• Consider the values of the electronic energy levels of an He atom. State which interactions would be expected to increase the energies of the electrons and which would decrease them.

There are 3 electrostatic interactions:

- Interaction between one electron and the 2 protons in the nucleus. This is attractive and lowers the energy of the electron.
- Interaction between the second electron and the 2 protons in the nucleus. This is attractive and lowers the energy of the electron.
- Interaction between the 2 electrons. This is repulsive and increases the energy of the electrons.

• Radon gas decays into polonium with a half-life of 3.82 days via the following mechanism:

\[
_{86}^{222}\text{Rn} \rightarrow _{84}^{218}\text{Po} + _2^4\text{He}
\]

Give three reasons why \(_{86}^{222}\text{Rn}\) is biologically a very harmful nuclide.

The half-life is relatively short and therefore it is highly radioactive.

The radioactive element is a gas and can therefore easily be inhaled into the lungs.

It produces alpha particles which are ionizing. They are stopped by tissue and do not escape the body: they do internal damage, especially to the lungs.
• Sketch the wavefunction of the 3s atomic orbital as described below. Clearly mark all nodes and the relative sign (+ or –) of the wavefunction.

a) using lobe representations

![Diagram showing spherical nodes and nucleus]

b) by plotting wavefunction versus distance from the nucleus

![Graph showing wavefunction ψ versus distance r]

Explain the significance of (a) the lobes, (b) the nodes and (c) the sign of the wavefunction, in terms of the probability of finding an electron at a given point in space relative to the nucleus.

The lobes define the volume within which there is a certain probability of finding the electron (usually 95%).

The nodes represent surfaces where there is zero probability of finding the electron.

The sign of the wavefunction is not relevant to the probability of finding the electron. The probability distribution depends on the square of the wavefunction, which is always positive.
The alkali hydrides are compounds of Group 1 metals with hydrogen in a 1:1 stoichiometry. Selected properties of the elements that make up these compounds are given in the following table.

<table>
<thead>
<tr>
<th>Element</th>
<th>First Ionisation Energy (kJ mol⁻¹)</th>
<th>Electron Affinity (kJ mol⁻¹)</th>
<th>Electronegativity (scale 0-4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>1314</td>
<td>−79</td>
<td>2.20</td>
</tr>
<tr>
<td>Li</td>
<td>526</td>
<td>−66</td>
<td>0.98</td>
</tr>
<tr>
<td>Na</td>
<td>502</td>
<td>−59</td>
<td>0.93</td>
</tr>
<tr>
<td>K</td>
<td>425</td>
<td>−55</td>
<td>0.82</td>
</tr>
<tr>
<td>Rb</td>
<td>409</td>
<td>−53</td>
<td>0.82</td>
</tr>
<tr>
<td>Cs</td>
<td>382</td>
<td>−52</td>
<td>0.79</td>
</tr>
</tbody>
</table>

Is CsH more or less ionic than LiH? Justify your answer with calculations of their partial ionic character.

**CsH is more ionic.**

The difference in electronegativity (ΔEN) of two elements is an indication of the polarity of the bond between them. The maximum possible value for ΔEN is 4 as the electronegativity scale goes from 0-4. The partial ionic character is given as:

\[ \text{partial ionic character} = \frac{\Delta \text{EN}}{4} \]

For CsH,

\[ \text{partial ionic character} = \left(2.20 - 0.79\right)/4 = 0.4 \]

For LiH,

\[ \text{partial ionic character} = \left(2.20 - 0.98\right)/4 = 0.3 \]

This predicts as Cs-H bond is 40% ionic whilst as Li-H bond is 30% ionic.

Explain the trend in the first ionisation energy of these elements.

The first ionisation energy is the energy needed to remove the single electron in the outermost occupied s orbital.

As you go down the group, the principal quantum number increases and the distance between the nucleus and the orbital increases. The coulombic attraction between nucleus and electron therefore decreases and less energy is required to remove the electron.
- In terms of their electronic origins, briefly explain the concept of allotropes. Use two of the allotropes of carbon as examples.

Allotropes are different molecular forms of the same element arising from the differences in bonding between the atoms.

For carbon, the stable allotropes are diamond, graphite and fullerenes such as $C_{60}$. The electronic bonding in diamond consists of 4 $\sigma$-bonds on each atom oriented tetrahedrally to give an “infinite” covalent, three-dimensional network.

