Topics in the June 2014 Exam Paper for CHEM1903

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- Nuclear and Radiation Chemistry

2014-J-3:

- Nuclear and Radiation Chemistry

2014-J-5:

- Wave Theory of Electrons and Resulting Atomic Energy Levels
- Atomic Electronic Spectroscopy
- Ionic Bonding

2014-J-6:

- Lewis Structures
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2014-J-7:

- Lewis Structures
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- Types of Intermolecular Forces

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- Chemical Equilibrium
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2014-J-11:

- First and Second Law of Thermodynamics
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- Batteries and Corrosion

2014-J-14:

- Batteries and Corrosion

Marks 6

- In March 2011 after a tsunami flooded the Fukushima Daiichi nuclear power plant, three of the six reactors went into meltdown, and by 31 March had released large quantities of the nuclides detailed in the table below.

Radioisotope	Initial activity of quantity released (10^{15} Bq)	Half-life
^{131}I	511	8.02 days
^{137}Cs	13.6	30.17 years

Given that the only stable nuclide of iodine is ^{127}I, would you expect the primary decay mechanism for ^{131}I to be α, β^-, or β^+ decay? Briefly explain your reasoning.

^{131}I has Z = 53 and N = 78 giving an N / Z ratio of 1.47. This ratio suggests that β^- will be the primary decay mechanism. α becomes impoortant after Z = 82.

This decay route will lower this ratio as it involves a neutron being converted into a proton and a β^- particle: N will decrease by 1 and Z will increase by 1.

Calculate the decay constant for ^{131}I.

The decay constant, λ, is related to the half life, $t_{1/2} = \ln 2 / \lambda$:

$$\lambda = \ln 2 / t_{1/2} = \ln 2 / (8.02 \times 24 \times 60 \times 60)\ s^{-1} = 1.00 \times 10^{-6}\ s^{-1}$$

Answer: **$1.00 \times 10^{-6}\ s^{-1}$**

Calculate the initial mass of ^{131}I released.

The initial activity of ^{131}I is 511×10^{15} Bq or 511×10^{15} nuclei s^{-1}. As activity, $A = \lambda N$:

$$N = A / \lambda = 511 \times 10^{15}\ \text{nuclei}\ s^{-1} / 1.00 \times 10^{-6}\ s^{-1} = 5.11 \times 10^{23}\ \text{nuclei}$$

The molar mass of ^{131}I is 131 g mol^{-1} so 6.022×10^{23} nuclei has a mass of 131 g. Therefore:

$$5.11 \times 10^{23}\ \text{nuclei corresponds to}\ 5.11 \times 10^{23} / 6.022 \times 10^{23} \times 131\ g = 111\ g$$

Answer: **111 g**

THIS QUESTION CONTINUES ON THE NEXT PAGE.

Marks 6

One method of determining whether further radionuclide leaks are occurring is to monitor the relative activities of the different nuclides as a function of time. Calculate the expected activity due to each of these nuclides exactly 3 years after the release. Assume no more has subsequently escaped from the reactors.

If the initial number of nuclei is N_0, the number of radioactive nucleus after time t is N_t where $\ln(N_0/N_t) = \lambda t$. As $A = \lambda N$, this can also be written in terms of activities:

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

From 2014-J-2, λ for ^{131}I is 1.00×10^{-6} s^{-1} and $A_0 = 511 \times 10^{15}$ Bq. Hence, after exactly 3 years:

$$\ln(511 \times 10^{15} \text{ Bq} / A_t) = (1.00 \times 10^{-6} \text{ s}^{-1}) \times (3.00 \times 365.25 \times 24 \times 60 \times 60 \text{ s})$$

$$A_t = 3.80 \times 10^{-24} \text{ Bq}$$

From 2014-J-2, $t_{1/2} = 30.17$ years for ^{137}Cs. Hence:

$$\lambda = \ln 2 / t_{1/2} = \ln 2 / (30.17 \times 365.25 \times 24 \times 60 \times 60) \text{ s}^{-1} = 7.28 \times 10^{-10} \text{ s}^{-1}$$

