YEAR 12

CHEMISTRY

REDOX

DEFINITIONS

The old definitions of redox were as follows. You don't use them now but they are useful when looking at the oxidation of alcohols in organic chemistry

	oxidation	reduction
oxygen (O)	gain	loss
hydrogen (H)	loss	gain

This enables us to identify the redox in the following reaction;

$$Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$$

- the CO has been oxidised to CO_2
- the Fe_2O_3 has been reduced to Fe

- Fe_2O_3 is the oxidant (oxidising agent)
- CO is the reductant (reducing agent)

- oxidants are themselves reduced
- reductants are themselves oxidised

However, these definitions are not much use for the following reaction;

$$2Mg + O_2 \rightarrow 2MgO$$

- The Mg has been oxidised to MgO
- ....but where is the reduction?

We need a further definition.

The above full equation can be broken down into two ½ equations'

oxidation; $Mg \rightarrow Mg^{2+} + 2e^-$

reduction; $O_2 + 4e^- \rightarrow 2O^{2-}$

	oxidation	reduction
electrons (e^-)	loss ('OIL')	gain ('RIG')

OXIDATION NUMBERS ('oxno')

'the hypothetical charge on each atom in species, assuming ionic character'

Rules for assigning oxnos

- elements have oxnos of 0
- sum of oxnos in neutral atoms/molecules is 0
- sum of oxnos in charged ions is equal to the charge on the ion
- H has oxno of +1 in compounds, except in metal hydrides (e.g NaH) when it is -1
- O has oxno of -2 in compounds, except in peroxides (e.g H_2O_2) when it is -1

e.g for nitrogen

+5	N_2O_5, HNO_3, NO_3^-
+4	NO_2, N_2O_4
+3	N_2O_3, HNO_2, NO_2^-
+2	NO
+1	N_2O
0	N_2
-1	NH_2OH
-2	N_2H_4
-3	N^{3-}, NH_3

	oxidation	reduction
oxidation number	increase'	decrease

for example

$$MnO_4^- \ + \ 5Fe^{2+} \ + \ 8H^+ \ \rightarrow \ Mn^{2+} \ + \ 5Fe^{3+} \ + \ 4H_2O$$
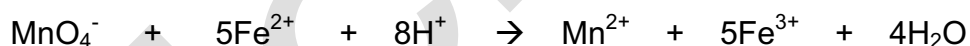
- Mn oxno has been decreased from +7 to +2......reduction
- Fe oxno has been increased from +2 to +3.......oxidation

note that the total increase in oxno in Fe [5x(+1)= +5] is equal and opposite to the total decrease in oxno in Mn [1x(-5)= -5]

DISPROPORTIONATION

"the simultaneous oxidation and reduction of a species"

e.g $2H_2O_2 \ \rightarrow \ 2H_2O \ + \ O_2$

- O oxidised from -1 to 0
- O reduced from -1 to -2

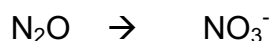And $Cl_2 \ + \ H_2O \ \rightarrow \ HCl \ + \ HClO$

CONSTRUCTING REDOX HALF-EQUATIONS AND FULL EQUATIONS

Rules for constructing redox ½ equations;

- balance for element X
- balance for O……………..using H_2O
- balance for H……………..using H^+
- balance for +/- charge…using e^-

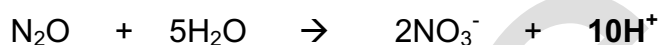**e.g 1; the oxidation of N_2O (oxno N = +1) to NO_3^- (oxno N = +5)**

$$N_2O \rightarrow NO_3^-$$

- balance for element X

$$N_2O \rightarrow \mathbf{2}NO_3^-$$

- balance for O……………..using H_2O

$$N_2O + \mathbf{5H_2O} \rightarrow 2NO_3^-$$

- balance for H……………..using H^+

$$N_2O + 5H_2O \rightarrow 2NO_3^- + \mathbf{10H^+}$$

- balance for +/- charge…using e^-

$$N_2O + 5H_2O \rightarrow 2NO_3^- + 10H^+ + \mathbf{8e^-}$$

e.g. 2; the reduction of $Cr_2O_7^{2-}$ (oxno Cr = +6) to Cr^{3+} (oxno Cr = +3)

