IB HL Redox 1

1   Define *oxidation* and *reduction* in terms of electrons.

Oxidation is loss of electrons

Reduction is gain of electrons

| Remember: OILRIG |

2   Define *oxidation* and *reduction* in terms of loss/gain of hydrogen/oxygen.

Oxidation is loss of hydrogen or gain of oxygen
Reduction is gain of hydrogen or loss of oxygen

3   Define *oxidation* and *reduction* in terms of oxidation state (oxidation number).

Oxidation is increase in oxidation state
Reduction is decrease in oxidation state

| They may use the term *oxidation state* or *oxidation number* – regard them as the same |

4   Determine the oxidation states of all elements in the following species:

P_4	SO_2	SO_3	SO_4^{2-}	HCl	$HClO_3$	ClO_4^-	$KMnO_4$	C_2H_5Cl
Ca	CrO_4^{2-}	$Cr_2O_7^{2-}$	H_2O_2	BaO_2	LiH	$LiAlH_4$	$Na_2S_2O_3$	$S_4O_6^{2-}$

	P_4	SO_2	SO_3	SO_4^{2-}	HCl	$HClO_3$	ClO_4^-	$KMnO_4$	C_2H_5Cl
elements	P 0	S +4 O -2	S +6 O -2	S +6 O -2	H +1 Cl -1	H + 1 Cl +5 O -2	Cl +7 O -2	K +1 Mn +7 O -2	Cl -1 H +1 C -2
	Ca	CrO_4^{2-}	$Cr_2O_7^{2-}$	H_2O_2	BaO_2	LiH	$LiAlH_4$	$Na_2S_2O_3$	$S_4O_6^{2-}$
	Ca 0	Cr +6 O -2	Cr +6 O -2	H +1 O -1	Ba +2 O -1	Li +1 H -1	Li +1 Al +3 H -1	Na +1 S +2 O -2	S +2.5 O -2

You **must** write + or – first and then the number.
2- ✗   -2 ✓

peroxides

Metal hydrides

Average oxidation state – the sulfur atoms are bonded differently within the ion so have different oxidation states

5   Name the following molecules/ions/compounds using oxidation states/numbers:

SO_2	SO_3	$Cr_2O_7^{2-}$	$FeCl_2$	$CuSO_4$	$KMnO_4$	$NaClO_4$	Cu_2O	$Fe_2(SO_4)_3$

SO_2	sulfur(IV) oxide
SO_3	sulfur(VI) oxide
$Cr_2O_7^{2-}$	dichromate(VI) ion
$FeCl_2$	iron(II) chloride
$CuSO_4$	copper(II) sulfate(VI)
$KMnO_4$	potassium manganate(VII)
$NaClO_4$	sodium chlorate(VII)
Cu_2O	copper(I) oxide
$Fe_2(SO_4)_3$	iron(III) sulfate(VI)

You must use Roman numerals

The (VI) is not usually included with the sulfate

6   Explain whether each of the following involves oxidation, reduction or neither:

$2Cl^- \rightarrow Cl_2 + 2e^-$ $Cu^{2+} + 2e^- \rightarrow Cu$

The conversion of Mn_2O_3 to MnO_2 The conversion of CH_3CH_2OH to CH_3CHO

The conversion of CH_3CH_2CHO to CH_3CH_2COOH

$2Cl^- \rightarrow Cl_2 + 2e^-$
oxidation – Cl^- loses an electron/the oxidation state of Cl increases from -1 to 0

$Cu^{2+} + 2e^- \rightarrow Cu$
Reduction – Cu^{2+} gains electrons/the oxidation state decreases from +2 to 0

The conversion of Mn_2O_3 to MnO_2
Oxidation – oxidation state of Mn increases from +3 to +4

The conversion of CH_3CH_2OH to CH_3CHO
Oxidation – average oxidation state of C increases from -2 to -1

> Could also be explained by 'loss of H' but probably better to stick to explanations involving oxidation state
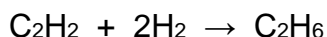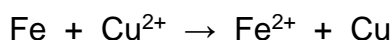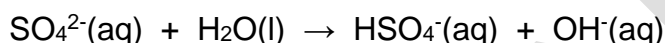
The conversion of CH_3CH_2CHO to CH_3CH_2COOH
Oxidation – average oxidation state of C increases from -1.33 to -0.67

> Could also be explained by 'gain of O'

> *Average* oxidation states – the carbon atoms are bonded to different types of atoms within the molecule so have different oxidation states

7   Explain which of the following equations represent Redox reactions

$I_2(s) + 2OH^-(aq) \rightarrow I^-(aq) + OI^-(aq) + H_2O(l)$

$SO_4^{2-}(aq) + H_2O(l) \rightarrow HSO_4^-(aq) + OH^-(aq)$

$Fe + Cu^{2+} \rightarrow Fe^{2+} + Cu$

$C_2H_2 + 2H_2 \rightarrow C_2H_6$

$2CrO_4^{2-} + 2H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O$
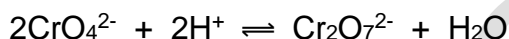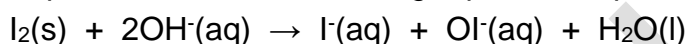
> Disproportionation – same element (I) oxidised and reduced

$I_2(s) + 2OH^-(aq) \rightarrow I^-(aq) + OI^-(aq) + H_2O(l)$
Redox – oxidation state of I in I_2 is 0 but -1 in I^- and +1 in OI^-
Change in oxidation states
Both oxidation and reduction occur therefore redox

$SO_4^{2-}(aq) + H_2O(l) \rightarrow HSO_4^-(aq) + OH^-(aq)$
Not redox – all oxidations states the same on right hand side and left hand side
No change in oxidations states, therefore not redox

