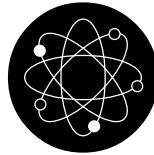


Chem Factsheet



Measuring Reducing and Oxidising Powers by Electrode Potentials

Prior Knowledge

Before you start this module you should be able to :

- (a) calculate oxidation numbers.
- (b) define and recognise oxidation, reduction and disproportionation processes in terms of oxidation number changes and electron transfer.
- (c) write half-equations.

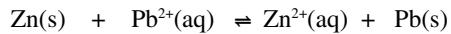
Introduction and Revision

Note: For “self-assessed” questions labelled S1, S2 etc, delete the incorrect alternatives to create a sensible explanation or answer to the question.

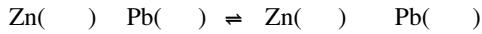
S1 During an OXIDATION process, the oxidation number of an atom becomes more **POSITIVE / NEGATIVE** and the species being oxidised **GAINS / LOSES** electrons.

S2 During a REDUCTION process, the oxidation number of an atom becomes more **POSITIVE / NEGATIVE** and the species being reduced **GAINS / LOSES** electrons.

S3 Consider the following redox equilibrium reaction:



Write the oxidation number of each species in the appropriate bracket.



Which atom / ion is :

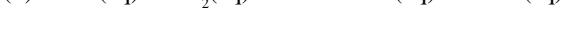
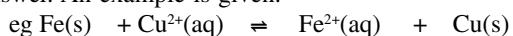
- (a) OXIDISED in FORWARD reaction? = _____
- (b) REDUCED in FORWARD reaction? = _____
- (c) the OXIDANT in FORWARD reaction? = _____
- (d) the REDUCTANT in FORWARD reaction? = _____

These examples show that, during the course of a redox reaction:

- (a) the OXIDANT (also called the “oxidising agent”) is **OXIDISED /REDUCED.**
- (b) the REDUCTANT (also called the “reducing agent”) is **OXIDISED/REDUCED.**

Q1 Identify EACH oxidant (“O”) and reductant (“R”) (for forward and backward reactions) in each of the following equations.

Write “O” or “R” below the atom, molecule or ion to show your answer. An example is given.



Q2 Metals “A”, “B”, “C” and “D” undergo the following reactions.

- (i) $\text{A(s)} + \text{B}^{2+}(\text{aq}) \rightarrow \text{A}^{2+}(\text{aq}) + \text{B(s)}$
- (ii) $\text{A(s)} + 2\text{C}^{+}(\text{aq}) \rightarrow \text{A}^{2+}(\text{aq}) + 2\text{C(s)}$
- (iii) $\text{B(s)} + 2\text{C}^{+}(\text{aq}) \rightarrow \text{B}^{2+}(\text{aq}) + 2\text{C(s)}$
- (iv) $\text{D(s)} + \text{B}^{2+}(\text{aq}) \rightarrow \text{D}^{2+}(\text{aq}) + \text{B(s)}$
- (v) $\text{D(s)} + \text{A}^{2+}(\text{aq}) \rightarrow \text{no reaction}$

Use this information to :

- (a) Place the metals “A”-“D” in order of **INCREASING reducing power.**
- (b) Place the metal ions in order of **INCREASING oxidising power.**

“Redox Conjugate Pairs” and “Half-equations”

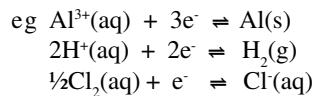
The species in any redox reaction can be “separated” into TWO pairs of reactants, each pair referred to as a **REDOX CONJUGATE PAIR**.

An **oxidant** and the species to which it is reduced form a “**REDOX CONJUGATE PAIR**”. A **reductant** and the species to which it is oxidised also form a “**REDOX CONJUGATE PAIR**”.

eg Zn²⁺ with Zn and Pb²⁺ with Pb are the “conjugate pairs” in $\text{Zn(s)} + \text{Pb}^{2+}(\text{aq}) \rightleftharpoons \text{Zn}^{2+}(\text{aq}) + \text{Pb(s)}$

The members of each conjugate pair can be connected by a **HALF-EQUATION**. This shows the **oxidant**, the **conjugate reductant** and the **number of electrons transferred**.

ie **OXIDANT + ne⁻ ⇌ REDUCTANT**



S4 Write the HALF-EQUATIONS for the conjugate pairs in the reaction studied in S3.

