by answering the following:

a. How is ultra-pure silicon made?

\[
\text{SiO}_2(s) \rightarrow \text{SiCl}_4(l)
\]

SiCl\(_4\)(l) is purified by distillation.

\[
\text{SiCl}_4(l) + 2 \text{Zn}(s) \rightarrow \text{Si}(s) + 2 \text{ZnCl}_2(s)
\]

This Si is about 99.9% pure. It is then ultrapurified using zone refining, where a heating coil melts a thin layer of the Si. As that thin layer is moved through the solid it collects all the impurities, leaving pure Si behind.

b. Creation of the semiconductor circuit is prepared by creating n-type or p-type semiconductors on different regions of the Si surface. How is this done?

1. coat the Si surface with a photo-reactive coating
2. irradiate the area where the p-type semiconductor will go
3. wash off the coating in that area
4. expose the surface with a Group 3A element (e.g. Al)
5. wash off the coating
6-10. repeat the above procedure but use a Group 5A element (e.g. P) for the n-type region

3. The band structures below are for three metals between Cs and Hg on the periodic table.

What does the y-axis represent? \textit{Energy}

Which represents the metal with the strongest metallic bonding? \textit{B}; in this case all the bonding orbitals are filled, but none of the antibonding orbitals.

Which represents the metal with the weakest metallic bonding? \textit{C}. Almost all the antibonding orbitals are filled.
4. Silicones are produced using compounds of the type $R_3SiCl$, $R_2SiCl_2$, and $RSiCl_3$, where $R$ = a hydrocarbon group such as $\text{-CH}_3$.

a. Draw a molecule that can be formed if 1 mole of $(\text{CH}_3)_3\text{SiCl}$ is reacted with water.

\[
\begin{align*}
\text{CH}_3 & \quad \text{Si} \quad \text{Si} \quad \text{Si} \quad \text{CH}_3 \\
\text{CH}_3 & \quad \text{Si} \quad \text{Si} \quad \text{Si} \quad \text{CH}_3 \\
\text{CH}_3 & \quad \text{Si} \quad \text{Si} \quad \text{Si} \quad \text{CH}_3 \\
\text{CH}_3 & \quad \text{Si} \quad \text{Si} \quad \text{Si} \quad \text{CH}_3 \\
\text{CH}_3 & \quad \text{Si} \quad \text{Si} \quad \text{Si} \quad \text{CH}_3
\end{align*}
\]

b. Is the compound you drew the only compound that can come about using the amounts listed in the question?

Yes or No

c. How would you make a silicone that was a liquid with a high boiling point? That is, what reactants would you use and in what proportions?

Use no $RSiCl_3$, and a mixture of $R_2SiCl_2$ and $R_3SiCl$, with the chain lengthening reactant ($R_2SiCl_2$) in greater amount than the chain capping reactant ($R_3SiCl$).

5. Consider the zeolite structure to the right.

a. Draw the atoms and bonds of the portion of the structure where $A$ is pointing.

\[
\begin{align*}
\text{O} & \quad \text{Si} \quad \text{O} \\
\text{O} & \quad \text{Si} \quad \text{O} \\
\text{O} & \quad \text{Si} \quad \text{O} \\
\text{O} & \quad \text{Si} \quad \text{O}
\end{align*}
\]

b. Draw the atoms and bonds of the portion of the structure where $B$ is pointing.

\[
\begin{align*}
\text{Si} & \quad \text{O} \quad \text{Si} \\
\text{Si} & \quad \text{O} \quad \text{Si} \\
\text{Si} & \quad \text{O} \quad \text{Si} \\
\text{Si} & \quad \text{O} \quad \text{Si}
\end{align*}
\]

c. Some zeolites have Al substituted for Si in the structure. That leads to differences in the zeolite structure and properties. What would be different if, instead of Al, a P atom was used to substitute for Si? How would it differ from an aluminosilicate? How would it act the same?

The P-containing structure will have one more proton than the pure SiO2 structure. There will be a positive charge at each P site, and a corresponding anion will be present in the zeolite structure. This zeolite will still absorb water molecules but chemical reactivity that depended on a negative charge in the aluminosilicate will differ.
6. Describe the chemistry of how a cave forms. Include the key chemical reaction.

