**Marks**
**4**

- A solution of 2.00 M NaOH (50.0 mL) at 44.9 ℃ is added to a constant pressure ("coffee cup") calorimeter containing 250.0 mL of 0.70 M $HNO_3$ at 21.5 ℃. The final temperature of the solution is 29.9 ℃. Calculate the enthalpy of neutralisation of $OH^-$(aq) and $H^+$(aq) in kJ mol$^{-1}$. Assume the density of these solutions is 1.000 g mL$^{-1}$ and the specific heat capacity of the solutions is 4.184 J K$^{-1}$ g$^{-1}$.

---

**The final temperature is due to both the mixing of two solutions with different initial temperatures and the chemical reaction. It is convenient to treat these two processes separately.**

**(i) Temperature change due to mixing:**

**The NaOH(aq) and $HNO_3$(aq) solutions are initially at 44.9 °C and 21.5 °C. When mixed, heat from the former will warm up the latter to give a solution with temperature $T_m$.**

**50.0 mL of NaOH(aq) corresponds to (50.0 mL $\times$ 1.000 g mL$^{-1}$) = 50.0 g. The heat *lost* by this mass is given by:**

$$q_1 = mC\Delta T = 50.0 \times 4.184 \times (T_m - 44.9)$$

**250.0 mL of $HNO_3$(aq) corresponds to (250.0 mL $\times$ 1.000 g mL$^{-1}$) = 250.0 g. The heat *gained* by this mass is given by:**

$$q_2 = mC\Delta T = 250.0 \times 4.184 \times (T_m - 21.5)$$

**As the heat lost by NaOH(aq) is gained by the $HNO_3$(aq), $q_1 = -q_2$ and so:**

$$50.0 \times 4.184 \times (T_m - 44.9) = -1 \times 250.0 \times 4.184 \times (T_m - 21.5)$$

**so $T_m$ = 25.4 °C**

**(ii) Temperature change due to reaction:**

**The final temperature is 29.9 °C so the temperature change due to the reaction must be (29.9 – $T_m$) = (29.9 – 25.4) = 4.5 °C. The mixed solution has a total volume of (50.0 + 250.0) = 300.0 mL.**

**This volume has a mass of (300.0 mL $\times$ 1.000 g mL$^{-1}$) = 300.0 g. The heat change corresponding to this mass and temperature increase is therefore:**

$$q_r = mC\Delta T = 300.0 \times 4.184 \times 4.5 = 5600 \text{ J} = 5.6 \text{ kJ}$$

**The reaction is a 1:1 neutralization reaction, $OH^-$(aq) + $H^+$(aq) → $H_2O$(aq).**

**ANSWER CONTINUES ON THE NEXT PAGE**

The number of moles of OH⁻(aq) present in 50.0 mL of the 2.00 M NaOH solution is:

number of moles = concentration × volume = 2.00 × 0.0500 = 0.100 mol

The number of moles of H⁺(aq) present in 250.0 mL of the 0.70 M HNO₃ solution is:

number of moles = concentration × volume = 0.70 × 0.2500 = 0.175 mol

The H⁺ is therefore in excess and the OH⁻ is the limiting reagent.

As 0.100 mol generates a heat change of 5.6 J, the enthalpy of neutralization is:

$$\Delta_r H = \frac{-5.6\,\text{kJ}}{0.1\,\text{mol}} = -56\ \text{kJ}\,\text{mol}^{-1}$$

The reaction increases the temperature and so must be exothermic.

| | |
|---|---|
| | Answer: **56 kJ mol⁻¹** |

Calculate the pH in the combined solution in the calorimeter at 21.5 °C.

As 0.100 mol of OH⁻(aq) reacts with 0.175 mol of H⁺(aq), the final solution contains (0.175 – 0.100) = 0.075 mol of unreacted H⁺(aq).

The final solution has a volume of 300.0 mL so,

$$[\text{H}^+(\text{aq})] = \frac{\text{number of moles}}{\text{volume}} = \frac{0.075\,\text{mol}}{0.3000\,\text{L}} = 0.25\,\text{M}$$

Hence,

$$\text{pH} = -\log_{10}[\text{H}^+(\text{aq})] = -\log_{10}(0.25) = 0.60$$

| | |
|---|---|
| | Answer: **pH = 0.60** |

- A 300.0 mL solution of HCl has a pH of 1.22. Given that the p$K_a$ of iodic acid, HIO₃, is 0.79, how many moles of sodium iodate, NaIO₃, would need to be added to this solution to raise its pH to 2.00?    **3**

Using pH = -log₁₀[H⁺(aq)],

[H⁺(aq)]ₒₙᵢₜᵢₐₗ = 10⁻¹·²² = 0.060 M

[H⁺(aq)]ₒₙᵢₙₐₗ = 10⁻²·⁰⁰ = 0.010 M

**ANSWER CONTINUES ON THE NEXT PAGE**

**Using pH = -log$_{10}$[H$^+$(aq)],**

**[H$^+$(aq)]$_{initial}$ = 10$^{-1.22}$ = 0.060 M**

**[H$^+$(aq)]$_{final}$ = 10$^{-2.00}$ = 0.010 M**

**The change of (0.060 – 0.010 M) = 0.050 M occurs due to the reaction with IO$_3^-$ (aq) to produce HIO$_3$(aq). If [IO$_3^-$(aq)] = $x$, the reaction table is:**

|  | H$^+$(aq) + | IO$_3^-$(aq) | ⇌ | HIO$_3$(aq) |
|---|---|---|---|---|
| **initial** | **0.060** | **$x$** | | **0** |
| **change** | **-0.050** | **-0.050** | | **+0.050** |
| **final** | **0.010** | **$x$ – 0.050** | | **0.050** |

