1) We have five equations:

- i) $\text{CH}_3\text{CHO}(g) + 2\text{H}_2(g) \rightarrow \text{C}_2\text{H}_6(g) + \text{H}_2\text{O}(l)$\hspace{1cm} $\Delta H^\circ = -205 \text{ kJ}$
- ii) $2\text{H}_2(g) + \text{O}_2(g) \rightarrow 2\text{H}_2\text{O}(g)$\hspace{1cm} $\Delta H^\circ = -484$
- iii) $2\text{C}_2\text{H}_5\text{OH}(l) + \text{O}_2(g) \rightarrow 2\text{CH}_3\text{CHO}(g) + 2\text{H}_2\text{O}(l)$\hspace{1cm} $\Delta H^\circ = -348 \text{ kJ}$
- iv) $\text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{O}(g)$\hspace{1cm} $\Delta H^\circ = 44 \text{ kJ}$
- v) $2\text{C}_2\text{H}_5\text{OH}(l) \rightarrow 4\text{C}(s) + 6\text{H}_2(g) + \text{O}_2(g)$\hspace{1cm} $\Delta H^\circ = 556 \text{ kJ}$

a) This is just an application of Hess’ Law of Heat Summation. The desired $\Delta H^\circ_f = -(v/2) + (iii/2) + (i) + 2(iv) - (ii)$ [verify this for yourselves] = $-278 + (-174) + (-205) + 44 + 484 = \textbf{-85 kJ}$, and the balanced equation is:

$$2\text{C}(s) + 3\text{H}_2(g) \rightarrow \text{C}_2\text{H}_6(g)$$

b) Our equation is now: $2\text{C}(s) + 3\text{H}_2(g) \rightarrow \text{C}_2\text{H}_6(g)$ for which we can find the following $S^\circ$:

$$5.7 \hspace{1cm} 130.6 \hspace{1cm} 229.5 \text{ (J/K)}$$

which leads to a $\Delta S^\circ_f = 229.5 - (2(5.7) + 3(130.6)) = \textbf{-173.7 J/K}$

c) Finally, the $\Delta G^\circ_f = \Delta H^\circ_f - T \Delta S^\circ_f = -85000 \text{ J} - (298.15\text{K})(-173.7 \text{ J/K}) = \textbf{-33.21 kJ}$

2a) We are given all the data we need to calculate both $\Delta H^\circ_f$ and $\Delta S^\circ_f$; from both of these, we can get $\Delta G^\circ_f$ and from this datum the $K_1$ requested. Here we go.

$$\Delta H^\circ_f = -635 + 0 -(-608) = -27 \text{ kJ/mol}; \Delta S^\circ_f = 109 + 0 - (234) = -125 \text{ J/K mol}.$$  

$$\Delta G^\circ_f = \Delta H^\circ_f - T \Delta S^\circ_f = -27000 - (298)(-125) = 10.25 \text{ kJ/mol}.$$  

We also know that $\Delta G^\circ_f = -RT\ln(K_0)$ which leads to, in this case, $\Delta G^\circ_f = -RT\ln(K_1)$. Substituting, we get: $10250 \text{ J/mol} = -(8.314 \text{ J/K mol})(298\text{K})\ln(K)$ which leads to $\ln(K) = -4.137$; taking the antilog, we get $K_1 = \textbf{1.6 \times 10^{-2} mol/L}$ which agrees pretty well with the value reported in Table 17.1 (p.727). [You didn’t have to do this last part; I just did for our edification.]

b) The entropic term here is fairly large, as things go, and it is this which probably shifts things to the non-spontaneous side of the argument. Note that this change in entropy is sort of anti to what we said in class; sometimes the qualitative arguments don’t work
quantitatively. On top of all this, the enthapic term is sort of small, relatively speaking. Coupled together, these two really affect the equilibrium.

3) Let us collect our data. We have a total volume of 30.0 L, and a temperature of 795°C (= 1068.15 K), plus 0.0175 mole CO and 0.0525 mole H₂. We also should have a balanced equation for this reaction. Here it is:

\[
\text{CO}(g) + 3\text{H}_2(g) \rightarrow \text{CH}_4(g) + \text{H}_2\text{O}(g)
\]

\[
\Delta H^\circ = -110.5 \quad 0.0 \quad -74.87 \quad -241.826 \quad (\text{kJ/mol})
\]

\[
\begin{align*}
\text{S} & = 197.5 \quad 130.6 \quad 186.1 \quad 188.72 & (\text{J/Kmol}) \\
\Delta G^\circ & = -137.2 \quad 0.0 \quad -50.81 \quad -228.60 \quad (\text{kJ/mol})
\end{align*}
\]

Note that we can't simply use the \(\Delta G^\circ\) values! These are given at 25°C, and we are not there. We need to use \(\Delta G = \Delta H - T \Delta S\) to get \(\Delta G\), and then use \(\Delta G = -RT \ln K\) to find the equilibrium constant.