$Fe + Cu^{2+} \rightarrow Fe^{2+} + Cu$
Redox – oxidation state of Fe changes from 0 to +2 (oxidation) and that of Cu changes from +2 to 0 (reduction)
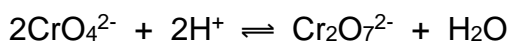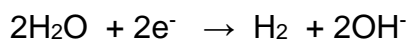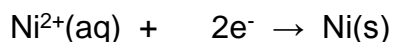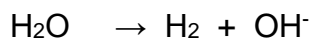Change in oxidation states
Both oxidation and reduction occur therefore redox
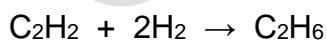
$C_2H_2 + 2H_2 \rightarrow C_2H_6$
Redox – oxidation state of C changes from -1 to -3 (reduction) and that of H changes from 0 to +1 (oxidation)
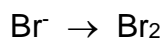Change in oxidation states
Both oxidation and reduction occur therefore redox
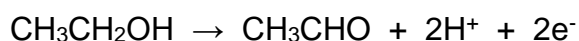
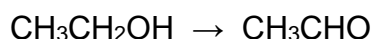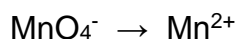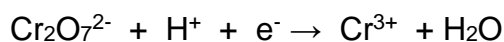$2CrO_4^{2-} + 2H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O$
Not redox – all oxidations states the same on right hand side and left hand side (Cr +6 on both sides)
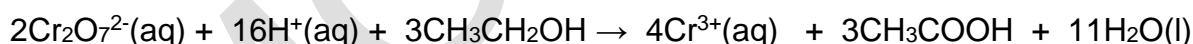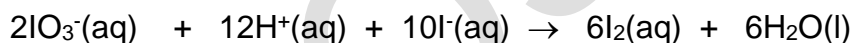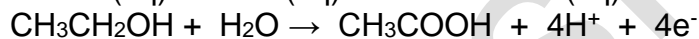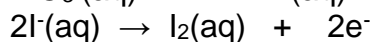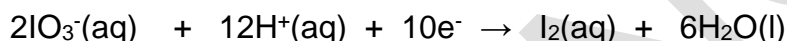No change in oxidations states, therefore not redox
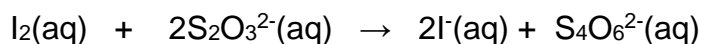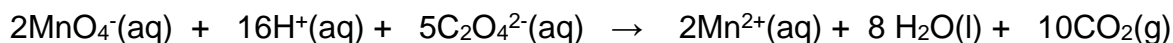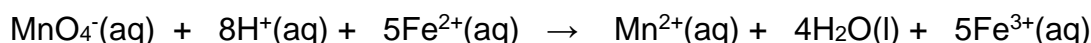
8   Balance the following half-equations in neutral solution:

$Ni^{2+}(aq) + \quad e^- \rightarrow Ni(s)$

$Br^- \rightarrow Br_2$

$H_2O \quad \rightarrow H_2 + OH^-$

$Ni^{2+}(aq) + \quad 2e^- \rightarrow Ni(s)$

$2Br^- \rightarrow Br_2 + 2e^-$

$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

9   Balance the following half-equations in acidic solution:

$Cr_2O_7^{2-} + H^+ + e^- \rightarrow Cr^{3+} + H_2O$

$MnO_4^- \rightarrow Mn^{2+}$

$CH_3CH_2OH \rightarrow CH_3CHO$

$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$

$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$

$CH_3CH_2OH \rightarrow CH_3CHO + 2H^+ + 2e^-$

10   Write balanced redox reactions from each pair of half equations

$2IO_3^-(aq) + 12H^+(aq) + 10e^- \rightarrow I_2(aq) + 6H_2O(l)$
$2I^-(aq) \rightarrow I_2(aq) + 2e^-$

$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$
$CH_3CH_2OH + H_2O \rightarrow CH_3COOH + 4H^+ + 4e^-$

$2IO_3^-(aq) + 12H^+(aq) + 10I^-(aq) \rightarrow 6I_2(aq) + 6H_2O(l)$

$2Cr_2O_7^{2-}(aq) + 16H^+(aq) + 3CH_3CH_2OH \rightarrow 4Cr^{3+}(aq) + 3CH_3COOH + 11H_2O(l)$

11   Balance the following redox equations:

$MnO_4^-(aq) + H^+(aq) + Fe^{2+}(aq) \rightarrow Mn^{2+}(aq) + H_2O(l) + Fe^{3+}(aq)$

$MnO_4^-(aq) + H^+(aq) + C_2O_4^{2-}(aq) \rightarrow Mn^{2+}(aq) + H_2O(l) + CO_2(g)$

$I_2(aq) + S_2O_3^{2-}(aq) \rightarrow I^-(aq) + S_4O_6^{2-}(aq)$

$MnO_4^-(aq) + 8H^+(aq) + 5Fe^{2+}(aq) \rightarrow Mn^{2+}(aq) + 4H_2O(l) + 5Fe^{3+}(aq)$

$2MnO_4^-(aq) + 16H^+(aq) + 5C_2O_4^{2-}(aq) \rightarrow 2Mn^{2+}(aq) + 8 H_2O(l) + 10CO_2(g)$

$I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$
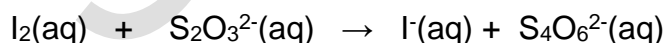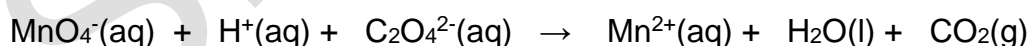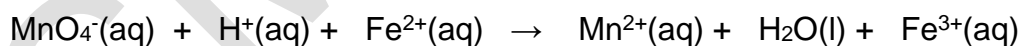
12   Define the terms *oxidising agent* and *reducing agent*.

Oxidising agent – species that oxidises something and in the process gets reduced – takes electrons away from something

Reducing agent – species that reduces something and in the process gets oxidised – gives electrons to something

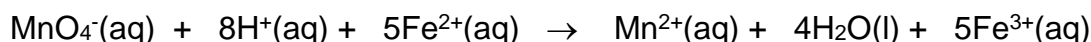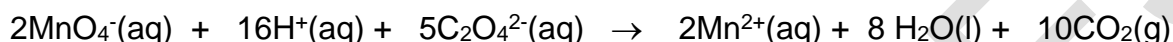13   Identify the oxidising and reducing agents in the equations in 11.

