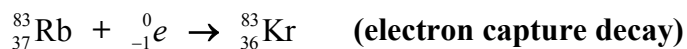
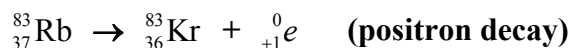


- Write two possible mechanisms for the radioactive decay of ^{83}Rb to ^{83}Kr .

Marks
5



The half-life of ^{83}Rb is 86.2 days. Calculate the activity (in Bq) of an isotopically pure 1.000 g sample of ^{83}Rb . (The molar mass of ^{83}Rb is 82.915110 g mol⁻¹.)

As 1 mol of ^{83}Rb has a mass of 82.915110 g, the number of nuclei, N , in 1.000 g is:

number of nuclei = number of moles \times Avogadro's constant

$$N = \left(\frac{1.000}{82.915110} \text{ mol} \right) \times (6.022 \times 10^{23} \text{ nuclei mol}^{-1}) = 7.263 \times 10^{21} \text{ nuclei}$$

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,

$$\lambda = \ln 2 / (86.2 \times 24 \times 60 \times 60 \text{ s}) = 9.31 \times 10^{-8} \text{ s}^{-1}$$

The activity is thus,

$$\begin{aligned} A &= \lambda N = (9.31 \times 10^{-8} \text{ s}^{-1}) \times (7.263 \times 10^{21} \text{ nuclei}) \\ &= 6.76 \times 10^{14} \text{ nuclei s}^{-1} = 6.76 \times 10^{14} \text{ Bq} \end{aligned}$$

Answer: $6.76 \times 10^{14} \text{ Bq}$

How many days will it take for this sample to diminish to 1 % of its initial activity?

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:

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

If the activity drops to 1% of its initial value, $A_0/A_t = (100/1) = 100$.

As $\lambda = 9.31 \times 10^{-8} \text{ s}^{-1}$:

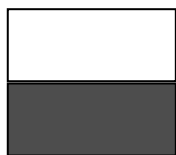
$$\ln(100) = (9.31 \times 10^{-8} \text{ s}^{-1})t$$

$$t = 49000000 \text{ s} = 600 \text{ days}$$

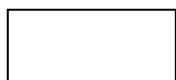
Answer: 600 days

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

Marks
4



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

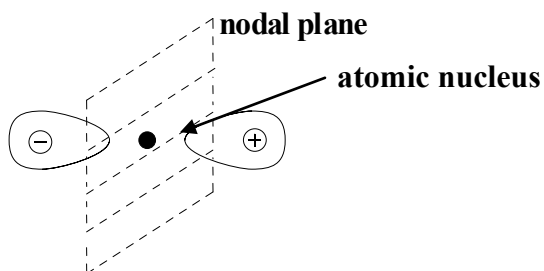


Si doped with Al

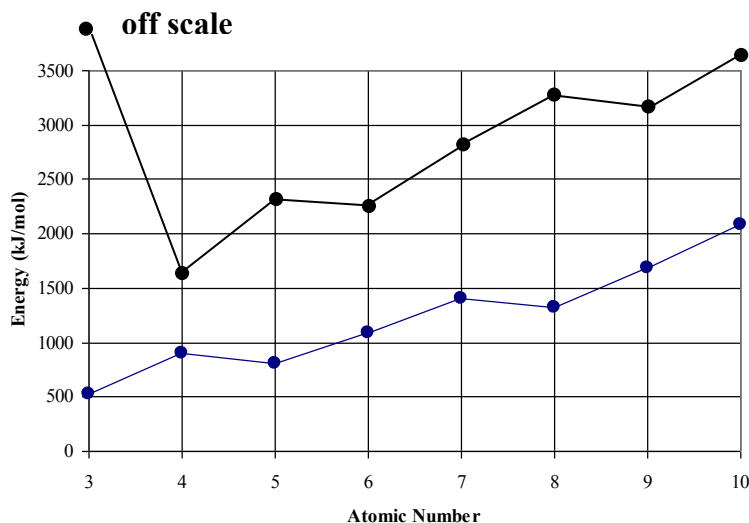
Replacing some Si atoms with Al (or other Group 13 element), means that the valence band will not be completely occupied with electrons. The gaps act as positive holes and allow the material to act as a semiconductor of the p-type.

