

Topics in the November 2008 Exam Paper for CHEM1101

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Write down an equation representing the decay mechanism of ^{14}C.	Marks 6
$^{14}_6\text{C} \rightarrow ^{14}_7\text{N} + ^0_{-1}\beta$	
The half-life of ^{14}C is 5730 years. What is the activity of precisely 1 g of this isotope, given that each atom weighs 14.00 amu? Give your answer in Bq.	
As 1 mol of ^{14}C has a mass of 14.00 g, the number of nuclei, N, in 1 g is: number of nuclei = number of moles $\times$ Avogadro's constant $N = \left(\frac{1.000}{14.00} \text{ mol}\right) \times (6.022 \times 10^{23} \text{ nuclei mol}^{-1}) = 4.301 \times 10^{22} \text{ nuclei}$ The activity (A) is related to N by $A = \lambda N$ where λ is the decay constant. The half life, $t_{1/2}$, is related to the decay constant, λ, by $t_{1/2} = \ln 2 / \lambda$. Hence, $\lambda = \ln 2 / (5730 \times 365 \times 24 \times 60 \times 60 \text{ s}) = 3.84 \times 10^{-12} \text{ s}^{-1}$ The activity is thus, $A = \lambda N = (3.84 \times 10^{-12} \text{ s}^{-1}) \times (4.301 \times 10^{22} \text{ nuclei})$ $= 1.65 \times 10^{11} \text{ nuclei s}^{-1} = 1.65 \times 10^{11} \text{ Bq}$	
Answer: $1.65 \times 10^{11} \text{ Bq}$	
Carbon-14 is used as a radioactive tracer in the urea breath test, a diagnostic test for <i>Helicobacter pylori</i>. Name an instrument which can be used to detect radioactive carbon dioxide in the breath of a patient.	
A scintillation counter	
A patient ingests 1.00 g of urea with a total activity of 1.00 μCi. What is the percentage, by weight, of carbon-14 in this sample?	
As 1 Ci = 3.70×10^{10} Bq, from above, the activity per gram of ^{14}C is, $A = \frac{1.65 \times 10^{11}}{3.70 \times 10^{10}} \text{ Ci} = 4.46 \text{ Ci}$ As the actual activity of urea is 1.00 μCi or 1.00×10^{-6} Ci, the percentage by weight that must be ^{14}C is, $\text{percentage } ^{14}\text{C} = \frac{1.00 \times 10^{-6}}{4.46} \times 100 \% = 2.2 \times 10^{-5} \%$	
Answer: $2.2 \times 10^{-5} \%$	

- Pure silicon is an insulator. Explain how incorporation of a small amount of nearby elements can bring about 'p-type' semiconduction. Explain your choice of dopant and use diagrams as required.

Marks
3

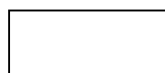


conductance band



valence band

The band gap in pure Si (between the full valence band and the empty conductance band) is large. Normal thermal energy does not give the electrons enough energy to make the jump and so Si is an insulator.



conductance band



valence band

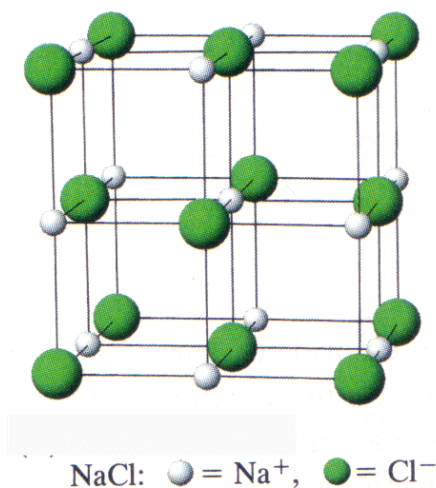
Si doped with Ga

As Si has 4 electrons per atom, replacing some Si atoms with Ga (or other Group 13 element), means that the valence band will not be completely occupied with electrons. The gaps act as positive holes and allow the material to act as a semiconductor of the p-type.

