

**Topics in the June 2008 Exam Paper for CHEM1101**

Click on the links for resources on each topic.

2008-J-2:

- [Nuclear and Radiation Chemistry](#)

2008-J-3:

- [Band Theory - MO in Solids](#)

2008-J-4:

- [Filling Energy Levels in Atoms Larger than Hydrogen](#)

2008-J-5:

- [Wave Theory of Electrons and Resulting Atomic Energy Levels](#)

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- [Lewis Structures](#)
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2008-J-8:

- [Bonding - MO theory \(larger molecules\)](#)

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2008-J-10:

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- [Polymers and the Macromolecular Consequences of Intermolecular Forces](#)
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2008-J-13:

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- [First and Second Law of Thermodynamics](#)

2008-J-14:

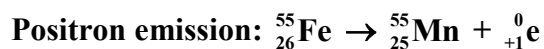
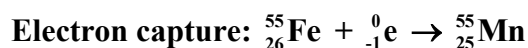
- [Electrochemistry](#)
- [Batteries and Corrosion](#)
- [Electrolytic Cells](#)

2008-J-15:

- [Electrolytic Cells](#)

**Marks**  
**5**

- Write two possible mechanisms for the radioactive decay of  $^{55}\text{Fe}$  to  $^{55}\text{Mn}$ .



The activity of an isotopically pure 1.000 g sample of  $^{55}\text{Fe}$  is measured as  $8.750 \times 10^{13}$  Bq. Calculate the half-life (in days) of  $^{55}\text{Fe}$ . (The molar mass of  $^{55}\text{Fe}$  is  $54.94 \text{ g mol}^{-1}$ .)

As the atomic mass of isotopically pure  $^{55}\text{Fe}$  is  $54.94 \text{ g mol}^{-1}$ , the number of moles in 1.000 g is:

$$\text{number of moles} = \frac{\text{mass (g)}}{\text{atomic mass (g mol}^{-1}\text{)}} = \frac{1.000 \text{ g}}{54.94 \text{ g mol}^{-1}} = 0.01820 \text{ g mol}^{-1}$$

This corresponds to:

$$\begin{aligned} \text{number of nuclei} &= \text{number of moles} \times \text{Avogadro's number} \\ &= (0.01820 \text{ mol}) \times (6.022 \times 10^{23} \text{ mol}^{-1}) = 1.096 \times 10^{22} \text{ nuclei} \end{aligned}$$

The activity ( $A$ ) is related to the number of nuclei ( $N$ ) by  $A = \lambda N$  where  $\lambda$  is the decay constant. Hence,

$$\lambda = \frac{A}{N} = \frac{8.750 \times 10^{13} \text{ Bq}}{1.096 \times 10^{22} \text{ nuclei}} = 7.983 \times 10^{-9} \text{ s}^{-1}$$

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

$$t_{1/2} = \ln 2 / (7.983 \times 10^{-9}) = 8.683 \times 10^7 \text{ s}$$

As 1 day is  $(24 \times 60 \times 60) \text{ s}$ , this corresponds to

$$t_{1/2} = \frac{8.683 \times 10^7 \text{ s}}{(24 \times 60 \times 60) \text{ s day}^{-1}} = 1005 \text{ days}$$

Answer: **1005 days**

ANSWER CONTINUES ON THE NEXT PAGE

How many years will it take for the activity of this pure 1.000 g sample of  $^{55}\text{Fe}$  to drop to  $1.000 \times 10^9$  Bq?

**The number of radioactive nuclei decays with time according to  $\ln(N_0/N_t) = \lambda t$ . As the activity is proportional to the number of nuclei ( $A = \lambda N$ ), this can be rewritten as:**

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

**As  $\lambda = 7.983 \times 10^{-9} \text{ s}^{-1}$ , the activity will decay from  $A_0 = 8.750 \times 10^{13}$  Bq to  $A_t = 1.000 \times 10^9$  Bq in a time  $t$  where**

$$\ln(8.750 \times 10^{13}/1.000 \times 10^9) = (7.983 \times 10^{-9} \text{ s}^{-1})t$$

$$t = 1.425 \times 10^9 \text{ s}$$

**As 1 year is  $(365 \times 24 \times 60 \times 60)$  s, this corresponds to:**

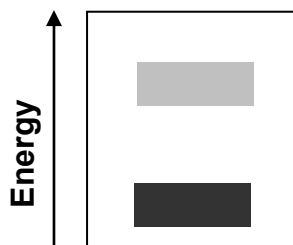
$$t = 1.425 \times 10^9 / (365 \times 24 \times 60 \times 60) = 45.19 \text{ years}$$

Answer: **45.19 years**

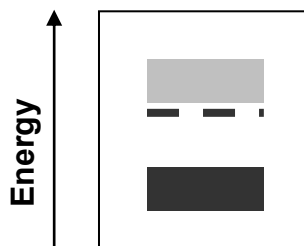
**Marks**  
**2**

- Pure silicon is an insulator. Explain, with sketches of band structure diagrams, how 'doping' pure silicon with a small amount of phosphorus can turn it into an 'n-type' semiconductor.