In graphite there are 3 $\sigma$-bonds in a trigonal planar arrangement to give a flat sheet of $C_6$ hexagons. The extra electrons occupy delocalised $\pi$-orbitals above and below the planes.

The bonding in fullerenes is similar to that in graphite. The atoms occur in $C_6$ hexagons and $C_5$ pentagons. This causes “puckering” of the sheets and leads to nearly spherical “balls” such as $C_{60}$.

The ability of carbon to form these allotropes are a reflection of its ability to form both $\sigma$ and $\pi$ bonds which are similar in strength. The $\pi$ bonds between silicon atoms, for example, are much weaker than the $\sigma$-bonds so that it only forms a diamond-like structure.

- Describe the nature of an ionic bond in terms of atomic and molecular orbitals.

When a covalent bond is formed between two elements of identical electronegativity, bonding and antibonding orbitals are formed which have equal contributions from both atoms. The covalent bonding arises from the increase in electron density between the two atoms.

As the electronegativity difference increases, the bonding orbital has a greater contribution from the more electronegative element. As a result the electron density is larger at the more electronegative element and the electron density between the two atoms is decreased. This decreases the covalent contribution to the bond.

However, the uneven sharing of the electron density leads to a build up of negative charge on the more electronegative atom and a build up of positive charge on the less electronegative atom. As a result, there is an electrostatic attraction between the atoms: an ionic contribution to the bond.

In the hypothetical case where the electronegativity difference is infinite, the ‘bonding’ orbital becomes the atomic orbital of the more electronegative atom. The electrons in the orbital are both located on this atom, giving it a full anionic charge. The other atom then has a full cationic charge. A fully ionic bond results.
• In order to predict if it is possible to form the He$_2^+$ cation, complete the following steps.

In the boxes below, draw an energy level diagram showing labelled electron orbitals and their occupancies for the two reacting species, He and He$^+$.

In the other box below, draw an energy level diagram showing labelled electron orbitals and their occupancies in a postulated He$_2^+$ molecule. Use the same energy scale.

Draw the lobe representation of the two occupied molecular orbitals in this molecule. Show all nuclei and nodal surfaces.

What is the bond order of this molecular ion?

It has 2 bonding ($\sigma$) and 1 antibonding ($\sigma^*$) electron. Hence:

\[
\text{bond order} = \frac{1}{2} (\text{number of bonding} - \text{number of antibonding electrons}) \\
= \frac{1}{2} (2 - 1) = \frac{1}{2}
\]

Make a prediction about the stability of He$_2^+$ in comparison to the H$_2$ molecule.

H$_2$ has a bond order of 1 and He$_2^+$ has a bond order of $\frac{1}{2}$ so the bond in H$_2$ is probably stronger.

As the nuclear charge in He is larger than H, the bonding orbital is more stable in He$_2^+$ than the bonding orbital in H$_2$ so the $\frac{1}{2}$ bond in He$_2^+$ is likely to be more than half as strong as the single bond in H$_2$. 
• Consider the process of electron capture by the manganese-54 isotope. Write a balanced nuclear formula.

In electron capture, a proton in the nucleus captures a core electron and is converted into a neutron. The atomic mass does not change but the atomic number decreases by 1:

\[
\frac{54}{25}\text{Mn} + \frac{0}{-1}\text{e} \rightarrow \frac{54}{24}\text{Cr}
\]

Explain why the wavelengths of the emitted X-rays after this process are identical to those of the peak X-ray fluorescence emissions obtained during bombardment of Cr by high energy electrons.

The newly formed \( ^{54}_{24}\text{Cr} \) has an electron missing (captured in the decay process) from its core orbitals.

Other electrons fall from higher energy orbitals emitting wavelengths characteristic of the differences in energy levels. The same transitions are observed during the electron bombardment of any Cr atom because all Cr atoms have the same energy levels and the bombardment is exciting or ejecting core electrons.
- Draw a plausible Lewis structures for isocyanic acid, HNCO.

\[
\begin{array}{c}
\text{H} \equiv \text{N} \equiv \text{C} = \text{O} \\
\end{array}
\]

<table>
<thead>
<tr>
<th>What are the NC and CO bond orders?</th>
<th>NC: 2 (double)</th>
<th>CO: 2 (double)</th>
</tr>
</thead>
<tbody>
<tr>
<td>How many lone pairs are on the nitrogen?</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Using the VSEPR model, what do you predict the H-N-C and N-C-O bond angles to be?</td>
<td>H-N-C: (\approx 120^\circ)</td>
<td>N-C-O: (180^\circ)</td>
</tr>
</tbody>
</table>

Draw two plausible Lewis structures for nitrous oxide, N\(_2\)O. (Connectivity: N–N–O)

\[
\begin{array}{c}
\equiv \text{N} \equiv \text{N} \equiv \text{O} \\
\equiv \text{N} \equiv \text{N} \equiv \text{O} \\
\end{array}
\]

Assuming these two resonance structures contribute equally, what are the NN and NO bond orders?