- Sketch the wave function of a $2p$ orbital as a lobe representation. Clearly mark all nodes (spherical and/or planar) and nuclear positions.

2



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



Explain the general trend and both anomalies.

The general trend of an *increase* in ionisation energy across the period is due to the increase in effective nuclear charge (Z_{eff}). The electrons feel a greater pull from the nucleus as Z_{eff} increases. This leads to a decrease in the size of the atom and an increase in the energy required to remove an electron.

First anomaly - the *decrease* in ionisation energy in going from Be (at. no. 4) to B (at. no. 5). Be has an electron configuration of $[\text{He}] 2s^2$ while B has a configuration of $[\text{He}] 2s^2 2p^1$. Due to shielding in a multi-electron atom, the $2p$ orbital is higher in energy than the $2s$ orbital and thus any electron in the $2p$ orbital is held less tightly than those in the $2s$ orbital. B therefore has a lower ionisation energy than Be, despite having a higher nuclear charge.

Second anomaly - another (slight) drop in ionisation energy going from N (at. no. 7) to O (at. no. 8). There are only three p orbitals, so the next electron to go into one of the p orbitals must pair up. Paired electrons in the same orbital suffer higher electron – electron repulsion so O has a lower ionisation energy than N, despite having a higher nuclear charge.

On the above graph, plot your estimates of the second ionisation energies for the second row elements. Make sure your graph clearly shows the general trends.

See figure above.

The second ionisation of Li is $> 7000 \text{ kJ mol}^{-1}$ as a core electron is ionised. The second ionisations of the other elements follow the same trends as the first ionisations (for exactly the same reasons), but displaced one atomic number to the right and at a slightly higher energy (as Z_{eff} is greater).

Marks
4

- 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.

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

If iron emits X-rays of 1.937 \AA when a $2s$ electron drops back to the $1s$ shell, determine the identity of the elements contained in an alloy found to emit the same type of X-rays at 1.435 \AA and 1.541 \AA ?

For iron, $Z = 26$. With $\lambda = 1.937 \text{ \AA} = 1.937 \times 10^{-10} \text{ m}$:

$$\frac{1}{\sqrt{1.937 \times 10^{-10} \text{ m}}} = k \times (26) \quad \text{so } k = 2764 \text{ m}^{-1/2}$$

For $\lambda = 1.435 \text{ \AA} = 1.435 \times 10^{-10} \text{ m}$:

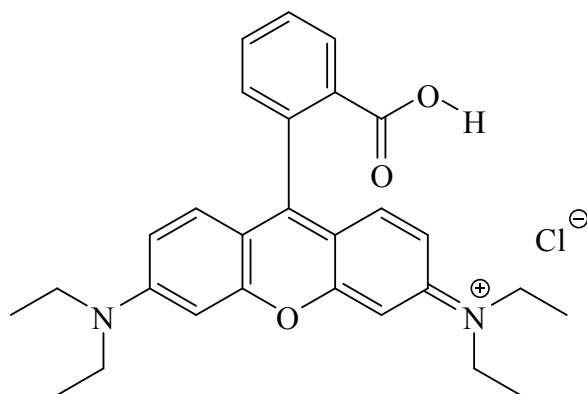
$$\frac{1}{\sqrt{1.435 \times 10^{-10} \text{ m}}} = (2764 \text{ m}^{-1/2}) \times Z \quad \text{so } Z = 30 \text{ corresponding to Zn}$$

For $\lambda = 1.541 \text{ \AA} = 1.541 \times 10^{-10} \text{ m}$:

$$\frac{1}{\sqrt{1.541 \times 10^{-10} \text{ m}}} = (2764 \text{ m}^{-1/2}) \times Z \quad \text{so } Z = 29 \text{ corresponding to Cu}$$

