Potentially useful information:

\[ R = 8.314 \text{ J/K mol} \]

Radius ratio rules

<table>
<thead>
<tr>
<th>R</th>
<th>CN</th>
<th>Typical structure type</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.225 - 0.414</td>
<td>4</td>
<td>cristobalite, zincblende</td>
</tr>
<tr>
<td>0.414 - 0.732</td>
<td>6</td>
<td>rocksalt, rutile</td>
</tr>
<tr>
<td>&gt;0.732</td>
<td>8</td>
<td>cesium chloride, fluorite</td>
</tr>
</tbody>
</table>

YOU CAN USE THE BACK OF THE SHEETS AS SCRATCH PAPER

Figure 1

Open circles are cations; closed circles anions

Figure 2
1. (14 pts total) Fill in the blanks in the following (1 pt each blank):

a) Crystalline materials have \textit{long-range} order and amorphous materials have \textit{short-range} order.

b) There are \(6/7\) crystal systems and \(14\) Bravais lattices.

c) An example of a metal that forms a hexagonal close-packed lattice is \(\text{Be, Mg, Cd}\).

d) \(\text{BaTiO}_3\) crystallizes in the \textit{perovskite} structure.

Such materials find use as \textit{piezoelectric transducers}.

e) The body-centered cubic lattice contains two types of voids. Name one \textit{tetrahedral} / \textit{octahedral}.

f) An example of a material other than diamond that crystallizes in the diamond structure is \(\text{Ge, Si, GaAs}\).

g) The critical radius ratio occurs in an ionic structure when \textit{anions touch cations}.

h) Describe in a few words the structure of any non-metallic element we have encountered in the course (4 pts)

\textit{e.g.) diamond, graphite, S\textsubscript{8}, Se, I\textsubscript{2}}
2. (16 pts total) Figure 1 shows the structure of an oxide of sodium that crystallizes in the antifluorite type structure. This structure is the same as the fluorite type of structure except that the anions and cations reverse positions.

(2 pts each):

a) in what sort of lattice are the anions arranged? \( \text{fcc} \)

b) what is the coordination number of the anions? 8

c) how would you describe the location of the cations? \( \text{Td void} \)

d) give a set of \((xyz)\) coordinates for any cation \( (1/4, 1/4, 1/4) \) etc.

e) what sort of void is not filled? \( \text{Oh} \)

f) what is the formula of the compound? \( \text{Na}_2\text{O} \)

g) the cube length \( a_0 \) for this compound is 555 pm. What is the Na-O distance? (4 pts):

\[
d (\text{Na-O}) = \sqrt{3 \left(\frac{1}{4}\right)^2} a_0 = \frac{\sqrt{3}}{4} a_0
\]

\[
\text{Na} (0, 0, 0) \quad \text{O} (1/4, 1/4, 1/4)
\]

\[
\text{Na-O} = 240 \text{ pm}
\]
3. (10 pts total)

What are the Miller indices of the planes in Figure 2? (3 pts each)

a) \( (1 2 3) \)  
b) \( (2 \overline{1} 1) \)

b) What is the spacing between the \((1 1 1)\) planes of Cu \((a_0 = 3.62 \text{ Å})\)? (4 pts)

Cu is cubic (fcc). The \((111)\) planes cut \((113)\) along the cube diagonal

so \( d_{111} = \frac{1}{3 \sqrt{2}} \cdot a_0 \).

\[ s = 2.09 \text{ Å} \]

(111) spacing = 2.09 Å
4. (13 pts total)

a) The table below show the interionic distances (Å) in several alkali halides.

<table>
<thead>
<tr>
<th>Anion</th>
<th>Li⁺</th>
<th>Na⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>Br⁻</td>
<td>2.75</td>
<td>2.97</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>2.57</td>
<td>2.79</td>
</tr>
<tr>
<td>F⁻</td>
<td>2.09</td>
<td>2.31</td>
</tr>
</tbody>
</table>

\[
\begin{align*}
\text{Na}^+ + \text{F}^- & \rightarrow \text{Na}^+ = 2.31 - 1.33 = 0.98 \\
\text{Na}^+ + \text{Br}^- & \rightarrow \text{Br}^- = 2.97 - 0.98 = 1.99 \\
\text{Li}^+ + \text{Br}^- & \rightarrow \text{Li}^+ = 2.75 - 1.99 = 0.76 \\
\text{Li}^+ + \text{F}^- & \rightarrow \text{F}^- = 2.57 - 0.98 = 1.59 \\
\text{So}, \quad \text{Na}^+ + \text{Cl}^- & = 0.98 + 1.81 = 2.79 \\
\text{Li}^+ + \text{F}^- & = 0.98 + 1.33 = 2.31
\end{align*}
\]