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY

Marks
4

- A cartoon representation of the structure of *halite* (NaCl) is shown below. The structure arises from the closest possible packing of anions stabilized by cations in the interstices. From a density of 2.16 g cm^{-3} , a nearest neighbour distance of 282 pm was calculated.



Crystal structure	Madelung constant (A)
ZnS (wurtzite)	1.641
NaCl	1.748
CsCl	1.763

What is the molar lattice energy of *halite*?

The molar lattice energy is given by the equation, $E = -A \frac{e^2}{4\pi\epsilon_0 r} N_a$ where A is the Madelung constant and r is the separation of the ions which is equal to the nearest neighbour distance. With $r = 282 \text{ pm} = 282 \times 10^{-12} \text{ m}$ and $A = 1.748$ for the NaCl structure from the table:

$$\begin{aligned}
 E &= -A \frac{e^2}{4\pi\epsilon_0 r} N_a \\
 &= -1.748 \times \frac{(1.602 \times 10^{-19})^2 \times (6.022 \times 10^{23})}{4 \times 3.142 \times (8.8524 \times 10^{-12}) \times (282 \times 10^{-12})} = -861000 \text{ J mol}^{-1}
 \end{aligned}$$

Answer: **-861 kJ mol⁻¹**

What would be the Madelung constant of lithium chloride given that it does not adopt the wurtzite structure? Explain your answer.

As the lattice energy is proportional to the Madelung constant, a salt will adopt the structure with the maximum *possible* Madelung constant. The Madelung constant is related to the number of anions surrounding each cation (and vice versa). Thus, the ZnS, NaCl and CsCl structures have 4, 6 and 8 anions around each cation respectively. The number of anions is limited by the radius ratio rules: the anions must physically fit around the cation.

Na^+ is large enough to fit 6 Cl^- around it but not large enough to fit 8 Cl^- and thus adopts the NaCl structure. Li^+ is smaller than Na^+ so is definitely also too small to fit 8 Cl^- around it. As the question states that it does not adopt the ZnS (wurtzite) structure, it must therefore adopt the NaCl structure so has $A = 1.748$.

Explain why, in general, there is a decrease in atomic radius from left to right across the second row of the periodic table (lithium to neon), but an abrupt increase in radius on going to the next row.	Marks 4
Across the period, the number of protons and the number of electrons increases. This leads to a greater pull from the nucleus and greater electron – electron repulsion. Because electrons are good at avoiding each other, the <i>net</i> effect is an increase in the effective nuclear charge, Z_{eff}. The effective nuclear charge (Z_{eff}) increases going from left to right across the period. The electrons feel a greater pull from the nucleus as Z_{eff} increases as they are all being added to the same $n = 2$ orbital. This leads to a decrease in the size of the atom across the period. When the 11th electron is added for Na, it goes into the $n = 3$ shell. The higher n quantum number leads to a much larger average radius and a big increase in the radius of the atom going from Ne to Na.	

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- Moseley discovered experimentally in 1913 that the atomic number, Z , of an element is inversely proportional to the square root of the wavelength, λ , of fluorescent X-rays emitted when an electron drops from the $n = 2$ to the $n = 1$ shell.

$$i.e. \quad \frac{1}{\sqrt{\lambda}} = kZ$$

What element would emit such X-rays with a wavelength one-quarter that of zirconium?

