1. Oxygen has an oxidation number of -2 so the oxidation number of N can be found so that the molecules are neutral. Molecules with odd numbers of electrons must have unpaired electrons and so are paramagnetic.

(b) NO
N II (+2)
Odd number of electrons \(\rightarrow\) paramagnetic

(c) \(\text{N}_2\text{O}\)
N I (+1)
Even number of electrons.

(d) \(\text{NO}_2\)
N IV (+4)
Odd number of electrons \(\rightarrow\) paramagnetic

(e) \(\text{N}_2\text{O}_4\)
N IV (+4)
Even number of electrons.

2. RDX \((\text{C}_3\text{H}_6\text{N}_6\text{O}_6)\) is a powerful explosive.

(a) \(2\text{C}_3\text{H}_6\text{N}_6\text{O}_6(\text{s}) + 3\text{O}_2(\text{g}) \rightarrow 6\text{CO}_2(\text{g}) + 6\text{H}_2\text{O}(\text{g}) + 6\text{N}_2(\text{g})\)

(b) In the explosive decomposition, it is unlikely that sufficient \(\text{O}_2(\text{g})\) will be available in the timescale of the reaction so that all of the oxygen available is that which is present in RDX. With less oxygen available, it is likely that \(\text{CO}\) rather than \(\text{CO}_2\) will be produced:

\(\text{C}_3\text{H}_6\text{N}_6\text{O}_6(\text{s}) \rightarrow 3\text{CO}(\text{g}) + 3\text{H}_2\text{O}(\text{g}) + 3\text{N}_2(\text{g})\)

(c) A solid reacts to form lots of gaseous molecules resulting in a large volume change and hence \(P\Delta V\) work. The reaction is highly exothermic as the products are very stable so considerable heat is generated. This heat also ensures that the volume of the gas is large (Charles’ Law)

(b) Using \(\Delta H^o = \Sigma m\Delta f H^o(\text{products}) - \Sigma n\Delta f H^o(\text{reactants})\)

For the complete combustion reaction as written:

\[
\Delta H^o = [6\times \Delta f H^o(\text{CO}_2) + 6\times \Delta f H^o(\text{H}_2\text{O})] - [2\times \Delta f H^o(\text{RDX})]
\]

\[
= [6\times -394 + 6\times -242] \text{kJ mol}^{-1} - [2\times +65] \text{kJ mol}^{-1} = -3946 \text{kJ mol}^{-1}
\]

As this is for the combustion of two moles of RDX,

\[
\Delta_{\text{comb}} H^o = -1970 \text{ kJ mol}^{-1}
\]

Molar mass = \((3\times 12.01 \text{ (C)} + 6\times 1.008 \text{ (H)} + 6\times 14.01 \text{ (N)} + 6\times 16.00 \text{ (O)}) \text{ g mol}^{-1}
\]

\[
= 222.138 \text{ g mol}^{-1}
\]

So,

\[
\Delta_{\text{comb}} H = -1970 \text{ kJ mol}^{-1} \text{ or } \frac{-1970 \text{ kJ mol}^{-1}}{222.138 \text{ g mol}^{-1}} = -8.88 \text{ kJ g}^{-1}
\]

Hence 100 g will generate \(100 \times 8.88 = 888 \text{ kJ}\).
3. (a) \[ \Delta r G^\circ = \Delta_r H^\circ - T \Delta r S^\circ = (-55.3 \times 10^3 \text{ kJ mol}^{-1}) - (298 \text{ K} \times -175.8 \text{ J K}^{-1} \text{ mol}^{-1}) \\
= -2912 \text{ J mol}^{-1} = -2.91 \text{ kJ mol}^{-1} \]

As \( \Delta r G^\circ = -RT \ln K_p \),

\[
\ln K_p = \frac{-\Delta r G^\circ}{RT} = \frac{-2912 \text{ J mol}^{-1}}{(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})} \quad \text{so} \quad K_p = 3.24
\]

Note that as SI units are used for energy, the gas constant is also used in SI units.

(b) \( \Delta r G^\circ = \Delta_r H^\circ - T \Delta r S^\circ \) and \( \Delta_r H^\circ \) and \( \Delta r S^\circ \) are both negative. As the temperature increases, the \( - T \Delta r S^\circ \) term will grow more and more positive and so \( \Delta r G^\circ \) will increase: become less negative and eventually positive. Hence \( K_p \) will decrease as the temperature increase.

