a) The equilibrium constants have similar set-ups. The $K_c = \frac{[C_2H_4][C_2H_6]}{[C_4H_{10}]}$, and the $K_p$

$$= \frac{(P_{\text{ethene}})(P_{\text{ethane}})}{(P_{\text{butane}})}.$$ 

b) Recall that $K_p = K_c(RT)^\Delta n$. We have our $K_p$ here (12 atm), and we have our temperature (500°C = 773 K). One mole of gas goes to two moles of gas, so $\Delta n = 1$. Thus, we can say: $12 = K_c[(0.08206 \text{ L} \cdot \text{atm}/\text{K} \cdot \text{mole})(773 \text{ K})]^1$ and $K_c = 1.89 \times 10^{-1} \text{ M}$

c) We can set up our I.C.E. table, with the initial pressure of butane as 50 atm.

<table>
<thead>
<tr>
<th></th>
<th>C$<em>4$H$</em>{10}$</th>
<th>C$_2$H$_4$</th>
<th>C$_2$H$_6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>50 atm</td>
<td>0 atm</td>
<td>0 atm</td>
</tr>
<tr>
<td>C</td>
<td>-x</td>
<td>+x</td>
<td>+x</td>
</tr>
<tr>
<td>E</td>
<td>(50-x) atm</td>
<td>x atm</td>
<td>x atm</td>
</tr>
</tbody>
</table>

Setting up the equation, we get: $12 = \frac{x(x)}{(50-x)}$, which, clearing fractions, gives us: $600 - 12x = x^2$. Putting this quadratic in normal form, we get: $x^2 + 12x - 600 = 0$. Solving, we get $x = 19.22, -31.22$. The negative number has no meaning in this context; therefore, the only acceptable value is 19.22. Since butane, ethane, and ethene are all in a 1:1:1 ratio. Therefore, the fraction butane converted $= \frac{19.22}{50} = 0.3844$.

d) The total pressure in the container is the pressure of butane, ethane, and ethene all added together. This is: $[(50 - 19.22) + 19.22 + 19.22] \text{ atm} = 69.22 \text{ atm}$.

2a) We are told that the equilibrium constant at 500 K is 23.6, and at 600 K it is 380; therefore, adding heat shifted the equilibrium to the right. Therefore, we can rewrite the equilibrium as:

$$\text{PCl}_5(\text{g}) + \text{heat} \leftrightarrow \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$$

meaning the reaction is endothermic.

b) (i) Increasing the volume of the vessel should result in a decrease in pressure and therefore will favor the side with more moles of gas, so we should see an increase in the concentrations of products, and a decrease in the concentration of reactants.

(ii) Adding an inert gas to the mixture, assuming (as seems reasonable) that the volume does not change would lead to an increase in the pressure, which would favor the
side of the equilibrium with fewer moles of gas, and result in a **decrease** in products, and an **increase** in reactants.

**iii** Adding a catalyst merely speeds up the attainment of equilibrium but does not affect the position of it, so there should be **no effect** observed on the concentration of reactants or products.

3) Starting with the both the hint (assume all molecules have dimerized and then dissociate) and the I.C.F. method that I proselytize, we get:

\[
(\text{CH}_3\text{CO}_2\text{H})_2 \leftrightarrow 2 \text{CH}_3\text{CO}_2\text{H}
\]

<table>
<thead>
<tr>
<th></th>
<th>(3.75 \times 10^{-3}) atm</th>
<th>0 atm</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>(-x)</td>
<td>+2x</td>
</tr>
<tr>
<td>C</td>
<td>((3.75 \times 10^{-3} - x)) atm</td>
<td>2x atm</td>
</tr>
</tbody>
</table>

\[
K_p = \frac{P(\text{CH}_3\text{CO}_2\text{H})^2}{P((\text{CH}_3\text{CO}_2\text{H})_2)} = \frac{(2x)^2}{(3.75 \times 10^{-3} - x)} = 7.692 \times 10^{-4}
\]

(Remember when you reverse an equilibrium, you take the inverse of the equilibrium constant).

Solving the quadratic which results \((4x^2 + 7.692 \times 10^{-4}x - 2.885 \times 10^{-6} = 0)\), we get, as the only sensible answer, \(x = 7.58 \times 10^{-4}\) atm. and the resultant pressures are:

monomer (= CH\(_3\)CO\(_2\)H) = \(1.52 \times 10^{-3}\) atm and dimer (=\((\text{CH}_3\text{CO}_2\text{H})_2\)) = \(2.99 \times 10^{-3}\) atm.

**b)** Hydrogen-bonding between the acidic groups, to provide some stabilization in the gas phase. The structure would be: (this structure was given on one of the problem sets from last semester!)

