Topics in the June 2014 Exam Paper for CHEM1101

Click on the links for resources on each topic.

2014-J-2:

- Atomic Electronic Spectroscopy
- Band Theory - MO in Solids
- Ionic Bonding

2014-J-3:

- VSEPR
- Types of Intermolecular Forces

2014-J-4:

- Nuclear and Radiation Chemistry

2014-J-5:

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

2014-J-6:

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

2014-J-7:

- Lewis Structures
- VSEPR

2014-J-8:

- Thermochemistry

2014-J-9:

- Chemical Equilibrium
- First and Second Law of Thermodynamics

2014-J-10:

- Chemical Equilibrium

2014-J-11:

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2014-J-12:

- Equilibrium and Thermochemistry in Industrial Processes

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- Electrolytic Cells

2014-J-14:

- Electrochemistry

2014-J-15:

- Electrochemistry

Marks

- An atomic absorption spectrometer with a path length of 1.0 cm is used to measure the concentrations of copper in tap water. The results are shown below. The standard solution contains 5.0 ppm Cu. **3**

Sample	Absorbance reading
Standard solution (5.0 ppm Cu)	22.3
Unknown tap water	14.5

Assuming the Beer-Lambert Law is applicable, what is the concentration of Cu in the unknown tap water?

According to the Beer-Lambert Law, absorbance, A, is proportional to concentration, c: $A \propto c$. The proportionality constant can be obtained from the standard solution:

constant = A / c = 22.3 / 5.0 = 4.46 ppm^{-1}

Using A = 4.46c, the concentration of copper in the tap water is:

c = A / 4.46 = 14.5 / 4.46 = 3.3 ppm

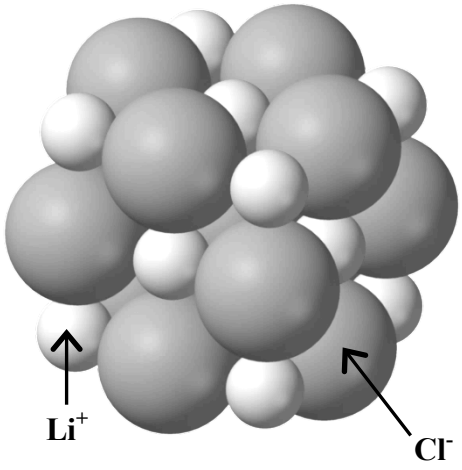
Answer: **3.3 ppm**

What is the absorption process that AAS measures?

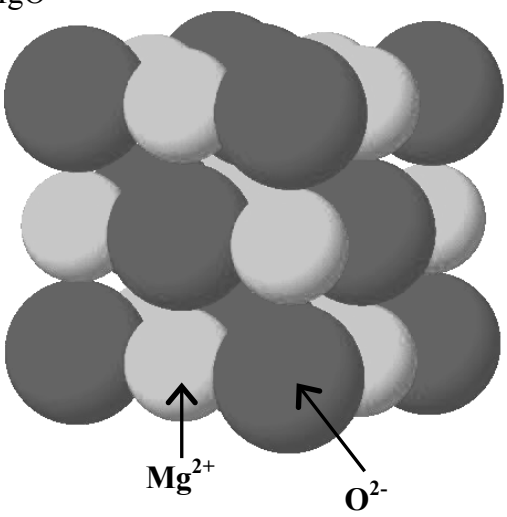
AAS measures the excitation of valence electrons into higher energy states.

- Below are fragments of the ionic crystals of LiCl and MgO (not to scale). On the diagrams, label the ions for each structure. **3**

LiCl



MgO



ANSWER CONTINUES ON THE NEXT PAGE

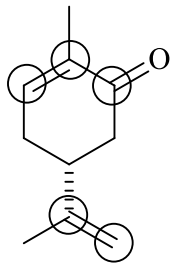
LiCl and MgO both adopt the same crystal lattice structure. Which of the two ionic compounds has the higher melting point? Why?

MgO has the higher melting point.

The higher charges of the ions in MgO (i.e. +2 and -2) compared to LiCl (+1 and -1) means the coulombic attraction between the ions is greater in MgO and hence MgO has the higher melting point.

