Topics in the June 2009 Exam Paper for CHEM1903

Click on the links for resources on each topic.

2009-J-2:

- Bonding in H_2 - MO theory
- Bonding in O_2, N_2, C_2H_2, C_2H_4 and CH_2O
- Band Theory - MO in Solids
- Polar Bonds
- Polymers and the Macromolecular Consequences of Intermolecular Forces

2009-J-3:

- Nuclear and Radiation Chemistry

2009-J-4:

- Bonding in O_2, N_2, C_2H_2, C_2H_4 and CH_2O

2009-J-5:

- Shape of Atomic Orbitals and Quantum Numbers
- Filling Energy Levels in Atoms Larger than Hydrogen
- Bonding in O_2, N_2, C_2H_2, C_2H_4 and CH_2O

2009-J-6:

- Lewis Structures
- VSEPR
- Wave Theory of Electrons and Resulting Atomic Energy Levels

2009-J-7:

- Types of Intermolecular Forces

2009-J-8:

- Thermochemistry
- First and Second Law of Thermodynamics

2009-J-9:

- Nitrogen Chemistry and Compounds

2009-J-10:

- Nitrogen in the Atmosphere

2009-J-11:

- Nitrogen in the Atmosphere

2009-J-12:

- First and Second Law of Thermodynamics
- Chemical Equilibrium

2009-J-14:

- Batteries and Corrosion

• In the spaces provided, explain the meaning of the following terms. You may use an example, equation or diagram where appropriate.	**Marks 6**

(a) covalent bond

A covalent bond describes the situation where an aggregation of 2 or more atoms is stabilised by the delocalisation of electrons among these atoms

(b) electronegativity

A measure of the tendency of an atom to attract electrons within a covalent bond.

(c) free radical

An atom or molecule with one or more unpaired electrons.

(d) band gap

The energy gap between the top of the valence band and the bottom of the conductance bands (the HOMO-LUMO gap) in a solid.

(e) hydrogen bond

The strong dipole interaction between a hydrogen bonded to a highly electronegative atom (usually F, N or O) and a lone pair on another atom.

(f) allotrope

Different physical forms of the same element, brought about by the different types of bonding exhibited by the element in its pure form (*e.g.* diamond and graphite).

	Marks
• The isotope ^{37}Ar has a half-life of 35 days. If each decay event releases an energy of 1.0 MeV, calculate how many days it would take for a 0.10 g sample of ^{37}Ar to release 22.57×10^3 kJ (enough energy to boil 10.0 L of water)?	**3**

1.0 MeV = 1.0 × 10^6 eV corresponds to (1.602×10^{-19} × 1.0×10^6) J = 1.602 × 10^{-13} J.

Each decay event releases 1.602 × 10^{-13} J and so to release 22.57 × 10^3 kJ requires:

$$\textbf{number of decay events required} = \frac{\textbf{22.57} \times \textbf{10}^3 \times \textbf{10}^3 \textbf{ J}}{\textbf{1.602} \times \textbf{10}^{-13} \textbf{ J}} = \textbf{1.409} \times \textbf{10}^{20}$$

0.10 g of ^{37}Ag corresponds to $\dfrac{\textbf{0.1 g}}{\textbf{37 g mol}^{-1}}$ = 0.0027 mol. This in turn corresponds to (0.00270 mol × 6.022 × 10^{23} mol^{-1}) = 1.63 × 10^{21} nuclei. N_0 = 1.63 × 10^{21}

As the initial number of nuclei present is 1.63 × 10^{21} and the number of decay events required is 1.409 × 10^{20}, the final number of nuclei will be:

(1.63 × 10^{21} – 1.409 × 10^{20}) = 1.49 × 10^{21} = N_t

As the half life is 35 days, the decay constant is $\dfrac{\textbf{ln2}}{\textbf{35 days}}$ = 0.0198 days^{-1}. Hence,
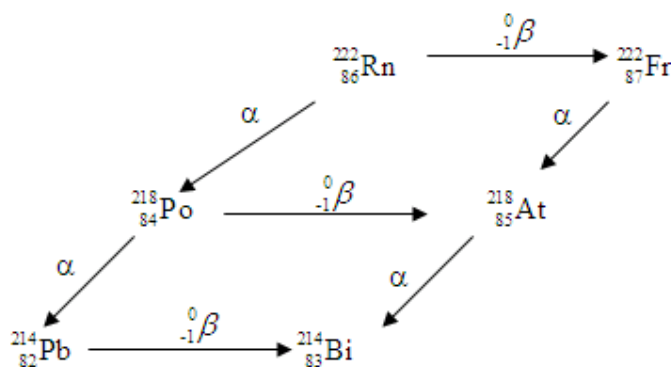
$$\ln\left(\frac{N_0}{N_t}\right) = \lambda t$$

$$\ln\left(\frac{\textbf{1.63} \times \textbf{10}^{21}}{\textbf{1.49} \times \textbf{10}^{21}}\right) = (\textbf{0.0198 days}^{-1})\, t$$

t = 4.5 days

| Answer: **4.5 days** |
|---|

• The isotope ^{222}Rn decays to ^{214}Bi in three steps. Identify all possible decay paths for this process, including all the intermediate isotopes along each path and the identity of the decay process involved in each individual step.	**3**

Marks
6

- The electronic energies of the molecular orbitals of diatomics consisting of atoms from H to Ne can be ordered as follows (with energy increasing from left to right):

$$\sigma \ \sigma^* \ \sigma \ \sigma^* \ 2\times\pi \ \sigma \ 2\times\pi^* \ \sigma^*$$
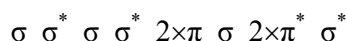
(the '2×' denotes a pair of degenerate orbitals)

Use this ordering of the molecular orbitals to identify the following species.

(i) The lowest molecular weight diatomic ion (homo- or heteronuclear) that has **all** of the following characteristics:
  a) a single negative charge,
  b) a bond order greater than zero *and*
  c) is diamagnetic.

HBe^- has 6 electrons (1 from He, 4 from Be and 1 from the negative charge) so has a configuration $\sigma^2 \ \sigma^{*2} \ \sigma^2$. It has a bond order of 1 and is diamagnetic.
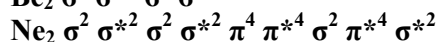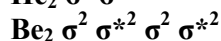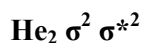
(ii) A diatomic species that has the same electronic configuration as O_2.

There are many: simply substitute one or both O by a cation with the same number of electrons (F^+, Ne^{2+} etc) or an anion with the same number of electrons (N^-, C^{2-} etc). For example:

NO^-, OF^+, NF, F_2^{2+}, CN^{3-}, N_2^{2-} .....
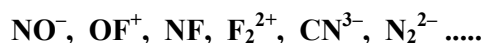
(iii) All of the atoms with atomic numbers less than or equal to 10 that cannot form stable, neutral, homonuclear diatomic molecules.

The neutral, homonuclear diatomic molecule would have a bond order of zero: He, Be and Ne.

$He_2 \ \sigma^2 \ \sigma^{*2}$
$Be_2 \ \sigma^2 \ \sigma^{*2} \ \sigma^2 \ \sigma^{*2}$
$Ne_2 \ \sigma^2 \ \sigma^{*2} \ \sigma^2 \ \sigma^{*2} \ \pi^4 \ \pi^{*4} \ \sigma^2 \ \pi^{*4} \ \sigma^{*2}$

Given that there are three degenerate *p* orbitals in an atom, why are there only two degenerate π orbitals in a diatomic molecule?

One *p*-orbital on each atom overlaps end-on with the matching *p*-orbital on the other atom. This produces a σ-bond.

This leaves only two *p*-orbitals on each atom to overlap in the side-on manner required for π bonding.

	Marks 3

- Imagine a Universe X in which electron spin did not exist. *i.e.* An electron has only a single internal state instead of the two spin states it has in our universe. Assume that all other properties of electrons and nuclei in Universe X are identical to those in our universe.

