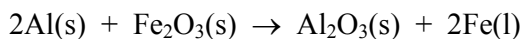


- The thermite reaction is written below. Show that the heat released in this reaction is sufficient for the iron to be produced as molten metal.



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

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

Marks  
6

Assume 1 mol of reactants at initial temperature of 25 °C. Need to show that  $\Delta H$  for the reaction is *greater* than the amount of energy required to melt 2 mol of Fe(s) and heat all the products (2 mol of Fe(s) + 1 mol of Al<sub>2</sub>O<sub>3</sub>(s)) to the melting point of Fe.

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

$\Delta H$  to heat 2 mol of Fe(s) to its melting point

$$\begin{aligned}\Delta H &= n_{\text{Fe}(\text{s})} \times C_p(\text{Fe}(\text{s})) \times \Delta T \\ &= (2 \text{ mol}) \times (25 \text{ J K}^{-1} \text{ mol}^{-1}) \times (1535 - 25) \text{ K} = 75.5 \text{ kJ}\end{aligned}$$

$\Delta H$  to heat 1 mol of Al<sub>2</sub>O<sub>3</sub>(s) to melting point of Fe(s)

$$\begin{aligned}\Delta H &= n_{\text{Al}_2\text{O}_3(\text{s})} \times C_p(\text{Al}_2\text{O}_3(\text{s})) \times \Delta T \\ &= (1 \text{ mol}) \times (79 \text{ J K}^{-1} \text{ mol}^{-1}) \times (1535 - 25) \text{ K} = 119 \text{ kJ}\end{aligned}$$

$\Delta H$  to melt 2 mol of Fe(s)

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

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

The energy generated by the reaction is more than enough to melt the iron.

<ul style="list-style-type: none"><li>• Explain the meanings of the following terms.</li></ul>	<b>Marks</b> <b>8</b>
<p>Heat</p> <p><b>Heat: energy contained in kinetic energies of molecules that flows from hotter to cooler temperatures.</b></p>	
<p><math>P\Delta V</math> work</p> <p><b><math>P\Delta V</math> work: work done by or on a system by a change in volume against a constant pressure.</b></p>	
<p>Internal energy</p> <p><b>Internal energy: the total energy contained within a system; the difference in internal energy in a system is the sum of the heat and work done by or on the system.</b></p>	
<p>Enthalpy change</p> <p><b>Enthalpy change: the difference in enthalpy between an initial and final state, the enthalpy being the heat of a system at constant pressure.</b></p>	
<p>Entropy</p> <p><b>Entropy: a measure of the distribution of heat, related to the number of ways or the probability of its distribution, hence to the level of disorder of the energy.</b></p>	
<p>Equilibrium constant</p> <p><b>Equilibrium constant: the ratio of the concentrations (or partial pressures) of reactants over products, each raised to its stoichiometric coefficient, when the system is at equilibrium.</b></p>	
<p>Reaction quotient</p> <p><b>Reaction quotient: the value of the equilibrium constant expression under any conditions, not at equilibrium.</b></p>	
<p>Triple point</p> <p><b>Triple point: The temperature and pressure at which a substance can exist as a solid, liquid and gas in equilibrium.</b></p>	

Marks  
6

- A champagne bottle is filled with 750 mL of wine, leaving 10.0 mL of air at atmospheric pressure when it is sealed with a cork. After fermentation, the pressure inside the bottle is 6.0 atm at 20 °C. Assume that the gas produced is entirely CO<sub>2</sub> and that its solubility in the wine is the same as in water. What mass of CO<sub>2</sub> has been produced by the fermentation?  
Data: The mole fraction solubility of CO<sub>2</sub> in water is  $7.1 \times 10^{-4}$  at 293 K and 1.0 atm.

The molar mass of H<sub>2</sub>O is (16.00 (O) + 2 × 1.008 (H)) g mol<sup>-1</sup> = 18.016 g mol<sup>-1</sup>. Assuming that the wine is entirely water with a density of 1.0 g mL<sup>-1</sup>, the bottle contains 750 g of water or:

$$\text{number of moles of water} = \frac{\text{mass}}{\text{molar mass}} = \frac{750 \text{ g}}{18.016 \text{ g mol}^{-1}} = 41.67 \text{ mol}$$

The mole fraction of CO<sub>2</sub> in water,  $X_{\text{CO}_2}$ , is given by:

$$X_{\text{CO}_2} = \frac{n_{\text{CO}_2(\text{aq})}}{n_{\text{CO}_2(\text{aq})} + n_{\text{H}_2\text{O}(\text{l})}} = \frac{n_{\text{CO}_2(\text{aq})}}{n_{\text{CO}_2(\text{aq})} + (41.67 \text{ mol})} = 7.1 \times 10^{-4}$$