**As p$K_a$ = 0.79 = -log$_{10}K_a$:**

$$K_a = \frac{[\text{H}^+(\text{aq})][\text{IO}_3^-(\text{aq})]}{[\text{HIO}_3(\text{aq})]} = \frac{(0.010) \times (x - 0.050)}{0.050} = 10^{-0.79}$$

**Thus, $x$ = 0.86 M = [IO$_3^-$(aq)]$_{initial}$. This concentration corresponds to a 300.0 mL solution so the number of moles that have been added is:**

**number of moles = concentration × volume**
**= (0.86 M) × (0.3000 L) = 0.26 mol**

Answer: **0.26 mol**

**Marks
4**

- Acetylene, $C_2H_2$, can be produced by reacting calcium carbide, $CaC_2$, with water:

$$CaC_2(s) + 2H_2O(l) \rightarrow Ca(OH)_2(s) + C_2H_2(g)$$
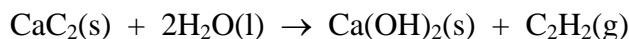
A 1.000 g sample of $CaC_2$ is placed in a sealed vessel that contains 250.0 mL of $H_2O(l)$ and 250.0 mL of $N_2(g)$ at 1.000 atm, and allowed to react completely with the water. The final pressure in the sealed vessel at 22.0 ℃ is 2.537 atm. Determine the vapour pressure of water in the sealed vessel at 22.0 ℃. Give your answer in mmHg. Ignore any change in the volume of the water.

**The formula mass of $CaC_2$ is (40.08 (Ca) + 2 × 12.01 (C)) g mol$^{-1}$ = 64.1 g mol$^{-1}$.**

**The amount of $CaC_2$ in 1.000 g is therefore, $n = \dfrac{m}{M} = \dfrac{1.000}{64.1} = 0.01560$ mol.**

**From the chemical equation, each mole of $CaC_2$ that reacts leads to one mole of $C_2H_2(g)$. Therefore, 0.0156 mol of $C_2H_2(g)$ is formed. The volume available to gas is 250.0 mL. Using the ideal gas equation, $pV = nRT$, the pressure due to this amount is therefore:**

$$p_{C_2H_2} = \frac{nRT}{V} = \frac{(0.01560\,\text{mol}) \times (0.08206\,\text{L atm K}^{-1}\,\text{mol}^{-1}) \times (22 + 273)\text{K}}{0.250\,\text{L}}$$

$$= 1.511 \text{ atm}$$

**As there is no change in the amount of $N_2(g)$, $p_{N_2} = 1.000$ atm. Hence,**

$$p_{\text{total}} = p_{H_2O} + p_{C_2H_2} + p_{N_2} = 2.537 \text{ atm}$$

$$p_{H_2O} + (1.511 \text{ atm}) + (1.000 \text{ atm}) = 2.537 \text{ atm}$$

**Hence, $p_{H_2O}$ = 0.026 atm. As 1 atm = 760 mmHg, this corresponds to.**

$$p_{H_2O} = 0.026 \times 760 = 20 \text{ mmHg}$$

| | |
|---|---|
| | Answer: **20 mmHg** |

The solubility of acetylene in water at 22.0 ℃ is small. If the temperature were raised, would you expect this solubility to increase or decrease?

**The solubility of gases in water decreases with temperature. The dissolution of a gas is entropically disfavoured and only occurs because it is exothermic. Like all exothermic process, the process becomes less favourable at higher temperatures (Le Chatelier's principle).**

**ANSWER CONTINUES ON THE NEXT PAGE**

- Draw all possible stereoisomers of the complex ion $[CoCl_2(en)_2]^+$. Label each as *cis* or *trans*.

**3**



mirror

*cis*                              *cis*                              *trans*
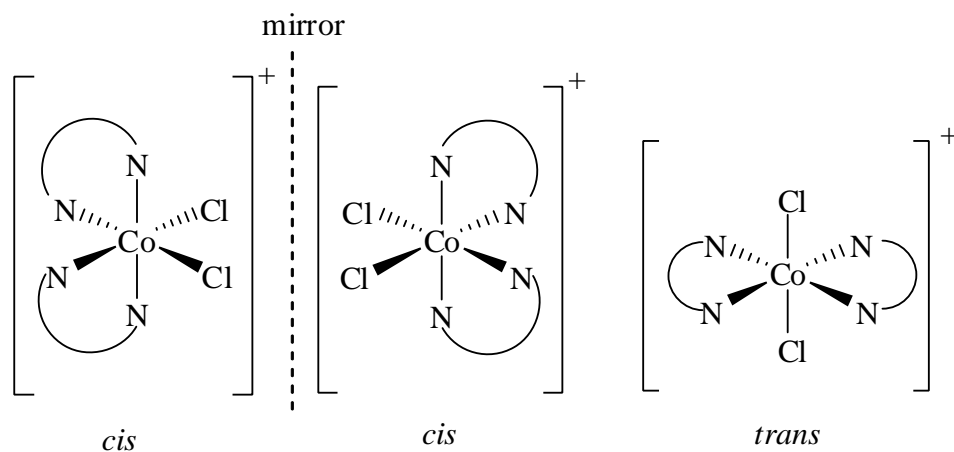
**dichlorobisethylenediaminecobalt(III) ion**

**The *cis* isomer is non-superimposable on its mirror image whereas the *trans* isomer is not chiral.**

**Marks
5**

- Consider the reaction          $2SO_2(g)$  +  $O_2(g)$  $\rightleftharpoons$  $2SO_3(g)$

$\Delta H° = -198.4$ kJ mol$^{-1}$ and $\Delta S° = -187.9$ J K$^{-1}$ mol$^{-1}$ at 25 °C.

