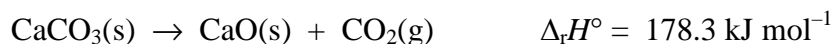


- Calculate $\Delta_r H^\circ$ for the reaction



given the following heats of reaction:



Marks
2

Using $\Delta_r H = \sum \Delta_f H(\text{products}) - \sum \Delta_f H(\text{reactants})$, the heats of the three reactions are, respectively:

$$\Delta_r H(1) = [\Delta_f H(\text{CaCO}_3(\text{s}))] - [\Delta_f H(\text{CO}_2(\text{g}))]$$

$$\Delta_r H(2) = [\Delta_f H(\text{CaO(s)})] = -635.1 \text{ kJ mol}^{-1}$$

$$\Delta_r H(3) = [\Delta_f H(\text{CaO(s)}) + \Delta_f H(\text{CO}_2(\text{g}))] - [\Delta_f H(\text{CaCO}_3(\text{s}))] = 178.3 \text{ kJ mol}^{-1}$$

Substituting $\Delta_r H(2)$ into $\Delta_r H(3)$ gives:

$$[(-635.1 \text{ kJ mol}^{-1}) + \Delta_f H(\text{CO}_2(\text{g}))] - [\Delta_f H(\text{CaCO}_3(\text{s}))] = 178.3 \text{ kJ mol}^{-1}$$

After rearrangement, this gives:

$$[\Delta_f H(\text{CaCO}_3(\text{s}))] - [\Delta_f H(\text{CO}_2(\text{g}))] = (-635.1 - 178.3) \text{ kJ mol}^{-1} = -813.4 \text{ kJ mol}^{-1}$$

This is equal to $\Delta_r H(1)$.

Answer: **-813.4 kJ mol⁻¹**

- Explain how the definition of the Gibbs free energy change

$$\Delta G = \Delta H - T\Delta S$$

expresses the Second Law of Thermodynamics.

3

The Second Law of Thermodynamics states that the entropy of the Universe increases for a spontaneous process.

$$\Delta S_{\text{univ}} = \Delta S_{\text{surr}} + \Delta S_{\text{sys}} \quad \text{where } \Delta S_{\text{surr}} = \frac{-\Delta H_{\text{sys}}}{T}$$

so,

$$\Delta S_{\text{univ}} = \frac{-\Delta H_{\text{sys}}}{T} + \Delta S_{\text{sys}}$$

or,

$$T\Delta S_{\text{univ}} = -\Delta H_{\text{sys}} + T\Delta S_{\text{sys}} = -\Delta G$$

$\Delta S_{\text{univ}} > 0$ for spontaneous reaction and hence $\Delta G < 0$ for spontaneous reaction.

Marks
4

- Calculate the density (in g L^{-1}) of $\text{CO}_2(\text{g})$ at 298 K and $1.013 \times 10^5 \text{ Pa}$ (1 atm).

From the ideal gas law, $PV = nRT$, so the volume occupied by one mol of CO_2 is

$$V = RT/P = (8.314 \text{ m}^3 \text{ Pa K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}) / (1.013 \times 10^5 \text{ Pa}) \\ = 0.02446 \text{ m}^3 = 24.5 \text{ L} \quad (\text{as } 1 \text{ m}^3 = 1000 \text{ L})$$

The molar mass of CO_2 is $(12.01 \text{ (C)} + 2 \times 16.00 \text{ (O)}) \text{ g mol}^{-1} = 44.01 \text{ g mol}^{-1}$. The mass of one mol of CO_2 is 44.01 g.

The density CO_2 is therefore:

$$\text{density} = \text{mass} / \text{volume} = (44.01 \text{ g}) / (24.5 \text{ L}) = 1.80 \text{ g L}^{-1}$$

Answer: **1.80 g L⁻¹**

How does the density change with an increase in temperature at constant pressure?

As $V = RT/P$, increasing the temperature will increase the volume occupied by one mol and so will *reduce* the density.

How does the density change with an increase in temperature at constant volume?