Hence, the number of moles of CO<sub>2</sub> in the wine *before* fermentation (1.0 atm) is given by:

$$\begin{aligned} n_{\text{CO}_2(\text{aq})} &= (7.1 \times 10^{-4})(n_{\text{CO}_2(\text{aq})} + 41.67) \\ &= 7.1 \times 10^{-4} n_{\text{CO}_2(\text{aq})} + (7.1 \times 10^{-4} \times 41.67) \end{aligned}$$

$$n_{\text{CO}_2(\text{aq})}(1.0 - 7.1 \times 10^{-4}) = (7.1 \times 10^{-4} \times 41.67)$$

$$n_{\text{CO}_2(\text{aq})} = 0.0296 \text{ mol}$$

After fermentation, the pressure is 6.0 atm so  $n_{\text{CO}_2(\text{aq})} = 6.0 \times 0.0296 \text{ mol}$ . The number of moles of CO<sub>2</sub> produced by the fermentation and dissolved in the wine is therefore:

$$n_{\text{CO}_2(\text{aq})} = (6.0 - 1.0) \times 0.0296 \text{ mol} = 0.148 \text{ mol}$$

The increase in air pressure of 5.0 atm is due to extra CO<sub>2</sub>(g). As 1 atm = 101.3 kPa,  $P = (5.0 \times 101.3) \text{ kPa} = 506.5 \text{ kPa}$ . The volume of air = 10.0 mL = 0.0100 L =  $1.00 \times 10^{-5} \text{ m}^3$ . Using the ideal gas equation,  $PV = nRT$ , the number of moles of CO<sub>2</sub>(g) is:

$$n_{\text{CO}_2(\text{g})} = \frac{PV}{RT} = \frac{(5.065 \times 10^5 \text{ Pa})(1.00 \times 10^{-5} \text{ m}^3)}{(8.314 \text{ m}^3 \text{ Pa K}^{-1} \text{ mol}^{-1})(20+273)\text{K}} = 0.00208 \text{ mol}$$

Overall:

$$n_{\text{CO}_2} = n_{\text{CO}_2(\text{aq})} + n_{\text{CO}_2(\text{g})} = (0.148 + 0.002) \text{ mol} = 0.150 \text{ mol}$$

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>. Hence, the mass of CO<sub>2</sub> produced by fermentation is given by:

$$\begin{aligned} \text{mass} &= \text{number of moles} \times \text{molar mass} \\ &= (0.150 \text{ mol}) \times (44.01 \text{ g mol}^{-1}) = 6.6 \text{ g} \end{aligned}$$

Answer: 6.6 g

ANSWER CONTINUES ON THE NEXT PAGE

After the bottle has been opened and all of the bubbles have been released, what volume of CO<sub>2</sub> has escaped? Assume all the CO<sub>2</sub> produced escapes.

**When the cork is released, the pressure returns to 1.0 atm. The amount of CO<sub>2</sub> that will remain dissolved is therefore, from above,  $n_{\text{CO}_2(\text{aq})} = 0.0296$  mol.**

**The amount of CO<sub>2</sub> which escapes is therefore:**

$$n_{\text{CO}_2(\text{g})} = (0.150 - 0.0296) \text{ mol} = 0.120 \text{ mol}$$

**At 1.0 atm = 101.3 kPa, this will occupy a volume:**

$$V = \frac{nRT}{P} = \frac{(0.120 \text{ mol})(8.314 \text{ m}^3 \text{ Pa K}^{-1} \text{ mol}^{-1})((20+273)\text{K})}{(1.013 \times 10^5 \text{ Pa})}$$

$$= 2.9 \times 10^{-3} \text{ m}^3 = 2.9 \text{ L}$$

$$\text{Answer: } 2.9 \times 10^{-3} \text{ m}^3 = 2.9 \text{ L}$$

- A solution is prepared by dissolving 0.050 mol of acetic acid, 0.020 mol of sodium acetate and 0.0010 mol of HCl in water to give a final volume of 250 mL. The  $pK_a$  of acetic acid is 4.76. What is the pH of this solution?

Marks  
3

HCl will react with the acetate to produce acetic acid:



As 0.020 mol of  $\text{CH}_3\text{CO}_2^-$  is initially present, the number of moles after this reaction is  $(0.020 - 0.0010)$  mol = 0.019 mol.

As 0.050 mol of  $\text{CH}_3\text{COOH}$  is initially present, the number of moles after this reaction is  $(0.050 + 0.0010)$  mol = 0.051 mol.

The final volume is 250 mL so the concentrations are:

$$[\text{CH}_3\text{CO}_2^-(\text{aq})] = \frac{\text{number of moles}}{\text{volume}} = \frac{0.019 \text{ mol}}{0.250 \text{ L}} = 0.076 \text{ M}$$

$$[\text{CH}_3\text{COOH}(\text{aq})] = \frac{\text{number of moles}}{\text{volume}} = \frac{0.051 \text{ mol}}{0.250 \text{ L}} = 0.204 \text{ M}$$

The pH of the solution containing both an acid ( $\text{CH}_3\text{COOH}$ ) and its conjugate base ( $\text{CH}_3\text{CO}_2^-$ ) is given by the Henderson-Hasselbalch equation:

$$\text{pH} = \text{p}K_a + \log \frac{[\text{base}]}{[\text{acid}]} = 4.76 + \log \frac{0.076}{0.204} = 4.33$$

$$\text{pH} = 4.33$$

- Consider the following reaction.