Using $A_0 = 13.6 \times 10^{15}$ Bq from 2014-J-2, after exactly 3 years:

$$\ln(13.6 \times 10^{15} \text{ Bq} / A_t) = (7.28 \times 10^{-10} \text{ s}^{-1}) \times (3.00 \times 365.25 \times 24 \times 60 \times 60 \text{ s})$$

$$A_t = 1.27 \times 10^{16} \text{ Bq}$$

Activities	^{131}I: **3.80×10^{-24} Bq**	^{137}Cs: **1.27×10^{16} Bq**

Caesium has no biological role in the human body, and is usually only present in trace amounts. On ingestion, even non-radioactive Cs isotopes are considered toxic as they are capable of partially substituting for chemically similar elements. Name a chemically similar element. State one chemically-significant difference between ions of this element and Cs^+ ions.

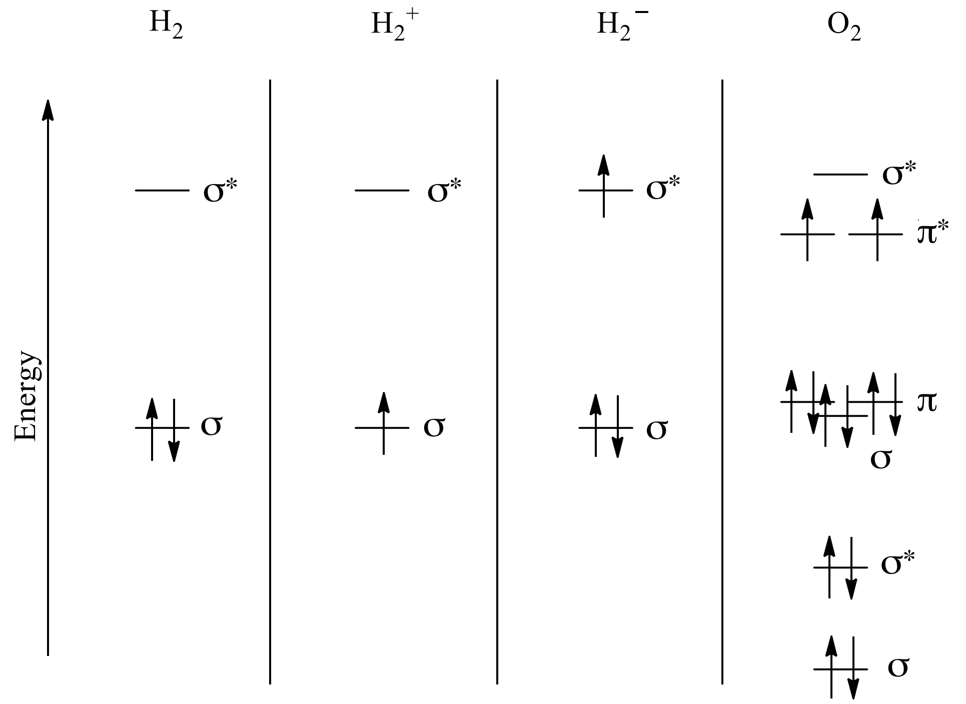
As a +1 ion, Cs^+ is chemically similar to Na^+ and K^+.

Cs^+ is larger than either of these ions. This will lead it to have higher coordination numbers: more anions will fit around it in ionic solids and more donor atoms (such as OH_2) will coordinate to it than can fit on Na^+ or K^+.

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

Marks
6

- The molecular orbital energy level diagrams for H_2, H_2^+, H_2^- and O_2 are shown below. Fill in the valence electrons for each species in its ground state and label the types of orbitals (σ, σ*, π, π*).



Give the bond order of each species.

H_2: ½ **(2 - 0) = 1**	H_2^+: ½ **(1 - 0) = ½**	H_2^-: ½ **(2 - 1) = ½**	O_2: ½ **(8 - 4) = 2**

Which of the four species are paramagnetic?

H_2^+, H_2^- and O_2

The bond lengths of H_2^+ and H_2^- are different. Which do you expect to be longer? Explain your answer.

H_2^- will be longer. Both have bond order of 0.5, but H_2^- is a multi-electron system so is destabilised by electron-electron repulsion. H_2^+ is single electron system so has no electron-electron repulsion.

