Topics in the June 2012 Exam Paper for CHEM1101

Click on the links for resources on each topic.

2012-J-2:

- Nuclear and Radiation Chemistry

2012-J-3:

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

2012-J-4:

- Wave Theory of Electrons and Resulting Atomic Energy Levels
- Shape of Atomic Orbitals and Quantum Numbers
- Filling Energy Levels in Atoms Larger than Hydrogen

2012-J-5:

- Band Theory - MO in Solids

2012-J-6:

- Bonding - MO theory (H_2)
- Bonding - MO theory (larger molecules)

2012-J-7:

- Lewis Structures
- VSEPR

2012-J-8:

- First and Second Law of Thermodynamics
- Gas Laws

2012-J-9:

- Thermochemistry
- Nitrogen Chemistry and Compounds
- Nitrogen in the Atmosphere

2012-J-10:

- Chemical Equilibrium

2012-J-11:

- Thermochemistry
- First and Second Law of Thermodynamics

2012-J-12:

- Thermochemistry
- First and Second Law of Thermodynamics
- Chemical Equilibrium
- Equilibrium and Thermochemistry in Industrial Processes

2012-J-13:

- Electrochemistry

2012-J-14:

- Electrochemistry
- Batteries and Corrosion

2012-J-15:

- Types of Intermolecular Forces

Marks 6

- On the 6th of April 2011, after the earthquake and tsunami in Japan, levels of ^{131}I in seawater were recorded at 7.5×10^6 times the legal limit. The half-life of ^{131}I is 8.02 days. How long will it take for the radioactivity of the initially sampled seawater to fall back to the legal limit?

The radioactivity is proportional to the number of radioactive nuclei, $A = \lambda N$. As the number of radioactive nuclei varies with time according to $\ln(N_0/N_t) = \lambda t$:

$$\ln(A_0/A_t) = \lambda t$$

Using $t_{1/2} = \ln 2 / \lambda$:

$$\lambda = \ln 2 / t_{1/2} = \ln 2 / 8.02 \text{ days}^{-1} = 0.0864 \text{ days}^{-1}$$

if $A_0 = 7.5 \times 10^6 \times A_t$,

$$\ln(7.5 \times 10^6) = (0.0864 \text{ days}^{-}1) \times t$$

$$t = 183 \text{ days}$$

Answer: **183 days**

Why is the ^{131}I nucleus unstable?

The $^{131}_{53}I$ nucleus lies outside the zone of stability - its neutron to proton ratio is too high.

Write a balanced equation for a likely decay mechanism of ^{131}I.

$$^{131}_{53}I \rightarrow {}^{131}_{54}Xe + {}^{0}_{-1}\beta$$

Another significant seawater contaminant detected after the tsunami was ^{137}Cs, which has a half-life of 30 years. If you were exposed to equal concentrations of both isotopes for 1 hour, which isotope, ^{137}Cs or ^{131}I, would do more damage? Explain your reasoning.

^{131}I would do more damage.

It has the shorter half-life so undergoes more disintegrations and produces more radiation in a given time period.

Marks

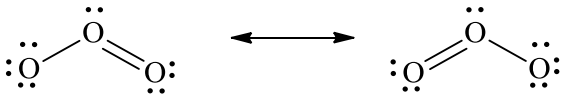
- Explain the physical significance of the square of the wavefunction, ψ^2. **2**

The square of the wavefunction provides a measure of electron density (*i.e.* the probability of finding an electron) at a given point around the nucleus of an atom.

- The σ-bonding in two plausible structures of ozone, O_3, is shown below. Complete each structure by adding electrons and/or π-bonds as appropriate. **4**

Predict the geometry of ozone? Give reasons for your answer.

Ozone adopts the non-cyclic structure. The cyclic structure is very strained with bond angles of 60° instead of 109.5°, making it very unstable. In contrast, the second structure is stabilised by resonance.