If the volume is constant, the density will be constant. Changing the temperature will not affect the mass.

Is there any temperature at which the density of $\text{CO}_2(\text{g})$ is less than that of air? Explain your answer.

No. The volume occupied is the same for all gases.

The relative density only depends on the molar masses. As the molar mass of CO_2 is 44.01 g mol^{-1} whilst that of air is about 28.8 ($0.2 \times 32 \text{ (O}_2) + 0.8 \times 28 \text{ (N}_2)$), so CO_2 is *always* more dense than air.

- At high temperatures (1100 K), $\text{CO}_2(\text{g})$ can be reduced to $\text{CO}(\text{g})$ by elemental carbon (graphite):



A vessel at 1100 K containing powdered graphite was filled with $\text{CO}_2(\text{g})$ to a pressure of 0.458 atm. After equilibration was established, the final pressure was 0.757 atm. With reference to a standard state of 1 atm, calculate K_p for the reaction.

Marks
6

The reaction table for this equilibrium is:

	$\text{CO}_2(\text{g})$	$\text{C}(\text{graphite})$	\rightleftharpoons	$2\text{CO}(\text{g})$
initial pressure	0.458	0		0
change	-x	0		+2x
equilibrium	0.458 - x	0		2x

$\text{C}(\text{graphite})$ is a solid and does not give rise to an appreciable contribution to the pressure.

The total pressure at equilibrium is therefore:

$$P_{\text{total}} = P_{\text{CO}_2} + P_{\text{CO}} = (0.458 - x + 2x) \text{ atm} = (0.458 + x) \text{ atm}$$

As $P_{\text{total}} = 0.757 \text{ atm}$,

$$x = (0.757 - 0.458) \text{ atm} = 0.299 \text{ atm}$$

So, $P_{\text{CO}_2} = (0.458 - x) \text{ atm} = (0.458 - 0.299) \text{ atm} = 0.159 \text{ atm}$ and $P_{\text{CO}} = 2x \text{ atm} = (2 \times 0.299 \text{ atm}) = 0.598 \text{ atm}$.

Hence, the equilibrium constant in terms of partial pressures, K_p , with a standard state of 1 atm is:

$$K_p = \frac{(P_{\text{CO}}/P^\circ)^2}{(P_{\text{CO}_2}/P^\circ)} = \frac{(0.598/1.000)^2}{(0.159/1.000)} = 2.25$$

$$K_p = 2.25$$

What do you expect to be the signs of ΔG and ΔS for this reaction? Explain the reasons for your predictions.

As $K_p > 1$, the forward reaction is favourable and so $\Delta G < 0$.

The reaction involves 1 mol of reactants leading to 2 mol of products. There is an increase in the dispersal of energy: $\Delta G > 0$

ANSWER CONTINUES ON THE NEXT PAGE

What experiment could be run in order to determine the sign of ΔH for this reaction?

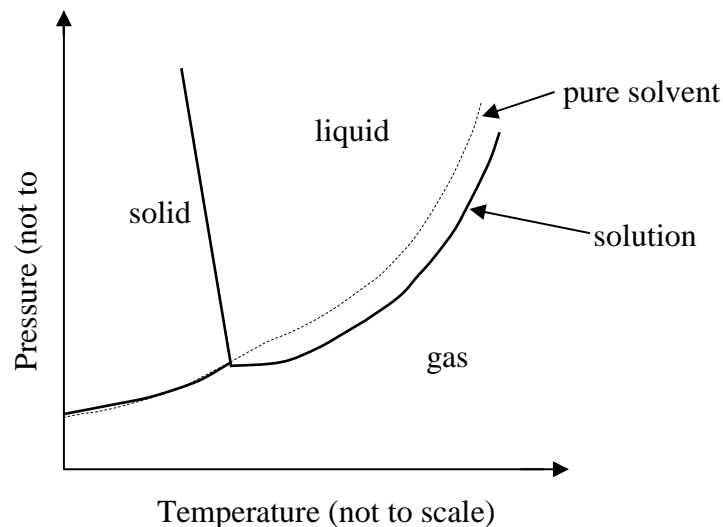
Two possible experiments are:

- (i) perform the reaction in a calorimeter and determine whether heat is lost or gained during the reaction, and**
- (ii) perform the experiment described in the first part of the question at a different temperature: if the reaction is exothermic, K_p will be smaller at the higher temperature and if the reaction is endothermic, K_p will be larger at the higher temperature.**

- Explain why the addition of salt to water raises the boiling point temperature of the solution but lowers the freezing point temperature.