Marks
3

From Moseley's equation, the atomic number is inversely proportional to the square root of the atomic number. The ratio of the wavelengths emitted by two elements is therefore:

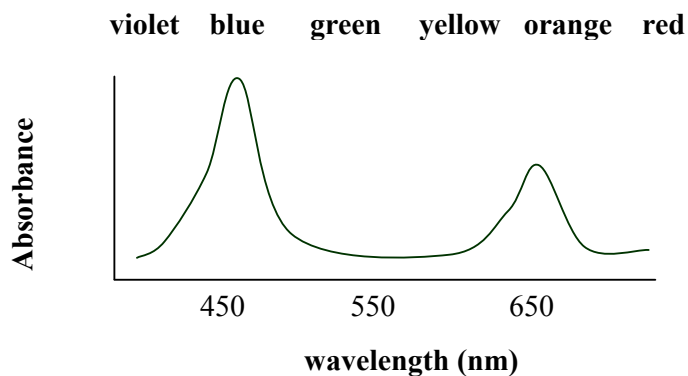
$$\frac{Z_1}{Z_2} = \sqrt{\frac{\lambda_2}{\lambda_1}}$$

As zirconium has $Z_1 = 40$ and $\frac{\lambda_2}{\lambda_1} = \frac{1}{4}$, the element has $Z = 80$. This corresponds to mercury.

Answer: **mercury**

- Many plants are green due to their high chlorophyll content. Draw on the diagram below the absorption spectrum of a green pigment such as chlorophyll.

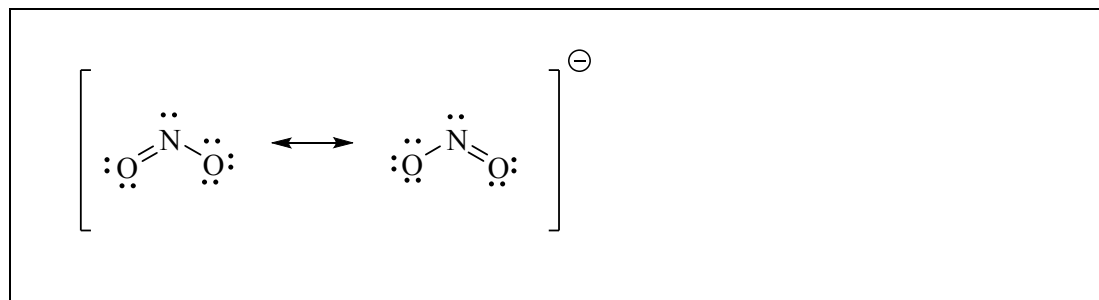
2



- Complete the following table showing the number of valence electrons, a Lewis structure and the predicted shape of each of the following species.

Marks
4

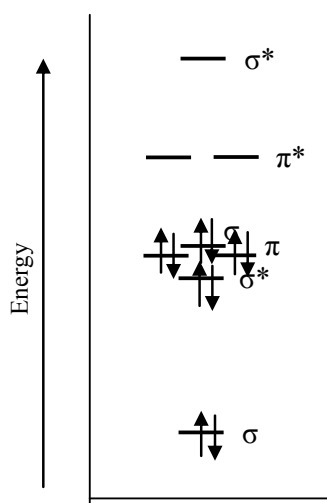
Formula	Number of valence electrons	Lewis structure	Name of molecular shape
e.g. NF_3	26	$\begin{array}{c} \text{:}\ddot{\text{F}}\text{--}\ddot{\text{N}}\text{--}\ddot{\text{F}}\text{:} \\ \\ \text{:}\ddot{\text{F}}\text{:} \end{array}$	trigonal pyramidal
BeF_2	16	$\text{:}\ddot{\text{F}}\text{--}\text{Be}\text{--}\ddot{\text{F}}\text{:}$	linear
BH_4^-	8	$\left[\begin{array}{c} \text{H} \\ \\ \text{H--B--H} \\ \\ \text{H} \end{array} \right]^\ominus$	tetrahedral

Draw the major resonance contributors of the nitrite ion, NO_2^- .**2****THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY**

- Carbon and oxygen can combine to form carbon monoxide, the second most abundant molecule in the universe.

Marks
6

The molecular orbital energy level diagram provided shows the energies of the orbitals for the valence electrons in CO. Indicate on this diagram the ground state electronic configuration of CO using the arrow notation for electron spins.