For Zn : _____

For Pb : _____

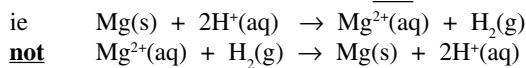
ANY redox reaction can be considered to be a “competition for electrons” between the two oxidants in the two half-equations.

Consider $\text{Mg}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Mg(s)}$ and $2\text{H}^{+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{H}_2(\text{g})$

One of the oxidants (H^+) will “take” electrons more strongly than the other oxidant (Mg^{2+}).

Equally, one of the reductants (Mg) will “give” electrons more easily than the other (H_2).

The net result is for the final equilibrium position to lie “AWAY FROM” the “STRONGER” oxidant and reductant, in other words “TOWARDS” the “WEAKER” oxidant and reductant .

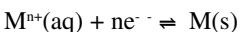


You should have used this principle in Q2!

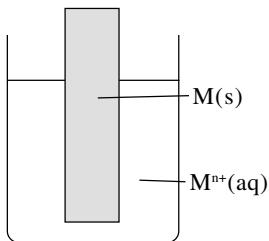
The Principle Behind Measuring Reducing and Oxidising Powers

To measure (ie QUANTIFY) the reducing power of a metal atom or the oxidising power of its ion, these HALF-REACTIONS must be used.

A GENERAL metal ion-metal half-equation would be :



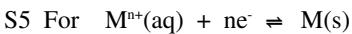
Suppose this equilibrium is setup by dipping M(s)(the reductant) into a solution of $M^{n+}(aq)$ (the oxidant) [as shown opposite] and allowing equilibrium to be reached at their interface (ie at the surface of the metal).



NB the metal (m) has many **DELOCALISED** electrons. It can easily give or absorb excess electrons, and so allow the half-reaction to proceed in its “natural (spontaneous) direction” to equilibrium.

ie METAL “M” ACTS AS AN “ELECTRODE” (a giver and taker of electrons) AS WELL AS THE REDUCTANT!

Use this and Le Chatelier’s Principle to answer S5, 6 and 7. Then check your answers.



(a) As the tendency of M^{n+} to **TAKE electrons** (i.e its OXIDISING power) **INCREASES**, this half-equation will move more to the **LEFT/RIGHT**.

This will **ADD / REMOVE** M^{n+} ions **TO / FROM** the solution causing the solution to become more **NEGATIVE / POSITIVE**.

It will also **ADD / REMOVE** electrons **TO / FROM** the delocalised “sea of electrons” of the metal causing the metal (M) to become more **NEGATIVELY / POSITIVELY** charged.

(b) As the tendency of M to **GIVE electrons** (i.e its REDUCING power) **INCREASES**, this half-equation will move more to the **LEFT/RIGHT**.

This will **ADD / REMOVE** M^{n+} ions **TO / FROM** the solution causing the solution to become more **NEGATIVE / POSITIVE**.

It will also **ADD / REMOVE** electrons **TO / FROM** the delocalised “sea of electrons” of the metal causing the metal (M) to become more **NEGATIVELY / POSITIVELY** charged.

S6 The answers from S5 suggest a method of **QUANTIFYING** redox powers. If such charges (“potentials”) can be measured then:

(a) A **MORE NEGATIVE** charge on the metal will indicate :
 (1) **LESSER / GREATER** oxidising power of the oxidant (M^{n+}) **AND**
 (2) **LESSER / GREATER** reducing power of the reductant (M)

(b) A **MORE POSITIVE** charge on the metal will show :
 (1) **LESSER / GREATER** oxidising power of the oxidant (M^{n+}) **AND**
 (2) **LESSER / GREATER** reducing power of the reductant (M)

S7 Experiment shows that zinc readily reduces **both** copper and silver ions but copper reduces only silver ions, not zinc ions. Use this information to place

- (a) the three metals in order of increasing reducing power **and**
 (b) the three metal ions in order of increasing oxidising power.

