1. **If x mol of ammonium carbamate decomposes, it will produce $2x$ mol of $NH_3(g)$ and x mol of $CO_2(g)$. As ammonium carbamate is a solid, it does not appear in the expression for K_c. Therefore:**

$$K_c = [NH_3(g)]^2[CO_2(g)] = (2x)^2(x) = 4x^3 = 1.58 \times 10^{-8}$$

Hence, $x = 0.00158$ M or

$$[NH_3(g)] = 2 \times 0.00158 \text{ M} = 0.00316 \text{ M and } [CO_2(g)] = 0.00158 \text{ M}.$$

For each component, $P = \dfrac{nRT}{V} = cRT$ so

$$
\begin{aligned}
P_{total} &= (0.00316 \times 10^3 \text{ mol m}^{-3}) \times RT + (0.00158 \times 10^3 \text{ mol m}^{-3}) \times RT \\
&= ((0.00316 + 0.00158) \times 10^3 \text{ mol m}^{-3}) \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times ((250+273) \text{ K}) \\
&= 2.06 \times 104 \text{ Pa} = 0.203 \text{ atm}
\end{aligned}
$$

2. (a) **For the reaction required,**
    $$H_2O(g) + \tfrac{1}{2}O_2(g) \rightleftharpoons H_2O_2(g)$$
    K_p is given by the expression,

    $$K_p = \frac{\left(p_{H2O2}/p^0\right)}{\left(p_{H2O}/p^0\right)\cdot\left(p_{O2}/p^0\right)^{1/2}}$$

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

    $$H_2(g) + O_2(g) \rightleftharpoons H_2O_2(g) \qquad K_p(1) = \frac{\left(p_{H2O2}/p^0\right)}{\left(p_{H2}/p^0\right)\cdot\left(p_{O2}/p^0\right)}$$

    $$2H_2(g) + O_2(g) \rightleftharpoons 2H_2O(g) \qquad K_p(2) = \frac{\left(p_{H2O}/p^0\right)^2}{\left(p_{H2}/p^0\right)^2 \cdot\left(p_{O2}/p^0\right)}$$

    To derive the expression above for K_p we need p_{H2O2} in the numerator. Therefore, take $K_p(1)$ as it stands.
    We need p_{H2O} in the denominator. Therefore, take $1/\sqrt{K_p(2)}$.
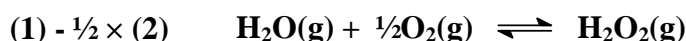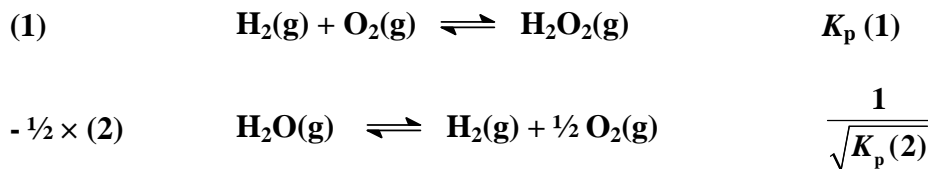   **Multiplying the two together:**

    $$
    \begin{aligned}
    K_p(1) \times \frac{1}{\sqrt{K_p(2)}} &= \frac{\left(p_{H2O2}/p^0\right)}{\left(p_{H2}/p^0\right)\cdot\left(p_{O2}/p^0\right)} \cdot \frac{\left(p_{H2}/p^0\right)\cdot\left(p_{O2}/p^0\right)^{1/2}}{\left(p_{H2O}/p^0\right)} \\
    &= \frac{\left(p_{H2O2}/p^0\right)}{\left(p_{H2O}/p^0\right)\cdot\left(p_{O2}/p^0\right)^{1/2}}
    \end{aligned}
    $$

    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:

(1)	$H_2(g) + O_2(g) \rightleftharpoons H_2O_2(g)$	K_p (1)
- ½ × (2)	$H_2O(g) \rightleftharpoons H_2(g) + \frac{1}{2} O_2(g)$	$\dfrac{1}{\sqrt{K_p(2)}}$
(1) - ½ × (2)	$H_2O(g) + \frac{1}{2}O_2(g) \rightleftharpoons H_2O_2(g)$	