What homonuclear diatomic molecule has the same electronic structure as CO? Comment on the bond orders of these two species.

N₂. This is has the same number of valence electrons – it is *isoelectronic*. N has 5 valence electrons so N₂ has 2 × 5 = 10 valence electrons. C has 4 and O has 6 valence electrons so CO has 4 + 6 = 10 valence electrons. They both have a triple bond: i.e. they both a bond order of 3:

$$\begin{aligned}\text{bond order} &= \frac{1}{2} (\text{no. of bonding electrons} - \text{no. of antibonding electrons}) \\ &= \frac{1}{2} (8 - 2) = 3\end{aligned}$$

How would adding an electron to CO to form CO⁻ affect the strength of the bond between the two atoms? Explain your answer.

The extra electron would go into the π* antibonding orbital. The bond order would consequently drop from 3 to 2.5: bond order = ½ (8 - 3) = 2.5

Hence the bond would be weaker.

Are the atomic orbital energies of oxygen lower or higher than carbon? Explain your answer and comment on how this may affect the electron density in bonding orbitals of the CO molecule.

Oxygen is more electronegative: the energies of its orbitals are lower than those of carbon. This is because oxygen is the smaller atom with a higher nuclear charge. The bond would therefore be polarised with a greater amount of the shared electron density on the oxygen end of the bond.

- Consider the following reaction.



An experiment was conducted in which 0.1000 mol of $\text{N}_2\text{O}_4(\text{g})$ was introduced into a 1.000 L flask. After equilibrium had been established at a particular temperature, the concentration of $\text{N}_2\text{O}_4(\text{g})$ was found to be 0.0491 M. Calculate the equilibrium constant, K_c , for the reaction as written at that temperature.

Marks
4

As initially 0.1000 mol of $\text{N}_2\text{O}_4(\text{g})$ is present in 1.000 L, its concentration is 0.1000 M. The reaction table is:

	$\text{N}_2\text{O}_4(\text{g})$	$\rightleftharpoons$	$2\text{NO}_2(\text{g})$
initial	0.1000		0
change	-x		+2x
equilibrium	0.1000 - x		2x

As $[\text{N}_2\text{O}_4(\text{g})]_{\text{eq}} = 0.1000 - x \text{ M} = 0.0491 \text{ M}$, $x = 0.0509 \text{ M}$.

Hence, $[\text{NO}_2(\text{g})]_{\text{eq}} = 2x = (2 \times 0.0509) \text{ M} = 0.102 \text{ M}$.

The equilibrium constant in terms of concentrations, K_c , is:

$$K_c = \frac{[\text{NO}_2(\text{g})]^2}{[\text{N}_2\text{O}_4(\text{g})]} = \frac{0.102^2}{0.0491} = 0.211$$