(a) _____

(b) _____

Hence, using the ideas from S6 and the above orders of reactivity, which of the **METALS** (Zn, Cu and Ag) should produce the **MOST**:

- (c) **POSITIVE** potential _____?
 (d) **NEGATIVE** potential _____?

Measuring Reducing and Oxidising Powers

These “absolute” potentials on the metal electrode **cannot be measured** because any attempt to connect a voltmeter would require a metallic connection and so create interfering potential differences.

Instead, a “**standard electrode**” is adopted. All other electrodes (redox systems) are then compared to this reference.

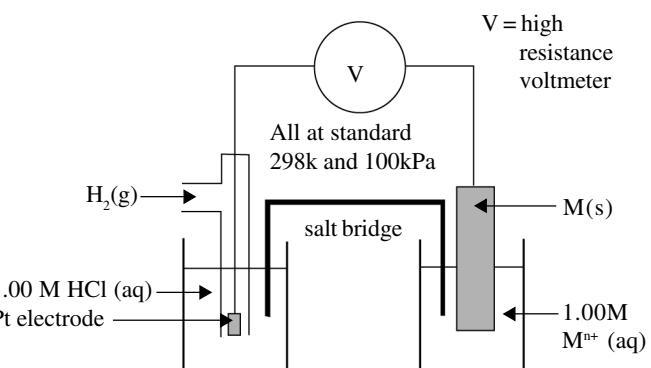
IUPAC has adopted the “**STANDARD HYDROGEN ELECTRODE (S.H.E.)**” which, by convention, is said to be at zero potential relative to all other electrode systems.

This standard hydrogen electrode consists of a platinum electrode in contact with both hydrogen ions (1.0M HCl) and hydrogen gas (see diagram).

The hydrogen ions (from fully ionised hydrochloric acid) and hydrogen molecules are at equilibrium at the surface of the platinum electrode.

The half-reaction to be measured is set up as the other half of a “cell”, allowing its potential to be measured via the high resistance voltmeter relative to the S.H.E.

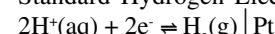
Such a general cell is shown in the following diagram. This would be used to assess the relative oxidising or reducing power of the $M^{n+}(aq) + ne^- \rightleftharpoons M(s)$ half-reaction.



The equilibria at the surface of each of the electrodes of this cell are :

Left-hand Side :

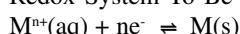
Standard Hydrogen Electrode



OA

Right-hand Side :

Redox System To Be Measured



OA

RA

Special Points

Any factor, other than “redox power”, which influences an equilibrium position must be STANDARDISED so that differences in potentials truly measure differences in redox power.

These factors include PRESSURE, TEMPERATURE and CONCENTRATION.

The standards adopted by I.U.P.A.C. are 10⁵ Pa (100kPa), 298K and 1.0 mol dm⁻³.

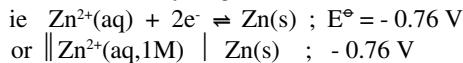
A very soluble salt must be chosen for use in the solution of Mⁿ⁺(aq) in this apparatus. The **NITRATE** of the metal is usually a good choice because they tend to be very water soluble.

The “salt bridge” is an ionic electrical connection between the two halves of the cell allowing the circuit to be completed so that the potential difference between the metals can be measured. It consists of a saturated solution of a salt such as potassium nitrate or ammonium nitrate supported in a porous medium such as filter paper or gelatin.

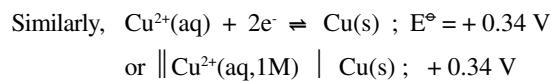
S8 Why is PLATINUM selected as the metal for use in a standard hydrogen electrode?