Water trickles through soil and picks up acids, which we will treat as CO₂. CO₂ reacts with H₂O to form carbonic acid, H₂CO₃.

\[
\text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{CO}_3.
\]

H₂CO₃ reacts with limestone in a favorable reaction:

\[
\text{H}_2\text{CO}_3(\text{aq}) + \text{CaCO}_3(\text{s}) \leftrightarrow \text{Ca}^{2+}(\text{aq}) + 2 \text{HCO}_3^{-}(\text{aq})
\]

A drop of water enters a cave after passing through overlying soil and limestone. What happens to the drop that leads to deposition of some CaCO₃ to form a stalactite?

When the drop enters the cave, it has a high CO₂ concentration.

The CO₂ degasses from the drop.

The drop in CO₂(aq) shifts the equilibrium CO₂ + H₂O ↔ H₂CO₃ to the left, reducing concentration of H₂CO₃.

Reduction of H₂CO₃ concentration shifts,

\[
\text{H}_2\text{CO}_3(\text{aq}) + \text{CaCO}_3(\text{s}) \leftrightarrow \text{Ca}^{2+}(\text{aq}) + 2 \text{HCO}_3^{-}(\text{aq})
\]

to the left, leading to precipitation of CaCO₃(s).

7. Draw a reasonable structure for B₂H₇⁻ ion. Account for all valence electrons by indicating where they are in your structure.

\[
\begin{array}{c}
\text{B} \quad \text{H} \\
2e^- \quad 2e^- \\
\text{H} \quad \text{H} \quad \text{B} \quad \text{H} \quad \text{B} \\
2e^- \quad \text{H} \quad \text{H} \\
\end{array}
\]

Is this ion expected to be a Lewis acid or a Lewis base? A Lewis Acid.

8. Why are silanes less stable than their corresponding alkanes?

Si-Si bonds are weaker than corresponding C-C bonds.

Si-H bonds are weaker than corresponding C-H bonds.

The main molecule available to react with either is O₂, to form CO₂ or SiO₂ and H₂O. Si-O bonds are stronger than C-O bonds.

So, silanes have weaker bonds to break when they react, and form stronger bonds in their products.
<table>
<thead>
<tr>
<th>Reduction Half-Reaction</th>
<th>$E^\circ$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$F_2(g) + 2 , e^- \rightarrow 2 , F^-(aq)$</td>
<td>2.87</td>
</tr>
<tr>
<td>$\text{MnO}_4^-(aq) + 8 , H^+(aq) + 5 , e^- \rightarrow \text{Mn}^{2+}(aq) + 4 , \text{H}_2\text{O(\ell)}$</td>
<td>1.51</td>
</tr>
<tr>
<td>$\text{Hg}^{2+}(aq) + 2 , e^- \rightarrow \text{Hg(\ell)}$</td>
<td>0.855</td>
</tr>
<tr>
<td>$O_2(g) + 4 , H^+(aq, , 10^{-7} , \text{M}) + 4 , e^- \rightarrow 2 , \text{H}_2\text{O(\ell)}$</td>
<td>0.82</td>
</tr>
<tr>
<td>$\text{Ag}^+(aq) + e^- \rightarrow \text{Ag(s)}$</td>
<td>0.799</td>
</tr>
<tr>
<td>$\text{Hg}_2^{2+}(aq) + 2 , e^- \rightarrow 2 , \text{Hg(\ell)}$</td>
<td>0.789</td>
</tr>
<tr>
<td>$\text{Fe}^{2+}(aq) + e^- \rightarrow \text{Fe}^{3+}(aq)$</td>
<td>0.771</td>
</tr>
<tr>
<td>$\text{Cu}^{2+}(aq) + 2 , e^- \rightarrow \text{Cu(s)}$</td>
<td>0.337</td>
</tr>
<tr>
<td>$\text{Sn}^{2+}(aq) + 2 , e^- \rightarrow \text{Sn(s)}$</td>
<td>-0.14</td>
</tr>
<tr>
<td>$\text{Ni}^{2+}(aq) + 2 , e^- \rightarrow \text{Ni(s)}$</td>
<td>-0.25</td>
</tr>
<tr>
<td>$\text{Cr}^{3+}(aq) + e^- \rightarrow \text{Cr}^{2+}(aq)$</td>
<td>-0.41</td>
</tr>
<tr>
<td>$\text{Fe}^{2+}(aq) + 2 , e^- \rightarrow \text{Fe(s)}$</td>
<td>-0.44</td>
</tr>
<tr>
<td>$\text{Cr}^{3+}(aq) + 3 , e^- \rightarrow \text{Cr(s)}$</td>
<td>-0.74</td>
</tr>
<tr>
<td>$\text{Zn}^{2+}(aq) + 2 , e^- \rightarrow \text{Zn(s)}$</td>
<td>-0.763</td>
</tr>
<tr>
<td>$\text{Al}^{3+}(aq) + 3 , e^- \rightarrow \text{Al(s)}$</td>
<td>-1.66</td>
</tr>
<tr>
<td>$\text{Mg}^{2+}(aq) + 2 , e^- \rightarrow \text{Mg(s)}$</td>
<td>-2.37</td>
</tr>
<tr>
<td>$\text{Na}^+(aq) + e^- \rightarrow \text{Na(s)}$</td>
<td>-2.714</td>
</tr>
</tbody>
</table>