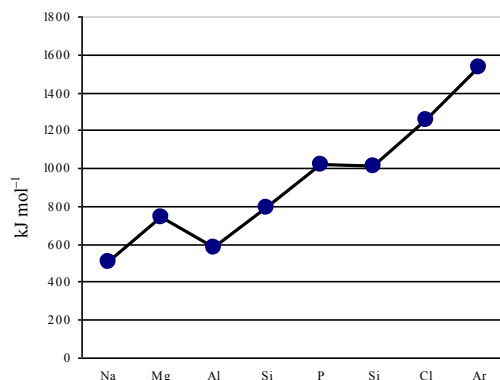
**Silicon is an insulator as the energy gap between the full valence band (shown in black below) and the empty conduction band (shown in grey below) is large:**



**Phosphorus has one extra electron compared to silicon. These occupy energy levels just below the bottom of the conduction band (shown as a dotted line below). Some electrons from these localised electronic states are thermally excited into the conduction band, where they become mobile and act as (negative) charge carriers.**



- The graph shows the first ionisation energies for third row elements of the periodic table.



Explain the general trend and both anomalies.

There are a number of factors to explain:

- There is an overall *increase* in ionization energy across the period. This is due to the increase in effective nuclear charge ( $Z_{\text{eff}}$ ) which leads to greater pull from the nucleus and an increase in the energy required to remove an electron.
- There is a *decrease* in ionization between Mg and Al *despite* the latter having a higher  $Z_{\text{eff}}$ . Mg has an atomic configuration of  $[\text{Ne}] 3s^2$  and Al has an atomic configuration of  $[\text{Ne}] 3s^2 3p^1$ . Thus, the electron being ionized in Mg is a  $3s$  electron and the electron being ionized in Al is a  $3p$  electron. The orbit of the  $3p$  electron is, on average, greater than that of a  $3s$  electron so the electron is held less tightly. Thus, Al has a lower ionization energy than Mg despite having a higher nuclear charge. Although a  $3p$  electron is also being removed in Si, it has a higher ionization energy than Mg because the increase in nuclear charge is more than enough to compensate for the sub-shell change.
- Between P and S there is also a drop in ionization *despite* the latter having a higher  $Z_{\text{eff}}$ . Between P and S, the extra electron *has* to pair up:

*p*-orbitals

P			
S			

Electrons which are paired and occupy the same orbital are forced to be close to one another in space, leading to higher repulsion. Because of this, the electron which is paired up is easier to remove and the ionization energy is lower.

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

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

Derive an expression for the constant of proportionality,  $k$ , for a hydrogen-like atom which would allow the value of  $k$  to be theoretically calculated.

The energy of an X-ray with wavelength  $\lambda$  is given by  $E = \frac{hc}{\lambda}$  where  $h$  is

Planck's constant and  $c$  is the speed of light. Using this and as  $\frac{1}{\sqrt{\lambda}} = kZ$

$$\frac{1}{\lambda} = (kZ)^2$$

$$E = hc(kZ)^2 \quad (1)$$

For a hydrogen like atom, an electron in an orbital with quantum number  $n$  has energy  $E = -Z^2 E_R (\frac{1}{n^2})$  where  $E_R$  is the Rydberg constant. The energy *emitted* when an electron moves from an orbital with quantum number  $n_i$  to an orbital with quantum number  $n_f$  is:

$$E = E_{n_i} - E_{n_f} = [-Z^2 E_R (\frac{1}{n_i^2})] - [-Z^2 E_R (\frac{1}{n_f^2})] = Z^2 E_R (\frac{1}{n_f^2} - \frac{1}{n_i^2}) \quad (2)$$

Equating (1) and (2) gives:

$$hc(kZ)^2 = Z^2 E_R (\frac{1}{n_f^2} - \frac{1}{n_i^2})$$

Rearranging for  $k$  gives:

$$k^2 = \frac{Z^2 E_R}{hcZ^2} (\frac{1}{n_f^2} - \frac{1}{n_i^2}) = \frac{E_R}{hc} (\frac{1}{n_f^2} - \frac{1}{n_i^2})$$

$$k = \sqrt{\frac{E_R}{hc} (\frac{1}{n_f^2} - \frac{1}{n_i^2})}$$

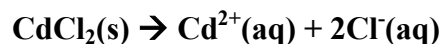
For the case where  $n_i = 2$  and  $n_f = 1$ , this becomes

$$k = \sqrt{\frac{E_R}{hc} (\frac{1}{1^2} - \frac{1}{2^2})} = \sqrt{\frac{3E_R}{4hc}}$$

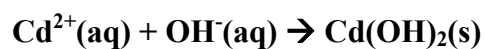
- Cadmium chloride and cadmium sulfate are both soluble in water. Cadmium carbonate, cadmium phosphate and cadmium hydroxide are all insoluble. Describe, using equations where appropriate, how to convert cadmium chloride into cadmium sulfate.

**One possible method is:**

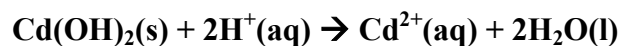
**(1) Dissolve cadmium chloride in water:**



**(2) Add aqueous sodium hydroxide. This leads to precipitation of cadmium hydroxide which can then be separated from the  $\text{Na}^{+}(\text{aq})$  and  $\text{Cl}^{-}(\text{aq})$  by filtration.**