Calculate  $\Delta G^\circ$  (in  $\text{J mol}^{-1}$ ) for this reaction.

3

$$\Delta G^\circ = -RT \ln K_p = -(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}) \times \ln(0.090) = 6.0 \times 10^3 \text{ J mol}^{-1}$$

$$\Delta G^\circ = 6.0 \times 10^3 \text{ J mol}^{-1}$$

Calculate the reaction quotient,  $Q$ , at 25 °C when  $p(\text{H}_2\text{O}) = 18$  mmHg,  $p(\text{Cl}_2\text{O}) = 2.0$  mmHg and  $p(\text{HOCl}) = 0.10$  mmHg.

The reaction quotient is given by:

$$Q_p = \frac{p(\text{HOCl})^2}{p(\text{H}_2\text{O})p(\text{Cl}_2\text{O})} = \frac{(0.10)^2}{(18)(2.0)} = 2.8 \times 10^{-4}$$

$$Q = 2.8 \times 10^{-4}$$

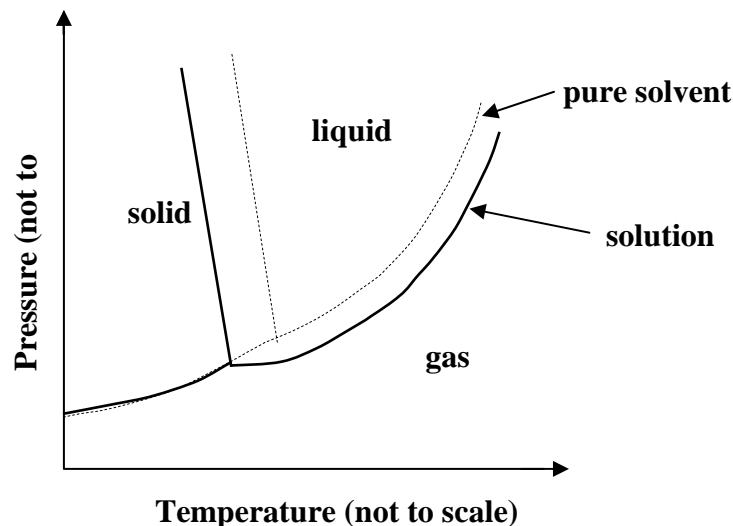
In which direction will the reaction proceed spontaneously at these partial pressures?

As  $Q < K$ , the reaction will proceed towards products (i.e. in the forward direction).

- Explain why the freezing temperature of an aqueous salt solution is lower than that of pure water.

**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 as shown in the phase diagram.



What mass of sugar (sucrose, MW  $342 \text{ g mol}^{-1}$ ) would have to be dissolved in 1.0 L of water to lower the freezing point as much as a water solution containing  $11.1 \text{ g L}^{-1}$  of  $\text{CaCl}_2$ ?

The molar mass of  $\text{CaCl}_2$  is  $(40.08 \text{ (Ca)} + 2 \times 35.45 \text{ (Cl)}) \text{ g mol}^{-1} = 110.98 \text{ g mol}^{-1}$ . The number of moles in 11.1 g of  $\text{CaCl}_2$  is therefore:

$$\text{number of moles} = \frac{\text{mass}}{\text{molar mass}} = \frac{11.1 \text{ g}}{110.98 \text{ g mol}^{-1}} = 0.100 \text{ mol}$$

As  $\text{CaCl}_2$  dissolves to give 3 particles per mole ( $\text{Ca}^{2+} + 2\text{Cl}^-$ ), the number of moles of sucrose required is  $(3 \times 0.100 \text{ mol}) = 0.300 \text{ mol}$ . This corresponds to a mass of:

$$\text{mass} = \text{number of moles} \times \text{molar mass} = (0.300 \text{ mol}) \times (342 \text{ g mol}^{-1}) = 103 \text{ g}$$

Answer: 103 g

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

- A 20.0 mL solution of nitrous acid ( $\text{HNO}_2$ ,  $\text{p}K_a = 3.15$ ) was titrated to its equivalence point with 24.8 mL of 0.020 M NaOH. What is the concentration of the  $\text{HNO}_2$  solution?