Marks

- Determine an electronic transition involving the $n = 5$ level of the He^+ ion that emits light in the visible region (400–700 nm) of the electromagnetic spectrum. **3**

Using Planck's relationship between wavelength and energy, $E = hc / \lambda$, visible light corresponds to the range:

$$E\ (400\ \text{nm}) = 6.626 \times 10^{-34}\ \text{J s} \times 2.998 \times 10^{8}\ \text{m s}^{-1} / 400 \times 10^{-9}\ \text{m} = 4.97 \times 10^{-19}\ \text{J}$$
$$E\ (700\ \text{nm}) = 6.626 \times 10^{-34}\ \text{J s} \times 2.998 \times 10^{8}\ \text{m s}^{-1} / 700 \times 10^{-9}\ \text{m} = 2.84 \times 10^{-19}\ \text{J}$$

For a 1-electron ion like He^+, the orbital energies are given by $E_n = -Z^2 E_R / n^2$ where $Z = 2$ for He^+ and E_R is the Rydberg constant, 2.18×10^{-18} J. For a transition from $n = 5$ to another level n_f, the energy difference is:

$$\Delta E = -4 \times 2.18 \times 10^{-18} \times (1/n_f^2 - 1/5^2)$$

With $n_f = 11$, the transition is just outside the visible range. As n_f must be an integer, the lowest value of n_f is 12. Any value of n_f above this will also be in the visible.

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

Examples include:

- **The diffraction of electron beams. Electrons can be diffracted just like ligt waves.**
- **The standing wave structure of atoms leading to atomic line spectra. Electrons can only exist in discrete orbits with certain energies, leading to absorption and emission at certain wavelengths rather than at every wavelength.**

- Consider the melting points of the following solids, which all have the halite crystal structure type. **3**

solid	AgCl	KBr	KCl	NaCl
m.p. (°C)	455	734	770	801

Rationalise the order of the melting points of KBr, KCl and NaCl in terms of the size of the constituents and the strength of the interactions holding them together.

Melting an ionic solid involves breaking up the lattice: the more energy it takes to do this, the higher the melting point will be. The lattice energy depends on the:

- **The crystal structure adopted: as these salts all adopt the same halite crystal structure type, this is not a factor here.**
- **The charges on the cations and anions: as these salts all have a +1 cation and a -1 anion, this is not a factor here.**
- **The size of the cation and anion: the smaller these are, the closer they can approach and the larger the lattice energy will be:**

ANSWER CONTINUES ON THE NEXT PAGE

(i) Br^- is bigger than Cl^- so KCl has a higher lattice energy and a higher melting point than KBr.

(ii) K^+ is larger than Na^+ so NaCl has a higher lattice energy and a higher melting point than KCl.

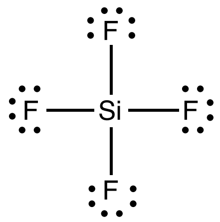
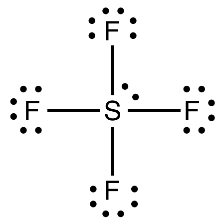
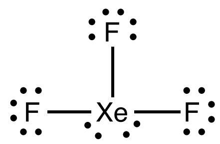
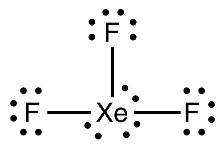
The Ag^+ ion is intermediate in size between Na^+ and K^+. Why does AgCl have a melting point considerably lower than both KCl and NaCl?

When the relative electronegativity of the anion and cation are very different as in NaCl and KCl, the bonding is predominately ionic. Melting the solid requires breaking up the ionic lattice with its strong and long distance interactions.

As Ag^+ is much less electronegative than Na^+ and K^+, AgCl is much less ionic than NaCl and KCl and has the lowest melting point. There is considerable ionic character to the bonding in AgCl.

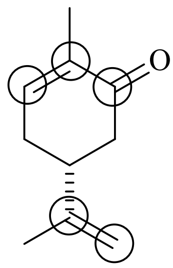
Marks 8

- Complete the table below showing the Lewis structures and the predicted shapes of the following species.