**(3) Add the filtered solid to aqueous sulfuric acid. This leads to dissolution as cadmium sulfate is soluble.**

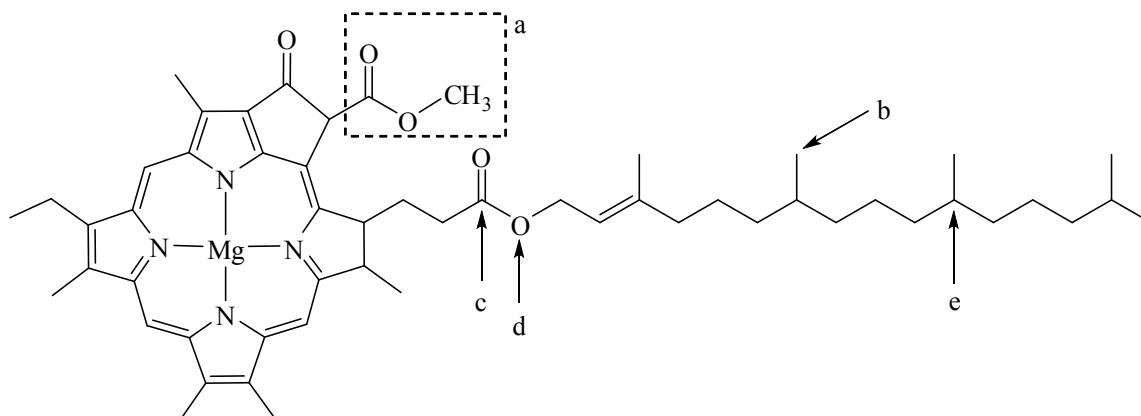


**(4) This solution contains only  $\text{Cd}^{2+}(\text{aq})$ ,  $\text{SO}_4^{2-}(\text{aq})$  and  $\text{H}_2\text{O}(\text{l})$  as all of the  $\text{Cl}^{-}$  and  $\text{Na}^{+}(\text{aq})$  were removed in the filtration in step (2). Simple evaporation of the solvent (water) then leaves  $\text{CdSO}_4(\text{s})$ .**

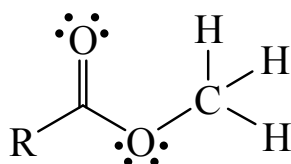


**Marks**  
**4**

- Modern plants, algae and cyanobacteria contain a class of pigments called chlorophyll. The structure of “chlorophyll *a*”, which absorbs both red and blue light, is shown below.



Draw the full Lewis structure of the functional group shown in box "a".



where 'R' represents the rest of the molecule

What type of functional group is it?

**It is an ester.**

Determine the local geometry of all other atoms bonded to each atom labelled on the structure above, and complete the table below.

Site	b	c	d	e
Geometry	tetrahedral	trigonal planar	bent	tetrahedral*

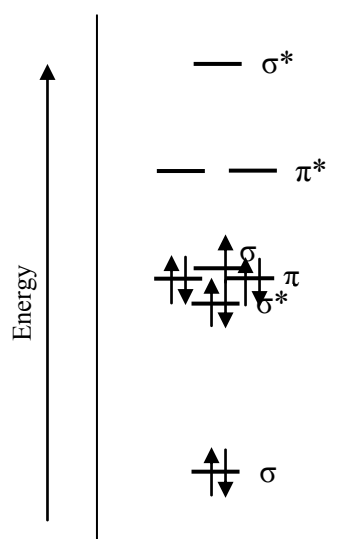
\* remember that this carbon atom has 2 hydrogen atoms attached to it that are not shown in the stick structure.

**Marks**  
**6**

- Carbon and nitrogen can combine to form a cyanide ion or a neutral free radical.

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

\* C has 4 valence electrons and N has 5 valence electrons, giving a total of 9 electrons to place on the diagram. These occupy orbitals from the bottom upwards, with a maximum of 2 in each. The overall configuration is shown and corresponds to  $(\sigma)^2(\sigma^*)^2(\pi)^4(\sigma)^1$



How would you expect the magnetic properties of CN to differ from that of  $\text{CN}^-$ ?

**CN has an unpaired electron. This makes it *paramagnetic* (it is attracted into a magnetic field).**

**$\text{CN}^-$  has an extra electron. This pairs up with the electron in the highest occupied  $\sigma$ -orbital. As all the electrons are now paired,  $\text{CN}^-$  is *diamagnetic* (it is weakly repelled by a magnetic field).**

**CN is paramagnetic whereas  $\text{CN}^-$  is diamagnetic.**

How would adding an electron to CN to form  $\text{CN}^-$  affect the strength of the bond between the two atoms? Explain your answer.

**The extra electron in  $\text{CN}^-$  occupies a  $\sigma$ -orbital. This is a bonding orbital and so  $\text{CN}^-$  has more bonding electrons than CN and would be expected to have a stronger bond as a result.**

**Equivalently, bond order can be used to rationalize the bond strength:**

$$\text{bond order} = \frac{1}{2} (\text{number of bonding} - \text{number of antibonding electrons})$$

**CN has 7 bonding and 2 antibonding electrons.  $\text{CN}^-$  has 8 bonding and 2 antibonding electrons. Hence,**

$$\text{bond order of CN} = \frac{1}{2} (7 - 2) = 2.5$$

$$\text{bond order of } \text{CN}^- = \frac{1}{2} (8 - 2) = 3$$

**$\text{CN}^-$  has a higher bond order than CN and would therefore be expected to have a stronger bond.**

ANSWER CONTINUES ON THE NEXT PAGE

Why do we only need to consider the valence electrons when discussing the bonding of CN?

**The core electrons are tightly held onto by the atoms. There is little overlap between the core orbitals on the two atoms.**

**Even if the 1s core electrons on each atom are considered, they would occupy *both* the bonding  $\sigma$  and antibonding  $\sigma^*$  orbitals formed from their overlap. This would not change the bond order. Their contribution to the bonding is minimal.**

**Marks**  
**2**

- Explain the difference between an equilibrium constant and a reaction quotient.