$MnO_4^-(aq) + 8H^+(aq) + 5Fe^{2+}(aq) \rightarrow Mn^{2+}(aq) + 4H_2O(l) + 5Fe^{3+}(aq)$

Oxidising agent: MnO_4^- (removes electrons from Fe^{2+}/gets reduced)
Reducing agent: Fe^{2+} (gives electrons to MnO_4^-/gets oxidised)

$2MnO_4^-(aq) + 16H^+(aq) + 5C_2O_4^{2-}(aq) \rightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 10CO_2(g)$

Oxidising agent: MnO_4^- (removes electrons from $C_2O_4^{2-}$/gets reduced)
Reducing agent: $C_2O_4^{2-}$ (gives electrons to MnO_4^-/gets oxidised)

$I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$
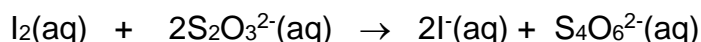
Oxidising agent: I_2 (removes electrons from $S_2O_3^{2-}$/gets reduced)
Reducing agent: $S_2O_3^{2-}$ (gives electrons to I_2/gets oxidised)

14   Explain whether A or Q is more reactive given the equation $A(s) + Q^{2+}(aq) \rightarrow A^{2+}(aq) + Q(s)$
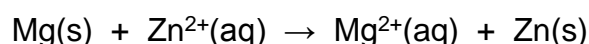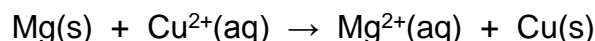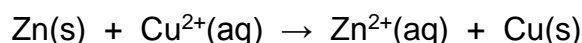
A is more reactive than Q
A displaces Q from solution/reduces Q^{2+} to the element
A has a greater tendency to form an ion/compound than Q

15   Complete the following table by predicting whether a 'reaction' or 'no reaction' will occur in each case and write an ionic equation for each **reaction**.

	$ZnSO_4(aq)$	$MgCl_2(aq)$	$CuSO_4(aq)$
Zinc			
Magnesium			
copper			

	$ZnSO_4(aq)$	$MgCl_2(aq)$	$CuSO_4(aq)$
Zinc	no reaction	no reaction	reaction
Magnesium	reaction	no reaction	reaction
copper	no reaction	no reaction	no reaction

$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

$Mg(s) + Cu^{2+}(aq) \rightarrow Mg^{2+}(aq) + Cu(s)$

$Mg(s) + Zn^{2+}(aq) \rightarrow Mg^{2+}(aq) + Zn(s)$

16   Solve redox titration problems involving iron(II) and manganate(VII)

$$MnO_4^-(aq) + 8H^+(aq) + 5Fe^{2+}(aq) \rightarrow Mn^{2+}(aq) + 4H_2O(l) + 5Fe^{3+}(aq)$$
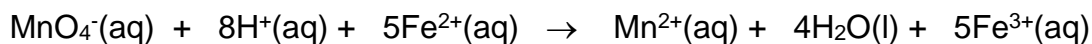
(a)   25.00 cm^3 of 1 mol dm^{-3} sulfuric acid was added to 25.00 cm^3 of a solution of iron(II) sulfate. This was then titrated against 0.02000 mol dm^{-3} potassium manganate(VII). 22.50 cm^3 of KMnO$_4$ was required to be added to the mixture to give the first permanent pink colour. Calculate the concentration of the original iron(II) sulfate solution.

Moles of KMnO$_4$ = 22.50/1000 x 0.02000 = 4.500x10^{-4} mol

From chemical equation

Moles of Fe^{2+} = 4.500x10^{-4} x 5 = 2.250x10^{-3} mol

Concentration of Fe^{2+} = 2.250x10^{-3}/(25.00/1000) = 0.09000 mol dm^{-3}

Same as concentration of FeSO$_4$
because 1 Fe^{2+} per FeSO$_4$ unit

(b)   Five iron tablets are dissolved in about 100 cm^3 of 1.0 mol dm^{-3} sulfuric acid and the solution is made up to a total volume of 250 cm^3 with distilled water. 25.0 cm^3 of the iron(II) solution is titrated with 0.0100 mol dm^{-3} potassium manganate(VII) solution until the first permanent pink colour is seen. 11.60 cm^3 of KMnO$_4$ was required. Calculate the mass of iron (in mg) in 1 tablet.

Moles of KMnO$_4$ = 11.60/1000 x 0.0100 = 1.16x10^{-4} mol

Moles of Fe^{2+} in 25.0 cm^3 of solution = 1.16x10^{-4} x 5 = 5.80x10^{-4} mol

Moles of Fe^{2+} in 250 cm^3 of solution = 5.80x10^{-4} x 10 = 5.80x10^{-3} mol

Mass of Fe in 5 tablets = 5.80x10^{-3} x 55.85 = 0.324 g

Mass of Fe in 1 tablet = 0.324/5 = 0.0648 g

Mass in mg is 0.0648 x 1000 = 64.8 mg

17   Solve redox titration problems involving sodium thiosulfate and iodine

$$I_2(aq) \; + \; 2S_2O_3^{2-}(aq) \; \rightarrow \; 2I^-(aq) \; + \; S_4O_6^{2-}(aq)$$
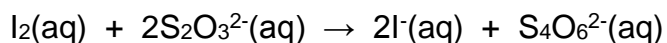
(a)   25.00 cm^3 of iodine solution is pipetted into a conical flask. 0.100 mol dm^{-3} sodium thiosulfate solution is added until the mixture becomes pale yellow. Starch indicator is added and the titration continued until the reaction mixture becomes colourless. The total volume of sodium thiosulfate solution required was 21.50 cm^3. Calculate the concentration of the iodine solution.

Moles of $Na_2S_2O_3$ = 21.50/1000 x 0.100 = 2.15x10^{-3} mol

Moles of I_2 = 2.15x10^{-3} / 2 = 1.075x10^{-3} mol

Concentration of I_2 = 1.075x10^{-3} /(25.00/1000) = 0.0430 mol dm^{-3}

(b)   x g of potassium iodate(V) is dissolved in distilled water and made up to a total volume of 250.0 cm^3. 25.00 cm^3 of this solution is pipetted into a conical flask and 20 cm^3 of 1 mol dm^{-3} sulfuric acid added – this is excess. Excess potassium iodide solution is added to the reaction mixture and the liberated iodine titrated against sodium thiosulfate solution. 25.30 cm^3 of 0.100 mol dm^{-3} sodium thiosulfate is required for the titration. Determine the value of x.

