1. Which of the following salts will be only sparingly soluble in water? Co(NO$_3$)$_2$, CePO$_4$, NH$_4$Cl, Na$_3$PO$_4$, TiO$_2$

Two of these salts are very insoluble, CePO$_4$ and TiO$_2$. Both involve combinations of multiply charged ions, which means high lattice energy to be overcome and unfavorable entropy terms for solvation. The other three involve singly charged anions and/or cations which most often leads to soluble materials.

2. CsCl has a simple cubic lattice. Calculate the density of CsCl given that the unit cell dimension is 4.12 Å.

The unit cell of CsCl has one formula unit in the cell. The density is given by

$$\text{density} = \frac{\text{mass of one formula unit}}{\text{volume of unit cell}}$$

To express this in the usual g cm$^{-3}$

$$\frac{168.35 \text{ g mol}^{-1}/6.022 \times 10^{23} \text{ mol}^{-1}}{(4.12 \times 10^{8} \text{ cm})^3} \approx 3.997 \text{ g cm}^{-3}$$

3. Using the data given below and the heat of formation (ΔH$_f$) of -1214.6 kJ/mol to calculate the lattice energy of CaF$_2$.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat of atomization (sublimation) of Ca</td>
<td>178 kJ/mol$^{-1}$</td>
</tr>
<tr>
<td>Bond dissociation energy of F$_2$</td>
<td>155 kJ/mol$^{-1}$</td>
</tr>
<tr>
<td>Electron affinity of fluorine</td>
<td>322 kJ/mol$^{-1}$</td>
</tr>
<tr>
<td>First ionization energy of Ca</td>
<td>590 kJ/mol$^{-1}$</td>
</tr>
<tr>
<td>Second ionization energy of Ca</td>
<td>1145 kJ/mol$^{-1}$</td>
</tr>
</tbody>
</table>

The cycle to the right allows the calculation of the lattice energy (here defined according to the direction of the arrow as a negative number)

$$\Delta H_f = \text{Sub} + \text{IP}_1 + \text{IP}_2 + \text{Diss} - 2 \text{ EA} - U$$

$$U = \Delta H_f - \text{Sub} - \text{IP}_1 - \text{IP}_2 - \text{Diss} + 2 \text{ EA}$$

$$U = -1214.6 - 178 - 590 - 1145 - 155 + 2(322)$$

$$U = 2639 \text{ kJ mol}^{-1}$$

Note that all of the terms leading to the formation of the gaseous ions are unfavorable except for the electron affinity. Thus the lattice energy and the electron affinity serve to
overcome all of these unfavorable terms and still give an overall favorable heat of formation.

4. Which of the following salts would be expected to have the highest lattice energy? Why? FeO, Fe$_2$O$_3$, FeS, Fe$_2$S$_3$

Fe$_2$O$_3$ would be expected to have the highest lattice energy. Although these salts do not necessarily have the same structure, the effect on lattice energy due to charge and internuclear distance are by far the most important. This salt, involving Fe$^{3+}$, will certainly have a larger lattice energy than for FeO, which contains Fe$^{2+}$. The smaller radius of O$^{2-}$ compared to S$^{2-}$ means that the oxides will have the larger lattice energy (most negative, in case anyone is worrying about signs here).

5. Which of the salts, MgTe or CaTe, would be most likely to adopt a structure in which the coordination number of the cation is 4? Give the reason(s) for your choice.

The answer here is based upon a consideration of radius ratios. Given that virtually no ionic materials are predicted to have occupancy of trigonal holes, then one expects that these will have the fcc lattice with either the tetrahedral holes (four coordination) or octahedral holes (six coordination) occupied. The one most likely to have four coordination is the one with the smallest cation/anion radius ratio. Without any calculation it can be concluded that the most likely is MgTe because magnesium has a smaller radius than calcium. (0.65 Å compared to 0.94 Å) Given that the radius for Te$^2-$ is 2.22 Å then one actually finds ratios of 0.29 and 0.42. The former actually predicts that tetrahedral sites would be occupied.

6. The unit cell of a rhenium oxide is shown below. What is the empirical formula of the compound?

There are four rhenium atoms on the edges of the cell; one fourth of each contribute to the cell. Therefore there is one Re atom.

There are four oxygen atoms in faces of the cell; these contribute one half each to the cell. There are eight oxygen atoms at the corners, which contribute one eighth to the cell. This is a total of three oxygen atoms. Therefore the formula of the rhenium oxide must be ReO$_3$. 