Show that this reaction is spontaneous at 25 °C.

**For a reaction to be spontaneous, $\Delta G°$ must be negative. As**

$\Delta G° = \Delta H° - T\Delta S°$

**At T = 25 °C,**

$\Delta G° = (-198.4 \times 10^3) - (25 + 273) \times (-187.9)$ **J mol$^{-1}$ = -140 kJ mol$^{-1}$**

**As $\Delta G°$ is negative at this temperature, the reaction is spontaneous.**

If the volume of the reaction system is increased at 25 °C, in which direction will the reaction move?

**The reaction involves 3 moles of gas being converted into 2 moles of gas. If the volume is increased, the pressure will decrease and the reaction will therefore shift to increase the number of moles of gas (Le Chatelier's principle).
It will shift to the left.**

Calculate the value of the equilibrium constant, $K$, at 25 °C.

**As $\Delta G° = -RT\ln K$, the equilibrium constant, $K$, at T = 25° is given by**

**$-140 \times 10^3 = -8.314 \times (25 + 273) \times \ln K$    or $K = e^{57}$**

**$K = 9.2 \times 10^{24}$**

| $K = 9.2 \times 10^{24}$    ($K$ has no units) |

Assuming $\Delta H°$ and $\Delta S°$ are independent of temperature, in which temperature range is the reaction non-spontaneous?
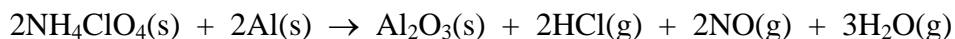
**The reaction is non-spontaneous when $\Delta G° > 0$. Assuming $\Delta H°$ and $\Delta S°$ are independent of temperature, this will occur when $\Delta H° - T\Delta S° > 0$:**

**$(-198.4 \times 10^3) - T \times (-187.9) > 0$**

**$T > \dfrac{198.4 \times 10^3}{187.9}$    or T > 1056 K**

| Answer: **T > 1056 K** |

**Marks**
**3**

- Ammonium perchlorate mixed with powdered aluminium powers the space shuttle booster rockets:

$$2NH_4ClO_4(s) + 2Al(s) \rightarrow Al_2O_3(s) + 2HCl(g) + 2NO(g) + 3H_2O(g)$$

Given the following thermochemical data, how much heat would be released per gram of Al(s)?

$\Delta H_f^o$ (H$_2$O(l)) = –285.1 kJ mol$^{-1}$     $\Delta H_f^o$ (Al$_2$O$_3$(s)) = –1669.8 kJ mol$^{-1}$

$\Delta H_f^o$ (NO(g)) = 90.4 kJ mol$^{-1}$     $\Delta H_f^o$ (NH$_4$ClO$_4$(s)) = –290.6 kJ mol$^{-1}$

$\Delta H_f^o$ (HCl(g)) = –92.3 kJ mol$^{-1}$     $\Delta H_{vap}^o$ (H$_2$O) = 44.1 kJ mol$^{-1}$

---

**Using $\Delta_{rxn}H^o = \sum m\Delta_f H^o (\text{products}) - \sum n\Delta_f H^o (\text{reac tan ts}):$**

$$\Delta_{rxn}H^o = \sum \Delta_f H°(Al_2O_3(s)) + 2\Delta_f H°(HCl(g)) + 2\Delta_f H°NO(g)) + 3\Delta_f H°(H_2O(g))$$
$$- \sum 2\Delta_f H°(NH_4ClO_4(s)) + 2\Delta_f H°(Al(s))$$
$$= [(-1669.8) + 2(-92.3) + 2(90.4) + 3(-285.1 + 44.1)] - [2(-290.6) + 2(0)]$$
$$= -1815.4 \text{ kJ mol}^{-1}$$

**In this calculation, $\Delta_f H°(Al(s)) = 0$ for an element in its standard state and $\Delta_f H°(H_2O(g)) = \Delta_f H°(H_2O(l)) + \Delta_{vap}H°(H_2O)$ have been used.**

**As written, this enthalpy change is for the reaction of two moles of Al(s). Therefore, per mole of Al(s), $\Delta H° = \frac{1}{2} \times$ -1815.4 kJ mol$^{-1}$ = 907.7 kJ mol$^{-1}$.**

**As the atomic mass of aluminium is 26.98 g mol$^{-1}$, the heat released per gram of Al is:**
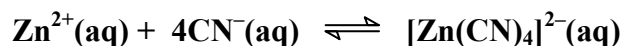
$$q = \frac{-907.7 \text{ kJ mol}^{-1}}{26.98 \text{ g mol}^{-1}} = 33.64 \text{ kJ g}^{-1}$$

Answer: **33.64 kJ g$^{-1}$**

**THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.**

**Marks
4**

- Zinc sulfate (8.07 g) is dissolved in 1.00 L of a 1.00 M solution of KCN. Write the chemical equation for the formation of the aqueous ion $[Zn(CN)_4]^{2-}$.

$$\textbf{Zn}^{2+}\textbf{(aq)} + \textbf{4CN}^-\textbf{(aq)} \rightleftharpoons [\textbf{Zn(CN)}_4]^{2-}\textbf{(aq)}$$

Calculate the concentration of $Zn^{2+}$(aq) in solution at equilibrium. Ignore any change in volume upon addition of the salt. $K_{stab}$ of $[Zn(CN)_4]^{2-} = 4.2 \times 10^{19}$ M$^{-4}$.

