

# 3A 1 Electrochemistry key facts

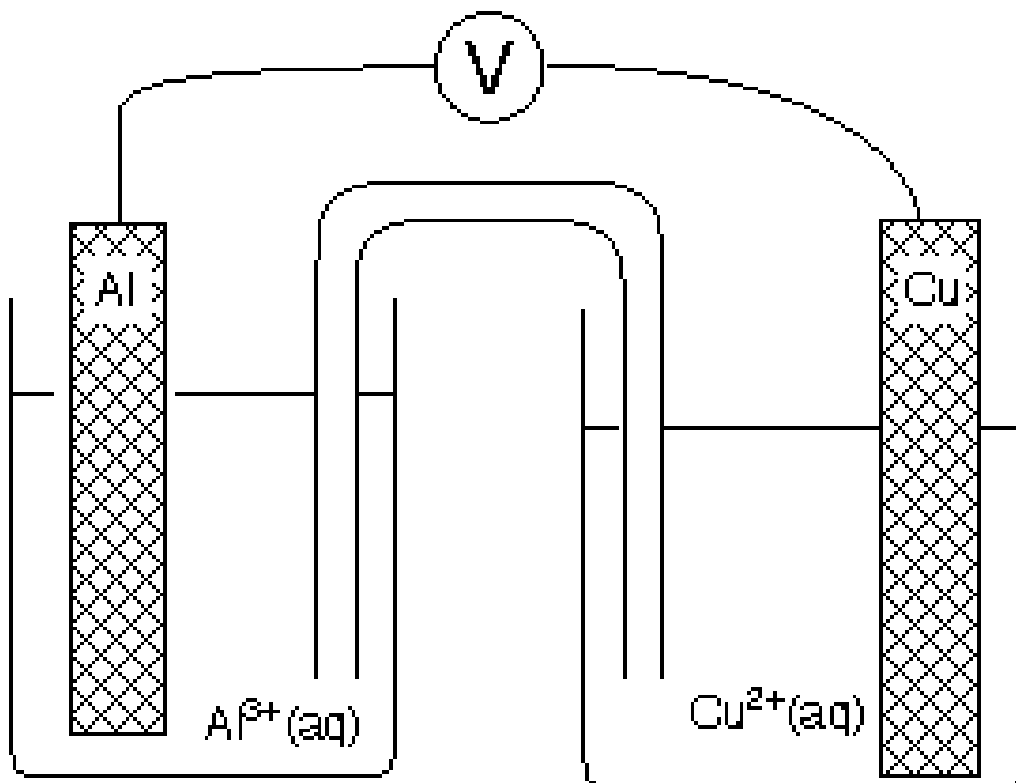
KF 25–36)

1	A _____ provides a path for ions to move from one half-cell to the other.	6	Standard $E^\circ$ potentials are measured with respect to the standard _____ half-cell.
2	In cell diagrams, a _____ separates species of the same phase.	7	In cell diagrams, the _____-hand cell is written as reduction.
3	_____ always occurs at the cathode.	8	_____ always occurs at the anode.
4	In cell diagrams, a _____ separates species of different phases.	9	$E^\circ$ values are measured at a temperature of _____ $^\circ\text{C}$ .
5	A series of electrochemical cells connected together is a _____.	10	In cell diagrams, the _____-hand cell is written as oxidation.

## 3A 1 Answers to: Electrochemistry key facts

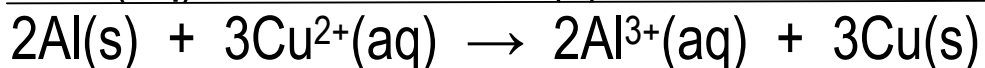
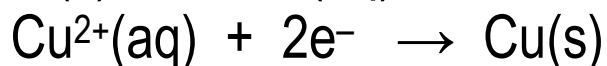
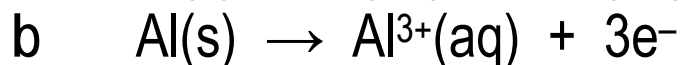
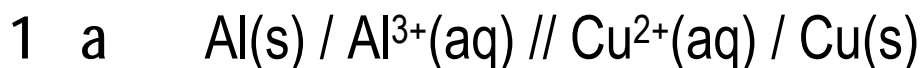
1	salt bridge	6	hydrogen
2	comma	7	right
3	reduction	8	oxidation
4	slash (/)	9	25
5	battery	10	left