What are the atomic numbers of the first two alkali metals in Universe X?	**2 and 6**
Write down the ground state electron configuration of the atom with atomic number 11 in Universe X.	$1s^1\ 2s^1\ 2p^3\ 3s^1\ 3p^3\ 4s^1\ 3d^1$

How would the energy difference between the 2*s* and 2*p* orbitals compare between our universe and Universe X? Provide a brief explanation of your answer.

For the atom with atomic number 1, there is no difference in energy between the 2*s* and 2*p* orbitals (in both our universe and Universe X).

The energy difference between 2*s* and 2*p* arises because of the difference in shielding for a 2*s* and 2*p* electrons (in both our universe and Universe X).

As there are fewer electrons per orbital in Universe X, the difference in shielding is smaller and so the energy difference would be smaller.

- In a linear molecule consisting of a carbon chain with alternating double and single bonds, the HOMO and LUMO are often extended over the whole length of the molecule. What will happen to the size of the HOMO-LUMO gap as the length of such a molecule is increased?

2

As the wavelength associated with an electron is given by $\lambda = h/mv$, a longer wavelength is associated with a lower velocity and hence a lower energy. The gap is reduced.

Assuming that the molecule absorbs in the visible range, how will its colour change as the molecule length increases? Give a reason for your answer.

The colour will become more blue.

The energy of the light *absorbed* decreases as the band gap decreases, so its wavelength increases and it becomes more red. The colour of the compound is *complementary* to the light absorbed.

		Marks
• Consider the molecule whose structure is shown below. Complete the table concerning the atoms **A**, **B** and **C** indicated by the arrows.		3

A   **B**   **C**

$$\mathrm{CH_3OCHCHCN}$$
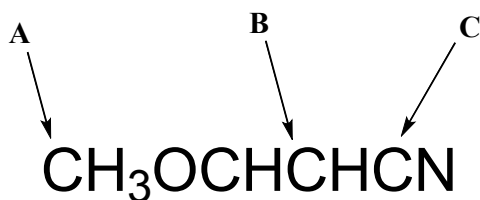
Selected atom	Number of σ-bonds associated with the selected atom	Geometry of σ-bonds about the selected atom
A	**4 (C-H × 3 + C-O)**	**tetrahedral**
B	**3 (C=C + C-H + C-C)**	**trigonal planar**
C	**2 (C-C + C≡N)**	**linear**

2

• Determine the value of n that corresponds to the lowest excited state of He^+ from which radiation with a wavelength of 600 nm is able to ionise the electron (*i.e.* excite it to a state of $n = \infty$). Show all working.

For a 1-electron atom or ion, the energy levels are given exactly by the equation,

$$E = -Z^2 E_R\left(\frac{1}{n^2}\right)$$

Ionization corresponds to excitation from level n_1 to level $n_2 = \infty$:

$$\Delta E = -Z^2 E_R\left(\frac{1}{\infty^2} - \frac{1}{n_1^2}\right) = Z^2 E_R\left(\frac{1}{n_1^2}\right)$$

Radiation with wavelength 600 nm has energy:

$$E = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34} \text{ J s})(2.998 \times 10^8 \text{ m s}^{-1})}{600 \times 10^{-9} \text{ m}} = 3.31 \times 10^{-19} \text{ J}$$

If this is able to provide the energy required to ionize He^+ ($Z = 2$) from level n_1:

$$Z^2 E_R\left(\frac{1}{n_1^2}\right) = 2^2 \times (2.18 \times 10^{-18} \text{ J}) \times \left(\frac{1}{n_1^2}\right) = 3.31 \times 10^{-19} \text{ J}$$

This gives $n_1 = 5.13$. As n must be an integer, the radiation can ionize from $n = 6$ or above.

Answer: $n = 6$

	Marks
• Describe one piece of experimental evidence supporting the conclusion that electrons have wave-like character.	**1**

> **Examples include:**
>
> - **the diffraction of electron beams**
> - **the standing wave structure of atoms leading to atomic line spectra**

	3
• The boiling points of H_2O and H_2S are 100 °C and –60 °C, respectively. Identify the single property whose difference for oxygen and sulfur is most responsible for this difference in boiling points.	