Marks
3

The presence of solute particles lowers the vapour pressure of the solution compared to that of the pure solvent. This results in a lowering of the freezing point and raising of the boiling point as shown in the phase diagram.



Alternatively, adding salt to water increases the entropy.

Boiling requires higher temperatures as it is driven by the increase in entropy associated with going to the gas phase which is decreased by the higher entropy of the solution.

Freezing requires lower temperatures as the opposite process (melting) becomes more favoured by the higher entropy of the solution.

- An aqueous solution with a volume of 10.0 mL contains 0.025 g of a purified protein of unknown molecular weight. The osmotic pressure of the solution was measured in an osmometer to be 0.0036 atm at 20.0 °C. Assuming ideal behaviour and no dissociation of the protein, estimate its molar mass.

3

The osmotic pressure is given by

$$\Pi = cRT$$

As 1 atm = 1.013×10^5 Pa, the osmotic pressure is

$$\Pi = (0.0036 \times 1.013 \times 10^5) \text{ Pa} = 365 \text{ Pa}$$

Hence

$$c = \Pi / RT = (365 \text{ Pa}) / ((8.314 \text{ m}^3 \text{ Pa K}^{-1} \text{ mol}^{-1}) \times (293 \text{ K})) = 0.15 \text{ mol m}^{-3}$$

ANSWER CONTINUES ON THE NEXT PAGE

As $1 \text{ m}^3 = 1000 \text{ L}$, this corresponds to

$$c = 1.5 \times 10^{-4} \text{ mol L}^{-1}$$

As 1 L contains $1.5 \times 10^{-4} \text{ mol}$, the amount in 10.0 mL is:

$$\text{amount of protein} = (0.0100 \text{ L}) \times (1.5 \times 10^{-4} \text{ mol L}^{-1}) = 1.5 \times 10^{-6} \text{ mol}$$

As this amount has a mass of 0.025 g , the mass of 1 mol is:

$$\begin{aligned} \text{molar mass} &= \text{mass} / \text{number of moles} \\ &= (0.025 \text{ g}) / (1.5 \times 10^{-6} \text{ mol}) = 17000 \text{ g mol}^{-1} \end{aligned}$$

Answer: $1.7 \times 10^4 \text{ g mol}^{-1}$

- Sketch the titration curve (pH against mL of added base) when 25.0 mL of 0.10 M hydrofluoric acid (HF) with a pK_a of 3.17 is titrated with 0.10 M NaOH.

Calculate the pH at the following four points:

- before any NaOH is added;
- when half of the HF has been neutralised;
- at the equivalence point; and
- 50% beyond the equivalence point, *i.e.* when 1.5 times the equivalence volume has been added.

(i) At this point, the solution contains only a weak acid.

As HF is a weak acid, $[H^+]$ must be calculated by considering the equilibrium:

	HF	\rightleftharpoons	F ⁻	H ⁺
initial	0.10		0	0
change	-x		+x	+x
final	0.10 - x		x	x

The equilibrium constant K_a is given by:

$$K_a = \frac{[F^-][H^+]}{[HF]} = \frac{x^2}{(0.10-x)}$$

As $pK_a = 3.17$, $K_a = 10^{-3.17}$. K_a is very small so $0.10 - x \sim 0.10$ and hence:

$$x^2 = 0.10 \times 10^{-3.17} \quad \text{or} \quad x = 0.00822 \text{ M} = [H^+]$$