Ozone does not contain 1 double and 1 single bond. Both the O-O bonds are exactly the same length and true structure is a sort of average of the two Lewis structures shown. The energy of the true structure is lower than the theoretical energy for either of the given structures. This energy difference is known as resonance stabilisation energy.

Marks 4

- The "Paschen" series of emission lines corresponds to emission from higher lying energy states to the n = 3 state in hydrogen-like atoms. Calculate the wavelength (in nm) of the lowest energy "Paschen" emission line in Li^{2+}.

The energy of an orbital in an 1-electron atom or ion is given by

$$E_n = -Z^2 E_R (1/n^2)$$

The energy difference between two levels is therefore:

$$\Delta E = E_{n1} - E_{n2} = [-Z^2 E_R (1/n_1^2)] - [-Z^2 E_R (1/n_2^2)] = Z^2 E_R (1/n_2^2 - 1/n_1^2)$$

The lowest energy line in the Paschen series corresponds to moving from n = 4 to n =3. As Li^{2+} has Z = 3, the energy of this transition is therefore:

$$\Delta E = (3)^2 E_R (1/3^2 - 1/4^2)$$
$$= 9.54\times 10^{-19} \text{ J}$$

Using $E = hc / \lambda$, this corresponds to a wavelength of:

$$\lambda = hc / E = (6.626 \times 10^{-34} \text{ J s})(2.998 \times 10^{8} \text{ m s}^{-1}) / (9.54 \times 10^{-19} \text{ J})$$
$$= 2.08\times 10^{-7} \text{ m}$$
$$= 208 \text{ nm}$$

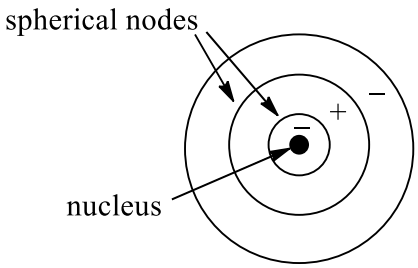
Answer: **208 nm**

What are the possible l states for the n = 4 level of Li^{2+}?

l = 0, 1, 2 and 3

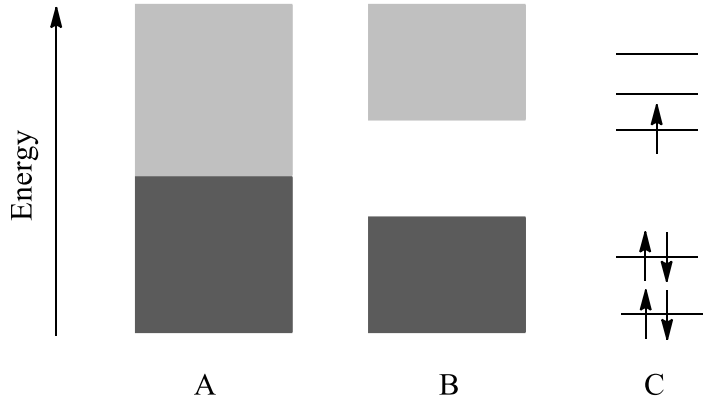
Sketch the atomic orbital with n = 3 and the lowest value of l.

The orbital is 3s:



Marks
5

- The diagram below shows the band structure of two solid elements, A and B. Dark grey denotes filled electron energy levels, light grey denotes unfilled levels. Also shown are the atomic energy levels (valence electron orbitals only) of another element, C.



Describe the electrical properties of elements A and B, explaining your reasoning.

A is a conductor. As there is no energy gap between them, electrons can easily be promoted from the filled to the unfilled electron energy levels. They are hence free to move if a voltage is applied.

B is an insulator. There is a large energy gap between the filled and unfilled electron energy levels. As the electrons can't get to the unfilled levels (the conductance band), B is unable to conduct.

If a small amount of element C is deliberately added to each of A and B, describe what effect this will have on the electrical properties of each. Give reasons.