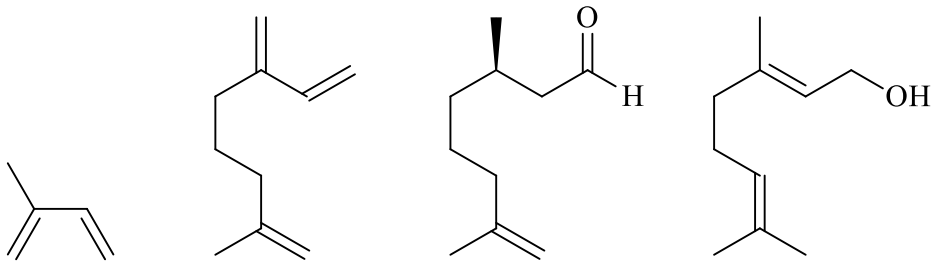
Marks 5

- (*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 ^{o}C	b.p. 167 ^{o}C	b.p. 201 ^{o}C	b.p. 230 ^{o}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 7

- Technetium-99m is an important radionuclide for medical imaging. It is produced from molybdenum-99. Fill in the box below to give a balanced nuclear equation for the production of Tc-99m from Mo-99.

$$^{99}_{42}\text{Mo} \rightarrow {}^{99m}_{43}\text{Tc} + \boxed{{}^{0}_{-1}\text{e}}$$

The half-life of Tc-99m is 6.0 hours. Calculate the decay constant, λ, in s^{-1}.

The half life, $t_{1/2}$, is equal to:

$$t_{1/2} = \ln 2 / \lambda = \ln 2 / (6.0 \times 60. \times 60.\ \text{s}) = 3.2 \times 10^{-5}\ \text{s}^{-1}$$

Answer: **$3.2 \times 10^{-5}\ \text{s}^{-1}$**

Calculate the molar activity in Bq mol^{-1}.

A mol of Tc-99m contains 6.022×10^{23} nuclei. As activity $A = \lambda N$ where N is the number of nuclei:

$$A = (3.2 \times 10^{-5}\ \text{s}^{-1}) \times (6.022 \times 10^{23}\ \text{nuclei mol}^{-1}) = 1.9 \times 10^{19}\ \text{Bq mol}^{-1}$$

Answer: **1.9×10^{19} Bq mol^{-1}**

Calculate the time in hours for 90% of the activity of a sample of Tc-99m to decay.

The number of nuclei changes with time according to $\ln(N_0/N_t) = \lambda t$. If 90% of the nuclei have decayed, $N_t = 0.10 \times N_0$ or $N_0 / N_t = 1 / 0.10$. Hence:

$$\ln(N_0/N_t) = \lambda t$$

$$\ln(1 / 0.10) = (3.2 \times 10^{-5}\ \text{s}^{-1}) \times t$$

$$t = 72000\ \text{s} = 20\ \text{hours}$$

Answer: **20 hours**

Why is Tc-99m suitable for medical imaging? Give two reasons.

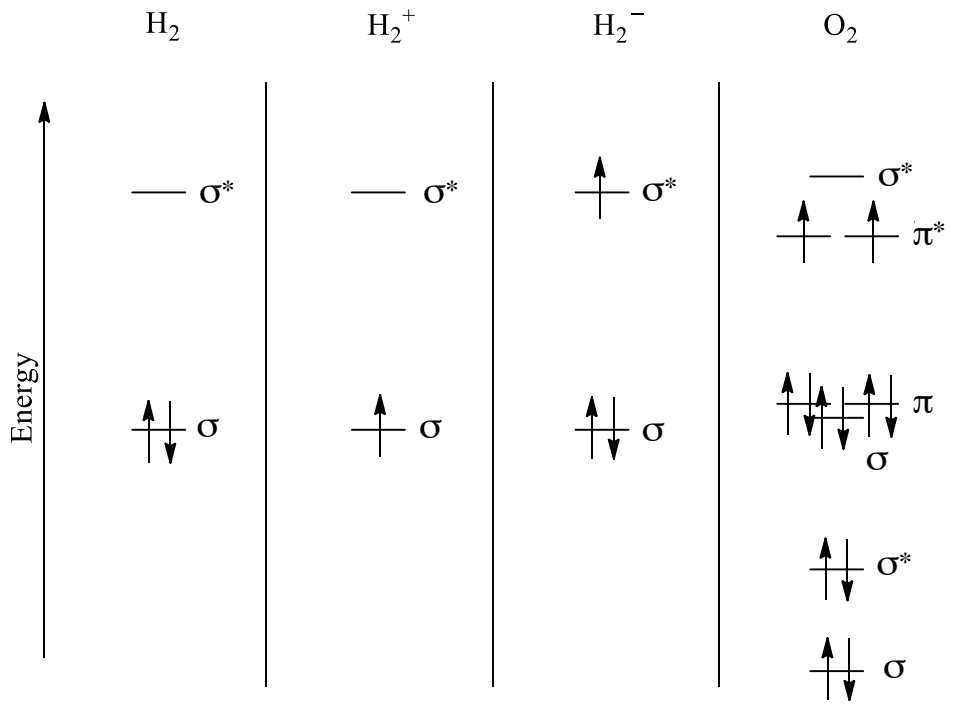
Appropriately short half-life allows time for production of nuclide, administration to patient, and for it to accumulate in the tissue of interest. Activity is high enough to give good quality image with small amount of nuclide.