S9 The platinum electrode is coated with “platinum black”. This is finely divided platinum. Why is it used?

eg If the cell shown above were set up using zinc and 1.0mol dm⁻³ zinc(II) solution for the electrode system a value of -0.76 v relative to a standard hydrogen electrode would be obtained.



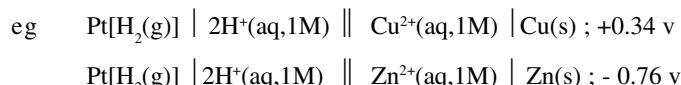
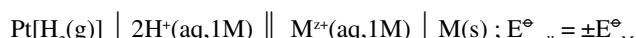
This means the zinc electrode is the negative electrode (connected to the black terminal of the voltmeter to give a forward reading) and the hydrogen electrode is the positive electrode (connected to the red terminal of the voltmeter) with a potential difference of 0.76 volts between these electrodes.



This means the copper electrode is the positive electrode (red) and the hydrogen electrode is the negative electrode (black) with a potential difference of 0.34 volts between the electrodes.

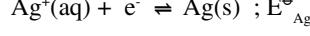
Additional Note

Using the IUPAC notation, the **whole cell** used for measuring E[⊖] values relative to a standard hydrogen electrode is represented by:



NB The reference electrode is conventionally shown on the **LEFT-HAND SIDE** of this cell representation.

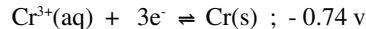
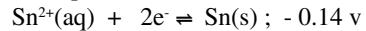
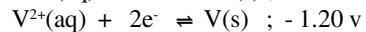
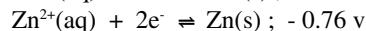
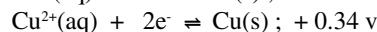
Q3(a) Draw a **fully labelled** diagram of a cell which could be used to measure the standard electrode potential for



(b) Give the IUPAC diagram for this cell.

(c) State clearly what readings need to be made in order to determine E[⊖]_{Ag}

Q4 Data: $\text{Fe}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Fe(s)} ; -0.44 \text{ v}$



(a) Use the E[⊖] values to list the metals **and hydrogen gas** in order of **increasing** reducing power

(b) Use the E[⊖] values to list the metal **and hydrogen ions** in order of **increasing** oxidising power

Q5(a) Standard electrode potentials, E[⊖] are measured relative to a standard reference electrode. What is the name of this standard reference electrode and what is its potential in volts?

(b) State **three** experimental conditions which must apply when values of E[⊖] are being determined

(c) What is the function of a *salt bridge*, and what might it contain?

The potential of a metal (M) in contact with its ions (under standard conditions) **relative** to a standard hydrogen electrode (ie as measured by the previous apparatus), is called the **STANDARD ELECTRODE POTENTIAL OF M (E[⊖]_M)**

Such “STANDARD ELECTRODE POTENTIALS” are usually quoted in data tables and provide a measure of the reducing power of the metal and the oxidising power of its cation.

If ordered in terms of E[⊖] values, this corresponds to a quantified version of the “reactivity series” or “electrochemical series”.

E[⊖]/V

$\text{Al}^{3+}(\text{aq}) + 3\text{e}^- \rightleftharpoons \text{Al(s)}$	-1.66
$\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Zn(s)}$	-0.76
$\text{Fe}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Fe(s)}$	-0.44
$\text{Pb}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Pb(s)}$	-0.13
$\text{2H}^+(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{H}_2\text{(g)}$	0.00
$\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Cu(s)}$	+0.34
$\text{Ag}^+(\text{aq}) + \text{e}^- \rightleftharpoons \text{Ag(s)}$	+0.80

As seen, E[⊖] data of this type are presented either as:

(a) A “half-equation” followed by its E[⊖] value

ie Oxidant + ne⁻ ⇌ Reductant ; E[⊖]

eg Cu²⁺(aq) + 2e⁻ ⇌ Cu(s) ; E[⊖] = +0.34 V or

(b) the “IUPAC representation” of the electrode

ie $\parallel \text{Oxidant} \mid \text{Reductant} ; E^\ominus$

eg $\parallel \text{Cu}^{2+}(\text{aq}, 1\text{M}) \mid \text{Cu(s)} ; +0.34 \text{ V}$

where “||“ represents the salt bridge and “|“ the surface of the electrode

Standard Electrode Potentials For Systems Other Than Metal-metal Ion Systems

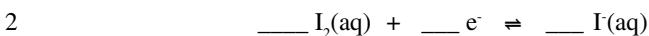
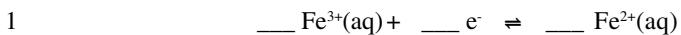
Earlier, discussion was limited to simple “metal-metal ion” redox systems.

These form a very small part of all redox reactions and the concept of “Electrode Potentials” needs to be extended to allow ALL redox systems to be quantified for oxidising or reducing power.

You will have met many such systems previously in your course. Again, they are best described by their half-equations.

S10 For each of the following examples, balance the half equations by inserting appropriate coefficients.

REMEMBER : number of electrons in half equation = oxidation number **change**



NB The oxidant and reductant are often **NOT** single substances.

eg In eg 3 of S10, oxidant = **ACIDIFIED manganese(VII) ions**

and reductant = **AQUEOUS manganese(II) ions**

This “combined” effect is shown by bracketing together (using **SQUARE** brackets) the species involved and including the coefficients from the half-equation:

eg Oxidant = $[\text{MnO}_4^-(\text{aq}) + 8\text{H}^+(\text{aq})]$

Reductant = $[\text{Mn}^{2+}(\text{aq}) + 4\text{H}_2\text{O}(\text{l})]$

As before (for metal-metal ion systems), the redox powers of these systems is quantified by measurement of E^\ominus values relative to a Standard Hydrogen Electrode.

In the metal - metal ion systems studied previously, the METAL acted as both reductant and electrode.

There is **no** metal involved in the half-reactions being considered here! Consequently an **INSERT metal electrode** has to be added to the system to allow measurement of the potential differences as before. **PLATINUM** is used for this purpose, much as it is used in the standard hydrogen electrode itself.

Experimental conditions for measurement are **standardised** as before.

S11 Standard (a) temperature = _____ (b) pressure = _____ (c) concentration = _____

NB “Standard concentration” refers **separately to EACH species** (except water) involved in the half-reaction.

eg For example 3 from S10, the cell would contain :

$1.0 \text{ mol dm}^{-3} \text{ MnO}_4^-(\text{aq})$, $1.0 \text{ mol dm}^{-3} \text{ H}^+(\text{aq})$ and $1.0 \text{ mol dm}^{-3} \text{ Mn}^{2+}(\text{aq})$

The **IUPAC system** used to represent electrodes or cells is extended to include these systems by making use of the “square bracketing” notation already mentioned.

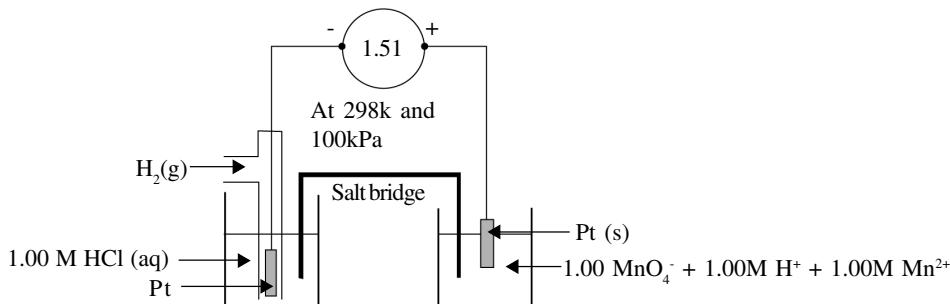
In general the electrode is represented by: $\| [\text{Oxidant}] , [\text{Reducant}] | \text{Pt}$

eg $\| [\text{MnO}_4^-(\text{aq}) + 8\text{H}^+(\text{aq})] , [\text{Mn}^{2+}(\text{aq}) + 4\text{H}_2\text{O}(\text{l})] | \text{Pt}$

eg $\| [\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14\text{H}^+(\text{aq})] , [2\text{Cr}^{3+}(\text{aq}) + 7\text{H}_2\text{O}(\text{l})] | \text{Pt}$

or $\| \text{Fe}^{3+}(\text{aq}) , \text{Fe}^{2+}(\text{aq}) | \text{Pt}$ and $\| \text{Cl}_2(\text{aq}) , 2\text{Cl}^-(\text{aq}) | \text{Pt}$ for simpler systems.

