1. If \( x \) mol of ammonium carbamate decomposes, it will produce \( 2x \) mol of \( \text{NH}_3(\text{g}) \) and \( x \) mol of \( \text{CO}_2(\text{g}) \). As ammonium carbamate is a solid, it does not appear in the expression for \( K_c \). Therefore:

\[
K_c = [\text{NH}_3(\text{g})]^2[\text{CO}_2(\text{g})] = (2x)^2(x) = 4x^3 = 1.58 \times 10^{-8}
\]

Hence, \( x = 0.00158 \) M or

\[
[\text{NH}_3(\text{g})] = 2 \times 0.00158 \text{ M} = 0.00316 \text{ M} \text{ and } [\text{CO}_2(\text{g})] = 0.00158 \text{ M}.
\]

For each component, \( P = \frac{nRT}{V} = cRT \) so

\[
P_{\text{total}} = (0.00316 \times 10^3 \text{ mol m}^{-3}) \times RT + (0.00158 \times 10^3 \text{ mol m}^{-3}) \times RT
\]

\[
= ((0.00316 + 0.00158) \times 10^3 \text{ mol m}^{-3}) \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times (250+273) \text{ K})
\]

\[
= 2.06 \times 10^4 \text{ Pa} = 0.203 \text{ atm}
\]

2. (a) For the reaction required,

\[
\text{H}_2\text{O}(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightleftharpoons \text{H}_2\text{O}_2(\text{g})
\]

\( K_p \) is given by the expression,

\[
K_p = \frac{\left(\frac{p_{\text{H}_2\text{O}_2}}{p^0}\right)}{\left(\frac{p_{\text{H}_2}}{p^0}\right)\cdot\left(\frac{p_{\text{O}_2}}{p^0}\right)^{\frac{1}{2}}}
\]

For the two reactions given, \( K_p \) is related to the partial pressures by:

\[
\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons \text{H}_2\text{O}_2(\text{g}) \quad K_p(1) = \frac{\left(\frac{p_{\text{H}_2\text{O}_2}}{p^0}\right)}{\left(\frac{p_{\text{H}_2}}{p^0}\right)\cdot\left(\frac{p_{\text{O}_2}}{p^0}\right)^{\frac{1}{2}}}
\]

\[
2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{H}_2\text{O}(\text{g}) \quad K_p(2) = \frac{\left(\frac{p_{\text{H}_2\text{O}}}{p^0}\right)^2}{\left(\frac{p_{\text{H}_2}}{p^0}\right)^2\cdot\left(\frac{p_{\text{O}_2}}{p^0}\right)}
\]

To derive the expression above for \( K_p \) we need \( p_{\text{H}_2\text{O}_2} \) in the numerator. Therefore, take \( K_p(1) \) as it stands.

We need \( p_{\text{H}_2\text{O}} \) in the denominator. Therefore, take \( 1/\sqrt{K_p(2)} \).

Multiplying the two together:

\[
K_p(1) \times \frac{1}{\sqrt{K_p(2)}} = \frac{\left(\frac{p_{\text{H}_2\text{O}_2}}{p^0}\right)}{\left(\frac{p_{\text{H}_2}}{p^0}\right)\cdot\left(\frac{p_{\text{O}_2}}{p^0}\right)^{\frac{1}{2}}} \cdot \frac{\left(\frac{p_{\text{H}_2\text{O}}}{p^0}\right)^2}{\left(\frac{p_{\text{H}_2}}{p^0}\right)^2\cdot\left(\frac{p_{\text{O}_2}}{p^0}\right)} = \frac{\left(\frac{p_{\text{H}_2\text{O}_2}}{p^0}\right)}{\left(\frac{p_{\text{H}_2\text{O}}}{p^0}\right)\cdot\left(\frac{p_{\text{O}_2}}{p^0}\right)^{\frac{1}{2}}}
\]

This is the relationship required (see above).
Thus, $K_p = 2.3 \times 10^6/\sqrt{1.8 \times 10^{37}} = 5.4 \times 10^{-13}$.