$$Cr_2O_7^{2} \rightarrow Cr^{3+}$$

- balance for element X

$$Cr_2O_7^{2-} \rightarrow \mathbf{2}Cr^{3+}$$

- balance for O……………..using H_2O

$$Cr_2O_7^{2-} \rightarrow 2Cr^{3+} + \mathbf{7H_2O}$$

- balance for H……………..using H^+

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

- balance **for +/-** charge…using e^-

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

These two redox half equations can now be combined to give a full equation

Oxidation

$$N_2O \ + \ 5H_2O \ \rightarrow \ 2NO_3^- \ + \ 10H^+ \ + \ 8e^-$$

Reduction

$$Cr_2O_7^{2-} \ + \ 14H^+ \ + \ 6e^- \rightarrow \ 2Cr^{3+} \ + \ 7H_2O$$
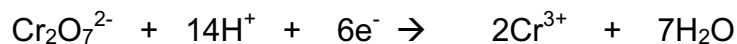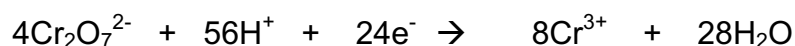
To cancel out the e^-, the oxidation ½ equation needs to be multiplied by 3 and the reduction ½ equation needs to be multiplied by 4. This gives us 24 e^- each side.

oxidation

$$3N_2O \ + \ 15H_2O \ \rightarrow \ 6NO_3^- \ + \ 30H^+ \ + \ 24e^-$$

reduction

$$4Cr_2O_7^{2-} \ + \ 56H^+ \ + \ 24e^- \rightarrow \ 8Cr^{3+} \ + \ 28H_2O$$
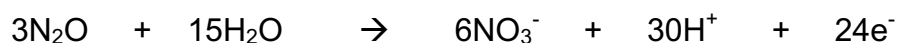
When adding these two ½ equations together, not only do the e^- cancel out, but the H_2O and H^+ must also be simplified.

$$\mathbf{4Cr_2O_7^{2-} \ + \ 26H^+ \ + \ 3N_2O \ \rightarrow \ 8Cr^{3+} \ + \ 6NO_3^- \ + \ 13H_2O}$$

Finally, check the numbers of each element and the charge on each side of the equation;

left		right
8	Cr	8
6	N	6
26	H	26
31	O	31
18+	+/-	18+

STANDARD REDUCTION POTENTIALS

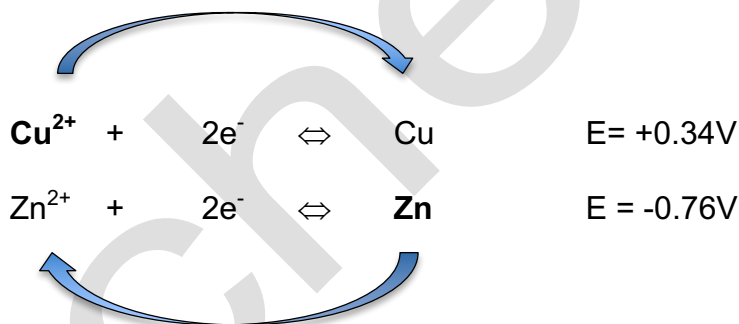The data sheet contains a list of about fifty standard reduction potentials (SRPs). Important things to note are;

- they are all ½ equations. Two ½ equations are needed to construct a full equation

- they are written as reductions (gain of e⁻) in the forwards direction
- and oxidations (loss of e⁻)in the backwards direction

- oxidants are on the left
- reductants are on the right

- the strongest oxidants are at the top left and the weakest at the bottom left
- the strongest reductants are at the bottom right and the weakest at the top right

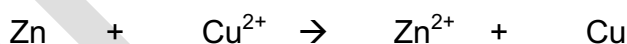SRPs can be used as predictors of the feasibility of chemical reactions;

"any oxidant on the left hand side of the SRP table is able to oxidise any reductant below it on the right hand side of the table"

e.g   does Zn metal react with Cu^{2+} ?