Species	Lewis Structure	Approximate F-X-F bond angle(s)	Name of molecular shape
SiF_4		**109.5°**	**tetrahedral**
SF_4		**90°, 120° and 180°**	**'see-saw'**
XeF_3^+		**90° and 180°**	**'T-shaped'**
XeF_3^-		**90°**	**trigonal pyramidal**

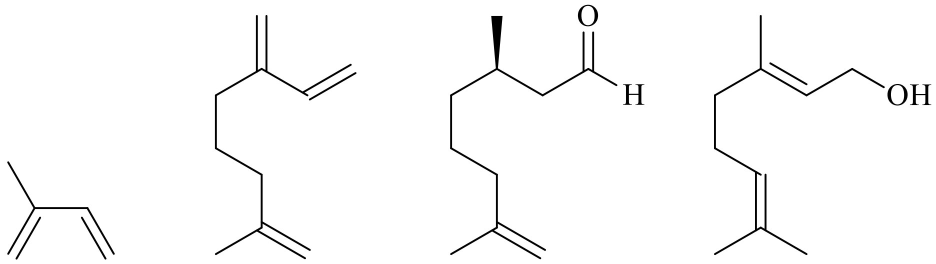
Marks
5

- (*R*)-Carvone is a typical terpene, a class of compounds widely distributed in nature. On the structure of (*R*)-carvone below, circle all of the carbon atoms with trigonal planar geometry.



(*R*)-carvone

All terpenes are derived from isoprene and many, such as myrcene, (*R*)-citronellal and geraniol, are used in the perfume industry.



isoprene	myrcene	(*R*)-citronellal	geraniol
b.p. 34 °C	b.p. 167 °C	b.p. 201 °C	b.p. 230 °C

Explain the differences in boiling points of these four compounds in terms of the type and size of the intermolecular forces present.

All the molecules experience dispersion forces. Dispersion forces are related to the polarisability of a molecule and increase as the number of electrons in the molecule increases (i.e. they increase with molecular size).

Dispersion forces are the only intermolecular forces present in isoprene and myrcene, but are stronger for the larger myrcene, so it has the higher boiling point.

Myrcene, citronellal and geraniol are all of similar size, so have similar dispersion forces.. Citronellal has a polar C=O group so can engage in dipole-dipole interactions so has a higher boiling point than myrcene.

Geraniol contains an –OH group so can engage in hydrogen bonding, a particularly strong intermolecular force, so it has a higher boiling point than citronellal.

Marks 5

- When 10.0 g of solid ammonium carbamate $NH_2CO_2NH_4$ is placed in an evacuated 1.0 L flask at 25 °C, the pressure in the flask rises to 88 mmHg. Write a balanced equation for the decomposition of ammonium carbamate into ammonia gas and carbon dioxide.

$NH_2CO_2NH_4(s) \rightarrow 2NH_3(g) + CO_2(g)$

Calculate the equilibrium constant in terms of partial pressures, K_p, for the decomposition of ammonium carbamate.

The total pressure at equilibrium is 88 mmHg corresponding to 88 / 760 atm. The total pressure is the sum of the partial pressures:

$$P(NH_3) + P(CO_2) = 88/760 \text{ atm} = 0.12 \text{ atm}$$

From the chemical equation, $P(NH_3) = 2 \times P(CO_2)$ and so:

$$3 \times P(CO_2(g)) = 0.12 \text{ atm}$$
$$P(CO_2) = 0.039 \text{ atm and } P(NH_3) = 0.077 \text{ atm}$$

The equilibrium constant in terms of partial pressures is given by:

$$K_p(1) = P(NH_3)^2 P(CO_2) = (0.077)^2(0.039) = 2.3 \times 10^{-4}$$

Answer: **2.3×10^{-4}**

This flask is connected by a hose (of negligible volume) to another 1.0 L flask at 25 °C containing 1.00 atm of $H_2S(g)$. A tap between the flasks is opened and the gaseous contents allowed to mix. Given the following reaction data:

$$NH_4SH(s) \rightleftharpoons NH_3(g) + H_2S(g) \quad K_p = 9.40 \times 10^{-2} \text{ at } 25\ °C,$$