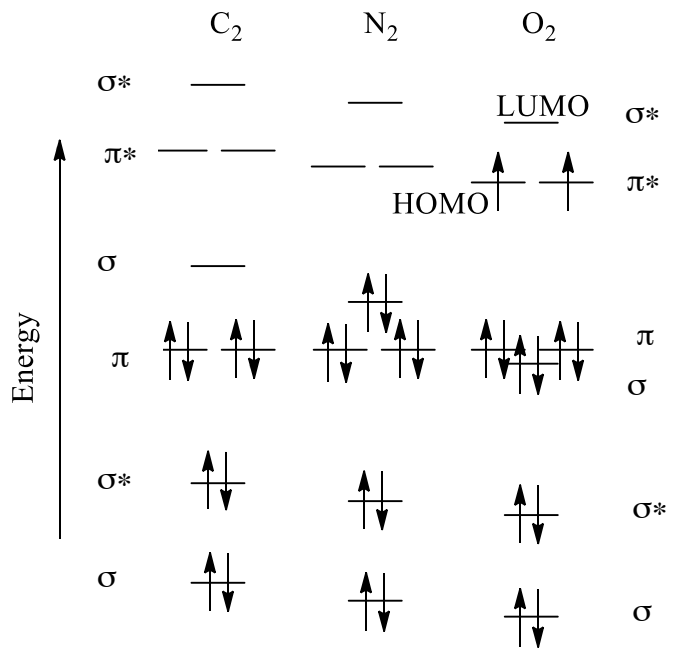
There is no effect on A. There is no effect on the energy levels so electrons can still be promoted easily into the conductance band.

B will become an n-type semi-conductor. The extra electrons are forced into the conductance band and are free to move when a voltage is applied. There are not very many of these extra electrons, so the result is a material which can conduct some current, but not a lot.

Marks 6

- The following diagram shows the molecular orbital energy level diagrams for the valence electrons in the homonuclear diatomic molecules C_2, N_2 and O_2.

  Complete the diagram by filling in the remaining *valence* electrons for each molecule and determining its bond order.



Bond order:	2	3	2

Explain why the energy of the lowest energy σ orbital shown above gets lower from left to right across the periodic table.

The atomic number of the elements increase moving across a period, reflecting an increase in the number of protons. This results in an increasing effective nuclear charge which pulls the electrons closer to the nucleus and lowers the energy of their orbitals.

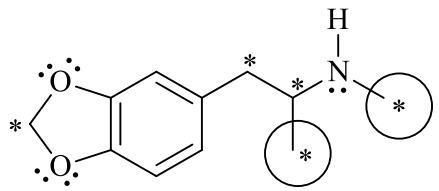
Clearly label the HOMO and LUMO of O_2 on the diagram above.

Marks

- The stick representation of 3,4-methylenedioxy-*N*-methylamphetamine ("ecstasy") is shown in the box below. **3**

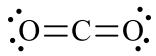
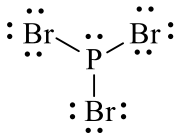
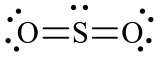
  (a) Identify clearly with asterisks (*) ALL the carbon atoms that have a tetrahedral geometry.

  (b) Circle all the CH_3 groups.



Name the N-containing functional group in ecstasy.	**amine**

- Complete the following table. The central atom is underlined. Carbon dioxide is given as an example. **3**

Molecule	Lewis structure	Shape of molecule
$\underline{C}O_2$		linear
$\underline{P}Br_3$		**trigonal pryamidal**
$\underline{S}O_2$		**bent (~120°)**

Marks

- Explain why quartz, $SiO_2(s)$, does not spontaneously decompose into silicon and oxygen at 25 °C, even though the standard entropy change of the reaction is large and positive. **2**

$$SiO_2(s) \rightarrow Si(s) + O_2(g) \qquad \Delta S° = 164 \text{ J K}^{-1} \text{ mol}^{-1}$$

Spontaneity requires a negative Gibbs free energy, *i.e.* $\Delta G = \Delta H - T\Delta S < 0$.