**Marks**  
**7**

The number of moles of  $\text{OH}^-$  required in the titration is:

number of moles = concentration  $\times$  volume

$$= (0.020 \text{ mol L}^{-1}) \times (0.0248 \text{ L}) = 4.96 \times 10^{-4} \text{ mol}$$

This is equal to the number of moles of  $\text{HNO}_2$  in 20.0 mL. Hence, the concentration of  $\text{HNO}_2$  is equal to:

$$\text{concentration} = \frac{\text{number of moles}}{\text{volume}} = \frac{4.96 \times 10^{-4} \text{ mol}}{0.0200 \text{ L}} = 0.025 \text{ M}$$

Answer: **0.025 M**

What was the pH at the start of the titration?

$\text{HNO}_2$  is a weak acid so the equilibrium concentrations need to be calculated using a reaction table:

	$\text{HNO}_2$	$\text{H}_2\text{O}$	$\rightleftharpoons$	$\text{H}_3\text{O}^+(\text{aq})$	$\text{NO}_2^-(\text{aq})$
<b>Initial</b>	<b>0.025</b>	<b>large</b>		<b>0</b>	<b>0</b>
<b>Change</b>	<b>-x</b>			<b>+x</b>	<b>+x</b>
<b>Equilibrium</b>	<b>0.025 - x</b>			<b>x</b>	<b>x</b>

As  $\text{p}K_a = -\log_{10}K_a$ , at equilibrium,

$$K_a = \frac{[\text{H}_3\text{O}^+(\text{aq})][\text{NO}_2^-(\text{aq})]}{[\text{HNO}_2(\text{aq})]} = \frac{(x)(x)}{(0.025-x)} = \frac{x^2}{(0.025-x)} = 10^{-3.15}$$

As  $K_a$  is so small,  $x$  will be tiny and  $0.025 - x \sim 0.025$  and so

$$x^2 = 10^{-3.15} \times 0.025 \text{ or } x = [\text{H}_3\text{O}^+(\text{aq})] = 0.00421 \text{ M}$$

As  $\text{pH} = -\log_{10}[\text{H}_3\text{O}^+(\text{aq})]$ ,

$$\text{pH} = -\log_{10}(0.00421) = 2.38$$

pH = **2.38**

**ANSWER CONTINUES ON THE NEXT PAGE**

What was the pH after (a) 12.4 mL and (b) 24.8 mL of the NaOH had been added?

(a) 12.4 mL represents the half equivalence point. At this point,  $[\text{HNO}_2(\text{aq})] = [\text{NO}_2^-(\text{aq})]$  and  $\text{pH} = \text{p}K_a$ . Hence  $\text{pH} = 3.15$

(b) 24.8 mL represents the equivalence point. At this point, all of the  $\text{HNO}_2$  has been converted into  $\text{NO}_2^-$  so:

$$\text{number of moles of } \text{NO}_2^- = 4.96 \times 10^{-4} \text{ mol}$$

The total volume of the solution is  $(20.0 + 24.8) \text{ mL} = 44.8 \text{ mL}$ . Hence:

$$[\text{NO}_2^-(\text{aq})] = \frac{\text{number of moles}}{\text{volume}} = \frac{4.96 \times 10^{-4}}{0.0448 \text{ L}} = 0.0111 \text{ M}$$

The solution contains a weak base. The pH needs to be calculated using a reaction table.

	$\text{NO}_2^-$	$\text{H}_2\text{O}$	$\rightleftharpoons$	$\text{HNO}_2(\text{aq})$	$\text{OH}^-(\text{aq})$
Initial	0.0111	large		0	0
Change	-y			+y	+y
Equilibrium	$0.0111 - y$			y	y

As  $\text{p}K_a + \text{p}K_b = 14.00$ ,  $\text{p}K_b = 14.00 - 3.15 = 10.85$ . At equilibrium,

$$K_b = \frac{[\text{HNO}_2(\text{aq})][\text{OH}^-(\text{aq})]}{[\text{NO}_2^-(\text{aq})]} = \frac{(y)(y)}{(0.025 - y)} = \frac{y^2}{(0.025 - y)} = 10^{-10.85}$$

As  $K_b$  is so small, y will be tiny and  $0.025 - y \sim 0.025$  and so

$$y^2 = 10^{-10.85} \times 0.025 \text{ or } y = [\text{OH}^-(\text{aq})] = 3.96 \times 10^{-7} \text{ M}$$

As  $\text{pOH} = -\log_{10}[\text{OH}^-(\text{aq})]$ ,

$$\text{pOH} = -\log_{10}(3.96 \times 10^{-7}) = 6.40$$

Finally, as  $\text{pH} + \text{pOH} = 14.00$ ,

$$\text{pH} = 14.00 - 6.40 = 7.60$$

(a) 12.4 mL:  $\text{pH} = 3.15$

(b) 24.8 mL:  $\text{pH} = 7.60$

ANSWER CONTINUES ON THE NEXT PAGE



Qualitatively, how would each of these three pH values be affected if 0.020 M  $\text{NH}_3$  had been used in place of the NaOH solution? The  $\text{p}K_b$  of  $\text{NH}_3$  is 4.76.