$$IO_3^-(aq) \; + \; 5I^-(aq) \; + \; 6H^+(aq) \; \rightarrow \; 3I_2(aq) \; + \; 3H_2O(l)$$
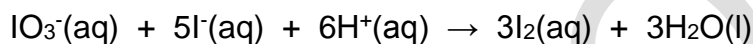
Moles of $Na_2S_2O_3$ = 25.30/1000 x 0.100 = 2.53x10^{-3} mol

Moles of I_2 = 2.53x10^{-3} / 2 = 1.265x10^{-3} mol

Moles of IO_3^- in 25.00 cm^3 = 1.265x10^{-3}/3 = 4.217x10^{-4} mol

Moles of IO_3^- in 250.0 cm^3 = 4.217x10^{-4} x 10 = 4.217x10^{-3} mol

Moles of KIO_3 = 4.217x10^{-3} mol

Mass of KIO_3 = 4.217x10^{-3} x (39.10 + 126.90 + 3x16.00) = 0.902 g

18 Calculate BOD from titrations using the Winkler Method

$$2Mn(OH)_2(s) + O_2(aq) \rightarrow 2MnO(OH)_2(s)$$

$$MnO(OH)_2(s) + 4H^+(aq) \rightarrow Mn^{4+}(aq) + 3H_2O(l)$$

$$Mn^{4+}(aq) + 2I^-(aq) \rightarrow Mn^{2+}(aq) + I_2(aq)$$

$$I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow S_4O_6^{2-}(aq) + 2I^- (aq)$$
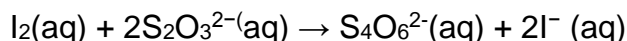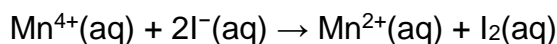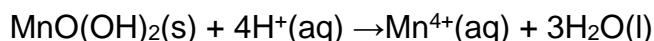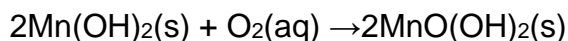
(a) The Winkler method was used to measure the concentration of dissolved oxygen in a sample of water. Manganese(II) sulfate, sulfuric acid and potassium iodide were added to 50.0 cm^3 of the water. The iodine that was formed was titrated against a sodium thiosulfate solution with a concentration of $2.00 \times 10^{-3} \text{ mol dm}^{-3}$. It was found that 17.40 cm^3 of sodium thiosulfate was required for the titration.

Another sample of water from the same source was incubated for 5 days at 20 °C. At the end of the incubation the Winkler method was used to determine concentration of dissolved oxygen. It was found that the concentration of dissolved oxygen in the sample was 3.50 ppm.

Calculate the concentration of dissolved oxygen (in ppm) in the original sample and the biochemical oxygen demand.

Moles of $Na_2S_2O_3 = 17.40/1000 \times 2.00 \times 10^{-3} = 3.48 \times 10^{-5}$ mol

> Moles of $O_2 = \dfrac{\text{moles of sodium thiosulfate}}{4}$

Moles of $I_2 = 3.48 \times 10^{-5} / 2 = 1.74 \times 10^{-5}$ mol

Moles of $Mn^{4+} = 1.74 \times 10^{-5}$ mol

Moles of $MnO(OH)_2 = 1.74 \times 10^{-5}$ mol

> Mass of O_2 is numerically equal to 8 x moles of sodium thiosulfate:
> $8 \times 3.48 \times 10^{-5} = 2.784 \times 10^{-4}$

Moles of $O_2 = 1.74 \times 10^{-5} / 2 = 8.70 \times 10^{-6}$ mol

Mass of $O_2 = 8.70 \times 10^{-6} \times 32.00 = 2.784 \times 10^{-4}$ g

> To convert to ppm

Concentration of O_2 in ppm $= 2.784 \times 10^{-4}/50.0 \times 10^6 = 5.57$ ppm

> Mass of 50.0 cm^3 of water in g

BOD $= 5.57 - 3.50 = 1.87$ ppm

(b) The Winkler method was used to measure the concentration of dissolved oxygen in a sample of water. Manganese(II) sulfate, sulfuric acid and potassium iodide were added to 25.0 cm^3 of the water. The iodine that was formed was titrated against a sodium thiosulfate solution with a concentration of $1.00 \times 10^{-3} \text{ mol dm}^{-3}$. It was found that 22.30 cm^3 of sodium thiosulfate was required for the titration.

Another sample of water from the same source was incubated for 5 days at 20 °C. At the end of the incubation the Winkler method was used to determine concentration of dissolved oxygen. It was found that the concentration of dissolved oxygen in the sample was 2.80 ppm.

Calculate the concentration of dissolved oxygen in the original sample and the biochemical oxygen demand.

Moles of $Na_2S_2O_3 = 22.30/1000 \times 1.00 \times 10^{-3} = 2.23 \times 10^{-5}$ mol