![Structure Diagram]

c) As the temperature increases, more energy is being input into the system. Since bond breaking is an endothermic process, adding thermal energy from the system would allow for a great deal of bond breaking. Since the hydrogen bonds can (or will) easily break, the amount of dimer should **decrease**. Another way to look at it is that forming the hydrogen bonds results in the release of some energy; from a LeChatelier principle argument, this is removing some product (heat) and therefore would shift the equilibrium to the **reactant side** (monomer) to ameliorate the affect of this change.
(An alternate argument can be made that increasing the temperature increases the pressure of the gas (assuming constant P, V); if true, this would lead to the prediction that the amount of dimer should increase as that is the side of the reaction with fewer moles of gas. This is a cogent argument, and should be taken seriously. It also, alas, complicates the problem a bit. One could argue both sides and predict no change; I find this last argument to be insubstantial to the question.)

4) We can figure out how many moles of CO\(_2\) we have, and then start our equilibrium work. 79.2 g of CO\(_2\)(s) represents \(\frac{79.2 g}{44.01 g/mol} = 1.80 \text{ moles}\).

a) We are given a gas density of 16.3 g/L at 1000K. We can calculate the density of the gases present under two unique conditions: (1) all CO\(_2\); (2) all CO.

If the gas failed to react at all, we have 79.2 g of CO\(_2\) in 5.00 L, for a density = 15.84 g/L.

If the gas totally went to produces, we would have (3.6 moles)(28 g/mol)/5.00 L for a density= 20.16 g/L.

Our densities given lie between these two values. Letting \(x = \text{fraction CO}_2\), (1-x) = fraction CO, so we can say: 16.3 g/L = (x)15.84 g/L + (1-x)20.16 g/L. Solving, we get \(x = 0.894\) which means that the gas mixture is 89.4% CO\(_2\) and 10.6% CO. This implies that 0.894(79.2 g) = 70.805 g CO\(_2\) remains (which equals 1.609 moles), and 8.395 g has reacted. This last mass of CO\(_2\) corresponds to 0.191 moles CO\(_2\), which gives 0.382 moles CO. We can now get partial pressures, and from that, finally, the K\(_p\). The P\(_{CO2}\) = \(\frac{(1.609)(0.08206)(1000)}{5} = 26.404 \text{ atm}\); the P\(_{CO}\) = \(\frac{(0.382)(0.08206)(1000)}{5} = 6.269 \text{ atm}\).

Finally, K\(_p\) = \(\frac{(P_{CO})^2}{(P_{CO2})^2}\) = \(\frac{(6.269)^2}{(26.404)^2}\) = 1.489 atm.

b) We can use a similar treatment here. Doing so yields a mixture of 75.5% CO\(_2\), 24.5% CO. Doing the same thing as in part (a), we have 59.796 g CO\(_2\) remaining (equaling 1.359 moles) and 24.69 g CO made (equaling 0.882 moles). These mole values yield partial pressures of: P\(_{CO2}\) = 24.534 atm, and P\(_{CO}\) = 15.923 atm, which yields a K\(_p\) = \(\frac{(P_{CO})^2}{(P_{CO2})^2}\) = \(\frac{(15.923)^2}{(24.534)}\) = 10.334 atm.

c) Based on these values for K\(_p\), which increase as temperature increases, I would be prone to say that the reaction is endothermic. More products are produced at higher temperature, which means we can write the reaction as:

\[
\text{CO}_2(g) + C(s) + \text{heat} \leftrightarrow 2\text{CO}_2(g)
\]

(This worked out to be a fairly tough problem!)
5) An exothermic reaction implies that $E_a(\text{forward}) < E_a(\text{reverse})$. (Think about the reaction coordinate.) Symbolically, this can be written: $E_{a,f} < E_{a,r}$. We can also say $k_f = Ae^{-E_{a,f}/RT}$, and $k_r = Ae^{-E_{a,r}/RT}$. Setting up our equilibrium constant in terms of these rate constants, we obtain: $K = \frac{k_f}{k_r} = \frac{A_f e^{-E_{a,f}/RT}}{A_r e^{-E_{a,r}/RT}}$. This last term can be rewritten as: $\frac{A_f}{A_r} e^{(E_{a,r} - E_{a,f})/RT}$.

Since $E_{a,r} > E_{a,f}$, their difference $(E_{a,r} - E_{a,f}) > 0$. Finally we can say that as $T$ gets larger, the fraction $\frac{(E_{a,r} - E_{a,f})}{RT}$ gets smaller, and the exponential term also gets smaller. Thus, $K_c$ decreases in this case.