The \(\Delta H\) for the reaction is: \((-241.826 + (-74.87)-(-110.5 + 0)) = -206.196\ \text{kJ}\). The \(\Delta S\) value is: \((188.72 + 186.1 - (197.5 + 3(130.6)) = -214.48\ \text{J/K}\). Therefore, our \(\Delta G\) is: \(-206196 - (1068.15)(-214.48) = 22.90\ \text{kJ}\), which leads to a \(K\) value of: \(-(8.314)(1068)\ln K_{\text{th}} = 22900\), and \(K = 7.59 \times 10^2\). Note that all the species in the balanced equation are gases, so we've just calculated a \(K_p\). As we are given moles and volumes, it seems best to work in molarities and concentrations, so we need a \(K_c\) value. Recall \(K_p = K_c(RT)^{\Delta n}\), or \(K_c = \frac{K_p}{(RT)^{\Delta n}}\); substituting, we get:

\[
\frac{7.59\times 10^{-2}}{(0.08206(1068.15))^{-2}} = 582.90.
\]

Now we can set up our I.C.F. table:

<table>
<thead>
<tr>
<th>(\text{CO}(g))</th>
<th>(3\text{H}_2(g))</th>
<th>(\rightarrow)</th>
<th>(\text{CH}_4(g))</th>
<th>(\text{H}_2\text{O}(g))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(0)</td>
<td>(5.83 \times 10^{-4})</td>
<td>(1.75 \times 10^{-3})</td>
<td>(x)</td>
<td>(x)</td>
</tr>
<tr>
<td>(0)</td>
<td>(-3x)</td>
<td>(+x)</td>
<td>(+x)</td>
<td>(+x)</td>
</tr>
<tr>
<td>(5.83 \times 10^{-4} - x)</td>
<td>(1.75 \times 10^{-3} - 3x)</td>
<td>(x)</td>
<td>(x)</td>
<td></td>
</tr>
</tbody>
</table>

Working out the equilibrium expression, we get:

\[
582.90 = \frac{x(x)}{(5.83 \times 10^{-4} - x)(1.75 \times 10^{-3} - 3x)^3} \quad \text{. Now comes the important realization; you don't need to solve this horrific quartic if you recognize that the bottom can be expressed}
\]
as a constant times an expression raised to the fourth. That is, 
\[ 582.90 = \frac{(x)^2}{(5.83 \times 10^{-4} - x)^4 (3)^4} \]. So take the square root on both sides and multiply by \( \sqrt{27} \) to get:

\[ 125.45 = \frac{x}{(5.83 \times 10^{-4} - x)^2} \]. Finally, expanding this fraction, we get, for our quadratic,

\[ 125.45x^2 - 1.1463x + 4.264 \times 10^{-5} = 0 \], and a value of \( x = 3.735 \times 10^{-5} \text{ M} \) as the only practical answer. (The other answer would not work with the above I.C.F. table.) This data leads us to \([\text{CH}_4] = [\text{H}_2\text{O}] = 4.082 \times 10^{-5} \text{ M} \). We are asked, however, for the number of moles of CH\(_4\) and H\(_2\)O; multiplying by 30.0 L, we get \(1.121 \times 10^{-3} \text{ moles CH}_4 \text{ and H}_2\text{O} \).

4) We are asked to find the \( K_{sp} \) for CdS at 45\(^\circ\)C, using thermodynamic data. Here is the balanced equation, with thermochemical data added:

\[
\text{CdS}(s) \leftrightarrow \text{Cd}^{2+}(aq) + \text{S}^{2-}(aq)
\]

\[
\Delta H^\circ_{rxn} = -144 - 72.38 + 41.8 \quad (\text{kJ/mol})
\]

\[
\Delta S^\circ = 71 - 61.1 + 22 \quad (\text{J/K/mol})
\]

\[
\Delta G^\circ = -141 - 77.74 + 83.7 \quad (\text{kJ/mol})
\]

Note we can't simply use the \( \Delta G^\circ \) values, since they are at 25\(^\circ\)C, and we are at 45\(^\circ\)C. We have to use \( \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \), and assume that the \( \Delta G \) value is nearly invariant over this temperature range. Here we go.

The \( \Delta H^\circ_{rxn} = -72.38 + 41.8 - (-144) = 113.42 \text{ kJ/mol} \); the \( \Delta S^\circ = -61.1 + 22 - 71 = -110.1 \text{ J/mol} \). Both of these combined lead to a \( \Delta G^\circ = 113420 - (318.15)(-110.1) \text{ J/K} = 148.45 \text{ kJ} \). Using this value in \( \Delta G^\circ = -RT \ln(K_{sp}) \) gives us: 148450 = - (8.314 J/K\text{mol})(318.15) \ln(K_{sp}) and a \( K_{sp} = 4.23 \times 10^{-25} \) (which compares favorably with the one at 25\(^\circ\)C of 8 x 10\(^{-27} \) [remember solids get more soluble as temperature rises!])

5) With a K>1, we can say that \( \Delta G^\circ < 0 \) since \( \Delta G^\circ = -RT\ln(K) \), which would be a negative number. Since \( \Delta G^\circ < 0 \), and \( \Delta H^\circ \approx 0 \), \( \Delta S^\circ > 0 \), since \( \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \). We can, therefore, be pretty confident in our assertion that entropy drives this reaction. (It is also a consequence of the qualitative rules—larger molecule breaking down into smaller molecules [or, at least, more of them!])