**The initial pH is unchanged as no base is present.**

**As  $\text{p}K_b$  for  $\text{NH}_3$  is 4.76,  $\text{p}K_a$  for its conjugate acid  $\text{NH}_4^+$  is  $(14.00 - 4.76) = 9.24$ . The half equivalence point is in the acidic region of the titration (it is at  $\text{pH} = 3.15$  for the weak acid / strong base titration above). This pH is considerably lower the  $\text{p}K_a$  value of  $\text{NH}_4^+$  and so essentially all of the  $\text{NH}_3$  will be present as  $\text{NH}_4^+$  and it will not contribute to  $[\text{H}_3\text{O}^+(\text{aq})]$ . The pH at the half-equivalence point will be the same as it depends only on the  $\text{p}K_a$  of  $\text{HNO}_2$ .**

**The pH at the equivalence point will be lower. At equivalence, the solution will contain  $\text{NO}_2^-$  as in the  $\text{HNO}_2 / \text{OH}^-$  titration. It will also contain  $\text{NH}_4^+$ , the conjugate acid of  $\text{NH}_3$ . As this is weakly acid, the pH will be lowered.**

- The general formula for a nickel(II) chloride compound complexed with ammonia is  $[\text{Ni}(\text{NH}_3)_x]\text{Cl}_2$ . A 0.59 g sample of the salt was dissolved in water and the ammonia from it was titrated with 153 mL of 0.100 M HCl. What is the value of the coefficient  $x$ ?

The molar mass of  $[\text{Ni}(\text{NH}_3)_x]\text{Cl}_2$  is:

$$\begin{aligned} & (58.69 \text{ (Ni)} + x (14.01 \text{ (N)} + 3 \times 1.008 \text{ (H)}) + 2 \times 35.45 \text{ (Cl)}) \text{ g mol}^{-1} \\ & = (129.59 + 17.034x) \text{ g mol}^{-1} \end{aligned}$$

A 0.59 g sample therefore corresponds to:

$$\text{number of moles} = \frac{\text{mass}}{\text{molar mass}} = \frac{0.59}{(129.59 + 17.034x)} \text{ mol} \quad (1)$$

The number of moles in 153 mL of 0.100 M HCl is:

$$\begin{aligned} \text{number of moles} &= \text{concentration} \times \text{volume} \\ &= 0.100 \text{ mol L}^{-1} \times 0.153 \text{ L} = 0.0153 \text{ mol} \end{aligned}$$

Ammonia reacts with HCl according to the reaction  $\text{NH}_3 + \text{HCl} \rightleftharpoons \text{NH}_4\text{Cl}$  and so this is equal to the number of moles of  $\text{NH}_3$  present. Each mol of  $[\text{Ni}(\text{NH}_3)_x]\text{Cl}_2$  contains  $x$  mol of  $\text{NH}_3$  so the number of moles of  $[\text{Ni}(\text{NH}_3)_x]\text{Cl}_2$  is:

$$\text{number of moles} = 0.0153 / x \text{ mol} \quad (2)$$

The value of  $x$  is calculated by equating (1) and (2). This is easiest to achieve by trial and error.

$x$	(1) / mol	(2) / mol
1	0.0040	0.015
2	0.0036	0.0077
3	0.0033	0.0051
4	0.0030	0.0038
5	0.0027	0.0031
6	0.0026	0.0026
7	0.0024	0.0022

The best agreement is for  $x = 6$  - a common coordination number for Ni(II).

Answer: 6

- A melt containing  $\text{Cr}^{3+}$  is electrolysed for exactly 1 hour with a current of 0.54 A. Calculate the quantity of chromium that is deposited in this time at the electrode.

Marks  
2

The number of moles of electrons delivered by a current  $I$  in time  $t$  is equal to  $\frac{It}{F}$ :

$$\text{number of moles of electrons} = \frac{It}{F} = \frac{(0.54 \text{ A}) \times (60 \times 60 \text{ s})}{96485 \text{ C mol}^{-1}} = 0.0201 \text{ mol}$$

The reduction reaction is  $\text{Cr}^{3+} + 3\text{e}^- \rightarrow \text{Cr}$  so 3 mol of electrons are required for each mol of Cr. The number of moles of Cr produced is therefore:

$$\text{number of moles of Cr} = \frac{1}{3} \times 0.0201 \text{ mol} = 0.00672 \text{ mol}$$

This corresponds to:

$$\begin{aligned} \text{mass of Cr} &= \text{number of moles} \times \text{molar mass} = \\ &(0.00672 \text{ mol}) \times (52.00 \text{ g mol}^{-1}) = 0.35 \text{ g} \end{aligned}$$

Answer: 0.35 g

- An Ag electrode immersed in an aqueous solution containing  $\text{AgNO}_3$  (0.010 M) and  $\text{NaCN}$  (1.00 M) has a potential of  $-0.66 \text{ V}$ . Calculate the stability constant of the complex ion,  $[\text{Ag}(\text{CN})_2]^-$ .