# 3B 1a Cell diagrams and reactions 1



- 1 a Write the cell diagram for the above system.
- b Write two half-equations, and hence the net cell equation for the reaction indicated by your cell diagram.
- c Calculate the  $E_{\text{cell}}$  for this system.  
 $E^{\circ}(\text{Al}^{3+}/\text{Al}) = -1.66 \text{ V}$ ,  $E^{\circ}(\text{Cu}^{2+}/\text{Cu}) = +0.34 \text{ V}$
- d Is the reaction in b spontaneous? Why/why not?

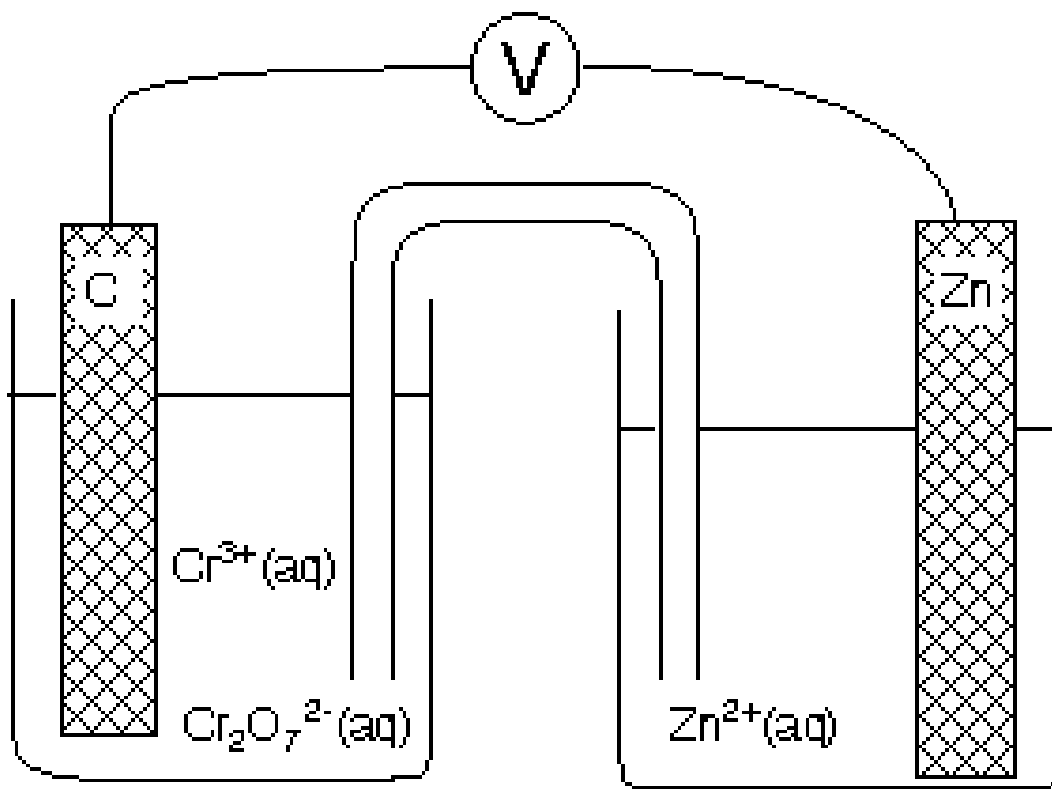
### 3B 1a Answers to: Cell diagrams and reactions 1



c 
$$\begin{aligned} E_{\text{cell}} &= E_{\text{RH}} - E_{\text{LH}} \\ &= 0.34 \text{ V} - (-1.66 \text{ V}) \\ &= 2.00 \text{ V} \end{aligned}$$