Answer: **Zn and Cu**

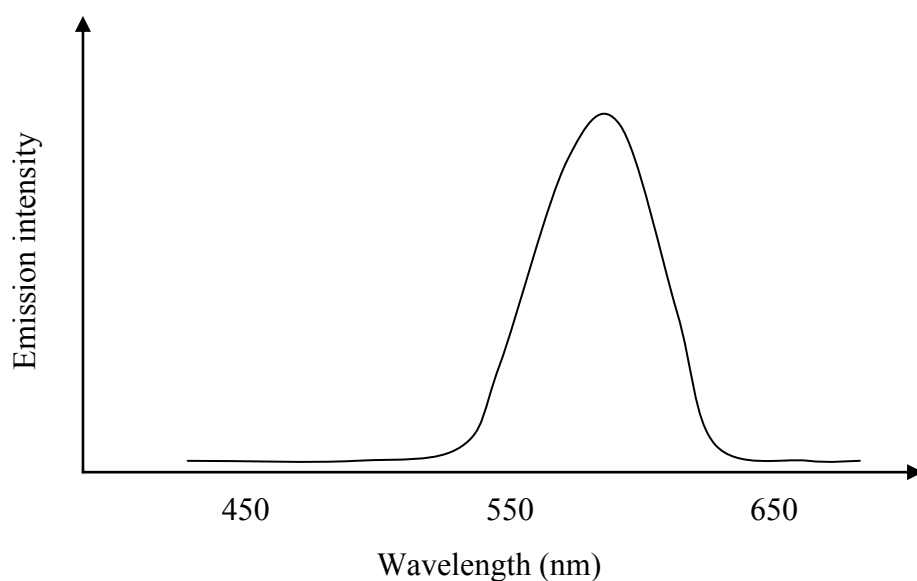
- Rhodamine 6G, whose structure is shown below, is a dye used in various applications such as lasers and environmental monitoring.



Name three functional groups present in the rhodamine 6G molecule.

carboxylic acid, ether, amine, aromatic ring

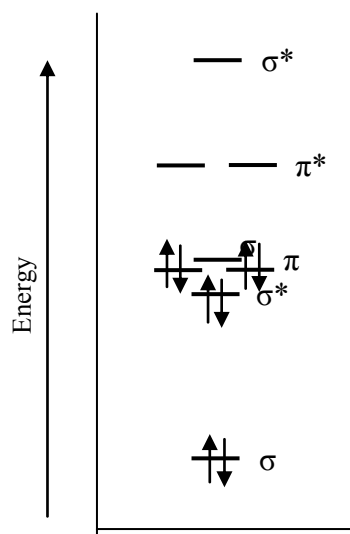
After absorbing green light, rhodamine 6G will emit yellow-orange light. Draw an indicative emission spectrum for this dye on the axes below.



Marks
6

- Carbon forms a homonuclear diatomic molecule which is observed in comets, flames and interstellar clouds.

The molecular orbital energy level diagram provided shows the energies of the orbitals for the valence electrons in the C_2 molecule. Indicate on this diagram the ground state electronic configuration of C_2 using the arrow notation for electron spins.



In its ground state, is C_2 paramagnetic or diamagnetic?

**all electrons are paired:
diamagnetic**

The lowest energy excited state of C_2 possesses two electrons with parallel, unpaired spins. What is the bond order of C_2 in this excited state?

The lowest energy excited state corresponds to an electron being excited from π to σ^* , leading to the configuration $\sigma^2 \sigma^{*2} \pi^3 \sigma^1$.

There are 6 bonding electrons ($1 \times \sigma + 3 \times \pi + 1 \times \sigma$) and 2 antibonding electrons ($2 \times \sigma^*$). The bond order is thus:

$$\begin{aligned} \text{bond order} &= \frac{1}{2} (\text{number of bonding } e^- - \text{number of antibonding } e^-) \\ &= \frac{1}{2} (6 - 2) = 2 \end{aligned}$$

Answer: 2

Starting in this excited state, further exciting an electron from the lowest σ^* orbital to the next lowest σ orbital brings about the doubly excited state responsible for green emission in flames. What is the bond order of this doubly excited state?