The equilibrium constant varies with temperature but not with pressure.

(c) (i) As the reaction is exothermic, Le Chatelier’s principle predicts that increasing the temperature will reduce the amount of product \((\text{N}_2\text{O}_4)\) and increase the amount of reactant \((\text{NO}_2)\) present at equilibrium.

(ii) As the reaction leads to a decrease in the number of moles of gas, it will also lead to a decrease in the volume. Le Chatelier’s principle predicts that increasing the pressure will favour product formation.

4. (a) \( K_c = \frac{[C]^3}{[A][B]} \)

(b) \( K_c = \frac{[C]^3}{[A]^2[B]} \)

(c) \( K_c = \frac{[C]^3}{[A]^2} \)

(d) \( K_c = \frac{1}{[A]^2[B]} \)

(e) \( K_c = \frac{1}{[A]^2} \)

5. The equilibrium is:

\[ \text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g}) \]

(i) The initial concentration of \text{PCl}_5(\text{g}) is \( \frac{\text{moles}}{\text{volume}} = \frac{2.00 \text{ mol}}{2.00 \text{ L}} = 1.00 \text{ M} \)

(ii) The reaction table is:

<table>
<thead>
<tr>
<th></th>
<th>\text{PCl}_5(\text{g})</th>
<th>\rightleftharpoons</th>
<th>\text{PCl}_3(\text{g})</th>
<th>+</th>
<th>\text{Cl}_2(\text{g})</th>
</tr>
</thead>
<tbody>
<tr>
<td>initial</td>
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<td>0</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>change</td>
<td>-x</td>
<td>+x</td>
<td>+x</td>
<td></td>
<td></td>
</tr>
<tr>
<td>equilibrium</td>
<td>1.00-x</td>
<td>x</td>
<td>x</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(iii) \( K = 1.00 \times 10^{-3} = \frac{[\text{PCl}_3(\text{g})][\text{Cl}_2(\text{g})]}{[\text{PCl}_5(\text{g})]} = \frac{x^2}{(1.00-x)} \)
As $K$ is small, the amount of PCl$_5$ that dissociates is also small. Hence, $1.00 - x \approx 1.00$. This approximation is useful as it means that solving the quadratic equation is unnecessary.

Using this approximation,

$$x^2 = (1.00 \times 10^{-3}) \times 1.00$$

$$x = 0.032.$$  

Hence,

$$[\text{PCl}_5(g)] = (1.00 - 0.032) \ M = 0.97 \ M,$$
$$[\text{PCl}_3(g)] = [\text{Cl}_2(g)] = 0.032 \ M$$

The assumption that $x$ is negligible compared to the amount of PCl$_5$ can be checked using the “5% rule”: if the assumption results in a change in concentration that is less than 5%, it is justified. The change in concentration is found to be 0.032 M so the percentage change compared to the initial concentration of 1.00 M is:

$$\text{percent change} = \frac{0.032}{1.00} \times 100 = 3.2\%$$

(The answer obtained using the quadratic formula is $x = 0.032$).

6. (a) C(graphite) + $\frac{1}{2}$ O$_2$(g) $\rightarrow$ CO (g)
Sn(s) + O$_2$(g) $\rightarrow$ SnO$_2$(s)

(b) The Ellingham diagram is shown below. The cross-over point is at about 600 K. This is the point where the reaction starts to favour products over reactants.

7. If the equilibrium partial pressure of N$_2$ is $x$, then the equilibrium partial pressure of H$_2$ is 3$x$, as the stoichiometric ratio of N$_2$ : H$_2$ is employed. With the equilibrium partial pressure of NH$_3$ being 50 atm. the equilibrium constant is:
\[ K_p = \frac{(p_{\text{NH}_3})^2}{(p_{\text{N}_2})(p_{\text{H}_2})^3} = \frac{(50)^2}{(x)(3x)^3} = \frac{(50)^2}{27x^4} = 1.00 \times 10^{-4} \] so \( x = 31 \) atm.

The equilibrium partial pressures are therefore:

\[ p_{\text{N}_2} = 31 \text{ atm}, \quad p_{\text{H}_2} = 3 \times 31 = 93 \text{ atm} \] and \( p_{\text{NH}_3} = 50 \) atm.

The total pressure is \((31 + 93 + 50) \text{ atm} = 174 \) atm.