Cu^{2+} is an oxidant and Zn is a reductant.

$$\textbf{Cu}^{\textbf{2+}} \quad + \quad 2e^{-} \quad \Leftrightarrow \quad Cu \qquad E= +0.34V$$

$$Zn^{2+} \quad + \quad 2e^{-} \quad \Leftrightarrow \quad \textbf{Zn} \qquad E = -0.76V$$

Combining the two ½ equations gives;

$$Zn \quad + \quad Cu^{2+} \quad \rightarrow \quad Zn^{2+} \quad + \quad Cu$$

Combining the two E values gives
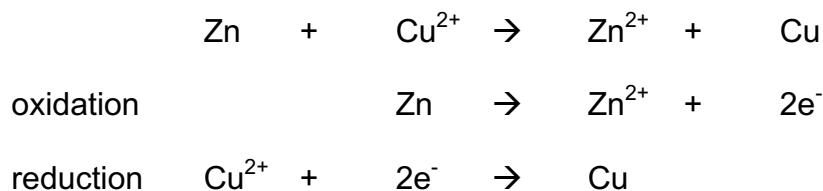
$$E_{tot} \quad = +0.34V \quad + \quad +0.76V$$

$$= +1.10V$$

note that

- when a ½ equation is reversed, its E value reverses
- a positive E_{tot} indicates a favourable reaction

Yes, the reaction should occur.

GALVANIC CELLS

We have already seen that redox reactions consist of two ½ reactions, an oxidation and a reduction. e.g. the displacement reaction when zinc metal is reacted with Cu^{2+} ions;

$$Zn \quad + \quad Cu^{2+} \quad \rightarrow \quad Zn^{2+} \quad + \quad Cu$$

oxidation $\quad\quad\quad\quad Zn \quad \rightarrow \quad Zn^{2+} \quad + \quad 2e^-$

reduction $\quad Cu^{2+} \quad + \quad 2e^- \quad \rightarrow \quad Cu$
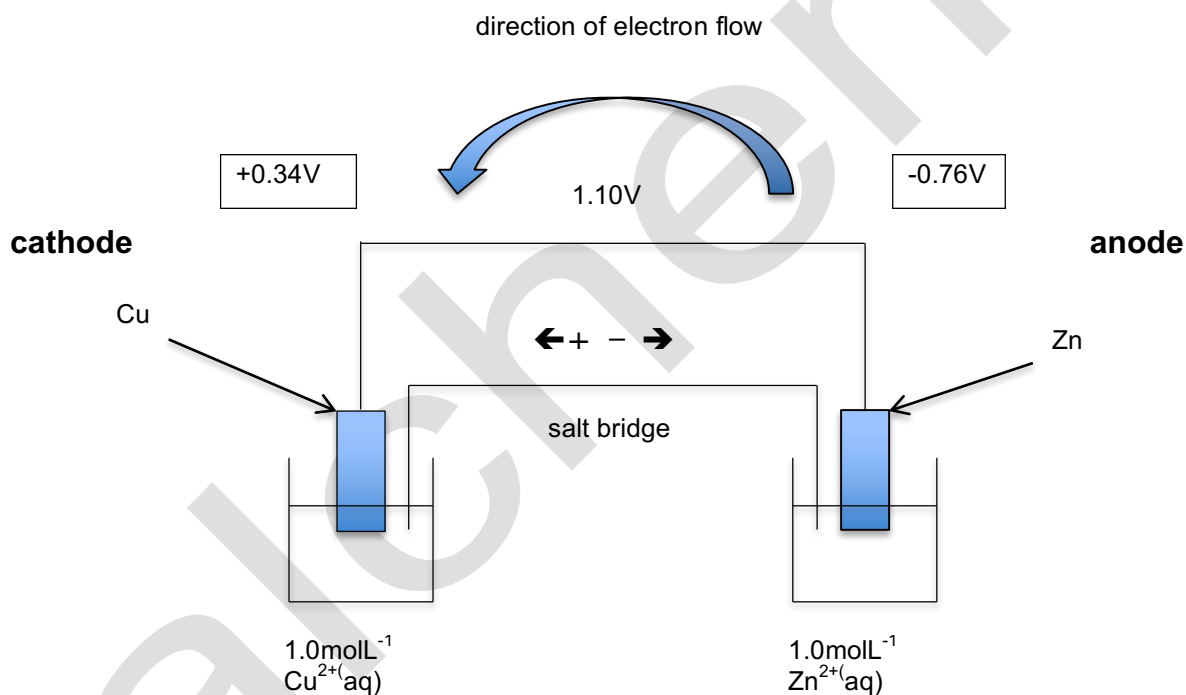
- electron transfer occurs within the reaction mixture