4

The standard reduction potential,  $E^\circ$ , for the reaction  $\text{Ag}^+(\text{aq}) + \text{e}^- \rightarrow \text{Ag}(\text{s})$  is  $+0.80 \text{ V}$ . The Nernst equation can be used to calculate the  $[\text{Ag}^+(\text{aq})]$  after  $\text{CN}^-$  is added. At this point,  $E = -0.66 \text{ V}$ .

Using the Nernst equation for this 1 electron process:

$$\begin{aligned} E &= E^\circ - \frac{RT}{nF} \ln Q \\ &= (+0.80 \text{ V}) - \frac{(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})}{1 \times 96485 \text{ C mol}^{-1}} \ln \frac{1}{[\text{Ag}^+(\text{aq})]} = -0.66 \text{ V} \end{aligned}$$

$$[\text{Ag}^+(\text{aq})] = 2.0 \times 10^{-25} \text{ M}$$

A reaction table can be used to calculate work out the stability constant:

	$\text{Ag}^+(\text{aq})$	$2\text{CN}^-(\text{aq})$	$\rightleftharpoons$	$\text{Ag}(\text{CN})_2^-(\text{aq})$
Initial	0.010	1.00		0
Change	-x	-2x		+x
Equilibrium	$2.0 \times 10^{-25}$	0.98		0.010

Hence,

$$K_{\text{stab}} = \frac{[\text{Ag}(\text{CN})_2^-(\text{aq})]}{[\text{Ag}^+(\text{aq})][\text{CN}^-(\text{aq})]^2} = \frac{(0.010)}{(2.0 \times 10^{-25})(0.98)^2} = 5.1 \times 10^{-22}$$

Answer:  $5.1 \times 10^{-22}$

- Explain the meaning of the terms  $\Delta G$ ,  $n$ , and  $E_{\text{cell}}$  in the equation  $\Delta G = -nFE_{\text{cell}}$ .

**Marks**  
**3**

**$\Delta G$  is the change in free energy due to the completion of a redox reaction. It is the maximum amount of energy that can be extracted from the reaction.**

**$n$  is the number of electrons exchanged.**

**$E_{\text{cell}}$  is the cell potential as defined in the Nernst equation:**

$$E = E^{\circ} - (RT/nF) \times \ln Q$$

**Marks**  
**3**

- Briefly describe collision theory and how it relates to the Arrhenius equation.

**Collision theory states that molecules must collide to react, and orientation, collision frequency and energy factors determine the reaction rate.**

**Not all collisions are effective - molecules need to be orientated correctly and they need to have enough energy (above the activation energy,  $E_a$ ) for a reaction to occur.**

**Increasing the temperature increases the number of collisions that exceed  $E_a$ .**

**Collision theory is summarised in the Arrhenius law,  $k = Ae^{-E_a/RT}$  where A is the “frequency factor”, or pre-exponential factor – related to collision frequency and orientation of colliding molecules.**

**Arrhenius law shows that the higher  $T$ , the larger the rate constant  $k$ , and the higher is the reaction rate.**

- Radioactive elements are used in medicine both as tracers and to treat diseases such as cancer. Describe what the ideal half-life of an element is for each application, and state the reasons for your choices.

**3**

**As a tracer, the element should ideally have a short half-life, of around a few hours, long enough for it to be produced, administered and imaged, but short enough for it to decay quickly so that it stops being radioactive in the body of the patient.**

**A longer half-life would be more suited for a topical treatment of cancer, to impose radiation to the affected area with a higher activity for a longer time.**

- Describe two alternative methods by which a colloidal suspension could be stabilised, and one by which a stable suspension could be destabilised.

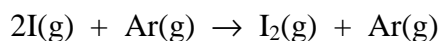
**3**

**Colloidal suspensions can be stabilised either electrostatically or sterically. Electrostatic repulsions between particles with the same charge can stabilise a suspension. The presence of an adsorbed polymer layer on the particles, can also stabilise the suspension because an entropic repulsion sets in between the polymer layers.**

**A suspension stabilised electrostatically can be destabilised by adding an electrolyte (e.g. NaCl), which decreases the repulsion between particles, causing the suspension to aggregate and precipitate. Heating or stirring vigorously can also destabilise a suspension by increasing the number of collisions between particles.**

- The following data were obtained for the reaction of iodine atoms in the gas phase in the presence of argon.