Using $\text{MnO}_4^-(\text{aq}) + 8\text{H}^+(\text{aq}) + 5\text{e}^- \rightleftharpoons \text{Mn}^{2+}(\text{aq}) + 4\text{H}_2\text{O}(\text{l})$ as an example, a practical set-up for such measurements would be :



S12 This set-up suggests the standard electrode potential for $\text{MnO}_4^-(\text{aq}) + 8\text{H}^+(\text{aq}) + 5\text{e}^- \rightleftharpoons \text{Mn}^{2+}(\text{aq}) + 4\text{H}_2\text{O}(\text{l})$ is **1.51V** / **+1.51V** / **-1.51V**

Such data can then be incorporated with previous metal-metal ion data to produce a more complete electrochemical series

	E^\ominus/V
$\text{Al}^{3+}(\text{aq}) + 3\text{e}^- \rightleftharpoons \text{Al}(\text{s})$	- 1.66
$\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Zn}(\text{s})$	- 0.76
$\text{Fe}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Fe}(\text{s})$	- 0.44
$\text{Pb}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Pb}(\text{s})$	- 0.13
$2\text{H}^+(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{H}_2(\text{g})$	0.00
$\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Cu}(\text{s})$	+ 0.34
$\text{I}^-_2(\text{aq}) + 2\text{e}^- \rightleftharpoons 2\text{I}^-(\text{aq})$	+ 0.54
$\text{Fe}^{3+}(\text{aq}) + \text{e}^- \rightleftharpoons \text{Fe}^{2+}(\text{aq})$	+ 0.77
$\text{Ag}^+(\text{aq}) + \text{e}^- \rightleftharpoons \text{Ag}(\text{s})$	+ 0.80
$\text{Br}_2(\text{aq}) + 2\text{e}^- \rightleftharpoons 2\text{Br}^-(\text{aq})$	+ 1.09
$\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14\text{H}^+(\text{aq}) + 6\text{e}^- \rightleftharpoons 2\text{Cr}^{3+}(\text{aq}) + 7\text{H}_2\text{O}(\text{l})$	+ 1.33
$\text{Cl}_2(\text{aq}) + 2\text{e}^- \rightleftharpoons 2\text{Cl}^-(\text{aq})$	+ 1.36

Q6(a) Draw a **fully labelled** diagram of a cell which could be used to measure the standard electrode potential for $\text{Fe}^{3+}(\text{aq}) + \text{e}^- \rightleftharpoons \text{Fe}^{2+}(\text{aq})$

(b) Give the IUPAC diagram for this cell.

Q7 Select:

- (a) the most oxidising species
- (b) the most reducing species shown in the previous data table.

Answers To Self-Assesed Questions

S1 — POSITIVE — LOSES

S2 — NEGATIVE — GAINS

S3 (0) (+2) (+2) (0) (a) Zn (b) Pb^{2+} (c) Pb^{2+} (d) Zn

S4 $\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Zn}(\text{s})$ and $\text{Pb}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Pb}(\text{s})$