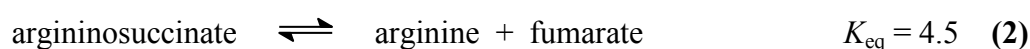
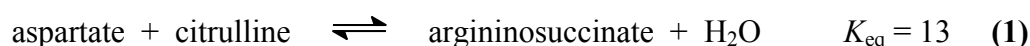
**Both the equilibrium constant ( $K$ ) and the reaction quotient ( $Q$ ) show the relationship between the amounts of product and reactant.**

**$K$  refers to equilibrium concentrations and so refers to a system at equilibrium. It is a constant for any system, depending only on the temperature.**

**$Q$  refers to concentrations that are not necessarily at equilibrium.**

**2**

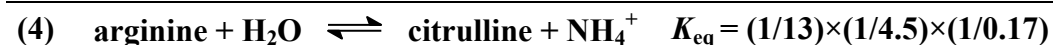
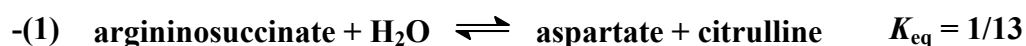
The following reactions have been demonstrated in mammalian liver at 37 °C and pH 7.5.



Calculate the equilibrium constant at 37 °C and pH 7.5 for the following reaction.



**If the first three reactions are combined by reversing each one and adding the reactions together, reaction (4) results:**



**When a reaction is reversed, the new equilibrium constant is the *reciprocal* of the original value. This has been used in the final column to obtain the equilibrium constants for the reverse of reactions (1), (2) and (3).**

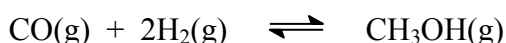
**When reactions are added together, the new equilibrium constant is the *product* of the equilibrium constants for the individual reactions.**

**Overall, this gives for reaction (4):**

$$K_{\text{eq}} = (1/13) \times (1/4.5) \times (1/0.17) = 0.10$$

Answer:  $K_{\text{eq}} = 0.10$

- Methanol,  $\text{CH}_3\text{OH}$ , is produced commercially by the catalysed reaction of carbon monoxide and hydrogen gas.  $K_p$  for this reaction at 600 K is  $1.13 \times 10^{-6}$ .



The reaction is exothermic, yet the equilibrium favours the reactants. Explain why this is the case.

**For a process to be spontaneous, the entropy of the universe must increase. Exothermic reactions lead to heat being given to the surroundings leading to an increase in the entropy of the surroundings,  $\Delta_{\text{surroundings}}S$ .**

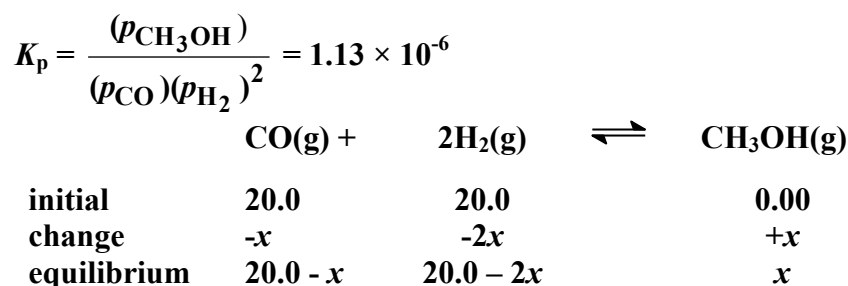
**Formation of *reactants* is endothermic so  $\Delta_{\text{surroundings}}S$  is negative. However, as formation of reactants leads to the formation of 3 molecules from each  $\text{CH}_3\text{OH}$ , it leads to an increase in the entropy of the system,  $\Delta_{\text{system}}S$  is positive..**

**For reactants to be favoured requires  $\Delta_{\text{system}}S$  to be more positive than  $\Delta_{\text{surroundings}}S$  is negative. As  $\Delta_{\text{surroundings}}S = q / T$ , it becomes less negative as  $T$  increases and so formation of reactants becomes more favourable at high  $T$ .**

S

The reaction vessel at 600 K is filled with 20.0 atm of  $\text{CO(g)}$  and 20.0 atm  $\text{H}_2\text{(g)}$ . What is the final pressure of  $\text{CH}_3\text{OH(g)}$  at equilibrium?

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



Thus, at equilibrium:

$$K_p = \frac{(p_{\text{CH}_3\text{OH}})}{(p_{\text{CO}})(p_{\text{H}_2})^2} = \frac{x}{(20.0 - x)(20.0 - 2x)^2} = 1.13 \times 10^{-6}$$

As  $K_p$  is very small,  $x$  will be tiny compared to 20.0 atm and so  $(20.0 - x) \sim 20.0$ . This approximation simplifies the expression for  $K_p$ :

$$K_p \sim \frac{x}{(20.0)(20.0)^2} = 1.13 \times 10^{-6} \quad \text{so } x = (1.13 \times 10^{-6}) \times (20.0) \times (20.0)^2$$

$$x = p_{\text{CH}_3\text{OH}} = 9.04 \times 10^{-3} \text{ atm}$$

Answer:  $p_{\text{CH}_3\text{OH}} = 9.04 \times 10^{-3} \text{ atm}$

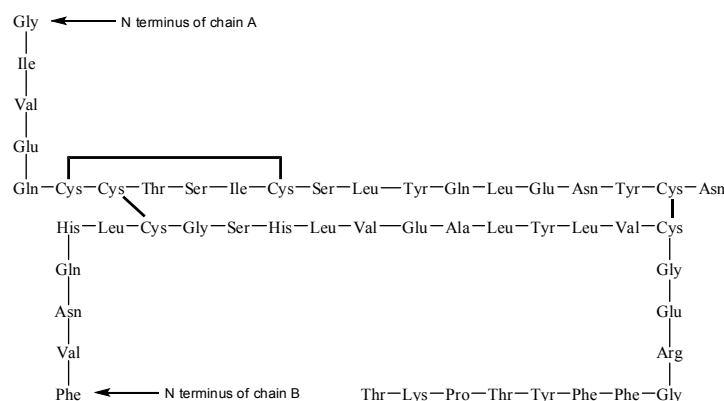
ANSWER CONTINUES ON THE NEXT PAGE

Under what conditions of temperature and pressure do you think an industrial reactor would function to optimise the production of methanol? Explain.