Answer: **0.211**

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY

A 50.0 mL solution contained 10.00 g of NaOH in water at 25.00 °C. When it was added to a 250.0 mL solution of 0.200 M HCl at 25.00 °C in a “coffee cup” calorimeter, the temperature of the solution rose to 27.24 °C.	Marks 6
Is the process an endothermic or exothermic reaction? Exothermic ($\Delta H < 0$) as the reaction causes the temperature of the solution to rise.	
Assuming the specific heat of the solution is $4.18 \text{ J K}^{-1} \text{ g}^{-1}$, that the calorimeter absorbs a negligible amount of heat, and that the density of the solution is 1.00 g mL^{-1}, calculate $\Delta_r H$ (in kJ mol^{-1}) for the following reaction. $\text{H}^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{H}_2\text{O}(\text{l})$	
The formula mass of NaOH is $(22.99 (\text{Na}) + 16.00 (\text{O}) + 1.008 (\text{H})) \text{ g mol}^{-1} = 39.998 \text{ g mol}^{-1}$. Hence the number of moles in 10.00 g is: $\text{number of moles} = \frac{\text{mass}}{\text{formula mass}} = \frac{10.00 \text{ g}}{39.998 \text{ g mol}^{-1}} = 0.2500 \text{ mol}$ The number of moles of H^+ in 250.0 mL of a 0.200 M solution is $\begin{aligned} \text{number of moles} &= \text{concentration} \times \text{volume} \\ &= (0.200 \text{ mol L}^{-1}) \times (0.2500 \text{ L}) = 0.0500 \text{ mol} \end{aligned}$ NaOH is in excess and H^+ is the limiting reagent. After the solutions are mixed, the total volume = $(50.0 + 250.0) \text{ mL} = 300.0 \text{ mL}$. If the density is 1.00 g mL^{-1}, this corresponds to a mass of: $\text{mass} = \text{density} \times \text{volume} = (1.00 \text{ g mL}^{-1}) \times (300.0 \text{ mL}) = 300. \text{ g}$ The temperature change, ΔT, of a substance with mass, m, is related to the heat change, q, using the specific heat capacity of the substance, c: $q = c \times m \times \Delta T$ In the experiment, $\Delta T = (27.24 - 25.00) \text{ K} = 2.24 \text{ K}$. Hence, $q = (4.18 \text{ J K}^{-1} \text{ g}^{-1}) \times (300. \text{ g}) \times (2.24 \text{ K}) = 28.1 \times 10^2 \text{ J}$ This is the heat from the reaction of 0.0500 mol, so the molar enthalpy change is: $\Delta_r H = -(28.1 \times 10^2 \text{ J}) / (0.0500 \text{ mol}) = -56200 \text{ J mol}^{-1} = -56.2 \text{ kJ mol}^{-1}$ where the negative sign corresponds to an exothermic reaction (see above).	
Answer: $-56.2 \text{ kJ mol}^{-1}$	

ANSWER CONTINUES ON THE NEXT PAGE

When the experiment was repeated using 12.00 g of NaOH in water, the temperature increase was the same. Explain.

$\text{H}^+(\text{aq})$ is the limiting reagent.

There is not enough $\text{H}^+(\text{aq})$ available to react with 10.0 g of NaOH, so no further reaction occurs when using 12.0 g instead.

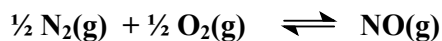
Hydrogen cyanide, HCN(g), is prepared commercially by the reaction of methane, CH₄(g), ammonia, NH₃(g), and oxygen, O₂(g), at high temperature. The other product is gaseous water. Write a chemical equation for the reaction.	Marks 2
$\text{CH}_4(\text{g}) + \text{NH}_3(\text{g}) + \frac{3}{2}\text{O}_2(\text{g}) \rightarrow \text{HCN}(\text{g}) + 3\text{H}_2\text{O}(\text{l})$	
What volume of HCN(g) can be obtained from 20.0 L of CH₄(g), 20.0 L of NH₃(g) and 20.0 L of O₂(g)? The volumes of all gases are measured at the same temperature and pressure.	
From the ideal gas law, $pV = nRT$, the number of moles is directly proportional to the volume of the substance, if the same temperature and pressure are used. As the volumes of CH₄(g), NH₃(g) and O₂(g) are the same, the number of moles of each is also the same. From the chemical equation, 1.5 mol of O₂(g) is required for every 1 mol of CH₄(g) and every 1 mol of NH₃(g). As the number of moles of O₂(g) is equal to the number of moles of CH₄(g) and NH₃(g), the limiting reagent is O₂(g). From the chemical equation, 1 mol of HCN(g) is made from every 1.5 mol of O₂(g). Each mole of O₂(g) will lead to $\frac{2}{3}$ mol of HCN(g). Hence, the volume of HCN(g) = $\frac{2}{3} \times 20.0 \text{ L} = 13.3 \text{ L}$. Answer: 13.3 L	
The reaction of carbon disulfide with chlorine is as follows. $\text{CS}_2(\text{g}) + 3\text{Cl}_2(\text{g}) \rightleftharpoons \text{CCl}_4(\text{g}) + \text{S}_2\text{Cl}_2(\text{g}) \quad \Delta H^\circ_{298} = -238 \text{ kJ mol}^{-1}$ In which direction will the reaction move when the following changes are made to the system initially at equilibrium? (a) The pressure on the system is doubled by halving the volume.	3
As the reaction involves 4 mol of gas $\rightarrow$ 2 mol of gas, increasing the pressure favours products (Le Chatelier's principle). The reaction will shift to the right.	
(b) CCl₄ is removed.	
Removing product will lead to the reaction shifting to produce more product (Le Chatelier's principle). The reaction will shift to the right.	
(c) The system is heated.	
The reaction is exothermic. Increasing the temperature will cause the reaction to reduce the amount of the exothermic reaction (Le Chatelier's principle). The reaction will shift to the left.	