> Mass of O_2 is numerically equal to 8 x moles of sodium thiosulfate

Mass of $O_2 = 2.23 \times 10^{-5} \times 8 = 1.784 \times 10^{-4}$ g

Concentration of O_2 in ppm $= 1.784 \times 10^{-4}/25.0 \times 10^6 = 7.14$ ppm

BOD $= 7.14 - 2.80 = 4.34$ ppm

19 Explain the connection between biochemical oxygen demand and the degree of pollution of a water sample.

The higher the BOD the more polluted the water.
The more polluted the water, the higher the concentration of organic waste – bacteria use up more oxygen breaking down the organic waste.
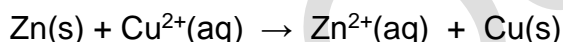
20 (a) Draw a labelled diagram showing a voltaic (Galvanic) cell made up of Zn/Zn²⁺ and Cu/Cu²⁺ half-cells. Labelling should include the anode, cathode, positive and negative electrodes and show the direction of electron flow in the external circuit and the direction of ion flow in the solutions.
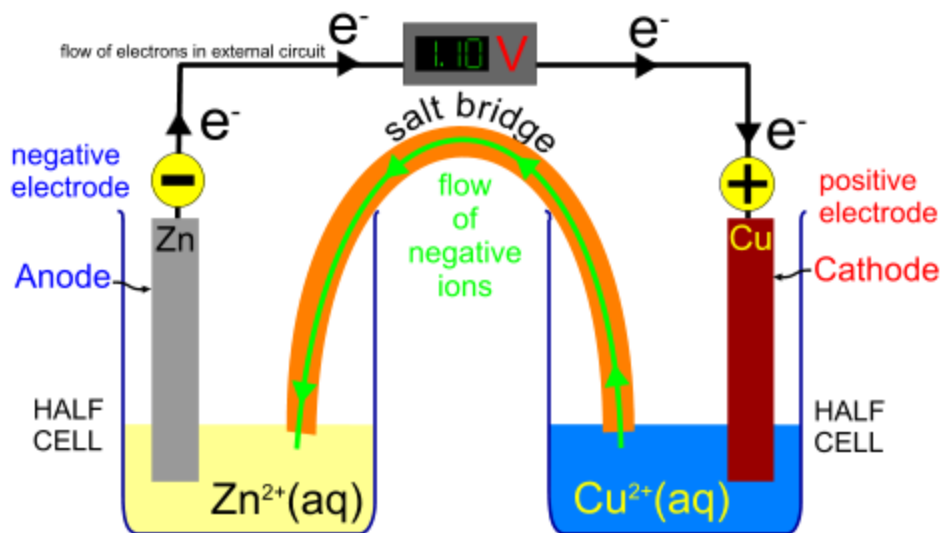
(b) Write half-equations for the reactions at each electrode

Anode (-): $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

Cathode (+): $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$
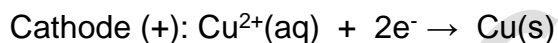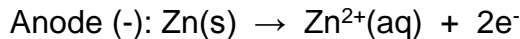
(c) Write the overall redox reaction that occurs in the cell.

$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

(d) State whether the overall reaction that occurs is exothermic or endothermic.

Exothermic

However, in the voltaic cell the energy is given out as electrical energy instead of heat energy.

21 Explain the purpose of the salt bridge in a voltaic (Galvanic) cell.

To complete circuit by allowing *ions* to flow into/out of half-cells.

22 State the energy conversion that occurs in a voltaic cell.

chemical energy → electrical energy

23 Explain what is meant by the term *standard electrode potential* and *standard cell potential*

standard electrode potential: the emf (voltage) of a half cell relative to a standard hydrogen electrode (SHE), measured under standard conditions - solutions of concentration 1 mol dm⁻³, pressure = 100kPa (and temperature = 298K)

A specific temperature is actually not included in the definition of standard conditions and should always be quoted. However, 298 K, is stated on the syllabus so it is probably best to include it.

standard cell potential: the emf (voltage) of a cell measured under standard conditions

24 Describe, with the aid of a labelled diagram, the standard hydrogen electrode
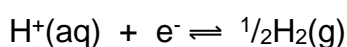

H₂(g) →
100 kPa pressure

298 K — As above - it is probably best to include 298 K

platinum
electrode

1 M H⁺(aq)
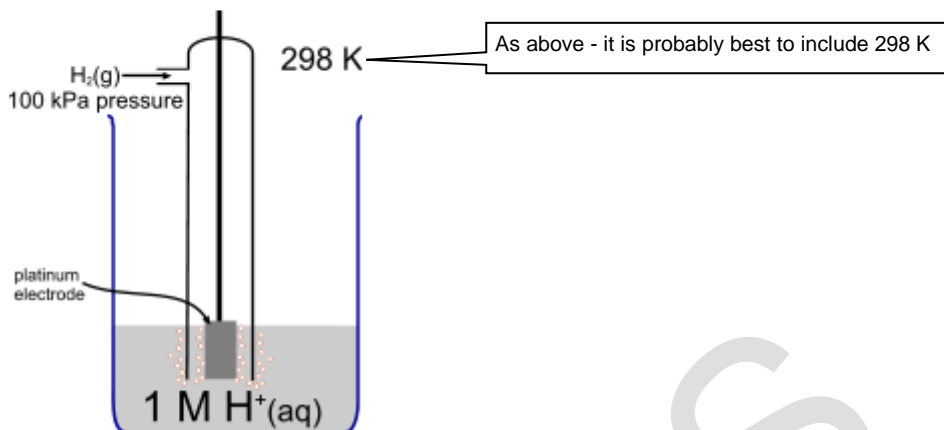
25 Write the half-equation for the standard hydrogen electrode and state the value of the standard electrode potential.

$H^+(aq) + e^- \rightleftharpoons \frac{1}{2}H_2(g)$ — Must be the *reduction* reaction but does not matter if you write it as:
$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$

$E^\ominus = 0.00$ V

26 Explain, with the aid of a diagram, how the standard electrode potential for Cu^{2+}/Cu could be measured
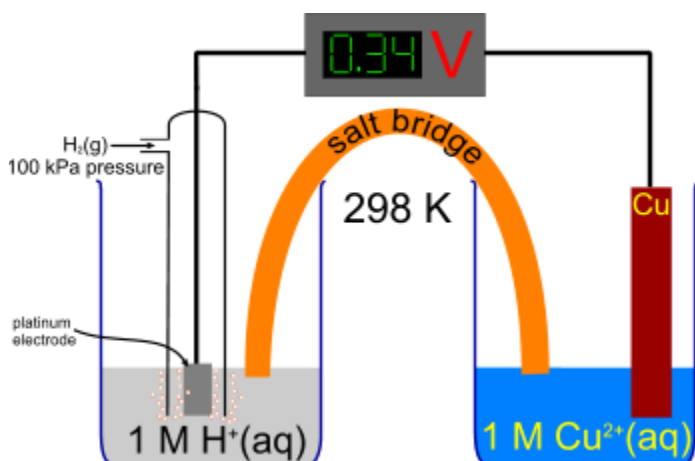
A standard Cu^{2+}/Cu half cell is connected to the standard hydrogen electrode and the voltage measured.
All concentrations must be 1.00 mol dm⁻³ and temperature would normally be 298 K.

27 State the significance of the fact that the standard electrode potential for a Cu^{2+}/Cu half-cell is positive but that for a Zn^{2+}/Zn half-cell is negative.

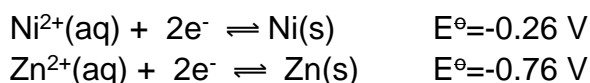Cu^{2+}/Cu - all the following are valid points:

• when this half-cell is attached to the standard hydrogen electrode the reduction of Cu^{2+} to Cu is the spontaneous reaction
• reduction of Cu^{2+} to Cu is favourable relative to the standard hydrogen electrode
• the reduction of Cu^{2+} to Cu is more favourable than the reduction of H^+ to H_2
• Cu^{2+} is a stronger oxidising agent than H^+.