Alternatively, the relationship between $K_p$, $K_p(1)$ and $K_p(2)$ can be derived by rearranging the reactions themselves, rather than the equilibrium expressions:

\[
\begin{align*}
(1) & \quad \text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons \text{H}_2\text{O}_2(\text{g}) & K_p(1) \\
- \frac{1}{2} \times (2) & \quad \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) & \frac{1}{\sqrt{K_p(2)}} \\
(1) - \frac{1}{2} \times (2) & \quad \text{H}_2\text{O}(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightleftharpoons \text{H}_2\text{O}_2(\text{g})
\end{align*}
\]

Hence, $K_p = K_p(1) \times \left(\frac{1}{\sqrt{K_p(2)}}\right) = (2.3 \times 10^6) \times \left(\frac{1}{\sqrt{1.8 \times 10^{37}}}\right) = 5.4 \times 10^{-13}$

Using $\Delta G^\circ = -RT\ln K_p$, at 600 K:

$\Delta G^\circ = -(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (600 \text{ K}) \times \ln(5.4 \times 10^{-13})$

$= +140000 \text{ J mol}^{-1} = 140 \text{ kJ mol}^{-1}$

As $K_p$ is very small, $\Delta G^\circ$ is positive and the reaction favours the reactants.

(b) The reaction involves $(1 + \frac{1}{2}) \text{ mol of gas reacting to give 1 mol of gas,}$ a change, $\Delta n$, of $-\frac{1}{2} \text{ mol}$. As $K_p = K_c \left(\frac{RT}{p^n}\right)^{\Delta n}$,

$K_c(1 \text{ mol m}^{-3}) = \frac{K_p}{(RT/p^n)^{\Delta n}} = \frac{(5.4 \times 10^{-13})}{\left((8.314 \times 600)/1 \times 10^5\right)^{1/2}} = 1.21 \times 10^{-13}$

This value of $K_c$ is based on a standard state of 1 mol m$^{-3}$. To convert $K_c$ based on the more usual standard standard concentration of 1 mol L$^{-1}$ requires a division by $(1000)^{\Delta n}$:

$K_c (1 \text{ mol L}^{-1}) = K_c (1 \text{ mol m}^{-3})/(1000)^{\Delta n}$

$= 1.21 \times 10^{-13} / (1000)^{-1/2}$

$= 3.8 \times 10^{-12}$

(c) As $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$, at $T = 600 \text{ K}$:

$\Delta H^\circ = \Delta G^\circ + T\Delta S^\circ = (140000 \text{ J mol}^{-1}) + (600 \text{ K}) \times (60 \text{ J K}^{-1} \text{ mol}^{-1})$

$= 176000 \text{ J mol}^{-1} = 176 \text{ kJ mol}^{-1}$.

(d) (i) If the volume of the container is decreased, the pressure will rise and the equilibrium amounts of reactant and product will change to reduce this pressure increase. As the reactants occupy a larger
volume than the product, the concentration of product will increase.

$[\text{H}_2\text{O}_2]$ increases.

(ii) As $\Delta H^\circ = +176 \text{ kJ mol}^{-1}$, the forward reaction is endothermic (and the backward reaction is exothermic). If the temperature is increased, the endothermic reaction, which acts to decrease the heat, is favoured. The concentration of product will again increase.

$[\text{H}_2\text{O}_2]$ increases.

(iii) A catalyst has no effect on the equilibrium so the equilibrium concentration of product will not change. This equilibrium concentration is achieved in less time, though.

$[\text{H}_2\text{O}_2]_{\text{equilibrium}}$ is unchanged.