• In the chlor-alkali process, three useful products are formed, including two of the “top ten” chemicals. Write the overall reaction, identify the two “top ten” chemicals, and propose why the third useful product is not usually harnessed in this process.	Marks 3				
$2\text{Cl}^-(\text{aq}) + 2\text{H}_2\text{O}(\text{l}) \rightarrow \text{Cl}_2(\text{g}) + \text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq})$ The two "top ten" chemicals produced are NaOH and Cl₂. H₂ is not harnessed as it is produced more cheaply in other ways.					
Explain why the Na⁺(aq) is not reduced to Na(s) in this process.					
Water is reduced preferentially. The reduction potentials are: <table><tr><td>$2\text{H}_2\text{O}(\text{l}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq})$</td><td>$E^\circ_{\text{red}} = -0.83 \text{ V}$</td></tr><tr><td>$\text{Na}^+(\text{aq}) + \text{e}^- \rightarrow \text{Na}(\text{s})$</td><td>$E^\circ_{\text{red}} = -2.71 \text{ V}$</td></tr></table> Even with an overpotential, it is much easier to reduce water than Na⁺(aq). (An equivalent explanation is that if Na(s) were produced, it would react very readily with H₂O to produce H₂(g) and OH⁻(aq).)	$2\text{H}_2\text{O}(\text{l}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq})$	$E^\circ_{\text{red}} = -0.83 \text{ V}$	$\text{Na}^+(\text{aq}) + \text{e}^- \rightarrow \text{Na}(\text{s})$	$E^\circ_{\text{red}} = -2.71 \text{ V}$	
$2\text{H}_2\text{O}(\text{l}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq})$	$E^\circ_{\text{red}} = -0.83 \text{ V}$				
$\text{Na}^+(\text{aq}) + \text{e}^- \rightarrow \text{Na}(\text{s})$	$E^\circ_{\text{red}} = -2.71 \text{ V}$				

- The heat of formation of nitric oxide, NO(g), is +90. kJ mol⁻¹. Why does nitric oxide form in a car engine when it does not form to any appreciable extent at room temperature? Make sure you include the appropriate chemical reactions in your answer.

Marks
3

NO(g) is produced by the reaction of N₂(g) and O₂(g):

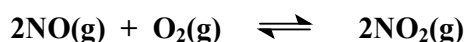


The formation of NO(g) is endothermic. From Le Chatelier's principle, it is favoured at high temperature, such as those in the car engine.

There is also a high activation energy for the reaction so the high temperature also speeds up the reaction.

What happens to the NO(g) once emitted from the tailpipe? Again, include any appropriate chemical reactions.