**As formation of methanol in this reaction is exothermic, its formation is favoured by low temperature. However, as a low temperature would also lead to a slow reaction, the temperature used would be chosen as a compromise between maximizing the yield whilst keeping the rate of its formation high.**

**As the reaction leads to a decrease in the number of moles of gas (3 mol of gas → 1 mol of gas), high pressure will favour product formation. Thus, the industrial process uses high pressures.**

- Insulin is an important hormone involved in the regulation of glucose availability in the body. It consists of two peptide chains, one consisting of 21 amino acids (the “A” chain) and one of 30 amino acids (the “B” chain). Below is a representation of insulin showing the amino acid sequence.



Define the terms *primary structure* and *secondary structure* in relation to proteins. In your definition, describe the atomic or molecular forces that are involved in the formation of the primary and secondary structure.

**The primary structure is the sequence of amino acids in the polypeptide chain of the protein. This sequence is held together by covalent bonds including the peptide C-N bond formed between the amine and carboxylate groups of the amino acids.**

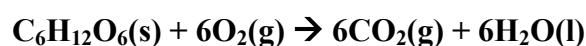
**The secondary structure is the ordered arrangement (conformation) of amino acids in parts of the protein. It includes structural motifs such as  $\alpha$ -helices and  $\beta$ -sheets. The secondary structure is due to intermolecular forces between the amino acids of the chain including hydrogen bonding, dipole-dipole and dispersion interactions.**

3

- The net amount of carbon dioxide fixed by photosynthesis on Earth has been estimated as  $5.5 \times 10^{16} \text{ g year}^{-1}$ . Calculate the energy stored by photosynthesis each year, assuming that all this carbon is converted into glucose,  $\text{C}_6\text{H}_{12}\text{O}_6$ .

$$\Delta_f H^\circ: \text{C}_6\text{H}_{12}\text{O}_6(\text{s}): -1273 \text{ kJ mol}^{-1}, \text{H}_2\text{O}(\text{l}): -285.8 \text{ kJ mol}^{-1}, \text{CO}_2(\text{g}): -393.5 \text{ kJ mol}^{-1}$$

**The chemical reaction for the combustion of glucose into carbon dioxide and water is:**



$$\text{As } \Delta_{\text{rxn}} H^\circ = \sum m \Delta_f H^\circ (\text{products}) - \sum n \Delta_f H^\circ (\text{reactants}),$$

$$\begin{aligned}
 \Delta_{\text{rxn}} H^\circ &= [6\Delta_f H^\circ (\text{CO}_2(\text{g})) + 6\Delta_f H^\circ (\text{H}_2\text{O}(\text{l}))] - [\Delta_f H^\circ (\text{C}_6\text{H}_{12}\text{O}_6(\text{s}))] \\
 &= [6 \times -393.5 + 6 \times -285.8] \text{ kJ mol}^{-1} - [-1273] \text{ kJ mol}^{-1} \\
 &= -2803 \text{ kJ mol}^{-1}
 \end{aligned}$$

ANSWER CONTINUES ON THE NEXT PAGE

**This is the energy released when 1 mol of glucose combusts. As this generates 6 mol of CO<sub>2</sub>(g), the energy release per mol of CO<sub>2</sub>(g) is**

$$\text{energy released per mol of CO}_2(\text{g}) = (-2803/6) \text{ kJ mol}^{-1} = 467.1 \text{ kJ mol}^{-1}$$

**The molar mass of CO<sub>2</sub> is (12.01 (C) + 2 × 16.00 (O)) g mol<sup>-1</sup> = 44.01 g mol<sup>-1</sup>.**

**The number of moles of CO<sub>2</sub> fixed per year is therefore:**

$$\text{number of moles} = \frac{\text{mass}}{\text{molar mass}} = \frac{5.5 \times 10^{16} \text{ g}}{44.01 \text{ g mol}^{-1}} = 1.25 \times 10^{15} \text{ mol}$$

**As combustion of glucose generates -467.1 kJ mol<sup>-1</sup> per mole of CO<sub>2</sub>(g) produced, photosynthesis of this amount stores**

$$\text{energy stored} = (467.1 \text{ kJ mol}^{-1}) \times (1.25 \times 10^{15} \text{ mol}) = 5.8 \times 10^{17} \text{ kJ}$$

**Answer:  $5.8 \times 10^{17}$  kJ**



- Sulfuric acid produced industrially must be diluted for many of its applications. This process is always carried out by adding the acid to water rather than by adding water to the acid. Use the data below to show that  $\Delta_r H^\circ$  for the dilution of 50.0 mL of  $\text{H}_2\text{SO}_4(\text{l})$  to 1.00 L of  $\text{H}_2\text{SO}_4(\text{aq})$  is  $-89 \text{ kJ}$ .