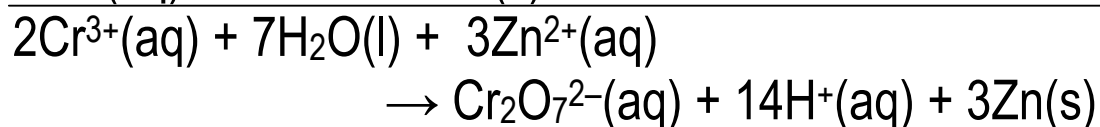
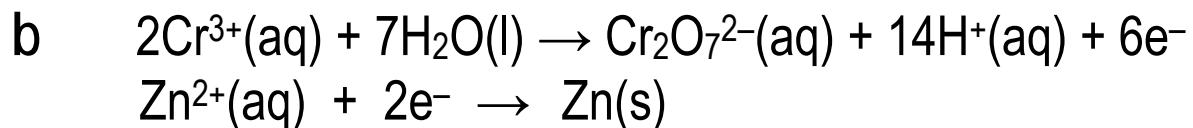
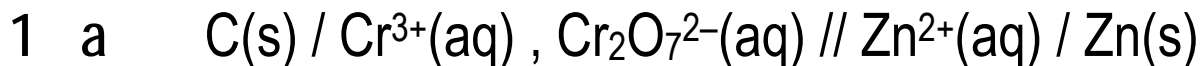
d The reaction is spontaneous, because  $E_{\text{cell}}$  is positive.

## 3B 1b Cell diagrams and reactions 2



- 1 a Write the cell diagram for the above system.
- b Write two half-equations, and hence the net cell equation for the reaction indicated by your cell diagram.
- c Calculate the  $E_{\text{cell}}$  for this system.  
 $E^\circ(\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}) = +1.33 \text{ V}$ ,  
 $E^\circ(\text{Zn}^{2+}/\text{Zn}) = -0.76 \text{ V}$
- d Is the reaction in b spontaneous? Why/why not?

### 3B 1b Answers to: Cell diagrams and reactions



c  $E_{\text{cell}} = E_{\text{RH}} - E_{\text{LH}}$   
 $= -0.76 \text{ V} - 1.33 \text{ V}$   
 $= -2.09 \text{ V}$

d The reaction does not occur as written, because  $E_{\text{cell}}$  is negative.

## 3B 2a Using $E_{\text{cell}}$ to predict reactions

1 Calculate the  $E_{\text{cell}}$  and hence determine whether  $\text{Cl}_2$  will oxidise  $\text{Mn}^{2+}$  to  $\text{Mn}^{3+}$ .

$$E^\circ(\text{Cl}_2/\text{Cl}^-) = 1.36 \text{ V} \quad E^\circ(\text{Mn}^{3+}, \text{Mn}^{2+}) = 1.49 \text{ V}$$

2 What would you observe when  $\text{BrO}_3^-$  solution is added to acidified  $\text{H}_2\text{O}_2$ ? Calculate the  $E_{\text{cell}}$  to support your answer.

$$E^\circ(\text{BrO}_3^-, \text{Br}_2) = 1.52 \text{ V} \quad E^\circ(\text{H}_2\text{O}_2/\text{H}_2\text{O}) = 1.77 \text{ V}$$
$$E^\circ(\text{O}_2/\text{H}_2\text{O}_2) = 0.68 \text{ V}$$

3 Which of these compounds does not form?  $\text{FeI}_2$  or  $\text{FeI}_3$ . Calculate the  $E_{\text{cell}}$  to support your answer.

$$E^\circ(\text{I}_2, \text{I}^-) = 0.54 \text{ V} \quad E^\circ(\text{Fe}^{3+}, \text{Fe}^{2+}) = 0.77 \text{ V}$$

## 3B 2a Answers to: Using $E_{\text{cell}}$ to predict reactions

- 1  $\text{Cl}_2$  is to be reduced,  $\text{Mn}^{2+}$  is to be oxidised:

$$\begin{aligned} E_{\text{cell}} &= E_{\text{red}} - E_{\text{ox}} \\ &= 1.36 \text{ V} - 1.49 \text{ V} \\ &= -0.13 \text{ V} \end{aligned}$$

Since the  $E_{\text{cell}}$  is negative, the reaction does not occur.