calculate K_p for the new equilibrium that is established, *viz.*

$$NH_2CO_2NH_4(s) + H_2S(g) \rightleftharpoons NH_3(g) + CO_2(g) + NH_4SH(s)$$

For $NH_4SH(s) \rightleftharpoons NH_3(g) + H_2S(g)$, the equilibrium constant is:

$$K_p(2) = P(NH_3)\, P(H_2S)$$

For $NH_2CO_2NH_4(s) + H_2S(g) \rightleftharpoons NH_3(g) + CO_2(g) + NH_4SH(s)$

$$K_p(3) = P(NH_3)\, P(CO_2) / P(H_2S)$$

The relationship between K_p (1), K_p (2) and K_p (3) is thus:

$$K_p(1) / K_p(2) = P(NH_3)^2 P(CO_2) / P(NH_3) P(H_2S)$$
$$= P(NH_3) P(CO_2) / P(H_2S) = K_p(3)$$

$$K_p(3) = 2.3 \times 10^{-4} / 9.40 \times 10^{-2} = 2.4 \times 10^{-3}$$

Answer: 2.4×10^{-3}

THIS QUESTION CONTINUES ON THE NEXT PAGE.

Hence calculate the total pressure in the flasks at equilibrium.

Marks
3

The initial partial pressures and equilibrium constant are given in 2014-J-8, $P(H_2S)$ = 1.00 atm, $P(CO_2)$ = 0.039 atm and $P(NH_3)$ = 0.077 atm) and K_p (3) = 2.4 × 10^{-3}. A reaction table can be used to work out the equilibrium partial pressures.

A reaction table can be used to calculate the equilibrium pressures. For the gases in the reaction $NH_2CO_2NH_4$(s) + H_2S(g) $\rightleftharpoons$ NH_3(g) + CO_2(g) + NH_4SH(s):

	H_2S(g)		NH_3(g)	CO_2(g)
initial	**1.00**	$\rightleftharpoons$	**0.077**	**0.039**
change	**-*x***		**+*x***	**+*x***
equilibrium	**1.00 - *x***		**0.077 + *x***	**0.039 + *x***

Hence,

$$K_p = P(NH_3)\,P(CO_2)\,/\,P(H_2S)$$
$$= (0.077 + x)(0.039 + x) / (1.00 - x) = 2.4 \times 10^{-3}$$

Expanding this gives:

$$0.00298 + 0.116x + x^2 = 2.4 \times 10^{-3} - 2.4 \times 10^{-3}x$$
$$x^2 + 0.118x + 0.000533 = 0$$

Solving this gives x = -0.0047 or x = -0.11. The latter would give negative partial pressures for NH_3 and CO_2. Using the former:

$P(H_2S)$ = (1.00 + 0.0047) atm,
$P(NH_3)$ = (0.077 – 0.0047) atm and
$P(CO_2)$ = (0.039 + 0.0047) atm.

The total pressure is then $P(H_2S) + P(NH_3) + P(CO_2)$ = 1.11 atm.

Answer: **1.11 atm**

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	Marks
• At a temperature of absolute zero, the entropy of deuterated methane CH_3D is 12 J K^{-1} mol^{-1}. Explain the significance of this value and suggest an explanation for it.	2

The 3rd Law of Thermodynamics is sometimes written in the form below:

- **The entropy of a perfect crystal at absolute zero is exactly equal to zero.**

CH_3D will adopt the same crystal structure as CH_4 as there is no difference in its shape or size. The relative position of the D atom in neighbouring molecules, however, will be completely random as there will minimal energy difference between them.

A crystal of CH_3D will not be perfect even at absolute zero.

• A concentration cell is constructed from two beakers containing 1 M $NiCl_2$ and 0.002 M $NiCl_2$. Describe the overall change that occurs as the concentration cell runs.	3

The overall process occurring is to equalise the concentrations:

- **In the beaker containing 0.002 M $NiCl_2$, oxidation of Ni(s) will occur to produce Ni^{2+}(aq) ions. This will increase [Ni^{2+}(aq)] in this beaker.**
- **The electrons from this oxidation will flow through the wire to the electrode in the second beaker.**
- **In this second beaker containing 1 M $NiCl_2$, reduction of Ni^{2+}(aq) will occur. This will decrease [Ni^{2+}(aq)].**
- **The cell will continue to operate until the concentrations have equalised.**

What would be the major driving force for the overall reaction, enthalpy or entropy? Explain your answer.