**The formula mass of zinc sulfate ($ZnSO_4$) is:**

**formula mass = 65.39 (Zn) + 32.07 (S) + 4 × 16.00 (O) = 161.46 g mol$^{-1}$**

**The number of moles in 8.07 g is therefore:**

$$\textbf{number of moles} = n = \frac{m}{M} = \frac{8.07\,\textbf{g}}{161.46\,\textbf{g mol}^{-1}} = \textbf{0.0500 mol}$$

**As $c = \dfrac{n}{V}$, [Zn$^{2+}$(aq)]$_{initial}$ = 0.0500 M when this is dissolved in a 1.00 L solution.**

**The reaction table is:**

|  | $Zn^{2+}$(aq) | $4CN^-$(aq) | $\rightleftharpoons$ | $[Zn(CN)_4^{2-}]$(aq) |
|---|---|---|---|---|
| **initial** | **0.0500** | **1.00** |  | **0** |
| **change** | **-x** | **-4x** |  | **+x** |
| **equilibrium** | **0.0500 – x** | **1.00 – 4x** |  | **x** |

**As $K_{stab}$ is *very* large, virtually all of the $Zn^{2+}$(aq) will have reacted. It is a good approximation, therefore, to take:**

**[CN$^-$(aq)]$_{equilibrium}$ = 1.00 – 4x ~ 1.00 – 4 × [Zn$^{2+}$(aq)]$_{initial}$**
**= (1.00 – 4 × 0.0500) M = 0.80 M**

**[[Zn(CN)$_4^{2-}$](aq)]$_{equilibrium}$ = x ~ [Zn$^{2+}$(aq)]$_{initial}$**
**= 0.0500 M**

**At equilibrium,**

$$K_{stab} = \frac{[[\textbf{Zn(CN)}_4]^{2-}\textbf{(aq)}]}{[\textbf{Zn}^{2+}\textbf{(aq)}][\textbf{CN}^-\textbf{(aq)}]^4} = \frac{0.0500}{(0.0500 - x)(0.80)^4} = 4.2 \times 10^{19}$$

**Hence, [Zn$^{2+}$(aq)]$_{equilibrium}$ = (0.0500 – x) M = 2.9 × 10$^{-21}$ M**

Answer: **2.9 × 10$^{-21}$ M**

Name the complex ion.

**tetracyanozincate(II) ion**

**ANSWER CONTINUES ON THE NEXT PAGE**

- The half life of the radioactive isotope $^{16}$N is 7.13 s.  Calculate how long it takes to reduce the radioactivity of a given sample to 71.6% of the initial value.

As the half life, $t_{1/2}$, is related to the decay constant, $\lambda$, by $t_{1/2} = \dfrac{\ln 2}{\lambda}$ :

$$\lambda = \frac{\ln 2}{t_{1/2}} = \frac{\ln 2}{7.13} = 0.0972 \text{ s}^{-1}$$

The number of radioactive nuclei, $N_t$, at time $t$ is related to the initial number $N_0$ by $\ln\dfrac{N_0}{N_t} = \lambda t$. As the activity is directly proportional to the number of radioactive nuclei, the radioactivity will be 71.6% of its initial value when $\dfrac{N_t}{N_0} = 0.716$ or $\dfrac{N_0}{N_t} = \dfrac{1}{0.716}$. Hence,

$$\ln(\frac{1}{0.716}) = (0.0972)t \quad \text{and so } t = 3.44 \text{ s}$$

Answer: **3.44 s**

| | Marks |
|---|---|
| • Lysozyme is an enzyme that breaks down bacterial cell walls.  A solution containing 0.150 g of this enzyme in 210 mL of solution has an osmotic pressure of 0.00125 atm at 25 $^{\circ}$C. What is the molar mass of lysozyme? | 3 |

**The osmotic pressure, $\pi$, is given by $\pi = cRT$**

**Hence, if $\pi$ = 0.00125 atm, the concentration at 25 °C is given by:**

$$c = \frac{\pi}{RT} = \frac{(0.00125\,\text{atm})}{(0.08206\,\text{L atm K}^{-1}\,\text{mol}^{-1}) \times ((25 + 272)\,\text{K})} = 5.1 \times 10^{-5}\,\text{M}$$

**As $c = \dfrac{n}{V}$, $n = cV = (5.1 \times 10^{-5}\ \text{mol L}^{-1}) \times (0.210\ \text{L}) = 1.1 \times 10^{-5}\ \text{mol}$**

**This amount corresponds to 0.150 g, so the molar mass, $M$, is:**

$$M = \frac{m}{M} = \frac{0.150\ \text{g}}{1.1 \times 10^{-5}\ \text{mol}} = 14000\ \text{g mol}^{-1}$$

Answer: **$1.4 \times 10^4$ g mol$^{-1}$**

| | Marks |
|---|---|
| • What mass of ethylene glycol, $HOCH_2CH_2OH$, is required to lower the freezing point of 1.00 L of water to –10.0 °C?  The freezing point depression constant of water is 1.86 °C kg mol$^{-1}$.  Assume the density of water is 1.00 g mL$^{-1}$ at 0 °C. | 3 |

**The freezing point depression, $\Delta T_f$, is related to the molality, $m$, and the freezing point depression constant, $K_f$, by $\Delta T_f = K_f m$**

**Hence, $m = \dfrac{\Delta T_f}{K_f} = \dfrac{10.0\ °C}{1.86\ °C\ \text{kg mol}^{-1}} = 5.38\ \text{mol kg}^{-1}$**

**If the density of water is 1.00 g mL$^{-1}$, 1000 mL will have a mass of 1.00 kg.**

**As the molality is given $m = \dfrac{\text{amount of solute (mol)}}{\text{mass of solvent (kg)}}$, the amount of solute is:**