> **The *electronegativity* difference between O and S. This leads to very polar O-H bonds and the occurrence of strong H-bonding in H_2O.**

The boiling points of HF and NH_3 are 20 °C and –30 °C, respectively. Explain why these boiling points are lower than that of water *and*, separately, explain why the boiling point of HF is greater than that of NH_3.

> **The high boiling points of NH_3, H_2O and HF are due to H-bonding.**
>
> **H-bonding requires the hydrogen atom to be bonded to an electronegative element, such as N, O or F, so that the X-H bond is very polar. It also requires at least one lone pair on an electronegative element to accept the H-bond.**
>
> **The H-F bond is more polar than the O-H or N-H bond so a H-bond between two H-F molecules is stronger than a H-bond between two H_2O molecules. Similarly, as an O-H bond is more polar than a N-H bond, a H-bond between two H_2O molecules is stronger than a H-bond between two NH_3 molecules.**
>
> **Each H_2O molecule has two H atoms and the O atom has two lone pairs: each H_2O molecule can make two H-bonds. HF has only 1 H atom and NH_3 has only one lone pair on N so both can only make only one H bond.**
>
> **Thus, H_2O has the highest boiling point has it makes more H-bonds than HF or NH_3. HF has a higher boiling point than NH_3 as its individual H-bonds are stronger.**

**Marks
5**

- A new process has been developed for converting cellulose from corn waste into the biofuel butanol, C_4H_9OH. A bomb calorimeter with a heat capacity of 3250 J K^{-1} was used to determine the calorific value by burning 5.0 g of butanol in excess oxygen.

Write a balanced reaction for the combustion of butanol in oxygen.

$$C_4H_9OH(l) + 6O_2(g) \rightarrow 4CO_2(g) + 5H_2O(g)$$
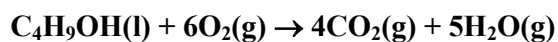
Calculate the heat released from this combustion if the temperature of the calorimeter increased from 23.0 to 78.6 °C during the test.

The heat, q, required to change the temperature of the bomb calorimeter by ΔT is given by:

$$q = C\,\Delta T$$

The temperature increases from 23.0 to 78.6 °C corresponding to $\Delta T = 55.6$ °C = = 55.6 K. Hence:

$$q = (3250 \text{ J K}^{-1})(55.6 \text{ K}) = 181000 \text{ J} = 181 \text{ kJ}$$

Answer: **181 kJ**

Use this value to determine the calorific value and molar enthalpy of combustion of butanol.

The calorific value is the energy content per gram. As 5.0 g of butanol releases 181 kJ, the calorific value is:

$$\text{calorific value} = \frac{181 \text{ kJ}}{5.0 \text{ g}} = 36 \text{ kJ g}^{-1}$$

The molar enthalpy of combustion is the energy released by combusting one mole. The molar mass of C_4H_9OH is:

$$\text{molar mass} = (4 \times 12.01 \text{ (C)} + 10 \times 1.008 \text{ (H)} + 16.00 \text{ (O)}) \text{ g mol}^{-1} = 74.12 \text{ g mol}^{-1}$$

5.0 g of butanol thus corresponds to:

$$\text{number of moles} = \frac{\text{mass}}{\text{molar mass}} = \frac{5.0 \text{ g}}{74.12 \text{ g mol}^{-1}} = 0.067 \text{ mol}$$

As 0.067 mol generates 181 kJ when combusted, the molar enthalpy of combustion is negative and is given by:

$$\Delta H = \frac{-181 \text{ kJ}}{0.067 \text{ mol}} = -2.7 \times 10^3 \text{ kJ mol}^{-1}$$

	Marks
• Many explosive compounds contain nitrogen, and form $N_2(g)$ upon decomposition. Briefly explain the significance of the formation of this molecule in terms of both (i) the heat generated and (ii) the spontaneity of such reactions.	**3**

(i) The decomposition reaction releases N_2. The formation of the very stable N≡N triple bond releases a large amount of heat into the surroundings. This means that the gaseous products are released with considerable energy, leading to a rapid increase in pressure.