<table>
<thead>
<tr>
<th>NN: 2.5 (average of 3 (left) and 2 (right))</th>
<th>NO: 1.5 (average of 1 (left) and 2 (right))</th>
</tr>
</thead>
<tbody>
<tr>
<td>How many lone pairs are on the central nitrogen?</td>
<td>None</td>
</tr>
<tr>
<td>Using the VSEPR model, what do you predict the N-N-O bond angle to be?</td>
<td>(180^\circ)</td>
</tr>
</tbody>
</table>

Draw two plausible Lewis structures for the \(\text{N}_2\text{O}^2-\) ion. (Connectivity: N–N–O)

\[
\begin{array}{c}
\equiv \text{N} \equiv \text{N} \equiv \text{O} \\
\equiv \text{N} \equiv \text{N} \equiv \text{O} \\
\end{array}
\]

Assuming these two resonance structures contribute equally, what are the NN and NO bond orders?

<table>
<thead>
<tr>
<th>NN: 1.5 (average of 2 (left) and 1 (right))</th>
<th>NO: 1.5 (average of 1 (left) and 2 (right))</th>
</tr>
</thead>
<tbody>
<tr>
<td>How many lone pairs are on the central nitrogen?</td>
<td>1</td>
</tr>
<tr>
<td>Using the VSEPR model, what do you predict the N-N-O bond angle to be?</td>
<td>(\approx 120^\circ)</td>
</tr>
</tbody>
</table>
Ethane $\text{C}_2\text{H}_6$ can be burnt in the presence of an excess of oxygen to give $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{l})$ or under restricted oxygen conditions to give $\text{CO}(\text{g})$ and $\text{H}_2\text{O}(\text{l})$. A balanced equation for the first process is

$$2\text{C}_2\text{H}_6(\text{g}) + 7\text{O}_2(\text{g}) \rightarrow 4\text{CO}_2(\text{g}) + 6\text{H}_2\text{O}(\text{l}) \quad (A)$$

Write a balanced equation for the combustion under restricted oxygen where $\text{CO}(\text{g})$ rather than $\text{CO}_2(\text{g})$ is produced.

$$2\text{C}_2\text{H}_6(\text{g}) + 5\text{O}_2(\text{g}) \rightarrow 4\text{CO}(\text{g}) + 6\text{H}_2\text{O}(\text{l}) \quad (B)$$

Using the heats of formation, calculate the difference (in kJ per mole of ethane) in heat released by the two different types of combustion of ethane, i.e. combustion with excess $\text{O}_2$ and combustion under restricted $\text{O}_2$ conditions.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\Delta H^\circ$ (kJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_2\text{O}(\text{l})$</td>
<td>$-285.9$</td>
</tr>
<tr>
<td>$\text{C}_2\text{H}_6(\text{g})$</td>
<td>$-84.67$</td>
</tr>
<tr>
<td>$\text{CO}_2(\text{g})$</td>
<td>$-393.5$</td>
</tr>
<tr>
<td>$\text{CO}(\text{g})$</td>
<td>$-110.5$</td>
</tr>
</tbody>
</table>

Using $\Delta_{\text{rxn}}H^\circ = \Sigma n\Delta H^\circ(\text{products}) - \Sigma m\Delta H^\circ(\text{reactants})$, the enthalpy of the combustion of the reaction with excess $\text{O}_2$ is:

$$\Delta H^\circ(A) = (4\Delta H^\circ(\text{CO}_2(\text{g}) + 6\Delta H^\circ(\text{H}_2\text{O}(\text{l}))) - (2\Delta H^\circ(\text{C}_2\text{H}_6(\text{g})))$$

$$= [(4 \times -393.5 + 6 \times -285.9) - (2 \times -84.67)] \text{kJ mol}^{-1} = -3120.1 \text{kJ mol}^{-1}$$