The ΔH component is very large and positive because of the very strong Si-O bonds in SiO_2, a network covalent compound.

Although ΔS is large and positive, it is not large enough to make the above expression negative, except at very high temperatures when $T\Delta S > \Delta H$.

- The equation for the detonation of nitroglycerine, $C_3H_5N_3O_9(l)$, is given below. **3**

$$4C_3H_5N_3O_9(l) \rightarrow 6N_2(g) + 12CO_2(g) + 10H_2O(g) + O_2(g)$$

What mass of nitroglycerine is required to produce 1000 L of product gases at 2000 °C and 1.00 atm? Assume all gases behave as ideal gases. Show all working.

Using the ideal gas equation, $PV = nRT$, the total number of moles of gas produced is:

$$n = PV / RT$$
$$= (1.00 \text{ atm} \times 1000 \text{ L}) / (0.08206 \text{ atm L K}^{-1} \text{ mol}^{-1} \times (2000 + 273) \text{ K})$$
$$= 5.36 \text{ mol}$$

From the chemical equation, detonation of 4 mol of nitroglycerine gives (6 + 12 + 10 + 1) mol = 29 mol of gases. Therefore:

number of moles of nitroglycerine required = (4/29) × 5.36 mol = 0.739 mol

The molar mass of nitroglycerine is:

$$\text{molar mass} = [3 \times 12.01 + 5 \times 1.008 \text{ (H)} + 3 \times 14.01 \text{ (N)} + 9 \times 16.00 \text{ (O)}] \text{ g mol}^{-1}$$
$$= 227.1 \text{ g mol}^{-1}$$

The mass of nitroglycerine is therefore:

$$\text{mass} = \text{number of moles} \times \text{molar mass} = (0.739 \text{ mol}) \times (227.1 \text{ g mol}^{-1}) = 168 \text{ g}$$
$$= 200 \text{ g (1 s.f.)}$$

Answer: **200 g**

Marks

- A 2.5 kg block of aluminium is heated to 80.0 °C and then placed into a thermally insulated water bath consisting of 10.0 L of water at 25.0 °C. Calculate the final temperature of the water once equilibrium has been reached. Show all working. **3**

  Data: Specific heat capacity of Al(s) is 0.900 J g^{-1} K^{-1}.
  Specific heat capacity of $H_2O(l)$ is 4.184 J g^{-1} K^{-1}.
  The density of water is 1 g mL^{-1}.

The aluminium will cool down and the water will heat up when the two are mixed. The final temperature, T_f, will be the same for both.

For the aluminium,

$$q_{aluminium} = m\ c\ \Delta T = (2500\ g) \times (0.900\ J\ g^{-1}\ K^{-1}) \times \Delta T_{aluminium}$$

For the water,

$$q_{water} = m\ c\ \Delta T = (10.0 \times 10^3\ g) \times (4.18\ J\ g^{-1}\ K^{-1}) \times \Delta T_{water}$$

As the heat lost by the aluminium is gained by the water, $q_{water} = -q_{aluminium}$:

$$(10.0 \times 10^3\ g) \times (4.18\ J\ g^{-1}\ K^{-1}) \times \Delta T_{water} = -(2500\ g) \times (0.900\ J\ g^{-1}\ K^{-1}) \times \Delta T_{aluminium}$$

or

$$41800 \times \Delta T_{water} = -2250 \times \Delta T_{aluminium}$$

Using $\Delta T_{water} = (T_f - 25.0)\ ^oC$ and $\Delta T_{aluminium} = (T_f - 80.0)\ ^oC$ gives:

$$T_f = 27.8\ ^oC$$

Answer: **27.8 °C**

- Provide a brief explanation of the term "nitrogen fixation". **1**

Nitrogen fixation is the conversion of relatively inert atmospheric nitrogen gas (N_2) into forms (*e.g.* NH_3, NO_3^-) that can be used by biological systems. Typically soil bacteria and leguminous plants convert N_2 into NH_4^+ ions.