There is enthalpy change in this process: the standard electrode potential is zero. The process is driven entirely by entropy: it is unfavourable for the concentration difference to be present.

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Marks 4

- Consider the following standard free energies of formation at 1000 K.

Compound	$CO(g)$	$CO_2(g)$	$Fe_2O_3(s)$	$Li_2O(s)$
$\Delta_f G°$ / kJ mol^{-1}	–200	–396	–562	–466

Predict whether the following oxides can be reduced to metals by carbon at that temperature, and state whether the products could be CO, CO_2 or both.

$Fe_2O_3(s)$

For reduction by C(s), the possible reactions are:

(i) $Fe_2O_3(s) + 3C(s) \rightarrow 2Fe(s) + 3CO(g)$

(ii) $Fe_2O_3(s) + 3/2C(s) \rightarrow 2Fe(s) + 3/2CO_2(g)$

Using $\Delta G° = \Sigma m \Delta_f G°(\text{products}) - \Sigma n \Delta_f G°(\text{reactants})$:

(i) $\Delta G° = 3\Delta_f G°(CO(g)) - \Delta_f G°(Fe_2O_3(s))$
$= [(3 \times -200) – (-562)]$ kJ mol^{-1} = -38 kJ mol^{-1}

(ii) $\Delta G° = 3/2\Delta_f G°(CO_2(g)) - \Delta_f G°(Fe_2O_3(s))$
$= [(3/2 \times -396) – (-562)]$ kJ mol^{-1} = -32 kJ mol^{-1}

Both reactions are possible and have similar $\Delta G°$ values. Both CO and CO_2 are possible products.

$Li_2O(s)$

For reduction by C(s), the possible reactions are:

(i) $Li_2O(s) + C(s) \rightarrow 2Li(s) + CO(g)$

(ii) $Li_2O(s) + 1/2C(s) \rightarrow 2Li(s) + 1/2CO_2(g)$

Using $\Delta G° = \Sigma m \Delta_f G°(\text{products}) - \Sigma n \Delta_f G°(\text{reactants})$:

(i) $\Delta G° = \Delta_f G°(CO(g)) - \Delta_f G°(Li_2O(s))$
$= [(-200) – (-466)]$ kJ mol^{-1} = +266 kJ mol^{-1}

(ii) $\Delta G° = 1/2\Delta_f G°(CO_2(g)) - \Delta_f G°(Li_2O(s))$
$= [(1/2 \times -396) – (-466)]$ kJ mol^{-1} = +268 kJ mol^{-1}

Neither reaction is possible.

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Marks 4

A voltaic cell consists of Cd^{2+}/Cd and Ag^+/Ag half cells with initial concentrations of $[Cd^{2+}]$ = 1.00 M and $[Ag^+]$ = 0.60 M. Each half cell contains 1.00 L of solution.

What is the voltage of the cell at 20 °C after equilibrium has been reached?	**0 V**

What are the concentrations of the Cd^{2+}(aq) and the Ag^+(aq) ions at 20 °C after equilibrium has been reached?

The standard reduction half-cell reactions are (from the data sheet):

$$Cd^{2+}(aq) + 2e^- \rightarrow Cd(s) \qquad E° = -0.40\ V$$
$$Ag^{+}(aq) + e^- \rightarrow Ag(s) \qquad E° = +0.80\ V$$

As the Cd^{2+} / Cd value is the least positive, it is reversed and the reaction and cell potential are:

$$2Ag^+(aq) + Cd(s) \rightarrow 2Ag(s) + Cd^{2+}(aq)$$

$$E° = (+0.40\ V) + (+0.80\ V) = +1.20\ V$$

Using $E° = \frac{RT}{nF}\ln K$, the equilibrium constant for this 2 e^- process at T = 20 °C is:

$$K = \exp\left(\frac{(1.20\ V) \times 2 \times (96485\ C\ mol^{-1})}{(8.314\ J\ K^{-1}\ mol^{-1}) \times (293\ K)}\right) = 2.03 \times 10^{44}$$