Zn^{2+}/Zn - all the following are valid points:

• when this half-cell is attached to the standard hydrogen electrode the oxidation of Zn to Zn^{2+} is the spontaneous reaction
• oxidation of Zn to Zn^{2+} is favourable relative to the standard hydrogen electrode
• the reduction of Zn^{2+} to Zn is less favourable than the reduction of H^+ to H_2
• Zn is a stronger reducing agent than H_2.
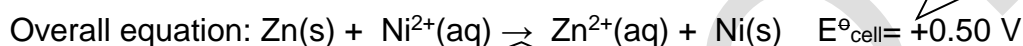
28   For each of the following cells

- calculate the cell potential,
- write an overall equation for the reaction that goes on in the cell
- state which is the positive and which the negative electrode
- identify the anode and cathode
- state which way electrons flow in the external circuit
- state which way ions flow in the salt bridge

$Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s)$ $Ag^+(aq) + e^- \rightleftharpoons Ag(s)$

$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$ $Sn^{2+}(aq) + 2e^- \rightleftharpoons Sn(s)$

$I_2(s) + 2e^- \rightleftharpoons 2I^-(aq)$ $Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$

$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$ $Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$

$Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s)$ $E^\ominus = -0.26$ V

$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$ $E^\ominus = -0.76$ V
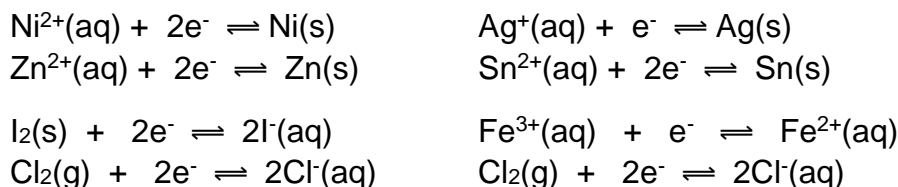
Reverse the half equation with the more negative $E^\ominus$ value

$Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s)$ $E^\ominus = -0.26$ V

$Zn(s) \rightleftharpoons Zn^{2+}(aq) + 2e^-$ $E^\ominus = +0.76$ V
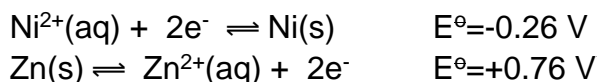
Positive value = spontaneous

Overall equation: $Zn(s) + Ni^{2+}(aq) \rightarrow Zn^{2+}(aq) + Ni(s)$ $E^\ominus_{cell} = +0.50$ V

Not a reversible arrow – you have determined in which direction the reaction is spontaneous

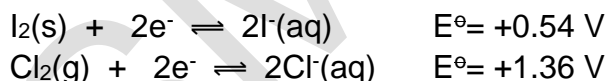Zn is negative electrode (oxidation occurs there/electrons produced)

Original $E^\ominus$ value was more -ve

Ni is the positive electrode

Original $E^\ominus$ value was more +ve

Zn is the anode – oxidation occurs

Ni is the cathode – reduction occurs

Electrons flow around the external circuit from Zn to Ni - from the negative to the positive electrode

Same continuous direction of flow of –ve charge around the circuit – electrons flow out of Zn/Zn^{2+} half-cell, therefore –ve ions must flow back in to the Zn/Zn^{2+} half-cell.

Negative ions flow through the salt bridge from the Ni/Ni^{2+} half-cell to the Zn^{2+}/Zn half-cell/positive ions flow in the opposite direction
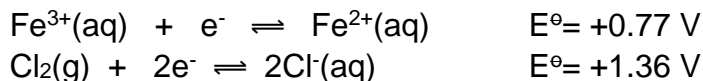
$I_2(s) + 2e^- \rightleftharpoons 2I^-(aq)$ $E^\ominus = +0.54$ V

$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$ $E^\ominus = +1.36$ V

Electrodes in both half-cells will actually be made of platinum

$Cl_2(g) + 2I^-(aq) \rightarrow 2Cl^-(aq) + I_2(s)$	I^- negative electrode	Cl_2 positive electrode	e^- flow from I_2/I^- half-cell to Cl_2/Cl^- half-cell
$E^\ominus_{cell} = +0.82$ V	I_2 anode	Cl_2 cathode	-ve ions flow from Cl_2/Cl^- half-cell to I_2/I^- half-cell

$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$ $E^\ominus = +0.80$ V

$Sn^{2+}(aq) + 2e^- \rightleftharpoons Sn(s)$ $E^\ominus = -0.14$ V
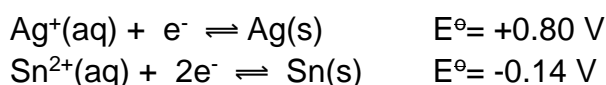
$2Ag^+(aq) + Sn(s) \rightarrow Sn^{2+}(aq) + 2Ag(s)$	Sn negative electrode	Ag positive electrode	e^- flow from Sn/Sn^{2+} half-cell to Ag^+/Ag half-cell
$E^\ominus_{cell} = +0.94$ V	Sn anode	Ag cathode	-ve ions flow from Ag^+/Ag Sn/Sn^{2+} half-cell to half-cell

$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$ $E^\ominus = +0.77$ V

$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$ $E^\ominus = +1.36$ V

Electrodes in both half-cells will actually be made of platinum

$Cl_2(g) + 2Fe^{2+}(aq) \rightarrow 2Cl^-(aq) + 2Fe^{3+}(aq)$	Fe^{2+} negative electrode	Cl_2 positive electrode	e^- flow from Fe^{2+}/Fe^{3+} half-cell to Cl_2/Cl^- half-cell
$E^\ominus_{cell} = +0.59$ V	Fe^{2+} anode	Ag cathode	-ve ions flow from Cl_2/Cl^- half-cell to Fe^{2+}/Fe^{3+} half-cell