Marks 4

- Consider the following reaction.

$$SO_2(g) + NO_2(g) \rightleftharpoons SO_3(g) + NO(g)$$

An equilibrium mixture in a 1.00 L vessel was found to contain $[SO_2(g)] = 0.800$ M, $[NO_2(g)] = 0.100$ M, $[SO_3(g)] = 0.600$ M and $[NO(g)] = 0.400$ M. If the volume and temperature are kept constant, what amount of NO(g) needs to be added to the reaction vessel to give an equilibrium concentration of $NO_2(g)$ of 0.300 M?

From the chemical equation,

$$K_{eq} = \frac{[SO_3(g)][NO(g)]}{[SO_2(g)][NO_2(g)]}$$

As the original mixture is at equilibrium:

$$K_{eq} = \frac{[SO_3(g)][NO(g)]}{[SO_2(g)][NO_2(g)]} = \frac{(0.600)(0.400)}{(0.800)(0.100)} = 3.00$$

This equilibrium is now disturbed by the addition of *x* M of NO(g). To re-establish equilibrium, the reaction will shift to the left by an unknown amount *y*. The reaction table for this is:

	$SO_2(g)$	$NO_2(g)$		$SO_3(g)$	NO(g)
initial	**0.800**	**0.100**	$\rightleftharpoons$	**0.600**	**0.400 + *x***
change	**+*y***	**+*y***		**-*y***	**-*y***
equilibrium	**0.800 + *y***	**0.100 + *y***		**0.600 – *y***	**0.400 + *x* - y**

As $[NO_2(g)] = 0.300$ M at the new equilibrium, *y* = (0.300 – 0.100) M = 0.200 M. Hence, the new equilibrium concentrations are:

$[SO_2(g)]$ = (0.800 + 0.200) M = 1.000 M
$[NO_2(g)]$ = 0.300 M
$[SO_3(g)]$ = (0.600 – 0.200) M = 0.400 M
[NO(g)] = (0.400 + *x* – 0.200) M = (0.200 + *x*) M

As the system is at equilibrium,

$$K_{eq} = \frac{[SO_3(g)][NO(g)]}{[SO_2(g)][NO_2(g)]} = \frac{(0.400)(0.200+x)}{(1.000)(0.300)} = 3.00$$

Solving this gives *x* = 2.05 M. As the reaction is carried out in a 1.00 L container, this is also the number of moles required.

Answer: **2.05 mol**

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY

Marks 4

- In a process called pyrolysis, a hydrocarbon fuel is partially dehydrogenated to produce hydrogen gas, which can then be combined with oxygen to produce water. Using ethane C_2H_6 as the fuel, the overall process is described by the following balanced equation:

$$2C_2H_6(g) + O_2(g) \rightarrow 2C_2H_4(g) + 2H_2O(l)$$

$H_2O(l)$	$C_2H_6(g)$	$C_2H_4(g)$	$CO_2(g)$	$CO(g)$
–285.9	–84.67	52.28	–393.5	–110.5

Using heats of formation, calculate the heat of reaction per mole of ethane consumed in the reaction described above.