(ii) The heat released increases the entropy of the surroundings and therefore the universe by q/T, favouring a spontaneous reaction.

	Marks 5

The diameter of Saturn's moon, Titan, is 5150 km and it orbits at an average of 1.427×10^9 km from the sun, or 9.54 times farther than the Earth. Its mean surface temperature is 94 K, it has an albedo of 0.09, and it has an atmosphere comprised of methane, nitrogen, ethane, argon and a trace of ammonia.

The temperature of the sun is 5780 K and its radius is 6.96×10^8 m. Determine the magnitude (in K) of the greenhouse effect on Titan's atmosphere.

The energy output from the sun is given by:

$$E_{sun,out} = 4\pi r^2 \times 5.67 \times 10^{-8} \times T^4 = 4\pi \times (6.96 \times 10^8 \text{ m})^2 \times 5.67 \times 10^{-8} \times (5780)^4$$

$$= 3.85 \times 10^{26} \text{ J}$$

The energy received by Titan, at a distance *d*, is given by :

$$E_{titan,in} = \frac{E_{sun,out}}{4\pi d^2} \times \pi r^2 \times (1 - \text{albedo})$$

$$= \frac{(3.85 \times 10^{26} \text{ J})}{4\pi \times (1.427 \times 10^{12} \text{ m})^2} \times \pi \times (\frac{5150}{2} \times 10^3 \text{ m})^2 \times (1 - 0.09)$$

$$= 2.852 \times 10^{15} \text{ J}$$

As Titan is in thermal equilibrium, $E_{titan,in} = E_{titan,out}$. In the absence of a greenhouse effect:

$$E_{titan,out} = 4\pi r^2 \times 5.67 \times 10^{-8} \times T^4 = E_{titan,in} = 2.852 \times 10^{15} \text{ J}$$

$$4\pi(\frac{5150}{2} \times 10^3 \text{ m})^2 \times 5.67 \times 10^{-8} \times T^4 = 2.852 \times 10^{15} \text{ J}$$

$$T = 88 \text{ K}$$

As the actual temperature is 94 K, the greenhouse effect contributes (94 – 88) K = 6 K.

	Answer: **6 K**

	Marks **2**

Calculate the wavelength of the maximum (black body) emission of Titan.

The wavelength, λ, emitted by a blackbody is related to its temperature by:

$$T\lambda \approx 2.898 \times 10^6 \text{ K nm}$$

With $T = 94$ K, the wavelength will be given by:

$$\lambda \approx \frac{2.898 \times 10^6 \text{ K nm}}{94 \text{ K}} = 31000 \text{ nm} = 3.1 \times 10^{-5} \text{ m}$$

Answer: **3.1×10^{-5} m**

Using the vibrational frequencies provided in the data table below, suggest the gas(es) most likely to be causing Titan's greenhouse effect.

CH$_4$ 3156 cm^{-1}; 3026 cm^{-1}; 1534 cm^{-1}; 1367 cm^{-1}

C$_2$H$_6$ 2969 cm^{-1}; 1468 cm^{-1}; 1388 cm^{-1}; 995 cm^{-1}; 823 cm^{-1}; 289 cm^{-1}

NH$_3$ 3337 cm^{-1}; 3444 cm^{-1}; 1627 cm^{-1}; 950 cm^{-1}

N$_2$ 2739 cm^{-1}

The *wavelength* 3.1×10^{-5} m corresponds to a wavenumber of 32000 m^{-1} or 320 cm^{-1}. The only molecule that is absorbing in this region is C$_2$H$_6$.