Hence, the pH is given by:

$$pH = -\log_{10}[H^+] = -\log_{10}[0.00822] = 2.09$$

(ii) At this point, half of the original HF has been converted to its conjugate base F⁻. The pH can be calculated using the Henderson-Hasselbalch equation:

$$pH = pK_a + \log \frac{[\text{base}]}{[\text{acid}]} = 3.17 + \log \frac{[F^-]}{[HF]} = 3.17 + \log(1) = 3.17$$

(iii) At this point, all of the original HF has been converted to F⁻. The number of moles of HF originally present is:

$$\begin{aligned} \text{number of moles of HF} &= \text{concentration} \times \text{volume} \\ &= (0.10 \text{ mol L}^{-1}) \times (0.025 \text{ L}) = 0.0025 \text{ mol} \end{aligned}$$

This is equal to the amount of F⁻ present at equivalence. As 25.0 mL of NaOH has been added at this point, the total volume is now (25.0 + 25.0) mL = 50.0 mL. The concentration of F⁻ is therefore:

$$[F^-] = \text{number of moles} / \text{volume} = (0.0025 \text{ mol}) / (0.050 \text{ L}) = 0.050 \text{ mol L}^{-1}$$

As F^- is a weak base. $[OH^-]$ must be calculated using a reaction table.

	F^-	H_2O	\rightleftharpoons	HF	OH^-
initial	0.050	large		0	0
change	-y	negligible		+y	+y
final	$0.050 - y$	large		y	y

The equilibrium constant K_b is given by:

$$K_b = \frac{[HF][OH^-]}{[F^-]} = \frac{y^2}{(0.050 - y)}$$

For an acid and its conjugate base:

$$pK_a + pK_b = 14.00$$

$$pK_b = 14.00 - 3.17 = 10.83$$

As $pK_b = 10.83$, $K_b = 10^{-10.83}$. K_b is very small so $0.050 - y \sim 0.050$ and hence:

$$y^2 = 0.050 \times 10^{-10.83} \text{ or } y = 8.59 \times 10^{-7} \text{ M} = [OH^-]$$

Hence, the pOH is given by:

$$pOH = -\log_{10}[OH^-] = \log_{10}[8.59 \times 10^{-7}] = 6.07$$

Finally, $pH + pOH = 14.00$ so

$$pH = 14.00 - 6.07 = 7.93$$

(iv) At this point, there is excess strong base present. Addition of 1.5 times the equivalence volume corresponds to addition of $(1.5 \times 25.0) \text{ mL} = 37.5 \text{ mL}$. This volume of 0.10 M NaOH contains

$$\begin{aligned} \text{number of moles of NaOH} &= \text{concentration} \times \text{volume} \\ &= (0.10 \text{ mol L}^{-1}) \times (0.0375 \text{ L}) = 0.00375 \text{ mol} \end{aligned}$$

From (iii), there was original 0.0025 mol of HF present so the excess of OH^- is:

$$\text{excess moles of } OH^- = (0.00375 - 0.0025) \text{ mol} = 0.00125 \text{ mol}$$

This is present in a total volume of $(25.0 + 37.5) \text{ mL} = 62.5 \text{ mL}$, so its concentration is:

$$\begin{aligned} [OH^-] &= \text{number of moles} / \text{volume} \\ &= (0.00125 \text{ mol}) / (0.0625 \text{ L}) = 0.020 \text{ mol L}^{-1} \end{aligned}$$

ANSWER CONTINUES ON THE NEXT PAGE

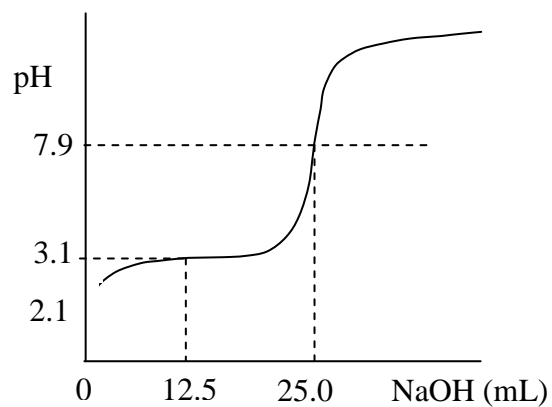
Hence,

$$\text{pOH} = -\log_{10}[\text{OH}^-] = -\log_{10}(0.020) = 1.70$$

Lastly, $\text{pH} = 14.00 - \text{pOH}$:

$$\text{pH} = 14.00 - 1.70 = 12.30$$

Putting these 4 points together gives the titration curve:



- Explain why iron storage proteins are necessary for the transport of iron both intracellularly and extracellularly within the bloodstream at a pH of 7.4.