3. (a) The molar mass of PCl$_5$ is $(30.97 \text{ (P)} + 5 \times 35.45 \text{ (Cl) g mol}^{-1}) = 208.22 \text{ g mol}^{-1}$. The number of moles of PCl$_5$ present before it dissociates is therefore:

$$\text{number of moles} = n = \frac{\text{mass}}{\text{molar mass}} = \frac{2.450 \text{ g}}{208.22 \text{ g mol}^{-1}} = 0.01177 \text{ mol}$$

Using the ideal gas law, $PV = nRT$, this amount will give rise to a pressure of:

$$P = \frac{nRT}{V} = \frac{(0.01177 \text{ mol}) \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (600 \text{ K})}{(500 \times 10^{-6} \text{ m}^3)} = 1.174 \times 10^5 \text{ Pa} = 1.159 \text{ atm}$$

(b) For the reaction $\text{PCl}_5(g) \rightleftharpoons \text{PCl}_3(g) + \text{Cl}_2(g)$, the reaction table is:

<table>
<thead>
<tr>
<th></th>
<th>PCl$_5$(g)</th>
<th>$\rightleftharpoons$</th>
<th>PCl$_3$(g)</th>
<th>Cl$_2$(g),</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_{\text{initial}}$</td>
<td>1.159</td>
<td></td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>change</td>
<td>-x</td>
<td>+x</td>
<td>+x</td>
<td></td>
</tr>
<tr>
<td>$P_{\text{equilibrium}}$</td>
<td>1.159-x</td>
<td>x</td>
<td>x</td>
<td></td>
</tr>
</tbody>
</table>

The equilibrium constant, in terms of partial pressures, $K_p$ is therefore:

$$K_p = \frac{(P_{\text{PCl}_3} / P^*) (P_{\text{Cl}_2} / P^*)}{(P_{\text{PCl}_5} / P^*)} = \frac{(x)(x)}{(1.159-x)} = \frac{x^2}{(1.159-x)} = 11.5$$

Rearranging this gives,

$$x^2 + 11.5x - (11.5 \times 1.159) = 0$$
Hence, \( a = 1, b = 11.5 \) and \( c = -13.33 \) and so:

\[
x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-11.5 \pm \sqrt{(11.5)^2 - 4 \times 1 \times (-13.33)}}{2} = \frac{-11.5 \pm \sqrt{185.6}}{2}
\]

\[
x = 1.061 \text{ atm} \quad \text{(only the positive root makes physical sense)}
\]

Hence, \( P_{\text{PCI}_3} = (1.159 - x) \text{ atm} = (1.159 - 1.061) \text{ atm} = 0.098 \text{ atm} \)

Note that as \( K_p \) is not very small, \( 1.159 - x \neq 1.159 \) and the quadratic formula needs to be used.

(c) The total pressure in the bulb at equilibrium is the sum of the partial pressures of \( \text{PCl}_5(g) \), \( \text{PCl}_3(g) \) and \( \text{Cl}_2(g) \):

\[
P_{\text{PCI}_3} = 0.098 \text{ atm}
\]

\[
P_{\text{PCI}_3} = P_{\text{Cl}_2} = x = 1.061 \text{ atm}
\]

\[
P_{\text{total}} = P_{\text{PCI}_3} + P_{\text{PCI}_3} + P_{\text{Cl}_2} = (0.098 + 1.061 + 1.061) \text{ atm} = 2.220 \text{ atm}
\]

(d) At equilibrium, \( P_{\text{PCI}_3} = 0.098 \text{ atm} \). Using the ideal gas law, \( PV = nRT \), this corresponds to:

\[
n = \frac{PV}{RT} = \frac{(0.098 \times 1.013 \times 10^5 \text{ Pa}) \times (500 \times 10^{-3} \text{ m}^3)}{(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (600 \text{ K})} = 10.0 \times 10^{-4} \text{ mol}
\]

As \( 0.01177 \text{ mol} \) \( \text{PCl}_5(g) \) were initially present, the amount that has dissociated is \( (0.01177 - 10.0 \times 10^{-4}) \text{ mol} = 0.01077 \text{ mol} \)

The degree of dissociation is therefore:

\[
\frac{\text{amount dissociated}}{\text{initial amount}} \times 100\% = \frac{0.01077}{0.01177} \times 100\% = 92\%
\]