It is a gamma emitter – highly penetrating radiation that can be detected outside the body and is not damaging to human tissue as it is non-ionising.

Its chemical properties allow it to be incorporated into molecules that will be absorbed by the organs to be investigated.

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**

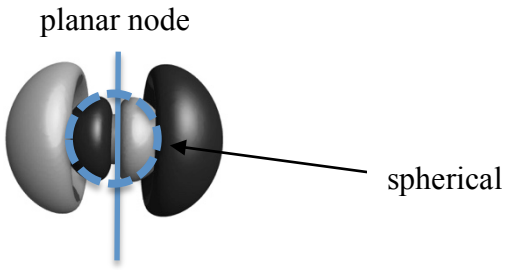
Which of the four species are paramagnetic?

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
• A schematic representation of a *p* orbital is shown below. The central sphere (mostly obscured) represents the atomic nucleus.	**2**



How many spherical and planar nodes does this orbital have? Label them on the diagram above.

Number of spherical nodes: **1**	Number of planar nodes: **1**

What is the principal quantum number, *n*, of this orbital? Explain your answer.

***n* = 3**

The total number of nodes is 1 fewer than the principal quantum number. As the total number of nodes is 1 + 1 = 2, the principal quantum number is 3.

• Shielding is important in multi-electron atoms. Briefly explain the concept of shielding.	**3**

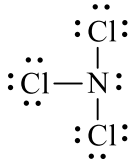
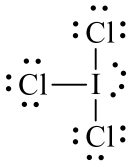
Electrons closer to the nucleus partially block the attractive force of the nucleus on the electrons that are further away, resulting in a lowering of the effective nuclear charge on such electrons.

Give one example of a consequence of shielding.

The elements in a group of the Periodic Table have similar reactivities but ionisation energies decrease and sizes increase.

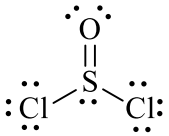
- Complete the following table for the molecules NCl_3 and ICl_3.

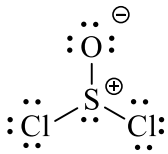
Marks 3

Molecule	Total number of valence electrons	Lewis structure	Shape of molecule
NCl_3	**26**		**trigonal pyramidal**
ICl_3	**28**		**T-shaped**

- Thionyl chloride ($SOCl_2$) is a common chlorinating agent in organic chemistry. Draw two possible Lewis structures for this molecule, assigning formal charges where appropriate.

3





Which is the more stable resonance form? Give a reason for your answer.

The first structure is more stable as it has minimised the formal charges.

Marks 3

- A 1.0 kg sample of copper metal is heated to 100.0 °C. The copper sample is immersed in a volume of water initially at 25.0 °C. What volume of water is required so that the final temperature of the copper is 40.0 °C? Show all working.

  Data: Specific heat capacity of Cu(s) is 0.39 J K^{-1} g^{-1}.
  Specific heat capacity of $H_2O(l)$ is 4.184 J K^{-1} g^{-1}.
  The density of water is 1.0 g mL^{-1}.