This excitation leads to the configuration $\sigma^2 \sigma^{*1} \pi^3 \sigma^2$.

There are now 7 bonding electrons ($1 \times \sigma + 3 \times \pi + 2 \times \sigma$) and 1 antibonding electrons ($2 \times \sigma^*$). The bond order is thus:

$$\text{bond order} = \frac{1}{2} (7 - 1) = 3$$

Answer: 3

- The value of the equilibrium constant, K_c , for the following reaction is 0.118 mol L^{-1} .



What is the equilibrium concentration of $\text{CO}(\text{g})$ if the equilibrium concentration of $[\text{CO}_2(\text{g})] = 0.492 \text{ M}$, $[\text{N}_2(\text{g})] = 0.319 \text{ M}$ and $[\text{NO}(\text{g})] = 0.350 \text{ M}$?

Marks
2

The equilibrium constant for the reaction is given by:

$$K_{\text{eq}} = \frac{[\text{CO}(\text{g})]^2 [\text{NO}(\text{g})]^2}{[\text{CO}_2(\text{g})]^2 [\text{N}_2(\text{g})]} = 0.118$$

When $[\text{CO}_2(\text{g})] = 0.492 \text{ M}$, $[\text{N}_2(\text{g})] = 0.319 \text{ M}$ and $[\text{NO}(\text{g})] = 0.350 \text{ M}$,

$$[\text{CO}(\text{g})]^2 = \frac{K_{\text{eq}} [\text{CO}_2(\text{g})]^2 [\text{N}_2(\text{g})]}{[\text{NO}(\text{g})]^2} = \frac{(0.118)(0.492)^2 (0.319)}{(0.350)^2} \text{ M} = 0.146 \text{ M}$$

$$[\text{CO}(\text{g})] = 0.273 \text{ M}$$

Answer: 0.273 M

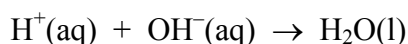
Marks
4

- A 50.0 mL solution contained 5.00 g of NaOH in water at 25.00 °C. When it was added to a 250.0 mL solution of 0.100 M HCl at 25.00 °C in a “coffee cup” calorimeter, the temperature of the solution rose to 26.12 °C.

Is the process an endothermic or exothermic reaction?

exothermic

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.



The total volume of the solution after mixing is $(50.0 + 250.0) \text{ mL} = 300.0 \text{ mL}$. As the density of the solution is 1.00 g mL^{-1} , the mass of the solution is:

$$\text{mass} = \text{density} \times \text{volume} = (1.00 \text{ g mL}^{-1}) \times (300.0 \text{ mL}) = 300. \text{ g}$$

The reaction produces a temperature change $\Delta T = (26.12 - 25.00) \text{ }^\circ\text{C} = 1.12 \text{ K}$. The heat change is therefore:

$$q = mC_v\Delta T = (300. \text{ g}) \times (4.18 \text{ J K}^{-1} \text{ g}^{-1}) \times (1.12 \text{ K}) = 1404 \text{ J}$$

The formula mass of NaOH is $(22.99 \text{ (Na)} + 16.00 \text{ (O)} + 1.008 \text{ (H)}) \text{ g mol}^{-1} = 40.00 \text{ g mol}^{-1}$. 5.00 g of NaOH therefore corresponds to:

$$\text{moles of NaOH} = \text{moles of OH}^- = \frac{\text{mass}}{\text{molar mass}} = \frac{5.00 \text{ g}}{40.00 \text{ mol}} = 0.125 \text{ mol}$$

A 250.0 mL solution of 0.100 M HCl corresponds to

$$\begin{aligned} \text{moles of HCl} &= \text{moles of H}^+ = \text{concentration} \times \text{volume} \\ &= (0.100 \text{ mol L}^{-1}) \times (0.250 \text{ L}) = 0.0250 \text{ mol} \end{aligned}$$

H^+ is therefore the limiting reagent in the reaction. The heat change of 1404 J corresponds to 0.025 mol of H^+ reacting with 0.025 mol of OH^- . The reaction is exothermic as it causes a temperature increase.