**Marks**  
**4**



Experiment Number	Initial [I] (M)	Initial [Ar] (M)	Initial Reaction Rate $-\text{d}[\text{I}(\text{g})]/\text{dt}$ ( $\text{M s}^{-1}$ )
1	$1.0 \times 10^{-5}$	$1.0 \times 10^{-3}$	$8.70 \times 10^{-4}$
2	$2.0 \times 10^{-5}$	$1.0 \times 10^{-3}$	$3.48 \times 10^{-3}$
3	$2.0 \times 10^{-5}$	$5.0 \times 10^{-3}$	$1.74 \times 10^{-2}$

Derive an expression for the rate law for the formation of  $\text{I}_2(\text{g})$  and calculate the value of the rate constant for this reaction.

Between experiments (1) and (2), [Ar] is constant and [I] is doubled. This leads to the rate increasing by  $\frac{3.48 \times 10^{-3}}{8.70 \times 10^{-4}}$ : a factor of 4. The rate is proportional to  $[\text{I}]^2$ .

Between experiments (2) and (3), [I] is constant and [Ar] is increased by a factor of 5. This leads to the rate increasing by  $\frac{1.74 \times 10^{-2}}{3.48 \times 10^{-3}}$ : a factor of 5. The rate is proportional to  $[\text{Ar}]^1$ .

Overall:

$$-\text{d}[\text{I}(\text{g})]/\text{dt} = k[\text{I}]^2[\text{Ar}]$$

From experiment (1), rate =  $8.70 \times 10^{-4} \text{ M s}^{-1}$  when  $[\text{I}] = 1.0 \times 10^{-5} \text{ M}$  and  $[\text{Ar}] = 1.0 \times 10^{-3} \text{ M}$ . Hence:

$$8.70 \times 10^{-4} \text{ M s}^{-1} = k \times (1.0 \times 10^{-5} \text{ M})^2 \times (1.0 \times 10^{-3} \text{ M})$$

$$k = 8.70 \times 10^9 \text{ M}^{-2} \text{ s}^{-1}$$

Rate law:  $-\text{d}[\text{I}(\text{g})]/\text{dt} = k[\text{I}]^2[\text{Ar}]$

Rate constant:  $8.70 \times 10^9 \text{ M}^{-2} \text{ s}^{-1}$

Calculate the rate of appearance of  $\text{I}_2(\text{g})$  when  $[\text{I}(\text{g})] = 1.0 \times 10^{-3} \text{ M}$  and  $[\text{Ar}(\text{g})] = 1.0 \times 10^{-2} \text{ M}$ .

$$\begin{aligned} -\text{d}[\text{I}(\text{g})]/\text{dt} &= k[\text{I}]^2[\text{Ar}] \\ &= (8.70 \times 10^9 \text{ M}^{-2} \text{ s}^{-1}) \times (1.0 \times 10^{-3} \text{ M})^2 \times (1.0 \times 10^{-2} \text{ M}) = 87 \text{ M s}^{-1} \end{aligned}$$

From the chemical equation, two I are lost for every  $\text{I}_2$  produced. Hence:

$$\text{d}[\text{I}_2(\text{g})]/\text{dt} = \frac{1}{2} \times -\text{d}[\text{I}(\text{g})]/\text{dt} = \frac{1}{2} \times (87 \text{ M s}^{-1}) = 44 \text{ M s}^{-1}$$

Answer:  $44 \text{ M s}^{-1}$

- The solubility of  $\text{BaF}_2$  in water is  $1.30 \text{ g L}^{-1}$ . Calculate the solubility product for  $\text{BaF}_2$ .

Marks  
2

The molar mass of  $\text{BaF}_2$  is  $(137.34 \text{ (Ba)} + 2 \times 19.00 \text{ (F)}) \text{ g mol}^{-1} = 175.34 \text{ g mol}^{-1}$ .  
As  $1.30 \text{ g}$  dissolves in one litre, this corresponds to:

$$\text{number of moles} = \frac{\text{mass}}{\text{molar mass}} = \frac{1.30 \text{ g}}{175.34 \text{ g mol}^{-1}} = 0.00741 \text{ mol}$$

As  $\text{BaF}_2$  dissolves to give  $\text{Ba}^{2+}(\text{aq}) + 2\text{F}^{-}(\text{aq})$ , dissolution of  $0.00741 \text{ mol}$  in one litre will produce  $[\text{Ba}^{2+}(\text{aq})] = 0.00741 \text{ M}$  and  $[\text{F}^{-}(\text{aq})] = 2 \times 0.00741 \text{ M} = 0.0148 \text{ M}$ . Hence:

$$K_{\text{sp}} = [\text{Ba}^{2+}(\text{aq})][\text{F}^{-}(\text{aq})]^2 = (0.00741)(0.0148)^2 = 1.6 \times 10^{-6}$$

Answer:  $1.6 \times 10^{-6}$

- A mixture of  $\text{NaCl}$  ( $5.0 \text{ g}$ ) and  $\text{AgNO}_3$  ( $5.0 \text{ g}$ ) was added to  $1.0 \text{ L}$  of water. What are the concentrations of  $\text{Ag}^{+}(\text{aq})$ ,  $\text{Cl}^{-}(\text{aq})$  and  $\text{Na}^{+}(\text{aq})$  ions in solution after equilibrium has been established?  $K_{\text{sp}}(\text{AgCl}) = 1.8 \times 10^{-10}$ .