The copper cools from 100.0 ^oC to 40.0 ^oC so ΔT = -60.0 K. As the specific heat capacity of Cu(s) is 0.39 J K^{-1} g^{-1}, the heat lost by 1.0 kg during this is given by:

$$q = mC\,\Delta T = (1.0 \times 10^3\ g) \times (0.39\ J\ K^{-1}\ g^{-1}) \times (-60.0\ K) = -23000\ J$$

This heat is gained by the water which is warmed from 25.0 ^oC to 40.0 ^oC – a change of 15.0 K. As the specific heat capacity of water is 4.184 J K^{-1} g^{-1} and a temperature change of 15.0 K is required:

$$q = mC\,\Delta T = m \times (4.184\ J\ K^{-1}\ g^{-1}) \times (15.0\ K) = 23000\ J$$

$$m = 370\ g$$

The density of water is 1.0 g mL^{-1} so the volume required is:

volume = mass / density = 370 g / 1.0 g mL^{-1} = 370 mL

Answer: **370 mL**

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

Marks

- Use the following equilibria:

$$2CH_4(g) \rightleftharpoons C_2H_6(g) + H_2(g) \qquad K_1 = 9.5 \times 10^{-13}$$

$$CH_4(g) + H_2O(g) \rightleftharpoons CH_3OH(g) + H_2(g) \qquad K_2 = 2.8 \times 10^{-21}$$

to calculate the equilibrium constant, K_3, for the following reaction:

$$2CH_3OH(g) + H_2(g) \rightleftharpoons C_2H_6(g) + 2H_2O(g).$$

Show all working.

2

The equilibrium constant expressions for reactions (1) and (2) are given by:

$$K_1 = \frac{[C_2H_6(g)][H_2(g)]}{[CH_4(g)]^2} \qquad \textbf{and} \qquad K_2 = \frac{[CH_3OH(g)][H_2(g)]}{[CH_4(g)][H_2O(g)]}$$

The equilibrium constant for reaction (3) is:

$$K_3 = \frac{[C_2H_6(g)][H_2O(g)]^2}{[CH_3OH(g)]^2[H_2(g)]}$$

K_3 can be obtained by multiplying K_1 by $1 / K_2^2$:

$$K_1 / K_2^2 = \frac{[C_2H_6(g)]\cancel{[H_2(g)]}}{\cancel{[CH_4(g)]^2}} \Big/ \frac{[CH_3OH(g)]^2[H_2(g)]\cancel{^2}}{\cancel{[CH_4(g)]^2}[H_2O(g)]^2} = \frac{[C_2H_6(g)][H_2O(g)]^2}{[CH_3OH(g)]^2[H_2(g)]} = K_3$$

$$K_3 = (9.5 \times 10^{-13}) / (2.8 \times 10^{-21})^2 = 1.2 \times 10^{29}$$

Answer: **1.2×10^{29}**

- The Second Law states that all observable processes must involve a net increase in entropy. When liquid water freezes into ice at 0 °C, the entropy of the water decreases. Since the freezing of water is certainly observable, the processes must still satisfy the Second Law. Provide a brief explanation of how this is so.

1

The freezing of water is exothermic and the heat evolved is passed to the surroundings. This causes an increase in the entropy of the surroundings equal to $\Delta S_{surroundings} = q/T$ where q is the heat gained by the surroundings and T is the temperature of the surroundings.

As long as the T is *low* enough, the *gain* in entropy in the surroundings, $\Delta S_{surroundings}$, overcomes the loss in entropy in the water, ΔS_{system}, so that the entropy of the universe increases. Freezing is spontaneous at temperatures below the freezing point.

Marks 4

- Consider the following reaction.

$$N_2O_4(g) \rightleftharpoons 2NO_2(g) \qquad K_c = 4.61 \times 10^{-3} \text{ at } 25\ ^\circ\text{C}$$

A 0.086 mol sample of NO_2 is allowed to come to equilibrium with N_2O_4 in a 0.50 L container at 25 °C. Calculate the amount (in mol) of NO_2 and N_2O_4 present at equilibrium. Show all working.

The initial concentration of $NO_2(g)$ is:

$[NO_2(g)]$ = number of moles / volume = 0.086 mol / 0.50 L = 0.172 mol L^{-1}

A reaction table can be used to calculate the equilibrium concentrations.