The molar enthalpy of reaction is $\frac{-1404 \text{ J}}{0.025 \text{ mol}} = -56200 \text{ J mol}^{-1} = -56.2 \text{ kJ mol}^{-1}$.

Answer: **-56.2 kJ mol⁻¹**

- Indicate the relative entropy of each system in the following pairs of systems. Use: “>”, “<”, or “=”.

$\text{H}_2\text{O}(\text{g})$

>

$\text{H}_2\text{O}(\text{s})$

$3\text{O}_2(\text{g})$

>

$2\text{O}_3(\text{g})$

- Consider butane (C_4H_{10}) and pentane (C_5H_{12}). Which gas has the higher entropy at 40 °C? Give reasons for your answer.

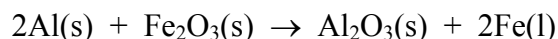
Pentane. It has more bonds and can therefore take on more conformations so has the higher entropy (disorder).

1

2

- The thermite reaction is written below. Show that the heat released in this reaction is sufficient for the iron to be produced as molten metal.

Marks
6



Assume that the values in the table are independent of temperature.

Substance	Enthalpy of formation, $\Delta_f H^\circ$ kJ mol ⁻¹	Molar heat capacity, C_p J K ⁻¹ mol ⁻¹	Melting point °C	Enthalpy of fusion kJ mol ⁻¹
Al	0	24	660	11
Al ₂ O ₃	-1676	79	2054	109
Fe	0	25	1535	14
Fe ₂ O ₃	-824	104	1565	138

Assume there is 1 mol of reactants at an initial temperature of 25 °C.

Need to show that ΔH for the reaction is greater than the amount of energy required to melt 2 mol of Fe *and* heat all the products (2 mol of Fe + 1 mol of Al₂O₃) to the melting point of Fe.

For the reaction:

$$\begin{aligned}\Delta H &= \sum \Delta_f H(\text{products}) - \sum \Delta_f H(\text{reactants}) \\ &= \Delta_f H(\text{Al}_2\text{O}_3) + 2\Delta_f H(\text{Fe}) - (2\Delta_f H(\text{Al}) + \Delta_f H(\text{Fe}_2\text{O}_3)) \\ &= -1676 + 2 \times 0 - (2 \times 0 - 824) = -852 \text{ kJ mol}^{-1}\end{aligned}$$

To melt 2 mol of Fe and heat all products to the melting point of Fe:

(i) ΔH to heat 2 mol of Fe to its melting point:

$$\Delta H = nC_p\Delta T = (2 \text{ mol}) \times (25 \text{ J K}^{-1} \text{ mol}^{-1}) \times ((1535-25) \text{ K}) = 75.5 \text{ kJ}$$

(ii) ΔH to heat 1 mol of Al₂O₃ to the melting point Fe

$$\Delta H = nC_p\Delta T = (1 \text{ mol}) \times (79 \text{ J K}^{-1} \text{ mol}^{-1}) \times ((1535-25) \text{ K}) = 119 \text{ kJ}$$

(iii) ΔH to melt 2 mol of Fe

$$\Delta H = n\Delta_{\text{fusion}}H = (2 \text{ mol}) \times (14 \text{ kJ mol}^{-1}) = 28 \text{ kJ}$$

Total energy required to melt the iron = 75.5 + 119 + 28 = +222.5 kJ

There is more than enough energy generated in the reaction for iron to be produced as a liquid.

- A helium balloon is filled on the ground, where the atmospheric pressure is 768 mmHg. The volume of the balloon is 8.00 m³. When the balloon reaches an altitude of 4200 m, its volume is found to be 16.8 m³. Assuming that the temperature remains constant, what is the air pressure at 4200 m in mmHg?

Marks
2

From the ideal gas law, $PV = nRT$. As the number of moles and the temperature is constant, the pressure and volume at the two heights are related by:

$$P_1V_1 = P_2V_2$$

Hence:

$$(768 \text{ mmHg}) \times (8.0 \text{ m}^3) = P_2 \times (16.8 \text{ m}^3)$$

$$P_2 = 366 \text{ mmHg}$$

Answer: **366 mmHg**

- The volume of a gas is 40.0 mL at -15 °C and 1.30 atm. At what temperature (°C) will the gas have a pressure of 1.00 atm and a volume of 65.0 mL?