**amount of solute (mol) = molality (mol kg$^{-1}$) × mass of solvent (kg)**
**= 5.38 × 1.00 mol = 5.38 mol**

**The molar mass of $HOCH_2CH_2OH$ ($C_2H_6O_2$) is (2 × 12.01 (C)) + (6 × 1.008 (H)) + (2 × 16.00 (O)) = 62.068 g mol$^{-1}$. The mass of 5.38 mol is therefore:**
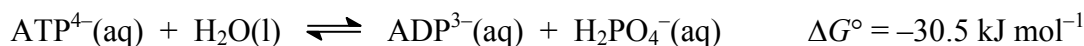
**mass (g) = molar mass (g mol$^{-1}$) × amount (mol) = 62.068 × 5.38 g = 334 g**
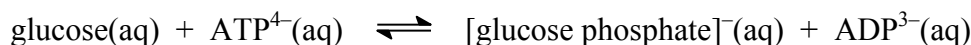
Answer: **334 g**

**Marks
6**

- The first step in the metabolism of glucose in biological systems is the addition of a phosphate group in a dehydration-condensation reaction:

  glucose(aq) + $H_2PO_4^-$(aq)  $\rightleftharpoons$  [glucose phosphate]$^-$(aq) + $H_2O$(l)
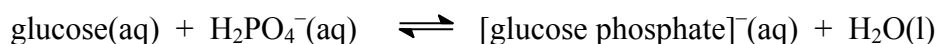
The free energy change associated with this reaction is $\Delta G° = 13.8$ kJ mol$^{-1}$. The reaction is driven forwards by harnessing the free energy associated with the hydrolysis of adenosine triphosphate, $ATP^{4-}$, to adenosine diphosphate, $ADP^{3-}$:

  $ATP^{4-}$(aq) + $H_2O$(l)  $\rightleftharpoons$  $ADP^{3-}$(aq) + $H_2PO_4^-$(aq)        $\Delta G° = -30.5$ kJ mol$^{-1}$

The overall reaction is thus:

  glucose(aq) + $ATP^{4-}$(aq)  $\rightleftharpoons$  [glucose phosphate]$^-$(aq) + $ADP^{3-}$(aq)

Calculate the equilibrium constant associated with this overall reaction at body temperature (37 °C).

---

**The overall reaction is the sum of the two reactions:**

|  | $\Delta G°$ (kJ mol$^{-1}$) |
|---|---|
| **glucose(aq) + $H_2PO_4^-$(aq) $\rightleftharpoons$ [glucose phosphate]$^-$(aq) + $H_2O$(l)** | **13.8** |
| **$ATP^{4-}$(aq) + $H_2O$(l) $\rightleftharpoons$ $ADP^{3-}$(aq) + $H_2PO_4^-$(aq)** | **-30.5** |
| **glucose(aq)+$ATP^{4-}$(aq) $\rightleftharpoons$ [glucose phosphate]$^-$(aq)+$ADP^{3-}$(aq)** | **-16.7** |

**For the overall reaction, $\Delta G° = ((13.8) + (-30.5))$ kJ mol$^{-1}$ = -16.7 kJ mol$^{-1}$. Using $\Delta G° = -RT\ln K$,**

**$-16.7 \times 10^3 = -8.314 \times (37 + 273)\ln K$   or $K = e^{6.48} = 652$**

> **Answer: $K = 652$   (no units)**

---

This overall equilibrium reaction is investigated by adding 0.0100 mol of $ATP^{4-}$ to a flask containing 175 mL of a 0.0500 M aqueous solution of glucose at 37 °C. What percentage of the $ATP^{4-}$ will have been consumed when the system reaches equilibrium?

---

**The initial concentration of $ATP^{4-}$ is $\dfrac{n}{V} = \dfrac{0.0100\,\text{mol}}{0.175\,\text{L}} = 0.0571$ M. The reaction table is then:**

|  | **glucose(aq)** | **$ATP^{4-}$(aq)** | $\rightleftharpoons$ | **[glucose phosphate]$^-$(aq)** | **$ADP^{3-}$(aq)** |
|---|---|---|---|---|---|
| **initial** | **0.0500** | **0.0571** | | **0** | **0** |
| **change** | **-x** | **-x** | | **+x** | **+x** |
| **equilibrium** | **0.0500-x** | **0.0571-x** | | **x** | **x** |

**At equilibrium,**

$$K = \frac{[\text{glucose-phosphate}^-(aq)][ADP^{3-}(aq)]}{[\text{glucose(aq)}][ATP^{4-}(aq)]} = \frac{x^2}{(0.0500 - x)(0.0571 - x)} = 652$$

**ANSWER CONTINUES ON THE NEXT PAGE**

**As the equilibrium constant is large so is x and this expression cannot be approximated. Instead, the full quadratic equation must be solved.**

**$x^2 = 652(0.0500-x)(0.0571-x)$ or**

**$651x^2 -652(0.0500+0.0571)+ (652×0.0500×0.0571) = 0$**

**The two roots are $x_1 = 0.0578$ M and $x_2 = 0.0495$ M. As $x_1$ gives a negative [glucose(aq)], it is not physically significant. As x is the concentration consumed, using $x_2$ gives:**

**percentage of $ATP^{4-}$(aq) consumed $= \dfrac{0.0495\,M}{0.0571\,M} \times 100\% = 87\%$**

Answer: **87%**

Suggest two simple ways of further reducing the remaining percentage of $ATP^{4-}$.