	$N_2O_4(g)$		$2NO_2(g)$
initial	**0.000**	$\rightleftharpoons$	**0.172**
change	**+x**		**-2x**
equilibrium	**x**		**0.172 – 2x**

Hence,

$$K_c = \frac{[NO_2(g)]^2}{[N_2O_4]} = \frac{(0.172-2x)^2}{x} = 4.61 \times 10^{-3}$$

So,

$(0.172 - 2x)^2 = 4.61 \times 10^{-3}\, x$

$0.0296 - 0.688x + 4x^2 = 4.61 \times 10^{-3}\, x$

$4x^2 - 0.693x + 0.0296 = 0$

Solving the quadratic gives x = 0.0766 and x = 0.0965. The second route would give a negative value for $[NO_2(g)]$. Using x = 0.0766:

$[N_2O_4(g)]$ = 0.0766 M and $[NO_2(g)]$ = (0.172 – 2 × 0.0766) M = 0.0188 M

As these concentrations are in a 0.50 L container:

number of moles of $N_2O_4(g)$ = concentration × volume

= 0.0766 mol L^{-1} × 0.50 L = 0.038 mol

number of moles of $NO_2(g)$ = 0.0188 mol L^{-1} × 0.50 L = 0.0094 mol

Amount of NO_2: **0.0094 mol**	Amount of N_2O_4: **0.038 mol**

Marks

- Give the balanced chemical equation for the combustion of butane gas, C_4H_{10}, in oxygen to produce CO_2 and water. **3**

$C_4H_{10}(g) + {}^{13}/_2O_2(g) \rightarrow 4CO_2(g) + 5H_2O(l)$

Use the standard enthalpies of formation provided to calculate the molar heat of combustion of butane gas. Show all working.

Data:

Compound	$H_2O(l)$	$CO_2(g)$	$C_4H_{10}(g)$
$\Delta_f H°$ / kJ mol^{-1}	–285.8	–393.5	–125.6

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

$\Delta_{combustion}H° = [4\Delta_f H°(CO_2(g)) + 5\Delta_f H°(H_2O(g))] - [\Delta_f H°(C_4H_{10}(g))]$

$\Delta_f H°(O_2(g))$ is zero as $O_2(g)$ is already an element in its standard state. Hence:

$\Delta_{combustion}H° = ([4 \times -393.5 + 5 \times -285.8] - [-125.6])$ kJ mol^{-1} = -2877.4 kJ mol^{-1}

Answer: **-2877.4 kJ mol^{-1}**

- Calculate the volume change when 20.0 g of solid trinitrotoluene $C_7H_5N_3O_6(s)$ explosively decomposes via the following process at 2000. °C and 2.0 atm. **3**

$$2C_7H_5N_3O_6(s) \rightarrow 12CO(g) + 5H_2(g) + 3N_2(g) + 2C(s)$$

Assume all gases behave as ideal gases and neglect the volume of any solid phases. Show all working.

The molar mass of $C_7H_5N_3O_6$ is:

molar mass = (7 × 12.01 (C) + 5 × 1.008 (H)
+ 3 × 14.01 (N) + 6 × 16.00 (O)) g mol^{-1}
= 227.14 g mol^{-1}

The number of moles in 20.0 g is therefore:

number of moles = mass / molar mass = 20.0 g / 227.14 g mol^{-1} = 0.0880 mol

The chemical reaction, when 2 mol of $C_7H_5N_3O_6$ decomposes, 12 mol of CO(g), 5 mol of H_2(g) and 3 mol of N_2(g) are produced. When 0.0880 mol decomposes,