Using $\Delta_{rxn}H° = \Sigma m\Delta_f H°$(products) - $\Sigma n\Delta_f H°$(reactants), the enthalpy of this reaction is:

$$\Delta H° = (2\Delta_f H°(C_2H_4(g) + 2\Delta_f H°(H_2O(l)) - (2\Delta_f H°(C_2H_6(g) + \Delta_f H°(O_2(g))$$

$$= [(2 \times 52.28 + 2 \times -285.9) – (2 \times -84.67 + 0)] \text{ kJ mol}^{-1} = -297.9 \text{ kJ mol}^{-1}$$

This is for the reaction as written, which consumes 2 mol of C_2H_6. The heat of reaction per mole of ethane is therefore

$$\Delta H° = ½ \times -297.9 \text{ kJ mol}^{-1} = -149.0 \text{ kJ mol}^{-1}$$

Answer: **-149.0 kJ mol^{-1}**

Simply burning ethane in oxygen to produce carbon dioxide and water releases 1560 kJ per mole of ethane consumed. Provide a brief explanation of the difference between the heats of combustion and the pyrolysis-based process described above.

The heat of combustion is for the reaction

$$C_2H_6(g) + 7/2\ O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$$

This reaction produces much more energy per mole of ethane as its products are more stable.

The C_2H_4 produced in the pyrolysis reaction can itself be burnt to produce more energy

$$C_2H_4(g) + 3O_2(g) \rightarrow 2CO_2(g) + 2H_2O(l)$$

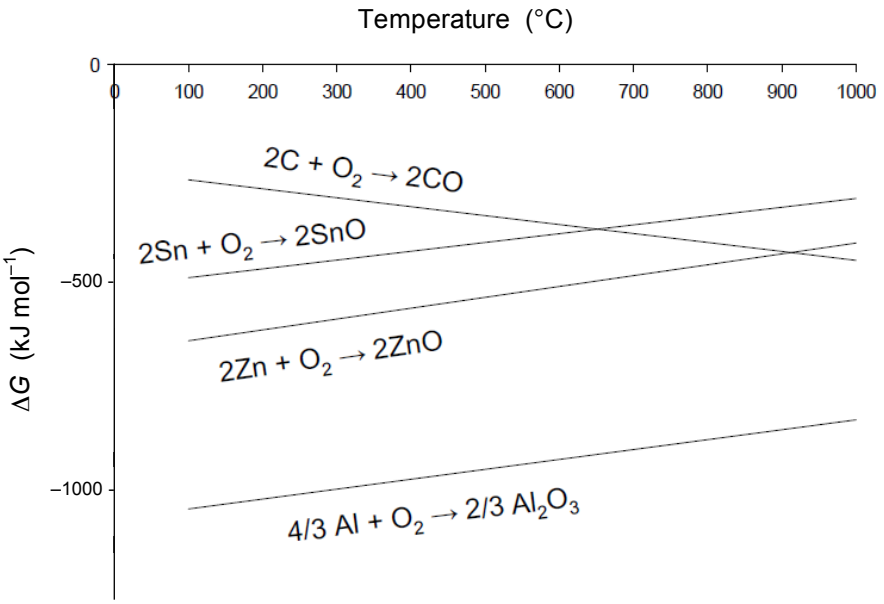
Briefly describe one environmental benefit of using the pyrolysis-based process for energy production.

The pyrolysis reaction does not produce $CO_2(g)$ which is known to contribute to the greenhouse effect.

However, the C_2H_4 gas produced is likely to be a greenhouse gas to so would have to be removed and stored for its effect to be removed.

Marks 4

- The diagram below represents the Gibbs Free energy change associated with the formation of 4 different oxides.



Using the free energy data above, write down the equation and indicate with an arrow the direction of the expected spontaneous reaction under the following conditions. If you think no reaction would occur, write "no reaction".

a) C and SnO are mixed at 400 °C

At 400 °C, the Sn / SnO line is *below* the C / CO line. Hence, there is no reaction.

b) C and SnO are mixed at 900 °C

SnO + C → Sn + CO

c) SnO, Sn, Zn and ZnO are mixed at 900 °C

Zn + SnO → ZnO + Sn

Of the 4 oxide formation reactions, write down one for which the entropy change is negative. Provide a brief explanation for your choice.