**The remaining $ATP^{4-}$ can be reduced by (i) adding more glucose and (ii) reducing the temperature. Removal of either product would also drive the reaction to the right but would be very difficult to achieve in practice.**

| | **Marks** |
|---|---|
| • The solubility product constant of AgCl is $K_{sp} = 1.8 \times 10^{-10}$ M$^2$. Using the relevant electrode potentials found on the data page, calculate the reduction potential at 298 K of a half-cell formed by:<br>(a) an Ag electrode immersed in a saturated solution of AgCl. | **6** |

**The standard electrode potential for Ag$^+$(aq) + e$^-$ → Ag(s) is $E° = +0.80$ V. This refers to the potential with [Ag$^+$(aq)] = 1 M.**

**For the dissolution of AgCl(s) $\rightleftharpoons$ Ag$^+$(aq) + Cl$^-$(aq), $K_{sp}$ = [Ag$^+$(aq)][Cl$^-$(aq)]. As [Ag$^+$(aq)] = [Cl$^-$(aq)],**

$$[Ag^+(aq)] = \sqrt{K_{sp}} = \sqrt{1.8 \times 10^{-10}} = 1.3 \times 10^{-5} \text{ M}$$

**Using the Nernst equation, the cell potential at 298 K (25 °C) is,**

$$E = E° - \frac{0.0592}{n} \log Q$$

**The Ag$^+$(aq) + e$^-$ → Ag(s) half cell involves one electron and so $n$ = 1. The reaction quotient is $\dfrac{1}{[Ag^+(aq)]}$. Hence,**

$$E = (+0.80) - \frac{0.0592}{1} \log\left(\frac{1}{1.3 \times 10^{-5}}\right) = +0.52 \text{ V}$$

| Answer: $E = +0.52$ V |
|---|

(b) an Ag electrode immersed in a 0.5 M solution of KCl containing some AgCl precipitate.

**[Cl$^-$(aq)] = 0.5 M and as $K_{sp}$ = [Ag$^+$(aq)][Cl$^-$(aq)],**

$$[Ag^+(aq)] = \frac{K_{sp}}{[Cl^-(aq)]} = \frac{1.8 \times 10^{-10} \text{ M}^2}{0.5 \text{ M}} = 3.6 \times 10^{-10} \text{ M}$$

**The electrode potential is now,**

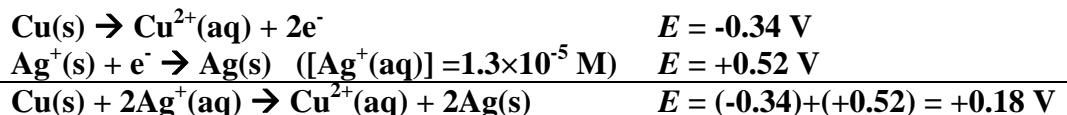$$E = (+0.80) - \frac{0.0592}{1} \log\left(\frac{1}{3.6 \times 10^{-10}}\right) = +0.24 \text{ V}$$

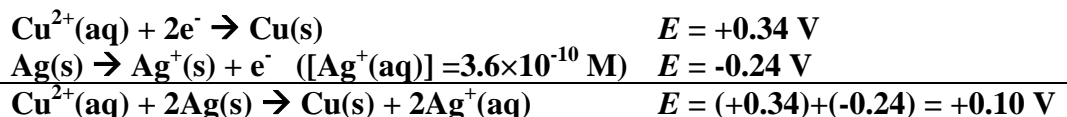| Answer: $E° = +0.24$ V |
|---|

**ANSWER CONTINUES ON THE NEXT PAGE**

Each of these half-cells is connected to a standard $Cu^{2+}$(1 M)/Cu(s) half-cell. In which half-cell, (a) or (b), will clear evidence of a reaction be seen? Describe the change(s) observed.

**For the $Cu^{2+}$ (1 M)/Cu(s) half cell, the reduction potential is $E° = +0.34$ V.**

**If the half cell is combined with half cell (a), the former has the least positive cell potential and is reversed:**

| | |
|---|---|
| $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$ | $E = -0.34$ V |
| $Ag^+(s) + e^- \rightarrow Ag(s)$   $([Ag^+(aq)] = 1.3 \times 10^{-5}$ M$)$ | $E = +0.52$ V |
| $Cu(s) + 2Ag^+(aq) \rightarrow Cu^{2+}(aq) + 2Ag(s)$ | $E = (-0.34)+(+0.52) = +0.18$ V |

**If the half cell is combined with half cell (b), the latter has the least positive cell potential and is reversed:**

| | |
|---|---|
| $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ | $E = +0.34$ V |
| $Ag(s) \rightarrow Ag^+(s) + e^-$   $([Ag^+(aq)] = 3.6 \times 10^{-10}$ M$)$ | $E = -0.24$ V |
| $Cu^{2+}(aq) + 2Ag(s) \rightarrow Cu(s) + 2Ag^+(aq)$ | $E = (+0.34)+(-0.24) = +0.10$ V |

**Although both reactions have $E > 0$ V and so are spontaneous, only the second reaction will give clear evidence of a reaction. The $Ag^+(aq)$ ions produced will react with the excess $Cl^-(aq)$ present to give a white precipitate of AgCl around the electrode**

|   | **Marks 2** |

- Describe how the addition of an electrolyte can alter the state of a colloidal dispersion.

**If the colloidal particle has a charge, a layer of oppositely charged ions will form on the surface (the Stern layer). In the region around the outside of the colloid, there is therefore a build-up of counter ions creating a double charge layer. The charge surrounding one colloid will repel the charge surrounding other particles and so coagulation is prevented.**

**Addition of an electrolyte leads to reduction in the net charge surrounding each colloid and prevents this electrostatic stabilization. As a result, the colloid particles tend to coagulate and the colloidal dispersion is lost.**

- An aqueous solution of $CuSO_4$ is electrolysed with a current of 1.00 A for 60 minutes. Calculate the mass of the products that are formed at the two electrodes.