moles of gas = 0.0880 × (12 / 2 (CO) + 5/2 (H_2) + 3/2 (N_2)) mol = 0.88 mol

ANSWER CONTINUES ON THE NEXT PAGE

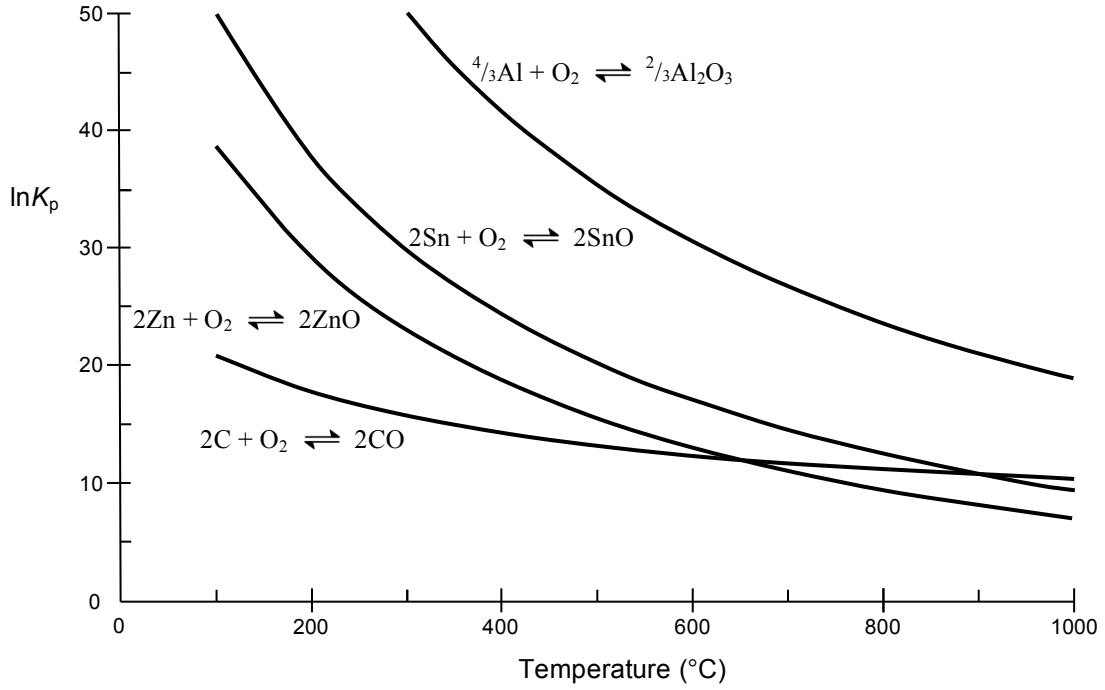
Using $PV = nRT$, the volume of this amount at 2000. ^{o}C (2273 K) and 2.0 atm is:

$$V = nRT / P$$
$$= (0.88 \text{ mol} \times 0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1} \times 2273 \text{ K}) / (2.0 \text{ atm}) = 82 \text{ L}$$

Answer: **82 L**

Marks 4

- The diagram below represents the equilibrium constant K_p associated with the formation of the four oxides indicated.



Using the equilibrium constant data above, describe the reaction that proceeds under the following conditions. If you think no reaction will occur, write 'no reaction'.

CO and Sn are combined at 400 °C

The C/CO line is below the Sn/SnO line at this temperature:

$Sn(s) + CO(g) \rightarrow SnO(s) + C(s)$

Al and SnO are combined at 400 °C

The Al/Al_2O_3 line is above the Sn/SnO line at this temperature:

$2Al(s) + 3SnO(s) \rightarrow Al_2O_3(s) + 3Sn(s)$

C and ZnO are mixed at 900 °C

The C/CO line is above the Zn/ZnO line at this temperature:

$C(s) + ZnO(s) \rightarrow CO(g) + Zn(s)$

ANSWER CONTINUES ON THE NEXT PAGE

Which oxide has the largest (most negative) enthalpy of formation?

$Al_2O_3(s)$

All of the formation reactions for the metallic oxides, $M(s) + O_2(g) \rightarrow MO(s)$, have very similar values of $\Delta_f S^o$ as they all involve loss of a mol of gas. In each case, $\Delta_f S^o < 0$. Hence, differences in $\Delta_f G^o$ are due to differences in $\Delta_f H^o$. As $\ln K_p$ is largest for Al_2O_3 it is the most stable with the most negative $\Delta_f G^o$.

For $2C(s) + O_2(g) \rightarrow 2CO(g)$, $\Delta_f S^o > 0$ because the formation reaction increases the number of moles of gas. As the formation reaction has the $\ln K_p$ value despite this, it must have the smallest (least negative) value for $\Delta_f H^o$.

Marks 6

- An aqueous solution of 1 M $CuSO_4$ undergoes electrolysis. At the minimum voltage necessary for a reaction to proceed, what products form at the anode and the cathode? Explain your answer.

At the cathode, reduction occurs. The two possible reduction reactions are of $Cu^{2+}(aq)$ and of $H_2O(l)$:

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s) \qquad E^o = +0.34\ V$$
$$2H_2O + 2e^- \rightarrow H_2(g) + 2OH^-(aq) \qquad E^o = -0.83\ V$$

Reduction of $Cu^{2+}(aq)$ has the more positive (least negative) reduction potential: it is easier and so this reduction occurs first:

Cu(s) produced at cathode: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

At the anode, oxidation occurs. In SO_4^{2-}, sulfur already has its highest possible oxidation number of +6 and so it cannot be oxidised. $H_2O(l)$ is oxidised at the anode;

$O_2(g)$ produced at anode: $2H_2O \rightarrow O_2(g) + 4H^+(aq) + 4e^-$

Write a balanced overall reaction for the electrolytic cell.