3

The molar mass of  $\text{NaCl}$  is  $(22.99 \text{ (Na)} + 35.45 \text{ (Cl)}) \text{ g mol}^{-1} = 58.44 \text{ g mol}^{-1}$ .  
Hence:

$$\text{number of moles} = \frac{\text{mass}}{\text{molar mass}} = \frac{5.0 \text{ g}}{58.44 \text{ g mol}^{-1}} = 0.0856 \text{ mol}$$

As  $\text{NaCl}$  dissolves to give  $\text{Na}^{+}(\text{aq}) + \text{Cl}^{-}(\text{aq})$ , dissolution of this amount in one litre will give  $[\text{Na}^{+}(\text{aq})] = 0.0856 \text{ M}$  and  $[\text{Cl}^{-}(\text{aq})] = 0.0856 \text{ M}$ .

The molar mass of  $\text{AgNO}_3$  is  $(107.87 \text{ (Ag)} + 14.01 \text{ (N)} + 3 \times 16.00 \text{ (O)}) \text{ g mol}^{-1} = 169.88 \text{ g mol}^{-1}$ . Hence:

$$\text{number of moles} = \frac{\text{mass}}{\text{molar mass}} = \frac{5.0 \text{ g}}{169.88 \text{ g mol}^{-1}} = 0.0294 \text{ mol}$$

As  $\text{AgNO}_3$  dissolves to give  $\text{Ag}^{+}(\text{aq}) + \text{NO}_3^{-}(\text{aq})$ , dissolution of this amount in one litre will give  $[\text{Ag}^{+}(\text{aq})] = 0.0294 \text{ M}$ .

Precipitation of  $\text{AgCl}(\text{s})$  follows  $\text{Ag}^{+}(\text{aq}) + \text{Cl}^{-}(\text{aq}) \rightarrow \text{AgCl}(\text{s})$ . As  $0.0294 \text{ mol}$  of  $\text{Ag}^{+}$  ions and  $0.0856 \text{ mol}$  of  $\text{Cl}^{-}$  ions are present, the former is limiting and so  $0.0294 \text{ mol}$  of  $\text{AgCl}(\text{s})$  will form leaving  $(0.0856 - 0.0294) \text{ mol} = 0.0562 \text{ mol}$  of  $\text{Cl}^{-}$  ions. Hence, after precipitation,  $[\text{Cl}^{-}(\text{aq})] = 0.0562 \text{ M}$ .

$\text{AgCl}(\text{s})$  has a very low solubility and dissolves to give  $\text{Ag}^{+}(\text{aq})$  and  $\text{Cl}^{-}(\text{aq})$  with

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

Hence:

$$[\text{Ag}^{+}(\text{aq})] = K_{\text{sp}} / [\text{Cl}^{-}(\text{aq})] = (1.8 \times 10^{-10}) / (0.0562) \text{ M} = 3.2 \times 10^{-9} \text{ M}$$

$$[\text{Ag}^{+}(\text{aq})] = 3.2 \times 10^{-9} \text{ M}$$

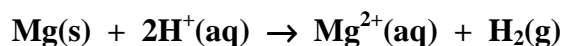
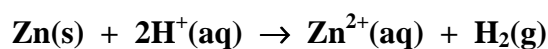
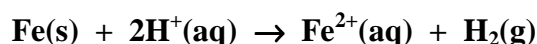
$$[\text{Cl}^{-}(\text{aq})] = 0.0562 \text{ M}$$

$$[\text{Na}^{+}(\text{aq})] = 0.0856 \text{ M}$$

**Marks**  
**4**

- Five strips of different metals were immersed in five different containers with concentrated HCl and the following observations were made.
  1. In the container with the strip of Cu, no change was observed.
  2. In the container with the strip of Sn, no change was observed.
  3. In the container with the strip of Fe, a yellow colour slowly emerged after immersion.
  4. From the container with the strip of Zn, gas started to bubble out.
  5. In the container with the strip of Mg, a vigorous reaction was observed and soon the strip disappeared.

Write down the reactions involved, if any occur.



Explain these experimental observations.

**Cu does not react as the oxidation potential for Cu is negative.**

**Sn would be expected to react as it has a slightly positive oxidation potential. The fact that it does not is due to a high overpotential for the formation of H<sub>2</sub> gas.**

**All the other metals react, evolving H<sub>2</sub>(g) as expected. The higher the oxidation potential (Mg > Zn > Fe), the more vigorous the reaction.**

Explain how cathodic protection can prevent the corrosion of iron.

**Fe, when placed in contact with another metal with a higher oxidation potential (e.g. Zn, Mg) will act as the cathode. The other metal will act as the sacrificial anode and will be oxidised preferentially.**