**4**

**If a current of 1.00 A is passed for 60 minutes, the number of electrons delivered is,**

$$\text{moles of e}^- = \frac{It}{F} = \frac{(1.00\,\text{A}) \times (60 \times 60\,\text{s})}{(96485\,\text{C mol}^{-1})} = 0.037\,\text{mol}$$

**At the cathode, the two possible reduction reactions are:**

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

**The reduction of $Cu^{2+}(aq)$ is much easier ($E$ is less negative) so Cu(s) is formed on the cathode.**

**[This potential for the reduction of water corresponds to $[H^+(aq)] = 1$ M. Using the Nernst equation gives $E = -0.42$ V for a pH 7 solution. An overpotential of 0.4 to 0.6 V must be added so that the reduction potential is actually ~1 V. Thus it is even more difficult to reduce water than the $E°$ value suggests.]**

**Each mole of Cu(s) requires 2 moles of electrons so,**

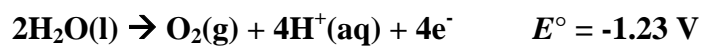$$\text{number of moles of Cu(s)} = \frac{1}{2} \times 0.037\,\text{mol} = 0.019\,\text{mol}$$

**The atomic mass of Cu is 63.55 g mol$^{-1}$ so the mass of copper deposited is,**

$$\text{mass of Cu(s)} = \text{number of moles} \times \text{molar mass}$$
$$= 0.019\,\text{mol} \times 63.55\,\text{g mol}^{-1} = 1.2\,\text{g}$$

**ANSWER CONTINUES ON THE NEXT PAGE**

**At the anode, oxidation of $H_2O$ occurs to produce $O_2(g)$.**

$$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^- \qquad E° = \text{-1.23 V}$$

**As $SO_4^{2-}$ contains S(VI), further oxidation is very difficult.**

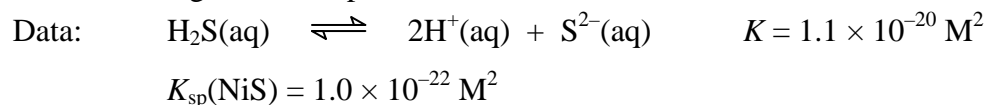**Production of each mole of $O_2(g)$ requires 4 moles of electrons so,**

   **number of moles of $O_2(g)$ = ¼ × 0.037 mol = 0.0093 mol**

**The molar mass of $O_2$ is $(2 \times 16.00) = 32.00$ g mol$^{-1}$ so the mass of $O_2(g)$ formed is,**

   **mass of $O_2(g)$ = number of moles × molar mass**
   **= 0.0093 mol × 32.00 g mol$^{-1}$ = 0.30 g**

**Marks
5**

- The pH of a solution can be controlled by adding small amounts of gaseous HCl. Assuming no change in volume, calculate what the pH of the solution must be to just dissolve 1.00 g of NiS suspended in 1.0 L of water.
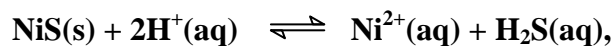
  Data:          $H_2S(aq) \rightleftharpoons 2H^+(aq) + S^{2-}(aq)$          $K = 1.1 \times 10^{-20} \text{ M}^2$

  $K_{sp}(\text{NiS}) = 1.0 \times 10^{-22} \text{ M}^2$

---

**For the dissolution NiS(s) $\rightleftharpoons$ Ni$^{2+}$(aq) + S$^{2-}$(aq),**

**$K_{sp} = [\text{Ni}^{2+}(aq)][\text{S}^{2-}(aq)]$.**

**For the acid dissociation, H$_2$S(aq) $\rightleftharpoons$ 2H$^+$(aq) + S$^{2-}$(aq),**

$$K = \frac{[\text{H}^+(aq)]^2[\text{S}^{2-}(aq)]}{[\text{H}_2\text{S}(aq)]}$$

**Combining these two equilibria gives, for the overall reaction,**

**NiS(s) + 2H$^+$(aq) $\rightleftharpoons$ Ni$^{2+}$(aq) + H$_2$S(aq),**

$$K_{eq} = \frac{[\text{Ni}^{2+}(aq)][\text{H}_2\text{S}(aq)]}{[\text{H}^+(aq)]^2} = \frac{K_{sp}}{K} = \frac{1.0 \times 10^{-22}}{1.1 \times 10^{-20}} = 9.1 \times 10^{-3}$$

**The formula mass of NiS is (58.69 (Ni) + 32.07 (S)) g mol$^{-1}$ = 90.76 g mol$^{-1}$. The amount in 1.00 g is therefore,**

$$\text{number of moles} = \frac{\text{mass (g)}}{\text{molar mass (g mol}^{-1})} = \frac{1.00\,\text{g}}{90.76\,\text{g mol}^{-1}} = 0.0110 \text{ mol}$$

**In the dissolution NiS(s) $\rightleftharpoons$ Ni$^{2+}$(aq) + S$^{2-}$(aq), so if 0.0110 mol of NiS(s) completely dissolves in 1.0 L, [Ni$^{2+}$(aq)] = 0.011 M. From the overall reaction, each mole of NiS which dissolves produces one mole of H$_2$S(aq) so [H$_2$S(aq)] = 0.011 M. Hence,**

$$[\text{H}^+(aq)]^2 = \frac{(0.011\,\text{M})(0.011\,\text{M})}{9.1 \times 10^{-3}} \quad \text{or} \quad [\text{H}^+(aq)] = 0.12 \text{ M}$$

**pH = -log$_{10}$[H$^+$(aq)] = -log$_{10}$(0.12) = 0.94**

| pH = **0.94** |
|---|

- A galvanic cell consists of a $Ni^{2+}/Ni$ half cell with $[Ni^{2+}]$ = 1.00 M, and a $Ag^+/Ag$ half cell with $[Ag^+]$ = 1.00 M. Calculate the electromotive force of the cell at 25 °C.