The entropy change is likely to be negative in three of them:

- **$2Sn + O_2 \rightarrow 2SnO$**
- **$2Zn + O_2 \rightarrow 2ZnO$**
- **$4/3Al + O_2 \rightarrow 2/3AlO$**

Each of these involves a *decrease* in the number of moles of gas. Gases have far higher entropy than solids.

The fourth reaction involves an increase in the number of moles of gas so is likely to produce an increase in entropy.

Marks

- Consider a voltaic cell in which oxidation of Cr to Cr^{3+} by O_2 in the presence of acid occurs. Write the half-reaction that occurs at each electrode and the overall balanced redox reaction. **3**

Reaction at anode	**$Cr(s) \rightarrow Cr^{3+}(aq) + 3e^-$**
Reaction at cathode	**$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$**
Overall balanced reaction	**$4Cr(s) + 3O_2(g) + 12H^+(aq) \rightarrow 4Cr^{3+}(aq) + 6H_2O(l)$**

- Is O_2 a stronger oxidizing agent under acidic or basic conditions? Give reasons for your answer. **2**

Acidic. Increasing the concentration of $H^+(aq)$ will favour the products in the reaction.

At standard conditions, $[H^+(aq)] = 1$ M. From the Nernst equation, the potential depends on the $H^+(aq)$ as

$$E_{cell} = E° - \frac{RT}{nF}\ln Q = E° - \frac{RT}{12F}\ln\frac{1}{[H^+(aq)]^{12}}$$

where $[Cr^{3+}(aq)]$ and $P(O_2)$ have been taken to be standard conditions for simplicity.

At low pH, $[H^+(aq)]$ is high so Q is small. The reduction potential is *decreased* so the oxidation potential is *increased.*

At high pH, $[H^+(aq)]$ is low so Q is large. The reduction potential is *increased* so the oxidation potential is *decreased.*

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY

Marks 6

- A voltaic cell utilises the following redox reaction.

$$Bi(s) + 3Fe^{3+}(aq) + H_2O(l) \rightarrow 3Fe^{2+}(aq) + BiO^{+}(aq) + 2H^{+}(aq)$$

What species is the oxidising agent in this reaction?	**$Fe^{3+}(aq)$**
How many electrons are transferred in the redox reaction?	**3**

Calculate the standard cell potential, $E°_{cell}$, for this electrochemical cell.

From the data page, the reduction potentials are

$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$ $E^o = +0.77$ V

$BiO^+(aq) + 2H^+(aq) + 3e^- \rightarrow Bi(s) + H_2O(l)$ $E^o = +0.32$ V

The latter is less positive so is reversed to become the oxidation reaction:

$$E^o = E^o_{reduction} + E^o_{oxidation} = (+0.77\text{ V}) + (-0.32\text{ V}) = +0.45\text{ V}$$

Answer: **+0.45 V**

Calculate the equilibrium constant for the redox reaction at 25 °C.

The equilibrium constant for this 3 electron reaction can be calculated using:

$$E_{cell} = \frac{RT}{nF}\ln K$$

$$0.45\text{ V} = \frac{(8.314\text{ J K}^{-1}\text{ mol}^{-1})(298\text{ K})}{(3)(96485\text{ C mol}^{-1})}\ln K$$

$\ln K = 52.6$ so $K = 6.8 \times 10^{22}$

Answer: **6.8×10^{22}**

What is the effect on the E_{cell} of decreasing the concentration of $BiO^+(aq)$ in the anode compartment?

BiO^+ is a product. Decreasing its concentration will favour formation of more product.

From the Nernst equation, shown below, if $[BiO^+(aq)]$ is decreased then E_{cell} will increase (i.e. become more positive).

$$E_{cell} = E° - \frac{RT}{nF}\ln Q = E° - \frac{RT}{3F}\ln\frac{[Fe^{2+}(aq)]^3[BiO^+(aq)][H^+(aq)]^2}{[Fe^{3+}(aq)]^3}$$

ANSWER CONTINUES ON THE NEXT PAGE

Calculate the cell potential, E_{cell}, when $[Fe^{3+}] = 8.2 \times 10^{-2}$ M, $[Fe^{2+}] = 0.45$ M, $[BiO^{+}] = 0.85$ M, and the pH is 2.15.