For the reaction in restricted $\text{O}_2$, this becomes:

$$\Delta H^\circ(B) = (4\Delta H^\circ(\text{CO}(\text{g}) + 6\Delta H^\circ(\text{H}_2\text{O}(\text{l}))) - (2\Delta H^\circ(\text{C}_2\text{H}_6(\text{g})))$$

$$= [(4 \times -110.5 + 6 \times -285.9) - (2 \times -84.67)] \text{kJ mol}^{-1} = -1988.1 \text{kJ mol}^{-1}$$

The difference between them is thus $(3120.1 - 1988.1) \text{kJ mol}^{-1} = 1132 \text{kJ mol}^{-1}$.

Both reactions were written for the combustion of two moles of ethane. The difference per mole of ethane is therefore $\frac{1}{2} \times 1132 \text{kJ mol}^{-1} = 566 \text{kJ mol}^{-1}$.

Answer: $566 \text{kJ mol}^{-1}$
Ammonia, \(\text{NH}_3(g)\), has a standard Gibbs free energy of formation equal to \(-16.4\, \text{kJ mol}^{-1}\). Consider the following reaction at 298 K.

\[
\text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g)
\]

In which direction will this reaction proceed if a mixture of gases is made with:
\[P_{\text{NH}_3} = 1.00\, \text{atm} \quad P_{\text{H}_2} = 0.50\, \text{atm} \quad P_{\text{N}_2} = 0.50\, \text{atm}\]

The reaction as written forms 2 moles of \(\text{NH}_3(g)\). The standard Gibbs free energy of the reaction is therefore \((2 \times -16.4\, \text{kJ mol}^{-1}) = -32.8\, \text{kJ mol}^{-1}\).

Using \(\Delta G^\circ = -RT\ln K_p\), the value of \(K_p\) can be determined:

\[
\ln K_p = -\frac{\Delta G^\circ}{RT} = \frac{-32.8 \times 10^3\, \text{J mol}^{-1}}{(8.314\, \text{J K}^{-1}\, \text{mol}^{-1})(298\, \text{K})} = 13.24
\]

\[K_p = 5.62 \times 10^5\]

The direction of the reaction can be determined by calculating the reaction quotient:

\[
Q = \frac{(P_{\text{NH}_3})^2}{(P_{\text{N}_2})(P_{\text{H}_2})^3} = \frac{(1.00)^2}{(0.50)(0.50)^3} = 16
\]

As \(Q < K_p\), the reaction will proceed to the right. This will increase the partial pressure of \(\text{NH}_3(g)\) and decrease the partial pressures of \(\text{N}_2(g)\) and \(\text{H}_2(g)\).

**Answer:** to the right

What pressure of hydrogen gas should be added to a mixture already containing 0.20 atm \(\text{NH}_3\) and 0.50 atm \(\text{N}_2\) so that the amounts of \(\text{NH}_3\) and \(\text{N}_2\) will not change?

If the partial pressures of \(\text{NH}_3(g)\) and \(\text{N}_2(g)\) do not change, these values must be the values at equilibrium. Hence:

\[
K_p = \frac{(P_{\text{NH}_3})^2}{(P_{\text{N}_2})(P_{\text{H}_2})^3} = \frac{(0.20)^2}{(0.50)(0.50)^3} = 5.62 \times 10^5
\]

\[(P_{\text{H}_2})^3 = 1.42 \times 10^{-7}\, \text{atm}^3
\]

\[P_{\text{H}_2} = 5.2 \times 10^{-3}\, \text{atm}\]

**Answer:** \(5.2 \times 10^{-3}\, \text{atm}\)
• Determine the value of the equilibrium constant (at 298 K) for the following reaction.

\[
\text{CO}_2(g) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_2\text{CO}_3(aq)
\]

<table>
<thead>
<tr>
<th>Substance</th>
<th>(\Delta H^\circ) / kJ mol(^{-1})</th>
<th>(S^\circ / J K^{-1} mol^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{H}_2\text{CO}_3(aq))</td>
<td>-700.</td>
<td>187</td>
</tr>
<tr>
<td>(\text{H}_2\text{O}(l))</td>
<td>-286</td>
<td>70.</td>
</tr>
<tr>
<td>(\text{CO}_2(g))</td>
<td>-394</td>
<td>214</td>
</tr>
</tbody>
</table>