$\text{H}_2\text{SO}_4(\text{l})$ :  $\Delta_f H^\circ = -814 \text{ kJ mol}^{-1}$ , density =  $1.831 \text{ g mL}^{-1}$ ,  $C = 1.42 \text{ J g}^{-1} \text{ K}^{-1}$

$\text{H}_2\text{SO}_4(\text{aq})$ :  $\Delta_f H^\circ = -909 \text{ kJ mol}^{-1}$ , density =  $1.060 \text{ g mL}^{-1}$ ,  $C = 3.50 \text{ J g}^{-1} \text{ K}^{-1}$

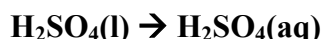
As the density of  $\text{H}_2\text{SO}_4(\text{l})$  is  $1.831 \text{ g mL}^{-1}$  and the dilution is of 50.0 mL, the mass of  $\text{H}_2\text{SO}_4(\text{l})$  requiring dilution is:

$$\text{mass} = \text{density} \times \text{volume} = (1.831 \text{ g mL}^{-1}) \times (50.0 \text{ mL}) = 91.55 \text{ g}$$

The molar mass of  $\text{H}_2\text{SO}_4$  is  $(2 \times 1.008 (\text{H}) + 32.07 (\text{S}) + 4 \times 16.00 (\text{O})) \text{ g mol}^{-1} = 98.086 \text{ g mol}^{-1}$ . This mass therefore corresponds to:

$$\text{number of moles} = \frac{\text{mass}}{\text{molar mass}} = \frac{91.55 \text{ g}}{98.086 \text{ g mol}^{-1}} = 0.9334 \text{ mol}$$

The dilution process involves the reaction:



For which:

$$\begin{aligned} \Delta_{\text{rxn}} H^\circ &= \sum m \Delta_f H^\circ (\text{products}) - \sum n \Delta_f H^\circ (\text{reactants}) \\ &= \Delta_f H^\circ (\text{H}_2\text{SO}_4(\text{aq})) - \Delta_f H^\circ (\text{H}_2\text{SO}_4(\text{l})) \\ &= (-909 \text{ kJ mol}^{-1}) - (-814 \text{ kJ mol}^{-1}) = -95 \text{ kJ mol}^{-1} \end{aligned}$$

Hence, 0.9334 mol will generate:

$$\Delta_{\text{rxn}} H^\circ = (0.9334 \text{ mol}) \times (-95 \text{ kJ mol}^{-1}) = -89 \text{ kJ mol}^{-1}$$

The dilution is carried out in a calorimeter. If the initial temperature of the system is  $25.0^\circ \text{C}$ , what is the final temperature after dilution?

After dilution, the calorimeter contains 1.00 L of  $\text{H}_2\text{SO}_4(\text{aq})$ . As this has a density of  $1.060 \text{ g mL}^{-1}$ , this corresponds to a mass of:

$$\text{mass} = \text{density} \times \text{volume} = (1.060 \text{ g mL}^{-1}) \times (1.00 \times 10^3 \text{ mL}) = 1060 \text{ g}$$

The dilution generates 89 kJ, causing the solution to warm. The temperature change is related to the heat change by:

$$q = C \times m \times \Delta T$$

ANSWER CONTINUES ON THE NEXT PAGE

**Hence,**

$$89 \times 10^3 \text{ J} = (3.50 \text{ J g}^{-1} \text{ K}^{-1}) \times (1060 \text{ g}) \times \Delta T$$

**Note that the heat capacity of  $\text{H}_2\text{SO}_4(\text{aq})$  has been used as this is what the calorimeter contains.**

**Hence,**

$$\Delta T = 24 \text{ K} = 24 \text{ }^\circ\text{C}$$

**As the original temperature is  $25.0 \text{ }^\circ\text{C}$ , the final temperature after this increase is**

$$T_{\text{final}} = T_{\text{initial}} + \Delta T = (25.0 + 24) \text{ }^\circ\text{C} = 49 \text{ }^\circ\text{C}$$

Final temperature: **49  $^\circ\text{C}$**

**Marks**  
**6**

Using the concept of heat capacity, explain why the dilution of sulfuric acid is carried out by adding acid to water rather than water to acid.



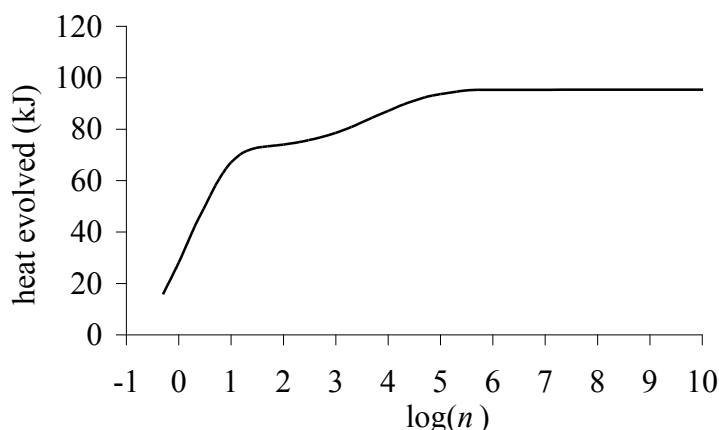
**The dilution of sulfuric acid generates  $95 \text{ kJ mol}^{-1}$  of heat.**

**As  $q = Cm\Delta T$ , the temperature change when a quantity of heat is generated is *inversely* proportional to the heat capacity of the substance.**

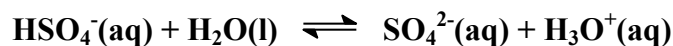
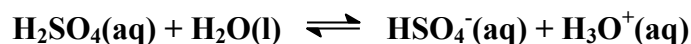
**If water is added to  $\text{H}_2\text{SO}_4(\text{l})$ , the *same* quantity of heat generates a much *larger* temperature change than occurs if  $\text{H}_2\text{SO}_4(\text{l})$  is added to water as the heat capacity of  $\text{H}_2\text{SO}_4(\text{l})$  is much *smaller* than that of water.**

**If water is added to acid, the temperature change is so large so it produces localized boiling of the solution at the surface. This causes the acid to spit out causing potential safety issues.**

The figure below shows the heat evolved when one mole of  $\text{H}_2\text{SO}_4$  is mixed with  $n$  moles of  $\text{H}_2\text{O}$ . Explain the shape of curve.