Marks
2

The K_{sp} of $\text{Fe}(\text{OH})_3$ is so low, that even at pH 7.4 there are sufficient OH^- ions present to precipitate the Fe^{3+} ions as $\text{Fe}(\text{OH})_3$.

To avoid precipitation and to allow a higher concentration of Fe^{3+} to be circulated, Fe^{3+} is complexed by *transferrin* in the bloodstream and iron is stored within *ferritin* within the cell.

Marks
6

- At present levels of $\text{CO}_2(\text{g})$ in the atmosphere, water in contact with air becomes acidic ($\text{pH} = 5.60$) through the hydrolysis of H_2CO_3 (*i.e.* $\text{CO}_2(\text{aq})$).



What is the concentration of H_2CO_3 in such natural waters?

The equilibrium constant is given by $K_a = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]}$.

From the reaction, $[\text{H}^+] = [\text{HCO}_3^-]$ and so:

$$K_a = \frac{[\text{H}^+]^2}{[\text{H}_2\text{CO}_3]} = 4.5 \times 10^{-7}$$

At $\text{pH} = 5.60$, $[\text{H}^+] = 10^{-5.60}$. Hence:

$$[\text{H}_2\text{CO}_3] = \frac{[\text{H}^+]^2}{K_a} = \frac{(10^{-5.60})^2}{(4.5 \times 10^{-7})} \text{ M} = 1.4 \times 10^{-5} \text{ M}$$

Answer: $1.4 \times 10^{-5} \text{ M}$

What is the total concentration of dissolved CO_2 ?

With $[\text{HCO}_3^-] = 10^{-5.60} \text{ M}$ and $[\text{H}_2\text{CO}_3] = 1.4 \times 10^{-5} \text{ M}$,

$$\text{total concentration of dissolved } \text{CO}_2 = (10^{-5.60} + 1.4 \times 10^{-5}) \text{ M} = 1.7 \times 10^{-5} \text{ M}$$

Answer: $1.7 \times 10^{-5} \text{ M}$

From Henry's law, a doubling of the atmospheric concentration will lead to the amount of dissolved CO_2 also doubling. Hence:

$$\text{total concentration of dissolved } \text{CO}_2 = 2 \times 1.7 \times 10^{-5} \text{ M} = 3.4 \times 10^{-5} \text{ M}$$

This will be present as both H_2CO_3 and HCO_3^- and the new point of equilibrium must be established to work out $[\text{H}^+]$:

	H_2CO_3	\rightleftharpoons	HCO_3^-	H^+
initial	3.4×10^{-5}		0	0
change	-x		+x	+x
final	$3.4 \times 10^{-5} - x$		x	x

The equilibrium constant K_a is given by:

$$K_a = \frac{[\text{HCO}_3^-][\text{H}^+]}{[\text{H}_2\text{CO}_3]} = \frac{x^2}{(3.4 \times 10^{-5} - x)} = 4.5 \times 10^{-7}$$

ANSWER CONTINUES ON THE NEXT PAGE

Assuming x is small compared to the initial concentration,

$$x \approx \sqrt{(3.4 \times 10^{-5}) \times (4.5 \times 10^{-7})} = 3.9 \times 10^{-6} = [\text{H}^+]$$

$$\text{pH} = -\log_{10}[\text{H}^+] = -\log_{10}(3.9 \times 10^{-6}) = 5.45$$

Without the approximation,

$$x^2 + (4.5 \times 10^{-7})x - (1.53 \times 10^{-11}) = 0$$

Solving this using the quadratic formula gives $\text{pH} = 5.44$.