29 For each of the cells in 28 write the cell diagram using the cell diagram convention

Salt bridge
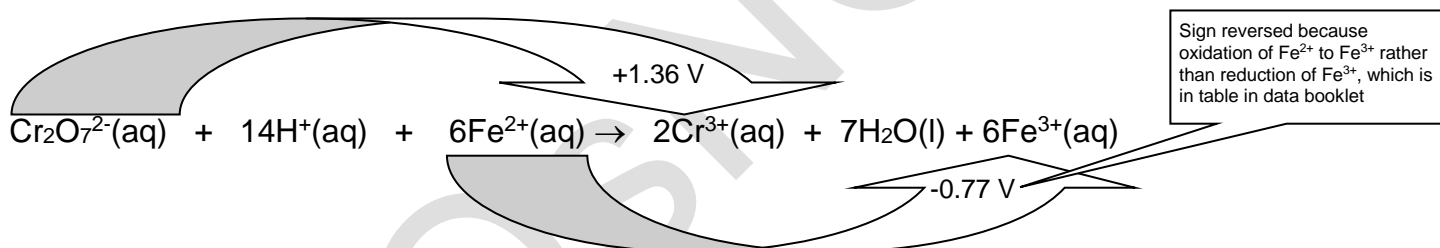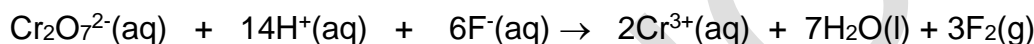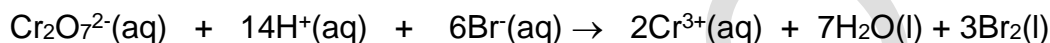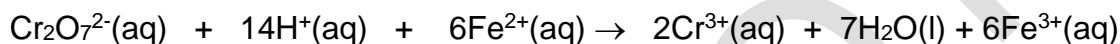
Phase boundary – species in different physical states

$Zn(s) + Ni^{2+}(aq) \rightarrow Zn^{2+}(aq) + Ni(s)$	$Zn(s)|Zn^{2+}(aq)||Ni^{2+}(aq)|Ni(s)$
$Cl_2(g) + 2I^-(aq) \rightarrow 2Cl^-(aq) + I_2(s)$	$Pt(s)|I^-(aq)|I_2(s)||Cl_2(g)|Cl^-(aq)|Pt(s)$
$2Ag^+(aq) + Sn(s) \rightarrow Sn^{2+}(aq) + 2Ag(s)$	$Sn(s)|Sn^{2+}(aq)||Ag^+(aq)|Ag(s)$
$Cl_2(g) + 2Fe^{2+}(aq) \rightarrow 2Cl^-(aq) + 2Fe^{3+}(aq)$	$Pt(s)|Fe^{2+}(aq),Fe^{3+}(aq)||Cl_2(g)|Cl^-(aq)|Pt(s)$

Both in same state therefore ,

30 Explain using electrode potentials below whether the reactions below will be spontaneous or not

$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6Fe^{2+}(aq) \rightarrow 2Cr^{3+}(aq) + 7H_2O(l) + 6Fe^{3+}(aq)$

$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6Br^-(aq) \rightarrow 2Cr^{3+}(aq) + 7H_2O(l) + 3Br_2(l)$

$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6F^-(aq) \rightarrow 2Cr^{3+}(aq) + 7H_2O(l) + 3F_2(g)$

Sign reversed because oxidation of Fe^{2+} to Fe^{3+} rather than reduction of Fe^{3+}, which is in table in data booklet

+1.36 V

$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6Fe^{2+}(aq) \rightarrow 2Cr^{3+}(aq) + 7H_2O(l) + 6Fe^{3+}(aq)$

-0.77 V

$E^\ominus_{cell} = 1.36 - 0.77 = +0.59$ V   value positive, therefore reaction is spontaneous

+1.36 V

$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6Br^-(aq) \rightarrow 2Cr^{3+}(aq) + 7H_2O(l) + 3Br_2(l)$

-1.09 V
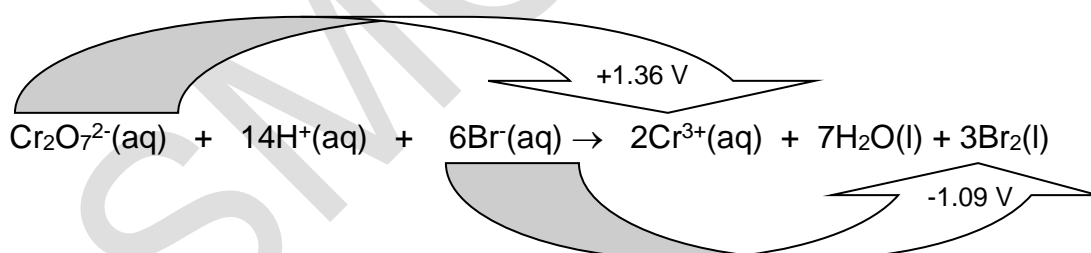
$E^\ominus_{cell} = 1.36 - 1.09 = +0.27$ V   value positive, therefore reaction is spontaneous

+1.36 V

$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6F^-(aq) \rightarrow 2Cr^{3+}(aq) + 7H_2O(l) + 3F_2(g)$

-2.87 V
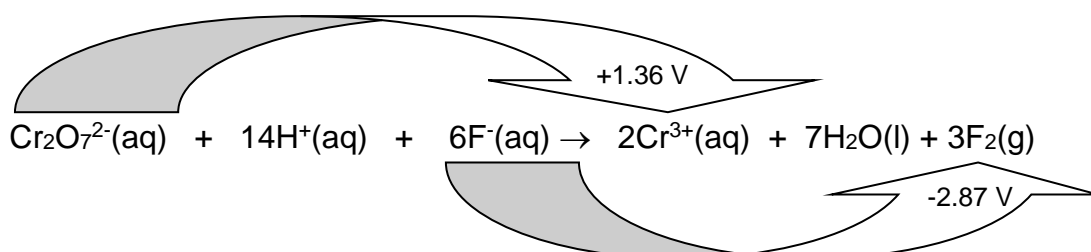
$E^\ominus_{cell} = 1.36 - 2.87 = -1.51$ V   value negative, therefore reaction is not spontaneous

31 Given the electrode potentials below select the strongest reducing agent and the strongest oxidising agent.

$U^{4+} + e^- \rightleftharpoons U^{3+}$ $E^\ominus = -0.61$ V

$Eu^{3+} + e^- \rightleftharpoons Eu^{2+}$ $E^\ominus = -0.43$ V

$Ho^{3+} + e^- \rightleftharpoons Ho$ $E^\ominus = -2.32$ V

$Ce^{4+} + e^- \rightleftharpoons Ce^{3+}$ $E^\ominus = +1.61$ V

$Pu^{4+} + e^- \rightleftharpoons Pu^{3+}$ $E^\ominus = +0.97$ V
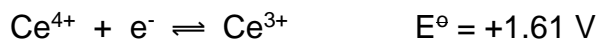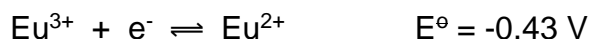
Strongest reducing agent: Ho – has most negative $E^\ominus$ value/greatest tendency to be oxidised/ greatest tendency to lose electrons.