(a) REDUCED (b) OXIDISED

S5 (a) - RIGHT - REMOVE - FROM - NEGATIVE - REMOVE - FROM - POSITIVELY -

(b) - LEFT - ADD - TO - POSITIVE - ADD - TO - NEGATIVELY

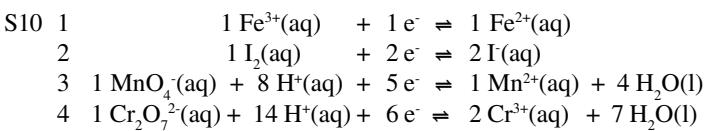
S6 (a) (1) — LESSER (2) — GREATER —

(b) (2) — GREATER (2) — LESSER —

S7 (a) $\text{Ag} < \text{Cu} < \text{Zn}$ (b) $\text{Zn}^{2+} < \text{Cu}^{2+} < \text{Ag}^+$ (c) Silver (d) Zinc

S8 It is chemically inert - it can act as an electrode without being involved in any chemical change

S9 The platinum black provides a very large surface area for adsorption of hydrogen molecules. This helps more RAPID equilibration with the H^+ ions.



S11 (a) 298K (b) 100kPa (c) 1.00 mol dm⁻³.

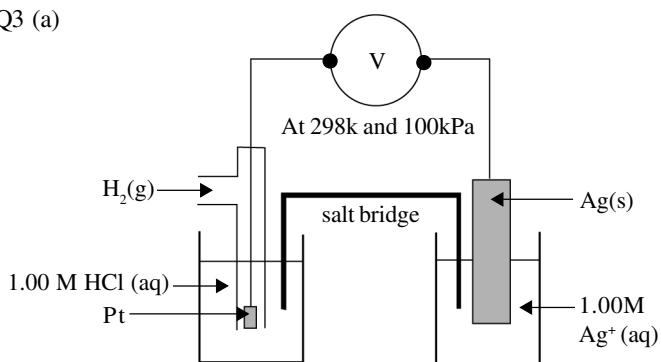
S12 +1.51V

Answers To Additional Questions

Q1 (a) O R R O (b) R O O R
 (c) O R R O (d) R O O R

Q2 (a) D < A < B < C (b) $\text{C}^+ < \text{B}^{2+} < \text{A}^{2+} < \text{D}^{2+}$

Q3 (a)



(b) $\text{Pt}[\text{H}_2(\text{g})] \mid 2\text{H}^+(\text{aq}, 1\text{M}) \parallel \text{Ag}^+(\text{aq}, 1\text{M}) \mid \text{Ag}(\text{s})$

(c) The value shown on the voltmeter and the polarity (+/-) of the silver electrode

Q4 (a) Cu < H₂ < Sn < Fe < Cr < Zn < V

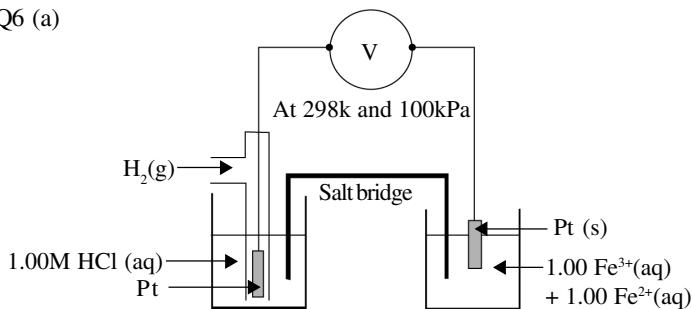
(b) $\text{V}^{2+} < \text{Zn}^{2+} < \text{Cr}^{3+} < \text{Fe}^{2+} < \text{Sn}^{2+} < \text{H}^+ < \text{Cu}^{2+}$

Q5 (a) Standard hydrogen electrode ; 0.00V

(b) 298K, 100kPa and 1.00 mol dm⁻³ for any solution

(c) To complete the circuit without use of metallic connections.
It could be a strip of filter paper soaked in saturated ammonium nitrate

Q6 (a)



(b) $\text{Pt}[\text{H}_2(\text{g})] \mid 2\text{H}^+(\text{aq}, 1\text{M}) \parallel \text{Fe}^{3+}(\text{aq}, 1\text{M}), \text{Fe}^{2+}(\text{aq}, 1\text{M}) \mid \text{Pt}(\text{s})$

Q7 (a) $\text{Cl}_2(\text{aq})$

(b) Al(s)

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