As pH = $-\log_{10}[H^{+}(aq)]$

$[H^{+}(aq)] = 10^{-2.15}$

From the Nernst equation,

$$E_{cell} = E^{\circ} - \frac{RT}{nF}\ln Q = E^{\circ} - \frac{RT}{3F}\ln\frac{[Fe^{2+}(aq)]^3[BiO^{+}(aq)][H^{+}(aq)]^2}{[Fe^{3+}(aq)]^3}$$

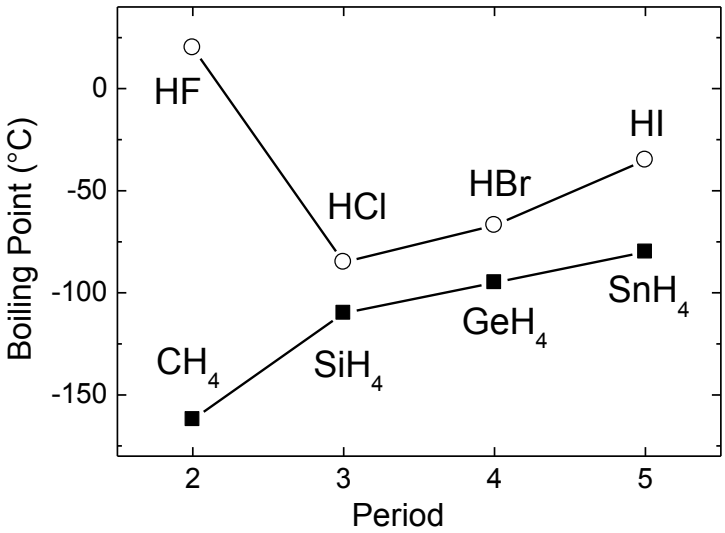
$$= (+0.45\text{ V}) - \frac{(8.314\text{ J K}^{-1}\text{ mol}^{-1})(298\text{ K})}{(3)(96485\text{ C mol}^{-1})}\ln\frac{[0.45]^3[0.85][10^{-2.15}]^2}{[8.2\times10^{-2}]^3}$$

$$= +0.49\text{ V}$$

Answer: **0.49 V**

Marks
4

- The figure below shows the boiling points of Group 14 and Group 17 hydrides as a function of the period (row) of the periodic table.



It is apparent from this figure that:
- the tetrahydrides have lower boiling points than the monohydrides,
- the boiling points increase with period, with the exception of HF.

Explain these features.

Boiling points depend on the strength of the intermolecular forces. Higher boiling points occur when these forces are strong and lower boiling points occur when these forces are weak.

Three kinds of intermolecular forces are present in these molecules:

- **Dispersion forces. These depend on the size of the molecule and the number of electrons.**
- **Dipole-dipole interactions. These require the presence of a dipole.**
- **Hydrogen bonds. They require H to be bonded to a very electronegative element like F.**

The tetrahydrides are all tetrahedral. As a result, none have dipole moments so there are no dipole-dipole interactions in tetrahydrides. The monohydrides are all polar, however. The higher boiling points in the monohydrides are due to the presence of these dipole-dipole interactions.

Note that the each monohydride is isoelectronic with the tetrahydride in the same period so dispersion forces are quite similar.

Down a period, the number of electrons is increasing and these are held further from the nucleus. As a result, dispersion forces increase and so boiling points increase.

An exception to this is HF. Because H is bonded to the very electronegative F atom, strong hydrogen bonds are present between HF molecules. Despite the weak dispersion forces in HF, it has a high boiling point as a result of the hydrogen bonds.