- 2  $\text{BrO}_3^-$  can only be reduced, so  $\text{H}_2\text{O}_2$  must be oxidised – to  $\text{O}_2$ .

$$\begin{aligned} E_{\text{cell}} &= E_{\text{red}} - E_{\text{ox}} \\ &= 1.52 \text{ V} - 0.68 \text{ V} \\ &= 0.84 \text{ V} \end{aligned}$$

Since this value is positive, the reaction can occur.

Therefore we would expect to see the colourless bromate solution turn brown as it reacts with the hydrogen peroxide solution, and we would also see bubbles of a colourless gas being produced.

- 3 When these half-cells are put together, oxidation would occur in the  $\text{I}_2$ ,  $\text{I}^-$  cell, and reduction in the  $\text{Fe}^{3+}$ ,  $\text{Fe}^{2+}$  cell:

$$\begin{aligned} E_{\text{cell}} &= E_{\text{red}} - E_{\text{ox}} \\ &= 0.77 \text{ V} - 0.54 \text{ V} \\ &= 0.23 \text{ V} \end{aligned}$$

This reaction is spontaneous, so whenever  $\text{Fe}^{3+}$  and  $\text{I}^-$  are combined they react to form  $\text{Fe}^{2+}$  and  $\text{I}_2$ , thus  $\text{FeI}_3$  cannot form.

## 3B 2b Cell observations



The system above shows a  $\text{Zn}^{2+}/\text{Zn}$  half-cell connected to a  $\text{Fe}^{3+}/\text{Fe}^{2+}$  half-cell.

- 1 Draw the cell diagram for this reaction.
- 2 Calculate the expected  $E_{\text{cell}}$  given  
 $E^\circ(\text{Zn}^{2+}/\text{Zn}) = -0.76 \text{ V}$  and  $E^\circ(\text{Fe}^{3+}, \text{Fe}^{2+}) = 0.77 \text{ V}$ .
- 3 The solutions used are  $1.0 \text{ mol L}^{-1}$  solutions. Why is the actual voltage not that calculated in 2?
- 4 If this system were left overnight, what changes would you expect to see?

## 3B 2b Answers to: Cell observations

1  $\text{Zn(s)} / \text{Zn}^{2+}(\text{aq}) // \text{Fe}^{3+}(\text{aq}) , \text{Fe}^{2+}(\text{aq}) / \text{C(s)}$

$$\begin{aligned} 2 \quad E_{\text{cell}} &= E_{\text{RHE}} - E_{\text{LHE}} \\ &= 0.77 \text{ V} - (-0.76 \text{ V}) \\ &= 1.53 \text{ V} \end{aligned}$$

3 The temperature may not be exactly 25 °C and the electrode used in the  $\text{Fe}^{3+}$ ,  $\text{Fe}^{2+}$  cell is carbon, not platinum.

4 The zinc electrode will be noticeably thinner; the orange colour of the solution in the right-hand beaker will have changed to a greener colour.

## 3B 3 Strongest and weakest

$$E^\circ(\text{Ag}^+/\text{Ag}) = 0.80 \text{ V}$$

$$E^\circ(\text{H}_2\text{O}_2/\text{H}_2\text{O}) = 1.77 \text{ V}$$

$$E^\circ(\text{Cu}^{2+}/\text{Cu}) = 0.35 \text{ V}$$

$$E^\circ(\text{Cl}_2/\text{Cl}^-) = 1.36 \text{ V}$$

$$E^\circ(\text{Mg}^{2+}/\text{Mg}) = -2.36 \text{ V}$$

$$E^\circ(\text{S}_4\text{O}_6^{2-}, \text{S}_2\text{O}_3^{2-}) = 0.08 \text{ V}$$

$$E^\circ(\text{MnO}_4^-, \text{Mn}^{2+}) = 1.70 \text{ V}$$

- 1 What species is:
  - a the strongest oxidant?
  - b the strongest elemental reductant?
- 2 Which anion is the weakest oxidant?
- 3 Write the cell diagram for the cell made with these half-cells which gives the largest voltage, and calculate this voltage.
- 4 What species will oxidise Ag but not  $\text{Mn}^{2+}$ ?