**$\text{H}_2\text{SO}_4$  is a diprotic acid as it has two acidic protons:**



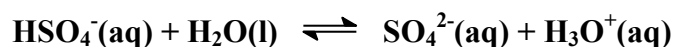
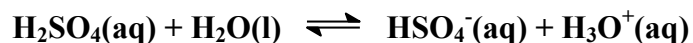
**At normal dilutions levels,  $\text{H}_2\text{SO}_4(\text{aq})$  is completely ionized into  $\text{SO}_4^{2-}$ . A 1 M solution contains roughly a 1 : 55 molar ratio of acid : water.**

**However, in the dilution curve above, the amount of  $\text{H}_2\text{O}$  is initially very low – when  $\log(n) = 0$ ,  $n_{\text{water}} = 1 \text{ mol}$  so there is a 1 : 1 molar ratio of acid : water. Low amounts of water lead both equilibria to shift towards the left.**

**Hence, the curve shows an initial increase in temperature as the first ionization occurs. Increasing the amount of water causes a higher percentage to be ionized and more heat to be generated.**

**ANSWER CONTINUES ON THE NEXT PAGE**

**H<sub>2</sub>SO<sub>4</sub> is a diprotic acid as it has two acidic protons:**



**At normal dilutions levels, H<sub>2</sub>SO<sub>4</sub>(aq) is completely ionized into SO<sub>4</sub><sup>2-</sup>. A 1 M solution contains roughly a 1 : 55 molar ratio of acid : water.**

**However, in the dilution curve above, the amount of H<sub>2</sub>O is initially very low – when  $\log(n) = 0$ ,  $n_{\text{water}} = 1$  mol so there is a 1 : 1 molar ratio of acid : water. Low amounts of water lead both equilibria to shift towards the left.**

**Hence, the curve shows an initial increase in temperature as the first ionization occurs. Increasing the amount of water causes a higher percentage to be ionized and more heat to be generated.**

**When  $\log(n) \sim 1$ ,  $n_{\text{water}} = 10$  mol. At this point, the first ionization is essentially complete and further dilution up to  $\log(n) \sim 3$  generates little extra heat as all the solution contains HSO<sub>4</sub><sup>-</sup>(aq).**

**As more water is added, the second ionization begins to occur. Again, addition of more water causes a higher percentage of the HSO<sub>4</sub><sup>-</sup> to ionize, generating more heat.**

**When  $\log(n) \sim 5$ , the second ionization is essentially completely and the solution contains only SO<sub>4</sub><sup>2-</sup>(aq). Further addition of water does not cause any additional ionization and no more heat is evolved.**

- Impure copper can be purified by electrolysis, with the impure copper as one electrode and the purified copper as the other. Is the impure copper the cathode or the anode in the electrolysis cell?

**The impure copper is the *anode*. As oxidation occurs at the anode, the impure copper is oxidized to give  $\text{Cu}^{2+}$ , leaving the impurities behind. The  $\text{Cu}^{2+}$  is then reduced at the cathode to pure  $\text{Cu(s)}$ .**

If a battery is used as the power source, is the positive terminal of the battery connected to the impure copper or to the pure copper electrode?

**In an electrolytic cell, oxidation at the anode must be forced to occur. This is achieved by making the anode *positive* so that it removes electrons from the reactant (impure copper) at the electrode.**

If electrolysis for 1.0 hour with a current of 5.2 A produces 5.9 g of pure copper, calculate the oxidation number of the copper dissolved in the cell.

**As the atomic mass of copper is  $63.55 \text{ g mol}^{-1}$ , 5.9 g corresponds to:**

$$\text{number of moles of copper} = \frac{\text{mass}}{\text{atomic mass}} = \frac{5.9 \text{ g}}{63.55 \text{ mol}^{-1}} = 0.093 \text{ mol}$$

**A current,  $I$ , of 5.2 A applied for a time,  $t$ , of 1.0 hour corresponds to:**

$$\text{number of moles of electrons} = \frac{It}{F} = \frac{(5.2 \text{ A}) \times (1.0 \times 60 \times 60 \text{ s})}{(96485 \text{ C mol}^{-1})} = 0.19 \text{ mol}$$

**Each mole of copper therefore requires  $\frac{0.19}{0.093} = 2.09$ . As the oxidation number is a whole number, this corresponds to an oxidation number of +2.**

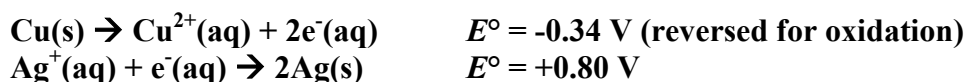
Oxidation number: +2 (II)

Explain, with the use of standard reduction potentials, why a silver impurity in the copper can be recovered from the cell as silver metal, but a nickel impurity is found dissolved in the electrolyte solution.