**9a.** Consider the table above. What is the strongest oxidizing agent? $F_2$

What is the strongest reducing agent? Na

**b.** What is the $E^\circ$ for a cell that uses the reaction: $\text{Cu}^{2+}(aq) + \text{Mg(s)} \rightarrow \text{Cu(s)} + \text{Mg}^{2+}(aq)$

$$E^\circ = 0.337 \, \text{V} - (-2.37 \, \text{V}) = +2.707 \, \text{V}$$

**c.** What is $\Delta G^\circ$ for the cell reaction? $\Delta G^\circ = -nFE^\circ = -2(96.5 \, \text{kJ/mol-V})(+2.707 \, \text{V}) = -522 \, \text{kJ/mol}$

**10.** Here’s the electrochemical cell from Figure 20.1.4.

a. Label the anode and cathode.

b. show which direction (and where) electrons travel

c. show which direction (and where) $\text{SO}_4^{2-}$ ions travel
11. In electrolysis of Al₂O₃ to obtain metallic Al, instead of using molten pure Al₂O₃, a mixture of Na₃AlF₆ and Al₂O₃ is used. Why?

The mixture of the two compounds has a lower melting point than does pure Al₂O₃.

Why are carbon electrodes used in this process?

The reaction of the C electrodes with the O²⁻ ions in Al₂O₃ produces CO₂. This is a more stable product than the O₂ that would be produced if Al₂O₃ were decomposed at a metal electrode. This lowers the voltage needed, lowering the cost of operation.

12. a. Why does the Earth have a molten core.

During the formation of Earth, metals react with nonmetals to form compounds. When our planet formed, metals were present in excess, compared with the nonmetals. All the nonmetals reacted, leaving the excess metal.

The metal sank to the core because it is more dense than the compounds formed between the compounds formed between metals and nonmetals.

The metals in the core have a lower melting point than do the chemical compounds in the mantle.

b. Is Zn expected to be found mainly in the core of the Earth, or in the mantle/crust?

Zn²⁺ has a highly negative reduction potential, meaning it is difficult to reduce relative to Fe²⁺. Therefore, Zn stays in the cationic form and is found in chemical compounds in the mantle and crust, not as a metal in the core.

13. What process is used to produce Mg from a Mg ore such as MgCl₂? Write the reaction and name the process.

Mg²⁺ has a very highly negative reduction potential and therefore Mg must be formed via electrolysis.

\[ \text{MgCl}_2(\text{l}) \rightarrow \text{Mg(s)} + \text{Cl}_2(\text{g}) \quad \text{the reaction is driven by an external voltage source} \]

14. What mass of copper can be deposited by electrolysis if a current of 2.5 A runs for 15 minutes? Assume the copper is in the form Cu(NO₃)₂.

15 min = 900 sec

900 sec x 2.5 A = 2250 C

\[
2250 \text{ C} \times \frac{1 \text{ mol e}^-}{96485 \text{ C}} \times \frac{1 \text{ mol Cu}}{2 \text{ mol e}^-} \times \frac{63.55 \text{ g Cu}}{1 \text{ mol Cu}} = 0.74 \text{ g Cu}
\]
TH1. You know what the band structure of a semiconductor that uses Si doped with a group 3A element looks like.