Using \(\Delta_{rxn}H^\circ = \Sigma m\Delta H^\circ(\text{products}) - \Sigma n\Delta H^\circ(\text{reactants})\), the enthalpy of this reaction is:

\[
\Delta H^\circ = (\Delta H^\circ(\text{H}_2\text{CO}_3(aq))) - (\Delta H^\circ(\text{CO}_2(g)) + \Delta H^\circ(\text{H}_2\text{O}(l)))
\]

\[
= [(-700.) - (-286 + -394)] \text{kJ mol}^{-1} = -20 \text{kJ mol}^{-1}
\]

Using \(\Delta_{rxn}S^\circ = \Sigma mS^\circ(\text{products}) - \Sigma nS^\circ(\text{reactants})\), the entropy change of this reaction is:

\[
\Delta S^\circ = (S^\circ(\text{H}_2\text{CO}_3(aq))) - (S^\circ(\text{CO}_2(g)) + S^\circ(\text{H}_2\text{O}(l)))
\]

\[
= [(187) - (214 + 70.)] \text{kJ mol}^{-1} = -97 \text{ J K}^{-1} \text{ mol}^{-1}
\]

Using \(\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ\):

\[
\Delta G^\circ = (-20 \times 10^3 \text{ J mol}^{-1}) - (298 \text{ K})(-97 \text{ J K}^{-1} \text{ mol}^{-1}) = +8906 \text{ J mol}^{-1}
\]

Using \(\Delta G^\circ = -RT\ln K_p\), the value of \(K_p\) can be determined:

\[
\ln K_p = -\frac{\Delta G^\circ}{RT} = -\frac{(+8906 \text{ J mol}^{-1})}{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298 \text{ K})}
\]

\[
= -3.595
\]

\[
K_p = 0.027
\]

Answer: \(0.027\)

• Consider the following equilibrium.

\[
\text{CO}(g) + \text{H}_2\text{O}(g) \rightleftharpoons \text{CO}_2(g) + \text{H}_2(g)
\]

\(K_c = 31.4 \text{ at 588 K}\)

If a 10.00 L vessel contains 2.50 mol \text{CO}(g), 2.50 mol \text{H}_2\text{O}(g), 5.00 mol \text{CO}_2(g) and 5.00 mol \text{H}_2(g) at 588 K, what are the concentrations of all species at equilibrium?

The initial concentrations are:

\[
[\text{CO}(g)] = \frac{\text{number of moles}}{\text{volume}} = 2.50 \text{ mol} / 10.00 \text{ L} = 0.25 \text{ M}
\]

\[
[\text{H}_2\text{O}(g)] = 2.50 \text{ mol} / 10.00 \text{ L} = 0.250 \text{ M}
\]

\[
[\text{CO}_2(g)] = 5.00 \text{ mol} / 10.00 \text{ L} = 0.500 \text{ M}
\]

\[
[\text{H}_2(g)] = 5.00 \text{ mol} / 10.00 \text{ L} = 0.500 \text{ M}
\]

Answer continues on the next page
The reaction table is therefore:

<table>
<thead>
<tr>
<th></th>
<th>CO(g)</th>
<th>H₂O(g)</th>
<th>⇋</th>
<th>CO₂(g)</th>
<th>H₂(g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>initial</td>
<td>0.250</td>
<td>0.250</td>
<td></td>
<td>0.500</td>
<td>0.500</td>
</tr>
<tr>
<td>change</td>
<td>-x</td>
<td>-x</td>
<td>+x</td>
<td>+x</td>
<td></td>
</tr>
<tr>
<td>equilibrium</td>
<td>0.250 - x</td>
<td>0.250 - x</td>
<td>0.500 + x</td>
<td>0.500 + x</td>
<td></td>
</tr>
</tbody>
</table>

The equilibrium constant is therefore:

\[ K_c = \frac{[\text{CO}_2 \text{(g)}][\text{H}_2 \text{(g)}]}{[\text{CO} \text{(g)}][\text{H}_2 \text{O} \text{(g)}]} = \frac{(0.500+x)(0.500+x)}{(0.250-x)(0.250-x)} = \frac{(0.500+x)^2}{(0.250-x)^2} = 31.4 \]