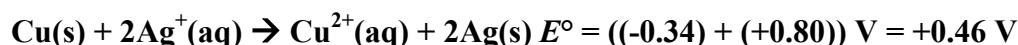
**The relevant reduction potentials are +0.34 V for  $\text{Cu}^{2+}(\text{aq})$ , +0.80 V for  $\text{Ag}^+(\text{aq})$  and -0.24 V for  $\text{Ni}^{2+}(\text{aq})$ .**

ANSWER CONTINUES ON THE NEXT PAGE

**For formation of silver metal,**

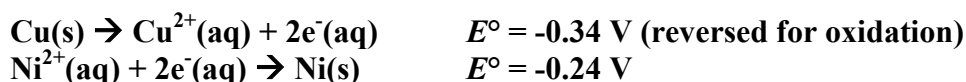


**A voltage of 0.34 V is sufficient to dissolve copper but not to dissolve silver. The silver thus remains as solid Ag(s). The reaction of Ag(s) with Cu<sup>2+</sup>(aq) is unfavourable as the *reverse* reaction is favourable:**

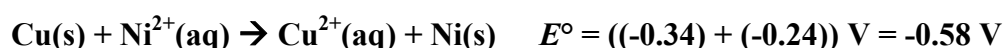


**As  $E^{\circ} > 0$ , the reaction should occur. Silver metal can thus be formed in the presence of copper metal.**

**For formation of nickel metal,**



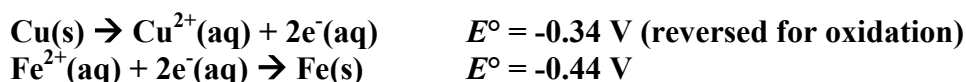
**The overall reaction is:**



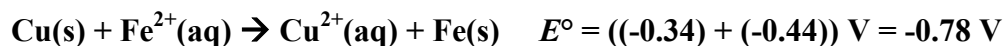
**As  $E^{\circ} < 0$ , the reaction will not occur. Nickel metal cannot be formed from Ni<sup>2+</sup> in the presence of copper metal.**

Explain what happens to an iron impurity in the Cu.

**The reduction potential for Fe<sup>2+</sup>(aq) is -0.44 V. Thus, for formation of iron metal,**

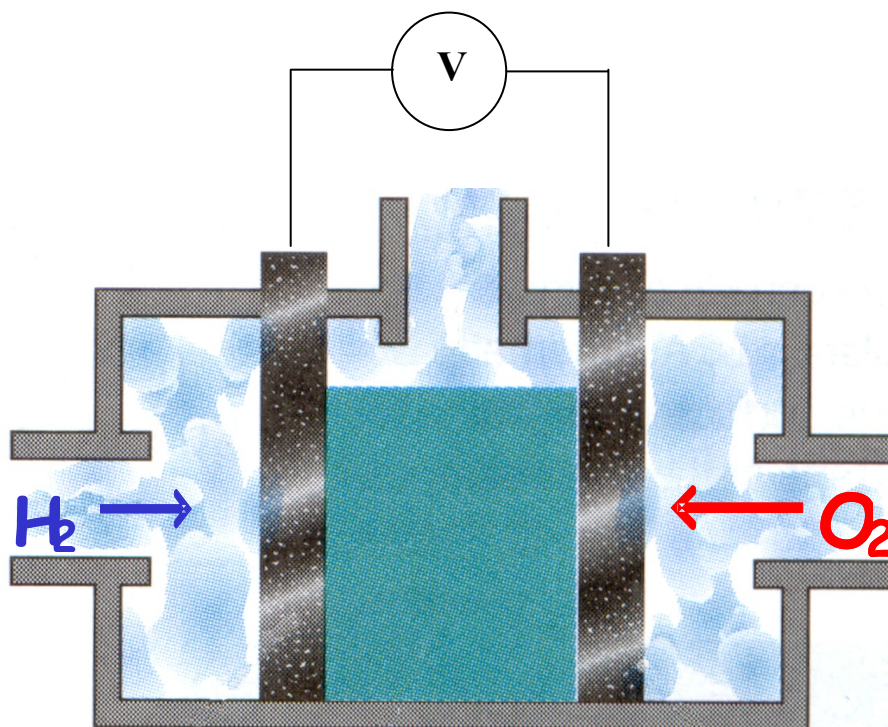


**The overall reaction is:**



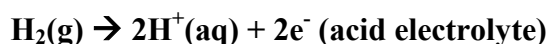
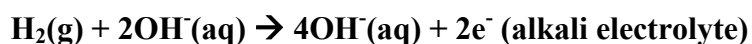
**As  $E^{\circ} < 0$ , the reaction will not occur. Iron metal cannot be formed from Fe<sup>2+</sup> in the presence of copper metal. The iron impurity will stay in the electrolyte solution as Fe<sup>2+</sup>.**

- Hydrogen burns or explodes when it reacts with oxygen, but hydrogen and oxygen can be used to generate electricity safely in a fuel cell.



What reaction occurs at the H<sub>2</sub> electrode?

**Hydrogen is oxidized:**



What reaction occurs at the O<sub>2</sub> electrode?

**Oxygen is reduced:**



In which direction do the electrons flow?

**Electrons flow from the H<sub>2</sub> electrode to the O<sub>2</sub> electrode.**

What is conducted through the inert membrane from the hydrogen to the oxygen electrode?

**M<sup>+</sup>(aq) counter ion such as K<sup>+</sup>(aq) (alkali electrolyte)**

**H<sup>+</sup>(aq) (acid electrolyte)**

What is the maximum voltage that this cell can generate under standard conditions?

**By definition, the oxidation half cell (H<sub>2</sub>) has  $E^0 = 0.00 \text{ V}$ . The reduction half cell has  $E^0 = +1.23 \text{ V}$ . Thus,  $E^0 = ((0.00) + (+1.23)) \text{ V} = +1.23 \text{ V}$**

How might this voltage be increased by changing the operating conditions?

**Standard conditions correspond to 1 atm pressure. The voltage can be increased by increasing the pressure of H<sub>2</sub>(g) and O<sub>2</sub>(g) gas.**