Assuming the ionic radius of F⁻ is 1.33 Å, fill in the missing values in this table (2 pts each).

\[
\begin{align*}
R(\text{LiBr}) & = \frac{0.98}{1.99} = 0.49 \\
\Rightarrow \text{CN} & = 4 \\
2nS & \\

R(\text{NaF}) & = \frac{0.98}{1.33} = 0.74 \\
\Rightarrow \text{CN} & = 8 \\
\text{CsCl structure} & \\
\end{align*}
\]

b) what structure according to the radius ratio rules would you expect from a) for (2 pts each)

i) LiBr \hspace{1cm} \text{zincblende (}4nS\text{)} \hspace{1cm} ii) NaF \hspace{1cm} \text{CsCl structure}

c) which do you expect to have the higher melting point NaCl or MgO? Both crystallize in the sodium chloride structure. Explain your reasoning (5 pts)

Assuming repulsive forces are not very different the m.p. should scale as the attractive part of the lattice energy:

\[
\frac{U(\text{NaCl})}{U(\text{MgO})} \approx \frac{4}{1}
\]

and MgO should have the higher m.p.
5. (10 pts total) a) Associate the correct name with the appropriate formula (1 pt each)

<table>
<thead>
<tr>
<th>Names</th>
<th>Formulae</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mie potential</td>
<td>$E_0 = - (N_A M e^2 / 4 \pi \epsilon_0 r_e) \left( 1 - \rho / r_e \right)$</td>
</tr>
<tr>
<td>Morse potential</td>
<td>$\phi = - \phi_e \left[ (r_e / r)^{12} - 2 (r_e / r)^{6} \right]$</td>
</tr>
<tr>
<td>Kapustinkii equation</td>
<td>$\phi = z_1 z_2 e^2 / r$</td>
</tr>
<tr>
<td>Dulong-Petit law</td>
<td>$C_v = 3 R (\theta_B / T)^2 \exp(\theta_B / T) / [\exp(\theta_B / T) - 1]^2$</td>
</tr>
<tr>
<td>Lennard-Jones potential</td>
<td></td>
</tr>
<tr>
<td>Born-Mayer potential</td>
<td></td>
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<tr>
<td>Coulomb potential</td>
<td></td>
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<tr>
<td>Hard-sphere potential</td>
<td></td>
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<tr>
<td>Einstein equation</td>
<td></td>
</tr>
</tbody>
</table>

b) (6 pts) sketch an approximate but realistic potential energy $V(r)$ vs. $r$ diagram for solid NaCl ($r_e = 399$ pm) and solid Ne ($r_e = 75$ pm) HINT: these curves will look somewhat different.
6. (17 pts total)
a) Fill in the blanks in these statements or select the best answer about the development of theories of heat capacity. (1 pt each)

The Dulong-Petit Law was based on the **Equi-partition of Energy** Principle and predicted that \( C_v = \frac{3R}{\theta} \). Einstein modelled the vibrations of atoms in solids as **simple harmonic** oscillators with no one a range of vibrational frequency(ies). Debye’s model regards the atomic vibrations as **coupled** oscillators give no / one / a range of vibrational frequency(ies).

All these models give values of \( C_v \) for metals at very low temperatures that are higher than those measured experimentally because they ignore **electronic specific heat**.

b) (4 pts) What does the Debye temperature (\( \theta_D \)) correspond to?

\[ \Theta_D = \frac{\hbar \omega_{\text{max}}}{k} \text{ and corresponds to the temperature at which } \hbar \omega_{\text{max}} = kT \]

c) for temperatures \( T \ll \theta_D \) the Debye theory predicts that \( C_v = \text{const} \left( \frac{T}{\theta_D} \right)^3 \). The Debye temperature of diamond is 1860 K. The value of \( R = 8.314 \text{ J/K mol} \)

i) if \( C_v \) for diamond is 1.944 J/K mol at 186 K, what is its value at 100K? (4 pts)

\[ 1.944 = \text{const} \left( \frac{186}{1860} \right)^3 \text{ so } \text{const} = 1944 \text{ so } \frac{C_v (100K)}{1944 \left( \frac{186}{1860} \right)^3} = 0.302 \text{ J/K mol} \]

ii) what is the numerical value of \( C_v \) at temperatures \( T \gg \theta_D \)? (2 pts)

\[ C_v \text{ at high } T = 3R = 24.94 \text{ J/K mol} \]