Answer: **5.44**

- ^{18}Ne is an unstable isotope of neon. Which force within the nucleus is responsible for its instability? Explain.

Marks
8

For the light elements, stable nuclei are those with the number of protons \approx the number of neutrons.

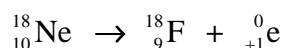
^{18}Ne has 10 protons and 8 neutrons so has too many protons relative to neutrons within the nucleus.

Therefore electrostatic repulsion between the protons destabilises the nucleus.

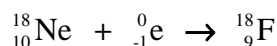
Write two possible mechanisms for the radioactive decay of ^{18}Ne to ^{18}F .

The ratio of protons to neutrons can be improved by positron emission (conversion of a proton to a neutron and positron) or electron capture (conversion of an electron and a proton to a neutron).

Positron emission:



Electron capture:



The molar mass of ^{18}Ne is $18.006 \text{ g mol}^{-1}$. The activity of an isotopically pure 1.000 g sample of ^{18}Ne is measured as $1.392 \times 10^{22} \text{ Bq}$. Calculate the half-life of ^{18}Ne .

As 18.006 g contains 1 mol, the number of nuclei in 1.000 g of ^{18}Ne is:

$$\begin{aligned} \text{number of nuclei} &= \frac{1.000 \text{ g}}{18.006 \text{ g mol}^{-1}} \times (6.022 \times 10^{23} \text{ nuclei g}^{-1}) \\ &= 2.402 \times 10^{10} \text{ nuclei} \end{aligned}$$

As the activity $A = \lambda N$:

$$\lambda = A / N = (1.392 \times 10^{22} \text{ nuclei s}^{-1}) / (2.402 \times 10^{10} \text{ nuclei}) = 0.4163 \text{ s}^{-1}$$

By definition,

$$t_{1/2} = \ln(2) / \lambda = \ln(2) / (0.4163 \text{ s}^{-1}) = 67.18 \text{ s}$$

Answer: **67.18 s**

ANSWER CONTINUES ON THE NEXT PAGE

How long will it take for the activity of this pure 1.000 g sample of ^{18}Ne to drop to 1.000×10^{10} Bq?

The number of radioactive nuclei decreases with time according to the equation:

$$\ln \frac{N_0}{N_t} = \lambda t$$

As $A = \lambda N$, this can be rewritten in terms of the change in activity with time:

$$\ln \frac{A_0}{A_t} = \lambda t$$

With $A_0 = 1.392 \times 10^{22}$ Bq, the activity will decrease to 1.000×10^{10} Bq when:

$$\ln \frac{(1.392 \times 10^{22})}{(1.000 \times 10^{10})} = (0.4163 \text{ s}) \times t$$

$$t = 67.18 \text{ s}$$

Answer: **67.18 s**

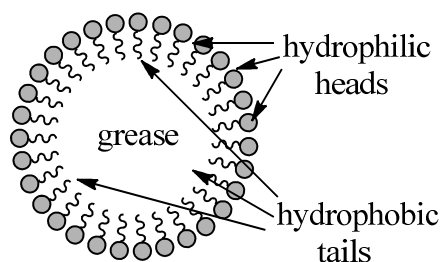
Marks
3

- Explain, with the aid of a diagram labelling all the key components, how sodium stearate ($C_{17}H_{35}COONa$) can stabilise long-chain non-polar hydrocarbons (“grease”) in water.

When dissolved in water, sodium stearate gives stearate ions which act as surfactant molecules.

The have hydrophobic non-polar tails and ionically charged hydrophilic polar heads.

This leads to formation of a stable, spherical micelle structure in which the grease molecules are contained within a monolayer of stearate ions with their heads pointing outwards.



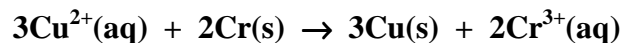
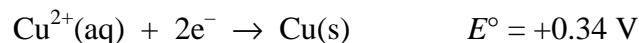
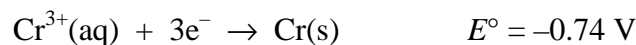
- Explain what is meant by a “non-oxidising acid” in aqueous solution.