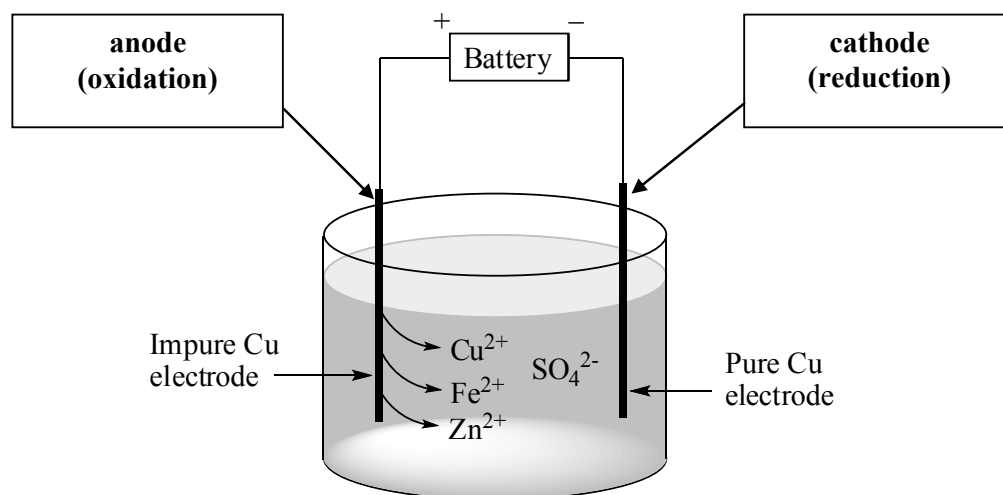
A catalytic converter will reverse the above reaction, leading to the re-formation of N₂(g) and O₂(g). If it escapes into the atmosphere, it reacts with oxygen in the atmosphere to give NO₂(g):



THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY

Marks
6

- In the refining of copper, impure copper electrodes are electrolysed in a manner such as described in the following figure. The impure Cu electrode contains varying amounts of metals such as zinc and iron as well as noble metals like gold, silver and platinum. Indicate in the boxes on the figure, which electrode is the anode and which is the cathode.

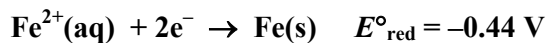


Why are noble metals left as a mud on the bottom of the reaction cell?

Noble metals do not undergo oxidation at the voltage used. As the metals do not form ions, the solid metal just falls to the bottom as the electrode dissolves. E°_{ox} for noble metals is more negative so Cu (and metals with higher E°_{ox}) are preferentially oxidized.

Explain why Zn^{2+} and Fe^{2+} are not deposited from solution during this reaction.

Cu^{2+} is preferentially reduced and hence preferentially deposited as it has the highest E°_{red} :



What mass of pure copper (in kg) will be obtained when the electrolytic cell is operated for 24.0 hours at a constant current of 100.0 A?

The total charge passed during 24.0 hours at a current of 100.0 A is:

$$\begin{aligned} \text{charge} &= (\text{current}) \times (\text{time in seconds}) \\ &= (100.0 \text{ A}) \times (24.0 \times 60 \times 60 \text{ s}) = 8.64 \times 10^6 \text{ C.} \end{aligned}$$

ANSWER CONTINUES ON THE NEXT PAGE

Using Faraday's constant, $F = 96485 \text{ C mol}^{-1}$, this charge corresponds to:

$$\text{moles of e}^{-} = \frac{\text{charge}}{F} = \frac{(8.64 \times 10^6 \text{ C})}{(96485 \text{ C mol}^{-1})} = 89.5 \text{ mol}$$

The reduction of Cu^{2+} to Cu(s) requires 2e^{-} so the total moles of Cu(s) obtained is $(\frac{1}{2} \times 89.5) \text{ mol} = 44.8 \text{ mol}$. As the atomic mass of Cu is 63.55 g mol^{-1} , this corresponds to:

$$\begin{aligned} \text{mass of copper} &= \text{moles} \times \text{atomic mass} \\ &= (44.8 \text{ mol}) \times (63.55 \text{ g mol}^{-1}) = 2850 \text{ g} = 2.85 \text{ kg} \end{aligned}$$

Answer: **2.85 kg**