Strongest oxidizing agent: Ce^{4+} – has most positive $E^\ominus$ value/greatest tendency to be reduced/ greatest tendency to gain electrons.

32 Using the values in 31 explain whether the following are true or false:

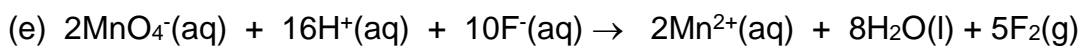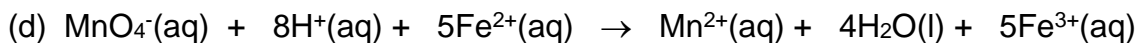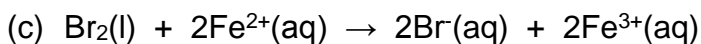(a) Eu^{3+} will oxidise Pu^{3+}
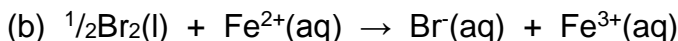
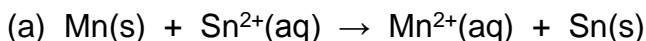(b) U^{3+} will reduce Ce^{4+}

(c) Pu^{4+} will oxidise U^{3+}

(a) FALSE Eu^{3+} is a weaker oxidising agent than Pu^{4+} since it has a less positive $E^\ominus$ value / Cell potential for $Eu^{3+} + Pu^{3+} \rightarrow Eu^{2+} + Pu^{4+}$ is negative, therefore reaction not spontaneous

(b) TRUE U^{3+} is a stronger reducing agent than Ce^{3+} since $E^\ominus$ is more negative for U^{4+}/U^{3+} / Cell potential for $U^{3+} + Ce^{4+} \rightarrow U^{4+} + Ce^{3+}$ is positive, therefore reaction is spontaneous

(c) TRUE Pu^{4+} is a stronger oxidising agent than U^{4+} since $E^\ominus$ is more positive / Cell potential for $U^{3+} + Pu^{4+} \rightarrow U^{4+} + Pu^{3+}$ is positive, therefore reaction is spontaneous

33 For each of the following reactions calculate the cell potential and ΔG and predict whether the reaction is spontaneous.

(a) $Mn(s) + Sn^{2+}(aq) \rightarrow Mn^{2+}(aq) + Sn(s)$

(b) $\frac{1}{2}Br_2(l) + Fe^{2+}(aq) \rightarrow Br^-(aq) + Fe^{3+}(aq)$

(c) $Br_2(l) + 2Fe^{2+}(aq) \rightarrow 2Br^-(aq) + 2Fe^{3+}(aq)$

(d) $MnO_4^-(aq) + 8H^+(aq) + 5Fe^{2+}(aq) \rightarrow Mn^{2+}(aq) + 4H_2O(l) + 5Fe^{3+}(aq)$

(e) $2MnO_4^-(aq) + 16H^+(aq) + 10F^-(aq) \rightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 5F_2(g)$

(a)
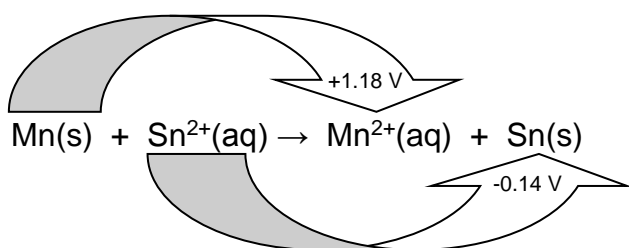
$E^{\ominus}_{cell} = 1.18 - 0.14 = +1.04$ V   value positive, therefore reaction is spontaneous

Half-equations: $Mn(s) \rightarrow Mn^{2+}(aq) + 2e^-$ $Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$
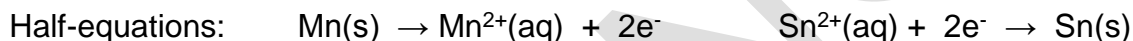
$2e^-$ transferred, therefore n=2

From data booklet

$\Delta G = -nFE = -2 \times 96500 \times 1.04 = -200720$ J mol^{-1} or -201 kJ mol^{-1}

ΔG negative, therefore reaction is spontaneous

(b)	$E^{\ominus}_{cell} = 1.09 - 0.77 = +0.32$ V	$\Delta G = -nFE = -1 \times 96500 \times 0.32 = -30880$ J mol^{-1} or -30.9 kJ mol^{-1}
Reaction is spontaneous because $E^{\ominus}_{cell}$ is positive / ΔG is negative		
(c)	$E^{\ominus}_{cell} = 1.09 - 0.77 = +0.32$ V	$\Delta G = -nFE = -2 \times 96500 \times 0.32 = -61760$ J mol^{-1} or -61.8 kJ mol^{-1}
Reaction is spontaneous because $E^{\ominus}_{cell}$ is positive / ΔG is negative		
(d)	$E^{\ominus}_{cell} = 1.51 - 0.77 = +0.74$ V	$\Delta G = -nFE = -5 \times 96500 \times 0.74 = -357050$ J mol^{-1} or -357 kJ mol^{-1}
Reaction is spontaneous because $E^{\ominus}_{cell}$ is positive / ΔG is negative		
(e)	$E^{\ominus}_{cell} = 1.51 - 2.87 = -1.36$ V	$\Delta G = -nFE = -10 \times 96500 \times (-1.36) = 1312400$ J mol^{-1} or 1312 kJ mol^{-1}
Reaction is **not** spontaneous because $E^{\ominus}_{cell}$ is negative / ΔG is positive		