**Marks
5**

- Write the equations for the combustion of graphite that occur in smelting processes to produce (i) CO(g) and (ii) CO$_2$(g), *in which one mole of O$_2$(g) is consumed.*

(i) | **2C(s) + O$_2$(g) → 2CO(g)**

(ii) | **C(s) + O$_2$(g) → CO$_2$(g)**
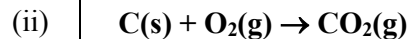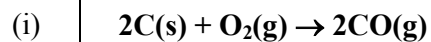
Use the standard enthalpy and entropy data provided to calculate the enthalpy and entropy of these two combustion reactions of graphite.

substance	$\Delta_f H°$ / kJ mol^{-1}	$S°$ / J K^{-1} mol^{-1}	substance	$S°$ / J K^{-1} mol^{-1}
CO(g)	−111	198	C(s)	6
CO$_2$(g)	−394	214	O$_2$(g)	205

Using $\Delta_{rxn}H° = \Sigma m \Delta_f H°$(products) - $\Sigma n \Delta_f H°$(reactants),

$\Delta_{comb}H°$ (i) = [(2 × -111) – (0)] kJ mol^{-1} = -222 kJ mol^{-1}

$\Delta_{comb}H°$ (ii) = [(-394) – (0)] kJ mol^{-1} = -394 kJ mol^{-1}

Using $\Delta_{rxn}S° = \Sigma m S°$(products) - $\Sigma n S°$(reactants),

$\Delta_{comb}S°$ (i) = [(2 × 198) – (2 × 6 + 205)] J K^{-1} mol^{-1} = +179 J K^{-1} mol^{-1}

$\Delta_{comb}S°$ (ii) = [(214) – (6 + 205)] J K^{-1} mol^{-1} = +3 J K^{-1} mol^{-1}

	Marks
Using calculations where necessary, sketch the temperature-dependence of the equilibrium constant for these two combustion reactions on the graph shown below. (Space for working is included below the graph.)	**6**
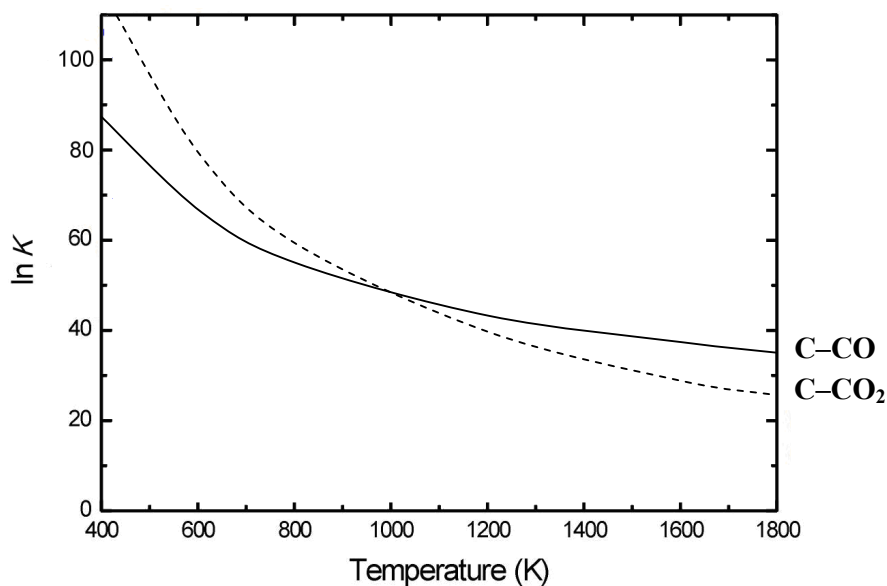
The equilibrium constant for the reaction is given by:

$$\Delta_{univ}S° = R\ln K$$

where

$$\Delta_{univ}S° = \Delta_{sys}S° + \Delta_{surr}S° = \Delta_{sys}S° - \frac{\Delta_{sys}H°}{T} \quad \text{as } \Delta_{surr}S° = \frac{\Delta_{surr}H°}{T} = -\frac{\Delta_{sys}H°}{T}$$

Using the results from 2009-J-12, at 400 K, for example:

$$\Delta_{univ}S° \text{ (i)} = (179 \text{ J K}^{-1}\text{ mol}^{-1}) - \frac{-222 \times 10^3 \text{ J mol}^{-1}}{400 \text{ K}} = 730 \text{ J K}^{-1}\text{ mol}^{-1}$$

$$\ln K \text{ (i)} = \Delta_{univ}S° \text{ (i)} / R = 88$$

The table below shows results for both reactions at several temperatures.