2

An acid whose anion is a weaker oxidising agent than H_3O^+ .

**Marks
8**

- Write the overall chemical reaction that takes place in a galvanic cell based on the following half-cell reactions:



Write the same reaction in shorthand voltaic cell notation.



Which metal electrode is acting as the cathode in this reaction?

copper

Calculate the potential of a battery based on this cell in which the concentration of $\text{Cu}^{2+}(\text{aq})$ is 0.0355 M, the concentration of $\text{Cr}^{3+}(\text{aq})$ is 1.6650 M and the temperature is 25 °C..

As Cr is being oxidised and Cu^{2+} is being reduced in the reaction, the standard cell potential is:

$$E^{\circ} = E^{\circ}_{\text{red}} + E^{\circ}_{\text{ox}} = (+0.34 \text{ V}) + (+0.74 \text{ V}) = +1.08 \text{ V}$$

The Nernst equation, $E_{\text{cell}} = E^{\circ} - \frac{RT}{nF} \ln Q$, can be used to work out the standard potential for the process in non-standard conditions. The reaction involves transfer of 6 electrons (as $2\text{Cr} \rightarrow 2\text{Cr}^{3+} + 6\text{e}^{-}$ and $3\text{Cu}^{2+} + 6\text{e}^{-} \rightarrow 3\text{Cu}$) and the reaction quotient is:

$$Q = \frac{[\text{Cr}^{3+}(\text{aq})]^2}{[\text{Cu}^{2+}(\text{aq})]^3}$$

Hence,

$$E_{\text{cell}} = E^{\circ} - \frac{RT}{nF} \ln Q = (+1.08 \text{ V}) - \frac{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298 \text{ K})}{(6 \times 96485 \text{ C mol}^{-1})} \ln \frac{(1.6650)^2}{(0.0355)^3}$$

$$E_{\text{cell}} = +1.03 \text{ V}$$

Answer: **+1.03 V**

ANSWER CONTINUES ON THE NEXT PAGE

How much free energy will be released as the battery described in the previous question runs down completely?

Using $\Delta G = -nFE$,

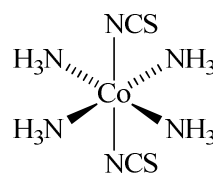
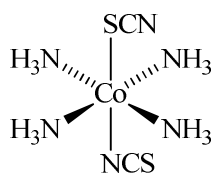
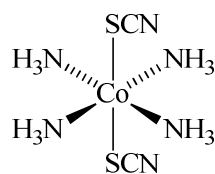
$$\Delta G = -(6 \times 96485 \text{ C mol}^{-1}) \times (+1.03 \text{ V}) = -598 \text{ kJ mol}^{-1}$$

i.e. 598 kJ will be released.

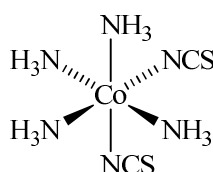
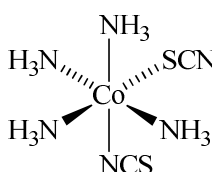
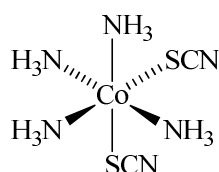
Answer: **598 kJ**

- Write out the full name in standard notation of $[\text{Co}(\text{NH}_3)_4(\text{SCN})_2]\text{Cl}$ and draw all the possible isomers of the complex ion.

tetraamminedithiocyanatocobalt(III) chloride



trans-isomers



cis-isomers

2 thiocyanato ligands

1 thiocyanato ligand &
1 isothiocyanato ligand

2 isothiocyanato ligands

Describe and contrast the nature of the chemical bonds:

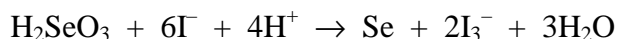
- between N and H in NH_3 ;
- between Co and NH_3 ; and
- between $[\text{Co}(\text{NH}_3)_4(\text{SCN})_2]^+$ and Cl^- in this compound.