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

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

$$\Delta G° = - (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (600 \text{ K}) \times \ln(5.4 \times 10^{-13})$$
$$= +140000 \text{ J mol}^{-1} = 140 \text{ kJ mol}^{-1}$$

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

(b) The reaction involves (1 + ½) mol of gas reacting to give 1 mol of gas., a change, Δn, of -½ mol. As $K_p = K_c (RT/p^o)^{\Delta n}$,

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

This value iof K_c is based on a standard state of 1 mol m^{-3}. To convert to Kc 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 $\Delta G° = \Delta H° - T\Delta S°$, at $T = 600$ K:

$$\Delta H° = \Delta G° + T\Delta S° = (140000 \text{ J mol}^{-1}) + (600 \text{ K}) \times (60 \text{ J K}^{-1} \text{ mol}^{-1})$$
$$= 176000 \text{ J mol}^{-1} = +176 \text{ kJ mol}^{-1}.$$

(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.

[H_2O_2] increases.

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

[H_2O_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.

[H_2O_2]$_{equilibrium}$ is unchanged.

3.   (a)   The molar mass of PCl$_5$ is (30.97 (P) + 5 × 35.45 (Cl) g mol^{-1}) = 208.22 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:

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

$$= 1.174 \times 10^5\,\text{Pa}$$

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

	PCl$_5$(g)	$\rightleftharpoons$	PCl$_3$(g)	Cl$_2$(g),
$P_{initial}$	1.174×10^5		0	0
change	-x		+x	+x
$P_{equilibrium}$	1.174×10^5 -x		x	x

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

$$K_p = \frac{(P_{PCl_3}/p^o)(P_{Cl_2}/p^o)}{(P_{PCl_5}/p^o)} = \frac{(x)(x)}{(1.174 \times 10^5 - x)} \cdot \frac{1}{p^o} = \frac{x^2}{(1.174 \times 10^5 - x)} \cdot \frac{1}{p^o} = 11.5$$

Substituting 1×10^5 Pa for p^0 and rearranging gives,

$$x^2 + (11.5 \times 10^5)x - (11.5 \times 10^5 \times 1.174 \times 10^5) = 0$$

Hence, $a = 1$, $b = 11.5 \times 10^5$ and $c = -1.35 \times 10^{11}$ and so:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-11.5 \times 10^5 \pm \sqrt{(11.5 \times 10^5)^2 - (4 \times 1 \times -1.35 \times 10^{11})}}{2} = \frac{-11.5 \times 10^5 \pm \sqrt{1.86 \times 10^{12}}}{2}$$

$x = 1.074 \times 10^5$ Pa   (only the positive root makes physical sense)

Hence, $P_{PCl_5} = (1.174 \times 10^5 - x)$ Pa $= (1.174 \times 10^5 - 1.074 \times 10^5)$ Pa $= 1.003 \times 10^4$ Pa

Note that as K_p is *not* very small, $1.174 \times 10^5 - x \neq 1.174 \times 10^5$ 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 $PCl_5(g)$, $PCl_3(g)$ and $Cl_2(g)$:

$P_{PCl_5} = 1.003 \times 10^4$ Pa

$P_{PCl_3} = P_{Cl_2} = x = 1.074 \times 10^5$ Pa

$P_{total} = P_{PCl_5} + P_{PCl_3} + P_{Cl_2} = (1.003 \times 10^4 + 1.074 \times 10^5 + 1.074 \times 10^5)$ Pa
$= 2.248 \times 10^5$ Pa

(d)   At equilibrium, $P_{PCl_5} = 1.003 \times 10^5$ Pa. Using the ideal gas law, $PV = nRT$, this corresponds to:

$$n = \frac{PV}{RT} = \frac{(1.003 \times 10^5 \, \text{Pa}) \times (500 \times 10^{-6} \, \text{m}^3)}{(8.314 \, \text{J K}^{-1} \, \text{mol}^{-1}) \times (600 \, \text{K})} = 1.005 \times 10^{-3} \, \text{mol}$$

As 0.01177 mol $PCl_5(g)$ were initially present, the amount that has dissociated is $(0.01177 - 1.005 \times 10^{-3})$ mol $= 0.01076$ mol

The degree of dissociation is therefore:

$$\frac{\text{amount dissociated}}{\text{initial amount}} \times 100\% = \frac{0.01076}{0.01177} \times 100\% = 91\%$$