5.29 a) From table on page 404.

<table>
<thead>
<tr>
<th></th>
<th>$\Delta G \text{ (kJ)}$</th>
<th>$V \text{ (cm}^3\text{)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>kyanite</td>
<td>-2.443.88</td>
<td>44.09</td>
</tr>
<tr>
<td>andalusite</td>
<td>-2.442.66</td>
<td>51.53</td>
</tr>
<tr>
<td>sillimanite</td>
<td>-2.440.99</td>
<td>49.90</td>
</tr>
</tbody>
</table>

Since kyanite has smallest $\Delta G$ it is certainly the stable phase at atmospheric pressure. We can see this conclusion is true at any pressure (at room temperature) by seeing that from eqn 5.41 $(\partial G/\partial P)_T^N = V$ and that kyanite has the lowest $V \Rightarrow$ its $G$ will increase the slowest with increasing pressure. Hence it will remain the lowest $G$.

b) By the rules of calculus

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,N} dT + \left(\frac{\partial G}{\partial P}\right)_{T,N} dP$$

If the pressure remains fixed, then $dP = 0$.

$$\Rightarrow dG = \left(\frac{\partial G}{\partial T}\right)_{P,N} dT$$

From equation 5.42, we have $\left(\frac{\partial G}{\partial T}\right)_{P,N} = -5$. 
\[ dG = -SdT \quad \text{at constant } P. \]

Integrating \( w.r.t. \) temperature,

\[ G(T_2) - G(T_1) = -\int_{T_1}^{T_2} S \, dT \]

This relation will be true for each phase. So if we substitute two such relations for each other, we will have:

\[ \Delta G(T_2) - \Delta G(T_1) = -\int_{T_1}^{T_2} \Delta S \, dT \]

which is what we were to show.

Schroeder then argues that \( \Delta S \) is independent of \( T \), at least at "high" temperatures. So this would simplify the relationship above to:

\[ \Delta G(T_2) - \Delta G(T_1) = -\Delta S \, \Delta T \]

\[ = -\Delta S \left( T_2 - T_1 \right) \]

<table>
<thead>
<tr>
<th>\text{Mineral}</th>
<th>\Delta G \text{ (kJ)}</th>
<th>S \text{ (J/k)}</th>
</tr>
</thead>
<tbody>
<tr>
<td>kyanite</td>
<td>-2443.88</td>
<td>83.81</td>
</tr>
<tr>
<td>andalusite</td>
<td>-2942.66</td>
<td>93.22</td>
</tr>
<tr>
<td>sillimanite</td>
<td>-2440.99</td>
<td>96.11</td>
</tr>
</tbody>
</table>
First consider stability of andalusite with respect to kyanite

\[ \Delta G(T_2) - \Delta G(T_1) = -\Delta S (T_2 - T_1) \]

\[ \begin{align*}
\downarrow & \\
0 - \left( -2443.88 + 2442.66 \right) \text{kJ} &= - \left( 83.81 - 93.22 \right) \frac{\text{kJ}}{\text{K}} \\
\uparrow & \\
x (T_2 - T_1)
\end{align*} \]

When equally stable at room temperature

\[ 1.220 \times 10^3 \text{ J} = 9.41 \frac{\text{J}}{\text{K}} (T_2 - T_1) \]

\[ \Rightarrow (T_2 - T_1) = 130 \text{ K} \]

\[ \Rightarrow \text{andalusite becomes stable w.r.t. kyanite above} \]

25 + 130 \approx 155 \text{ °C.}

Repeat exercise with sillimanite and kyanite

\[ 0 - \left( -2443.88 + 2440.99 \right) \text{kJ} = - \left( 83.81 - 96.11 \right) (T_2 - T_1) \]

\[ T_2 - T_1 = 235 \text{ K} \Rightarrow \text{sillimanite becomes stable w.r.t. kyanite above} \]

\[ T_2 = 260 \text{ °C.} \]

But, of course, by then andalusite has been established as favored phase over kyanite. So repeat with sillimanite and...
andalusite

\[ \Delta G = (2442.66 + 2440.99) \text{kJ} = -(93.22 - 96.11) \frac{\text{J}}{\text{K}} \frac{(T_2 - T_1)}{10} \]

\[ (T_2 - T_1) = 578 \text{ K} \Rightarrow T_2 = 603 \text{ °C}. \]

So, based on this calculation, we expect kyanite to be the stable phase from room temperature up to 158 °C, when andalusite takes over. Then above 603 °C, sillimanite becomes the most stable phase.

d) At constant pressure, the change in entropy (of a given phase) is given by

\[ \Delta S = C_p \frac{\Delta T}{T} \]

So the approximation that \( \Delta S \) between phases is a constant implies that the heat capacity of the two phases is the same. We see from the table that this isn't exactly true at room temperature

<table>
<thead>
<tr>
<th>Phase</th>
<th>( C_p ) (J/K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>kyanite</td>
<td>121.71</td>
</tr>
<tr>
<td>andalusite</td>
<td>122.72</td>
</tr>
<tr>
<td>sillimanite</td>
<td>129.52</td>
</tr>
</tbody>
</table>

Let's look at the worst case scenario, andalusite vs. sillimanite over a \( \Delta T \) of 578 K.
\[ \Delta (\Delta S) = \Delta C_p \cdot \Delta T / T \]

\[ = (124.52 - 122.72) \text{ J/K} \cdot 578 \text{ K} / 589 \text{ K} \]

\[ = 1.8 \text{ J/K} \]

So significant correction possible. Need more data.