N–H bonds are covalent in NH_3 . These bonds are relatively short, strong and highly directional. They involve the sharing of electrons from both atoms involved in the bond.

$\text{Co}:\text{NH}_3$ coordination bonds are due to the donation of the lone pair of electrons on N to the Co^{3+} . These bonds are highly polar and are generally weaker, longer and less directional than covalent bonds.

$[\text{Co}(\text{NH}_3)_4(\text{SCN})_2]^+$ and Cl^- are ionically bonded in the solid state due to Coulombic attraction between the oppositely charged ions. These bonds are strong but not directional (i.e. they occur between every pair of ions in the solid with a strength that decreases with their separation).

- The following reaction is run from 4 different starting positions.



Marks
7

Experiment Number	Initial $[\text{H}_2\text{SeO}_3]$ (mol L ⁻¹)	Initial $[\text{I}^-]$ (mol L ⁻¹)	Initial $[\text{H}^+]$ (mol L ⁻¹)	Initial rate of increase of $[\text{I}_3^-]$ (mol L ⁻¹ s ⁻¹)
1	0.100	0.100	0.100	1.000
2	0.100	0.075	0.100	0.422
3	0.075	0.100	0.100	0.750
4	0.100	0.075	0.075	0.237

Determine the rate law for the reaction.

The rate law has the form:

$$\text{rate} = k[\text{H}_2\text{SeO}_3]^x[\text{I}^-]^y[\text{H}^+]^z$$

Between experiments (1) and (2), only $[\text{I}^-]$ is varied:

$$\frac{\text{rate}_{(1)}}{\text{rate}_{(2)}} = \frac{([\text{I}^-]_{(1)})^x}{([\text{I}^-]_{(2)})^x} \quad \text{so} \quad \frac{1.000}{0.422} = \left(\frac{0.100}{0.075}\right)^x$$

Solving this gives $x = 3$.

Between experiments (1) and (3), only $[\text{H}_2\text{SeO}_3]$ is varied:

$$\frac{\text{rate}_{(1)}}{\text{rate}_{(3)}} = \frac{([\text{H}_2\text{SeO}_3]_{(1)})^y}{([\text{H}_2\text{SeO}_3]_{(3)})^y} \quad \text{so} \quad \frac{1.000}{0.750} = \left(\frac{0.100}{0.075}\right)^y$$

Solving this gives $y = 1$.

Between experiments (2) and (4), only $[\text{H}^+]$ is varied:

$$\frac{\text{rate}_{(2)}}{\text{rate}_{(4)}} = \frac{([\text{H}^+]_{(2)})^z}{([\text{H}^+]_{(4)})^z} \quad \text{so} \quad \frac{0.422}{0.237} = \left(\frac{0.100}{0.075}\right)^z$$

Solving this gives $z = 2$.

Rate law: $\text{rate} = k[\text{H}_2\text{SeO}_3][\text{I}^-]^3[\text{H}^+]^2$

ANSWER CONTINUES ON THE NEXT PAGE

Calculate the value of the rate constant.

Using experiment (1):

$$(1.000 \text{ mol L}^{-1} \text{ s}^{-1}) = k \times (0.100 \text{ mol L}^{-1}) \times (0.100 \text{ mol L}^{-1})^3 \times (0.100 \text{ mol L}^{-1})^2$$

$$k = 1.00 \times 10^6 \text{ mol}^{-5} \text{ L}^5 \text{ s}^{-1}$$

$$\text{Answer: } k = 1.00 \times 10^6 \text{ mol}^{-5} \text{ L}^5 \text{ s}^{-1}$$

Suggest an appropriate technique for measuring the rate of increase of $[\text{I}_3^-]$ in the above experiments.

I_3^- is coloured whereas I^- is not so visible spectroscopy could be used. The absorption of light is proportional to $[\text{I}_3^-]$.

Alternatively, $[\text{I}_3^-]$ can be measured using a titration with a reducing agent, such as thiosulfate, and starch as an indicator.