Hence,

\[ \frac{(0.500+x)}{(0.250-x)} = (31.4)^{1/2} = 5.60 \]

\[ 0.500 + x = 5.60 \times (0.250 - x) \]

\[ 0.500 + x = 1.40 - 5.60x \]

\[ x = 0.136 \text{ M} \]

Finally:

\[ [\text{CO(g)}] = (0.250 - 0.136) \text{ M} = 0.114 \text{ M} \]
\[ [\text{H}_2\text{O(g)}] = (0.250 - 0.136) \text{ M} = 0.114 \text{ M} \]
\[ [\text{CO}_2\text{(g)}] = (0.500 + 0.136) \text{ M} = 0.636 \text{ M} \]
\[ [\text{H}_2\text{(g)}] = (0.500 + 0.136) \text{ M} = 0.636 \text{ M} \]

\[ [\text{CO}] = 0.114 \text{ M} \quad [\text{H}_2\text{O}] = 0.114 \text{ M} \quad [\text{CO}_2] = 0.636 \text{ M} \quad [\text{H}_2] = 0.636 \text{ M} \]
Hydrogen peroxide, $\text{H}_2\text{O}_2$, can decompose to water and oxygen. Using the following redox potentials, determine whether this decomposition reaction is spontaneous or not.

\[
\begin{align*}
\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- & \rightleftharpoons 2\text{H}_2\text{O} \quad E^\circ = 1.76 \text{ V} \\
\text{O}_2 + 2\text{H}^+ + 2\text{e}^- & \rightleftharpoons \text{H}_2\text{O}_2 \quad E^\circ = 0.70 \text{ V}
\end{align*}
\]

The decomposition reaction is:

\[2\text{H}_2\text{O}_2(\text{l}) \rightarrow 2\text{H}_2\text{O}(\text{l}) + \text{O}_2(\text{g})\]

This is combines the first half cell as the reduction half cell and the second half cell as the oxidation half cell:

\[E^\circ = (+1.76 \text{ V}) + (-0.70 \text{ V}) = +1.06 \text{ V}\]

As $E^\circ > 0$, the reaction is spontaneous.
The net reaction discharging the lead acid storage battery is:

\[ \text{PbO}_2 + \text{Pb} + 2\text{H}_2\text{SO}_4 \rightarrow 2\text{PbSO}_4 + 2\text{H}_2\text{O} \]

What reaction occurs at the cathode?

\[ \text{PbO}_2 + 2\text{H}_2\text{SO}_4 + 2e^- \rightarrow \text{PbSO}_4 + 2\text{H}_2\text{O} + \text{SO}_4^{2-} \]

What reaction occurs at the anode?

\[ \text{Pb} + \text{H}_2\text{SO}_4 \rightarrow \text{PbSO}_4 + 2\text{H}^+ + 2e^- \]

Why are the cathode and anode not in separate compartments, as in the Cu/Zn battery?

All the redox active species are solids so can be kept apart without needing separate compartments.

How does \( \text{H}_2\text{SO}_4 \) serve as the ‘salt bridge’? Which ions flow in which direction to maintain electroneutrality?

\( \text{H}_2\text{SO}_4 \) dissociates to give \( \text{H}^+ \), \( \text{HSO}_4^- \) and \( \text{SO}_4^{2-} \) ions which carries the current. The \( \text{H}^+ \) ions migrate to the cathode, whilst the \( \text{HSO}_4^- \) and \( \text{SO}_4^{2-} \) ions migrate to the anode.

What is the formula for the equilibrium constant for the discharge reaction above?

Solids do not appear in the equilibrium constant, as their ‘concentration’ is constant. Water is present as the solvent and is at very high and effectively constant concentration. Hence, only \([\text{H}_2\text{SO}_4]\) varies:

\[ K = [\text{H}_2\text{SO}_4]^{-2} \]

The cell potential for this battery is 2.05 V. If the concentration of the \( \text{H}_2\text{SO}_4 \) is 4.5 M, what is the standard potential of the cell at 25 °C?

The Nernst equation, \( E_{\text{cell}} = E^o - \frac{RT}{nF}\ln Q \), can be used to work out the standard potential for this two electron process. As \( E_{\text{cell}} = 2.05 \) V when \([\text{H}_2\text{SO}_4] = 4.5 \) M:

\[
2.05 \text{ V} = E^o - \frac{(8.314 \text{ JK}^{-1} \text{mol}^{-1})(298 \text{ K})}{(2)(96485 \text{ C mol}^{-1})}\ln(4.5)^{-2}
\]

\[ E^o = 2.01 \text{ V} \]

Answer: +2.01 V
• Rationalise the order of the boiling points of the following liquids in terms of their intermolecular forces.