T / K	$\ln K$ (i)	$\ln K$ (ii)
400	88	120
600	60	79
800	55	60
1000	48	48
1200	44	40
1400	41	34
1600	38	30
1800	36	27

ANSWER CONTINUES ON THE NEXT PAGE

Over what temperature range is carbon monoxide the favoured product?

The temperature at which both reactions are equally favoured occurs when
$\Delta_{univ}S°$ **(i)** $= \Delta_{univ}S°$ **(ii):**

$$\Delta_{sys}S° \text{ (i) } - \frac{\Delta_{sys}H° \text{ (i)}}{T} = \Delta_{sys}S° \text{ (ii) } - \frac{\Delta_{sys}H° \text{ (ii)}}{T}$$

$$(179 \text{ J K}^{-1} \text{ mol}^{-1}) - \frac{-222 \times 10^3 \text{ J mol}^{-1}}{T} = (3 \text{ J K}^{-1} \text{ mol}^{-1}) - \frac{-394 \times 10^3 \text{ J mol}^{-1}}{T}$$
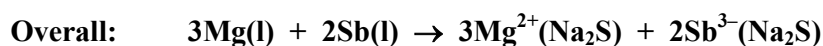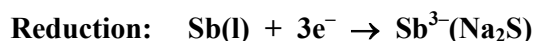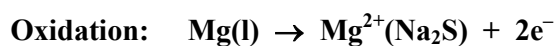
$T = 977 \text{ K}$

The reaction favours CO_2 at lower temperatures as $\ln K$ (ii) $> \ln K$ (i) and favours CO at higher temperatures as $\ln K$ (i) $> \ln K$ (ii). Hence, CO is favoured when $T >$ 977 K.

- MIT researcher Donald Sadoway has developed a novel kind of battery that uses molten magnesium and antimony electrodes, which react as the cell discharges to form magnesium and antimonide ions dissolved in molten sodium sulfide. The cell potential is 2.76 V. This kind of cell is proposed as a way of storing energy from solar photovoltaic cells to supply electricity at night.

Write out the spontaneous oxidation and reduction half-cell reactions, and overall (balanced) cell reaction.

Oxidation: $Mg(l) \rightarrow Mg^{2+}(Na_2S) + 2e^-$

Reduction: $Sb(l) + 3e^- \rightarrow Sb^{3-}(Na_2S)$

Overall: $3Mg(l) + 2Sb(l) \rightarrow 3Mg^{2+}(Na_2S) + 2Sb^{3-}(Na_2S)$

Identify the cathode and the anode.

Oxidation occurs at the anode: Mg(l) is the anode.
Reduction occurs at the cathode: Sb(l) is the cathode.

Is this a primary or secondary battery, or a fuel cell? Explain your answer briefly.

The cell can be recharged so it is a secondary battery.

A prototype cell provided the extraordinary current of 12,000 A. How long would this discharging cell take to consume 1.0 kg of Mg electrode?

As the atomic mass of Mg is 24.31 g mol^{-1}, the number of moles in 1.0 kg is:

$$\text{moles of Mg} = \frac{\text{mass}}{\text{molar mass}} = \frac{1.0 \times 10^3 \text{ g}}{24.31 \text{ g mol}^{-1}} = 41.1 \text{ mol}$$

Oxidation of Mg is a 2e$^-$ process so oxidation of 41.1 mol will produce 82.2 mol of electrons. The number of moles of electrons is related to the current produced by:

$$\text{number of moles of e}^- = \frac{It}{F}$$

Hence, the time required to pass a current of 12000 A (= 12000 C s^{-1}) with a supply of 82.2 mol of electrons is:

$$t = \frac{\text{number of moles of electrons} \times F}{I} = \frac{82.2 \text{ mol} \times 96485 \text{ C mol}^{-1}}{12000 \text{ C s}^{-1}} = 660 \text{ s}$$

Answer: **660 s or 11 mins**