2

As the number of moles is constant, the pressure, volume and temperature of the gas are related by;

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

Hence:

$$\frac{(1.30 \text{ atm})(40.0 \text{ mL})}{(-15+273)\text{K}} = \frac{(1.00 \text{ atm})(65.0 \text{ mL})}{T_2}$$

$$T_2 = 322.5 \text{ K} = 49.5 \text{ °C}$$

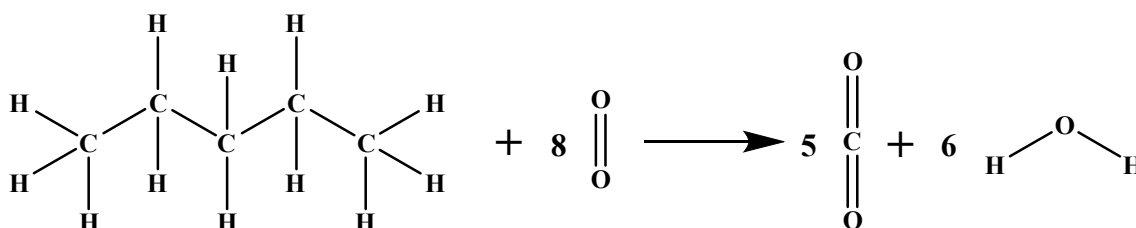
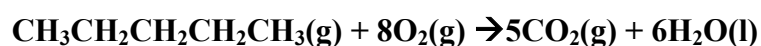
Answer: **49.5 °C**

Marks
3

- Pentane, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$, burns completely in oxygen to form $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{g})$. Use the bond enthalpies given below to estimate the enthalpy change for this process.

Bond	Bond enthalpy (kJ mol^{-1})	Bond	Bond enthalpy (kJ mol^{-1})
C-H	414	O-H	463
C-C	346	O-O	144
C=O	804	O=O	498

The combustion reaction is:



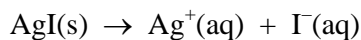
$$\begin{aligned} \Delta_{\text{comb}}H &= \{ [\Delta_{\text{atom}}H(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3)] + 8 \times [\Delta_{\text{atom}}H(\text{O}_2)] \} \\ &\quad - \{ 5 \times [\Delta_{\text{atom}}H(\text{CO}_2)] + 6 \times \Delta_{\text{atom}}H(\text{H}_2\text{O}) \} \\ &= \{ [4 \times 346 (\text{C-C}) + 12 \times 414 (\text{C-H})] + 8 \times [498 (\text{O=O})] \} \\ &\quad - \{ 5 \times [2 \times 804 (\text{C=O})] + 6 \times [2 \times 463] \} \text{ kJ mol}^{-1} \\ &= \{ [10336] - [13596] \} \text{ kJ mol}^{-1} \\ &= -3260 \text{ kJ mol}^{-1} \end{aligned}$$

Answer: $-3260 \text{ kJ mol}^{-1}$

- The measured potential of the following cell is -0.742 V at 298 K .



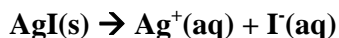
Calculate the standard cell potential and determine the equilibrium constant, K_{sp} , for the following reaction at 298 K .

**Marks****4**

The two half cell reactions are:



The overall cell reaction is:



The cell potential is given by the Nernst equation:

$$E_{\text{cell}} = E^\circ - 2.303 \times \frac{RT}{nF} \log Q$$

The reaction is a 1 electron process, $n = 1$, with $Q = Q_{\text{sp}} = [\text{Ag}^+(\text{aq})][\text{I}^-(\text{aq})]$