What type of semiconductor is that: \( \text{intrinsic} \quad \text{n-type} \quad \text{p-type} \)

b. What is a “band” in the context of band theory? That is, what does the term “band” describe?

A set of closely spaced (energetically) molecular orbitals in a solid.

c. Finish drawing the band structure of that group 3A semiconductor, and right next to it, draw one for a semiconductor that uses a group 2A element instead. Be precise about the relative energy levels of the two.

Will the structure with the 2A element conduct better or worse than that with the 3A element? Give a one-sentence explanation.

Either answer is reasonable:

Better: The 2A element has two orbital vacancies and therefore twice as many orbitals that can accept an electron.

Worse: The 2A elements has higher energy orbitals and therefore the energy gap is larger.
TH2. Explain the chemistry involved in an iron blast furnace.

What is “coke”? What role does coke play?

Coke is a purified form of coal; essentially elemental carbon. Coke serves as the reducing agent for the reaction to reduce $\text{Fe}^{3+}$ ions to Fe metal.

What chemical entity directly reduces the iron oxides? Why does it play this role instead of other reactants added to the system?

Carbon monoxide. The reducing agent added is C(s) but two solids will not react rapidly so a gas phase reducing agent is needed to react with the solid $\text{Fe}_2\text{O}_3$. CO serves this purpose.

TH3. Draw a detailed diagram of a battery that might be constructed using Cd and MnO$_2$. Write reactions that would take place and note how electrons and any ions would transfer. What voltage would this battery have?
TH4. Consider the extraction of Cd from the compound CdO. Calculate the temperature at which this would be favorable for the direct decomposition of CdO, and for the reaction of CdO with C to form Cd and CO₂. Which process would be used to extract Cd: decomposition, reaction with C, or electrolysis?

<table>
<thead>
<tr>
<th></th>
<th>ΔH°f (kJ/mol)</th>
<th>ΔG°f (kJ/mol)</th>
<th>S° (J/mol K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C (s, graphite)</td>
<td>0</td>
<td>0</td>
<td>5.7</td>
</tr>
<tr>
<td>CO₂ (g)</td>
<td>-393.5</td>
<td>-394.4</td>
<td>213.7</td>
</tr>
<tr>
<td>Cd (s)</td>
<td>0</td>
<td>0</td>
<td>52.0</td>
</tr>
<tr>
<td>CdO (s)</td>
<td>-258.0</td>
<td>-228.0</td>
<td>55.0</td>
</tr>
<tr>
<td>O₂ (g)</td>
<td>0</td>
<td>0</td>
<td>205.1</td>
</tr>
</tbody>
</table>

Decomposition: \( 2 \text{CdO(s)} \rightarrow 2\text{Cd(s)} + \text{O}_2(g) \)

\[ \Delta H^\circ = 0 - 2 \times -258 \text{kJ/mol} = +516 \text{kJ/mol} \]

\[ \Delta S^\circ = (2 \times 52.0 + 205.1) - (2 \times 55.0) \text{J/Kmol} = +199.1 \text{J/Kmol} \]

Crossover \( T = \frac{516,000 \text{J/mol}}{199.1 \text{J/Kmol}} = 2592 \text{ K} \)

Reaction with C: \( 2 \text{CdO(s)} + \text{C(s)} \rightarrow 2 \text{Cd(s)} + \text{CO}_2(g) \)

\[ \Delta H^\circ = (2 \times 0 + -393.5) \text{kJ/mol} - (2 \times -258) \text{kJ/mol} = +122.5 \text{kJ/mol} \]

\[ \Delta S^\circ = (2 \times 52.0 + 213.7) - (2 \times 55.0 + 5.7) \text{J/Kmol} = +202 \text{J/Kmol} \]

Crossover \( T = \frac{122,500 \text{J/mol}}{202 \text{J/Kmol}} = 606 \text{ K} \)

The temperature for decomposition is too high to be commercially viable. The temperature for reduction with carbon is very reasonable, so that process would be used.