The equilibrium constant is so large that the reaction essentially goes to completion. Initially, $[Cd^{2+}(aq)]_{initial}$ = 1.00 M and $[Ag^+(aq)]_{initial}$ = 0.60 M. If essentially all of the Ag^+(aq) reacts then $[Cd^{2+}(aq)]$ = 1.30 M. If the small amount of Ag^+(aq) left over has $[Ag^+(aq)] = x$ M:

$$E_{cell} = E° - \frac{RT}{nF}\ln Q = E° - \frac{RT}{2F}\ln\frac{[Cd^{2+}(aq)]}{[Ag^+(aq)]^2} = 0$$

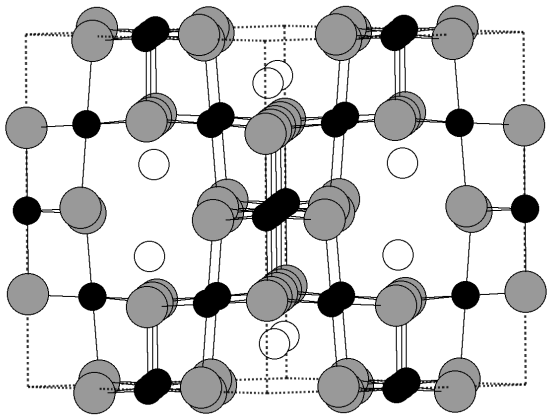
$$= (1.20\ V) - \frac{(8.314\ J\ K^{-1}\ mol^{-1}) \times (293\ K)}{2 \times (96485\ C\ mol^{-1})}\ln\frac{(0.13)}{[Ag^+(aq)]^2}$$

This gives $[Ag^+(aq)] = 2.6 \times 10^{-21}$

$[Cd^{2+}]_{eq}$ = **1.3 M**	$[Ag^+]_{eq}$ = **2.6×10^{-21} M**

Marks
3

- $LiMn_2O_4$ (s) is an infinite network solid with the spinel-type structure, shown below. White circles are Li atoms, black circles are Mn atoms and grey circles are oxygen atoms. Dashed lines represent the unit cell.



What are the most important types of chemical bonds responsible for making $LiMn_2O_4$ a stable solid?

Ionic bonds

$LiMn_2O_4$ is commonly used as a cathode in rechargeable lithium-ion batteries. The battery is charged by moving Li^+ ions out of this cathode to give $Li_{1-x}Mn_2O_4$. Explain how this is possible.

The structure contains channels through which the Li^+ ions can diffuse. When Li^+ is removed, the oxidation of Mn increases to ensure that charge balance is maintained.

The anode is C (graphite), which gives Li_xC_6 on charging. Describe how the lithium is incorporated into the graphite anode.

Graphite consists of hexagonal sheets. The bonding between the carbon atoms in the sheets is strong but the forces between the sheets are weak. The Li^+ ions can occupy ('intercalate') the space between the sheets.

For every Li^+ that is incorporated, an electron is transferred onto the carbon atoms and is delocalised over the sheets.

THIS QUESTION IS CONTINUED ON THE NEXT PAGE

Marks
5

Write out the anode and cathode half-cell reactions, and the overall cell reaction, for this battery as it discharges.

Cathode	**$Li_{1-x}Mn_2O_4 + xLi^+ + xe^- \rightarrow LiMn_2O_4(s)$**
Anode	**$Li_xC_6 \rightarrow xLi^+ + xe^- + C_6$**
Overall	**$Li_{1-x}Mn_2O_4 + Li_xC_6 \rightarrow LiMn_2O_4(s) + C_6$**

Many researchers are exploring the possibility of replacing Li^+ with Na^+ in these batteries, because sodium is much cheaper and less toxic than lithium. Explain two potential *disadvantages* of switching to sodium, in terms of battery performance.

Na is heavier than Li: the batteries will need to be heavier.

Na^+ is larger than Li^+ so the diffusion of the ions will be slower: the rate at which the battery discharges and recharges will be slower.

Na is more reactive: there are safety and stability considerations due to reactions with water for example.

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