$2Cu^{2+}(aq) + 2H_2O(l) \rightarrow 2Cu(s) + O_2(g) + 4H^+(aq)$

Assuming no overpotential, what would be the minimum voltage required to drive the overall reaction at a pH of 0?

For the reduction of $Cu^{2+}(aq)$, E^o(reduction) = +0.34 V. For the oxidation of $H_2O(l)$, E^o(oxidation) = -1.23 V.

For the overall cell, E^o = ((-0.83) + (-1.23)) V = -0.89 V

To drive this reaction to occur, a voltage of greater than 0.89 V needs to be supplied.

Answer: **0.89 V**

At a pH of 7, would a higher or lower voltage be required to drive the reaction? Explain your answer.

The standard oxidation potential of $H_2O(l)$ assumes standard concentrations and so $[H^+(aq)]$ = 1.0 M. At pH = 7, $[H^+(aq)]$ is much less, so from Le Chatelier's principle the forward reaction will be favoured to produce more $H^+(aq)$. Hence lower voltage would be required.

Marks 6

- An electrochemical cell consists of an Fe^{2+}/Fe half cell with unknown $[Fe^{2+}]$ and a Sn^{2+}/Sn half-cell with $[Sn^{2+}] = 1.10$ M. The electromotive force (electrical potential) of the cell was measured at 25 °C to be 0.35 V. What is the concentration of Fe^{2+} in the Fe^{2+}/Fe half-cell?

From the reduction potential table,

$$E_{cell}^{o}\ (Fe^{2+}(aq) + e^- \rightarrow Fe(s)) = -0.44\ V$$

$$E_{cell}^{o}\ (Sn^{2+}(aq) + e^- \rightarrow Sn^{2+}(aq)) = -0.136\ V$$

The Fe^{2+}/Fe half cell has the more negative reduction potential so it is the half cell that is turned around to act as the oxidation half cell:

$$E_{cell}^{o}\ (Fe(s) \rightarrow Fe^{2+}(aq) + e^-) = +0.44\ V$$

In combination with the Sn^{2+}/Sn reduction half cell, this gives an overall reaction and cell potential of:

$$Fe(s) + Sn^{2+}(aq) \rightarrow Fe^{2+}(aq) + Sn(s) \qquad E^{o} = ((+0.44) + (-0.136))\ V = 0.30\ V$$

For this reaction with $[Sn^{2+}(aq)] = 1.10$ M:

$$Q = \frac{[Fe^{2+}(aq)]}{[Sn^{2+}(aq)]} = \frac{[Fe^{2+}(aq)]}{(1.10)}$$

For the $2e^-$ reaction, the Nernst equation gives the cell potential as:

$$E_{cell} = E^{\circ} - \frac{RT}{nF}\ln Q$$

$$= (0.30\ V) - \frac{(8.314\ J\ K^{-1}\ mol^{-1})(298\ K)}{(2 \times 96485\ C\ mol^{-1})}\ln\frac{[Fe^{2+}(aq)]}{(1.10)} = 0.35\ V$$

Solving this gives, $[Fe^{2+}(aq)] = 0.031$ M.

Answer: **0.031 M**

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

Using $E^{o} = (RT/nF)\ \ln K$:

$$0.30\ V = \frac{(8.314\ J\ K^{-1}\ mol^{-1})(298\ K)}{(2 \times 96485\ C\ mol^{-1})}\ln K$$

Solving this gives $K = 1.9 \times 10^{10}$

Answer: **1.9×10^{10}**

ANSWER CONTINUES ON THE NEXT PAGE

Calculate the standard Gibbs free energy change for the reaction at 25 °C.

Using $\Delta G^o = -nFE^o$:

$\Delta G^o = -2 \times (96485\ \text{C mol}^{-1}) \times (0.30\ \text{V}) = -59\ \text{kJ mol}^{-1}$

Answer: **$-59\ \text{kJ mol}^{-1}$**

Marks 3

- 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.

$[Ni^{2+}(aq)]$ will reduce in the more concentrated solution and Ni(s) will be deposited on the electrode.

Simultaneously, $[Ni^{2+}(aq)]$ will increase in the less concentrated solution and the Ni(s) electrode will dissolve.

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

Entropy

The overall enthalpy change of the reaction is zero. Maximum entropy is reached when the concentrations of the two cells are equal.

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.