As $E_{\text{cell}} = -0.742\text{ V}$, $[\text{Ag}^+(\text{aq})] = 0.010\text{ M}$ and $[\text{I}^-(\text{aq})] = 0.030\text{ M}$:

$$-0.742\text{ V} = E^\circ - 2.303 \times \frac{(8.314\text{ J K}^{-1}\text{ mol}^{-1})(298\text{ K})}{1 \times 96485\text{ C mol}^{-1}} \log(0.010 \times 0.030)$$

$$E^\circ = -0.95\text{ V}$$

At equilibrium, $E = 0$ and $E^\circ = 2.303 \times \frac{RT}{nF} \log K_{\text{sp}}$:

$$-0.95 = 2.303 \times \frac{(8.314\text{ J K}^{-1}\text{ mol}^{-1})(298\text{ K})}{1 \times 96485\text{ C mol}^{-1}} \log K_{\text{sp}}$$

$$K_{\text{sp}} = 8.5 \times 10^{-17}$$

$$E^\circ_{\text{cell}} = -0.95\text{ V}$$

$$K_{\text{sp}} = 8.5 \times 10^{-17}$$

- Circle the molecule in the following pairs that has the stronger intermolecular forces. Identify the types of forces present for the species selected.

2

molecule pair	types of intermolecular forces
H_2 or <u>N_2</u>	dispersion (more electrons in N_2)
<u>CH_3Cl</u> or CH_4	dipole-dipole and dispersion (dipole present and more electrons in CH_3Cl)
<u>SO_2</u> or CO_2	dipole-dipole and dispersion (dipole present and more electrons in SO_2)
<u>H_2O</u> or H_2S	hydrogen bonding (only present in H_2O)

- How does nitric oxide, NO(g), form in a car engine? What happens to the NO once emitted from the tailpipe? Make sure you include the appropriate chemical reactions in your answer.

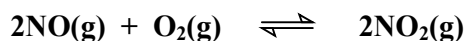
Marks
2

NO(g) forms from the reaction of N₂(g) with O₂(g):



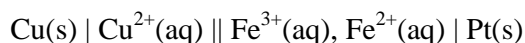
The formation of NO(g) is endothermic, so it is favoured at the high temperatures that exist in the car engine. The high temperatures also speed up the reaction.

NO(g) reacts with oxygen in the atmosphere to give NO₂(g).



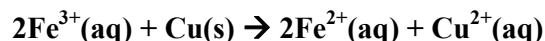
- Calculate the standard potential at 298 K of the following electrochemical cell.

5



Data:	$\Delta_f H^\circ / (\text{kJ mol}^{-1})$	$S^\circ / (\text{J K}^{-1} \text{ mol}^{-1})$
Fe ³⁺ (aq)	-49	-316
Fe ²⁺ (aq)	-89	-138
Cu ²⁺ (aq)	65	-100
Cu(s)	0	33

The reaction is:



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

$$\Delta_{\text{rxn}}H^\circ = [(2 \times -89 + 65) - (2 \times -49 + 0)] \text{ kJ mol}^{-1} = -15 \text{ kJ mol}^{-1}$$

Using $\Delta_{\text{rxn}}S^\circ = \sum S^\circ(\text{products}) - \sum S^\circ(\text{reactants})$,

$$\Delta_{\text{rxn}}S^\circ = [(2 \times -138 + -100) - (2 \times -316 + 33)] \text{ J K}^{-1} \text{ mol}^{-1} = 223 \text{ J K}^{-1} \text{ mol}^{-1}$$

As $\Delta_{\text{rxn}}G^\circ = \Delta_{\text{rxn}}H^\circ - T\Delta_{\text{rxn}}S^\circ$, at $T = 298 \text{ K}$:

$$\Delta_{\text{rxn}}G^\circ = (-15 \times 10^3 \text{ J mol}^{-1}) - (298 \text{ K})(223 \text{ J K}^{-1} \text{ mol}^{-1}) = -81454 \text{ J mol}^{-1}$$

The reaction is a 2 electron process as it involves $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu}(\text{s})$ and as $\Delta_{\text{rxn}}G^\circ = -nFE^\circ$:

$$-81454 \text{ J mol}^{-1} = -2 \times (96485 \text{ C mol}^{-1}) \times E^\circ$$

$$E^\circ = +0.422 \text{ V}$$

Answer: +0.422 V