**As the concentrations of $Ni^{2+}$ and $Ag^+$ are both 1.00 M, the 'electromotive force' (i.e. the cell potential) refers to standard potentials. The two half-cell reactions and standard reduction potentials are:**

$$Ag^+(aq) + e^- \rightarrow Ag(s) \qquad\qquad E° = +0.80 \text{ V}$$
$$Ni^{2+}(aq) + 2e^- \rightarrow Ni(s) \qquad\qquad E° = -0.24 \text{ V}$$

**The least positive ($Ni^{2+}/Ni$) cell is reversed – Ni is oxidized in this reaction and $Cu^{2+}$ is reduced. This gives the overall reaction and potential:**

$$2Ag^+(aq) + Ni(s) \rightarrow 2Ag(s) + Ni^{2+}(aq) \quad E° = (+0.80) + (+0.24) = +1.04 \text{ V}$$
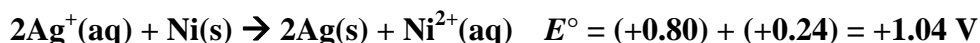
| Answer: +**1.04 V** |
|---|

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

**The equilibrium constant $K$ and the standard cell potential are related by,**

$$E° = \frac{RT}{nF} \ln K$$

**The reaction involves two electrons, $n = 2$, and so at $T = 25$ °C,**

$$+1.04 = \frac{8.314 \times (25+273)}{2 \times 96485} \ln K$$

**$\ln K = 81$ or $K = e^{81} = 1.5 \times 10^{35}$**

| Answer: **$1.5 \times 10^{35}$** |
|---|

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

**The standard free energy change is directly related to the standard cell potential, $\Delta G° = -nFE°$,**

$$\Delta G° = -2 \times 96485 \times 1.04 = -201 \text{ kJ mol}^{-1}$$

**Alternatively, the standard free energy change is related to the equilibrium constant by $\Delta G° = -RT\ln K$,**

$$\Delta G° = -(8.314) \times (25 + 273) \times \ln(1.5 \times 10^{35}) = -2.0 \times 10^2 \text{ kJ mol}^{-1}$$

| Answer: **-201 kJ mol$^{-1}$** |
|---|

**ANSWER CONTINUES ON THE NEXT PAGE**

Is the reaction spontaneous?  Give reasons for your answer.

**As $E° > 0$, or, equivalently, as $\Delta G° < 0$, the reaction is spontaneous (2$^{nd}$ Law of Thermodynamics).**

Express the overall reaction in the shorthand voltaic cell notation.

**The oxidation half cell (the anode) is written on the left and the reduction half cell (the cathode) is written on the right. The two half-cells are connected by a salt bridge:**

$$\textbf{Ni(s)} \,\big|\, \textbf{Ni}^{2+}\textbf{(aq)} \,\big\|\, \textbf{Ag}^{+}\textbf{(aq)} \,\big|\, \textbf{Ag(s)}$$

**Marks
5**

- Phosgene is a toxic gas prepared by the reaction of carbon monoxide with chlorine:

$$CO(g) + Cl_2(g) \rightarrow COCl_2(g)$$
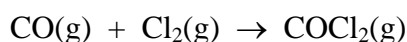
The following data were obtained in a kinetics study of its formation at 150 °C.

| Experiment | initial [CO] (M) | initial [Cl$_2$] (M) | Initial rate  (M s$^{-1}$) |
|:---:|:---:|:---:|:---:|
| 1 | 1.00 | 0.100 | $1.29 \times 10^{-29}$ |
| 2 | 0.100 | 0.100 | $1.33 \times 10^{-30}$ |
| 3 | 0.100 | 1.00 | $1.30 \times 10^{-29}$ |
| 4 | 0.100 | 0.0100 | $1.32 \times 10^{-31}$ |

Determine the rate law for the reaction.

**Between experiments (1) and (2), [Cl$_2$]$_{initial}$ is kept constant and [CO]$_{initial}$ is reduced by a factor of 10. The rate decreases by a factor of $\dfrac{1.29 \times 10^{-29}}{1.33 \times 10^{-30}} \sim 10$. Hence the reaction is first order with respect to CO.**

**Between experiments (1) and (3), [Cl$_2$] is increased by a factor of 10 and [CO]$_{initial}$ is decreased by a factor of 10. The rate does not change. As this change in [CO]$_{initial}$ is known from above to increase the rate by a factor of 10, the change in [Cl$_2$]$_{initial}$ must be decreasing the rate by a factor of 10. Hence, the reaction is also first order with respect to Cl$_2$.**

**Hence, overall,
    rate = $k$[CO][Cl$_2$]**

Calculate the value of the rate constant at 150 °C.

**Using experiment (1), when [CO] = 1.00 M and [Cl$_2$] = 0.100 M, the rate is $1.29 \times 10^{-29}$ M s$^{-1}$. Hence from the rate law:**

**$1.29 \times 10^{-29}$ M s$^{-1}$ = $k \times$ (1.00 M) $\times$ (0.100 M)**

**$k = \dfrac{1.29 \times 10^{-29} \text{ M s}^{-1}}{(1.00 \text{ M}) \times (0.100 \text{ M})} = 1.29 \times 10^{-28} \text{ M}^{-1} \text{ s}^{-1}$**

Answer: **$1.29 \times 10^{-28}$ M$^{-1}$ s$^{-1}$**

Calculate the rate of appearance of phosgene when [CO] = [Cl$_2$] = 1.3 M.

**rate = $k$[CO][Cl$_2$] = (1.29 $\times$ 10$^{-28}$ M$^{-1}$ s$^{-1}$)$\times$(1.3 M)$\times$(1.3 M) = 2.2 $\times$ 10$^{-28}$ M s$^{-1}$**

Answer: **$2.2 \times 10^{-28}$ M s$^{-1}$**