<table>
<thead>
<tr>
<th>liquid</th>
<th>F_2</th>
<th>HCl</th>
<th>HBr</th>
<th>HI</th>
<th>Cl_2</th>
<th>HF</th>
<th>Br_2</th>
<th>I_2</th>
</tr>
</thead>
<tbody>
<tr>
<td>b.p. (° C)</td>
<td>−188</td>
<td>−85</td>
<td>−67</td>
<td>−35</td>
<td>−34</td>
<td>20</td>
<td>59</td>
<td>184</td>
</tr>
</tbody>
</table>

The boiling points in F_2, Cl_2, Br_2 and I_2 are determined by the size of the dispersion forces between molecules. The bigger the atoms, the more polarisable their electron clouds and the greater the dispersion forces. Hence boiling points are in order:

I_2 > Br_2 > Cl_2 > F_2.

Dispersion forces also operate in HF, HCl, HBr and HI, but here the dipole formed between the halogen atom and the hydrogen also needs to be considered. F is a very small and very electronegative atom. The H–F bond is therefore highly polarised and H-bonds form in this liquid. These are much stronger than dispersion forces and so HF has an anomalously high boiling point.

Cl, Br and I are not as electronegative as F: the dispersion forces in HCl, HBr and HI are more significant than the dipole-dipole forces as can be evidenced by the order of boiling points

HF > HI > HBr > HCl.

The values given tell us that the total of the dispersion forces in Br_2 is greater than the H-bonds in HF. Similar comparisons can be made between other members of the two series.
• You would like to make a gas thermometer using a mole of N\textsubscript{2} at 1 atm. Assuming that you can treat the gas as ideal, determine how much the volume increases (in mL) per degree °C.

The ideal gas law is \( PV = nRT \). At a constant pressure of 1 atm and with \( n = 1 \) mol, the change in temperature and volume are thus related by:

\[
\Delta V = \left( \frac{nR}{P} \right) \times \Delta T \\
= \left( \frac{0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1}}{1 \text{ atm}} \right)(1 \text{ mol}) / (1 \text{ atm}) \times \Delta T \\
= 0.080 \text{ L} = (80 \text{ mL}) \times \Delta T
\]

The volume increases by 80 mL for every Kelvin (and therefore for every °C).

Answer: 80 mL

• Most of the solar radiation is arriving at the Earth’s surface in the form of visible light. Explain, briefly, why the principal contributions to the Greenhouse Effect come from gases that do not absorb in the visible but, instead, in the infrared frequencies.

Visible light passes through the atmosphere and is absorbed by the Earth’s surface. It is then re-emitted as black body radiation, mainly in the infrared region. It is this black body radiation that is absorbed by the greenhouse gases.

• Consider two blocks of steel: block A is 1.00 kg and block B is 600. g. Both blocks start from the same temperature and are heated so that 600. J flows into each of the blocks in the form of heat. What is the final difference in temperature, \( T_A - T_B \), between block A and block B. The specific heat of steel is 0.460 J g\textsuperscript{-1} K\textsuperscript{-1}. Show all working.

The specific heat capacity \( C \) can be used to calculate the increase in temperature, \( \Delta T \) from a heat change, \( q \) as:

\[
q = m \times C \times \Delta T
\]

where \( m \) is the mass of the substance.

For block A, \( m = 1.00 \times 10^3 \) g so that the temperature increase is:

\[
\Delta T = \frac{q}{mC} = \frac{600. \text{ J}}{(1.00 \times 10^3 \text{ g}) \times (0.460 \text{ J g}^{-1} \text{ K}^{-1})} = 1.30 \text{ K}
\]

For block A, \( m = 600. \times 10^3 \) g so that the temperature increase is:

\[
\Delta T = \frac{q}{mC} = \frac{600. \text{ J}}{(600. \text{ g}) \times (0.460 \text{ J g}^{-1} \text{ K}^{-1})} = 2.17 \text{ K}
\]

The final temperature difference, \( T_A - T_B \), is therefore \( (1.30 - 2.17) \text{ K} = -0.87 \text{ K} \)

Note that block B is lighter so ends up as the hotter of the two.

Answer: \(-0.87 \text{ K}\)