### 3B 3 Answers to: Strongest and weakest

- 1 a  $\text{H}_2\text{O}_2$   
b  $\text{Mg}$



- 3  $\text{Mg(s)} / \text{Mg}^{2+}(\text{aq}) // \text{H}_2\text{O}_2(\text{aq}) , \text{H}_2\text{O(l)} / \text{C(s)}$

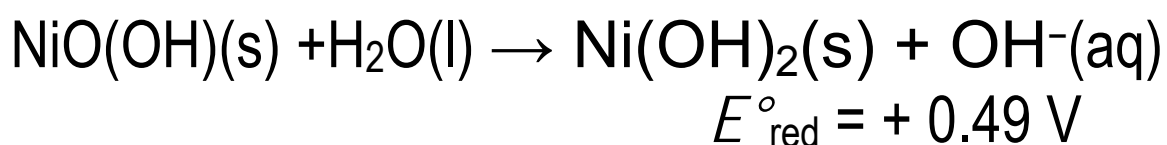
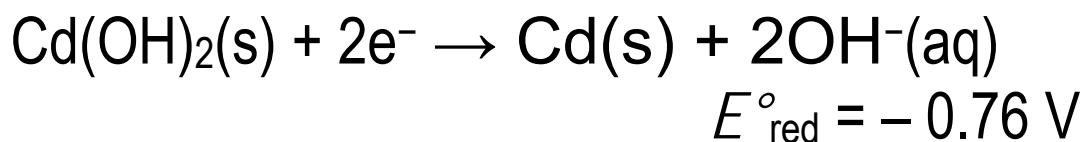
$$\begin{aligned} E^\circ_{\text{cell}} &= E_{\text{RHE}} - E_{\text{LHE}} \\ &= 1.77 \text{ V} - (-2.36 \text{ V}) \\ &= 4.13 \text{ V} \end{aligned}$$

- 4  $\text{Cl}_2$

## 3C 1 The nicad battery

One of the most common rechargeable batteries is the nicad (nickel-cadmium) battery.

Given the following information, namely:

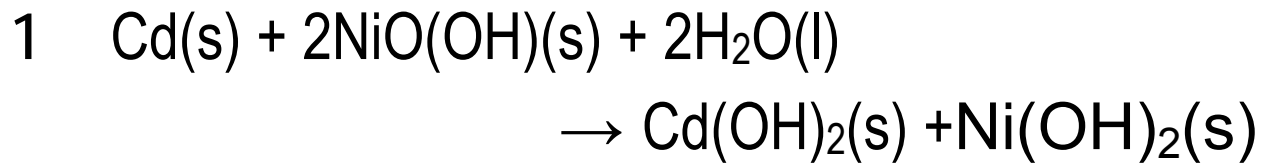


- 1 Write the overall reaction for the discharge of the cell.
- 2 How does the charging reaction differ?
- 3 Calculate the expected  $E_{\text{cell}}$ .

A typical nicad battery gives an emf of 1.30V.

- 4 What might cause the difference between this value and the one calculate in 3?

### 3C 1 Answers to: The nicad battery



Note: Cd is oxidised at LHE.

2 In charging the reaction is reversed.

$$\begin{aligned} 3 \quad E_{\text{cell}} &= E_{\text{RHE}} - E_{\text{LHE}} \\ &= 0.49 \text{ V} - (-0.76 \text{ V}) \\ &= 1.25 \text{ V} \end{aligned}$$

4 The materials are not at standard conditions  
eg the concentrations are non standard.