In galvanic cells

- the two ½ reactions are physically separated
- electron transfer occurs through an external circuit
- an electric current is produced

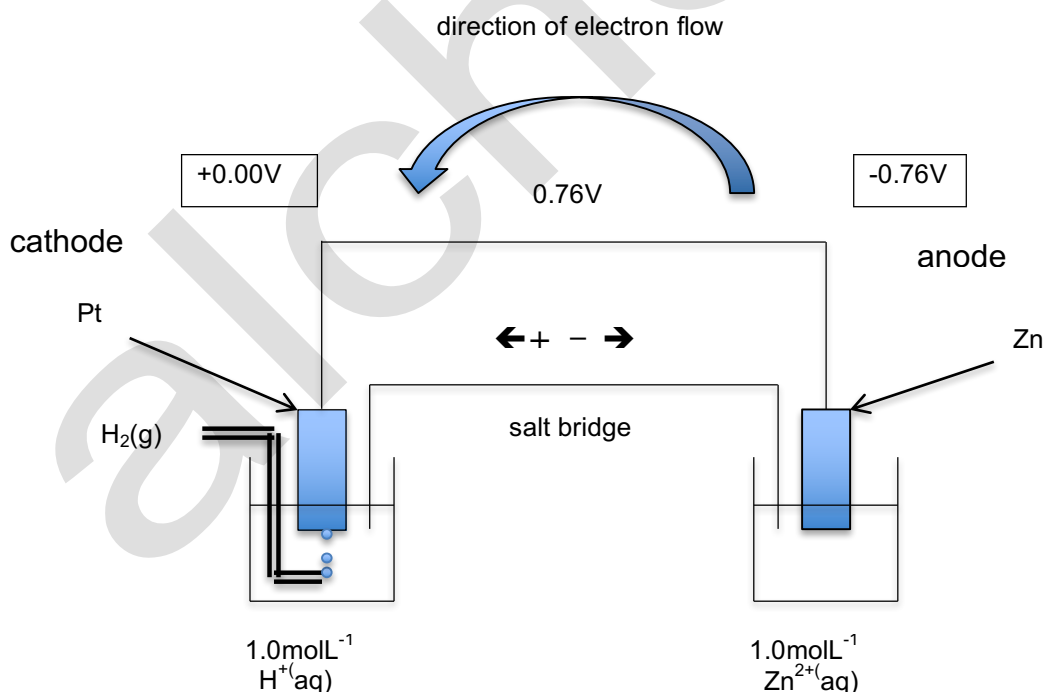e.g. for the same reaction as above;

- the two electrodes are connected by a wire

- the two solutions are connected by a salt bridge, usually $KNO_3(aq)$......soluble so ions can conduct electric current ....and does not interfere with redox reactions by forming precipitates or acting as oxidant/reductant itself.

- electrons in the wire flow from the more negative electrode to the more positive electrode

- ions in the salt bridge flow as shown, note the flow of e^- in the wire and negative ions in the salt bridge make a circuit.

- **r**eduction occurs **a**t the **c**athode ("RAC") ($Cu^{2+} + 2e^- \rightarrow Cu$)
- oxidation occurs at the anode ($Zn \rightarrow Zn^{2+} + 2e^-$)

- the copper cathode increases in mass
- the zinc anode decreases in mass
- the blue colour of the Cu^{2+} solution fades

- the cell EMF (voltage) is equal to the difference between the E values of the two ½ cells; in this case 1.10V

- as the cell discharges, the difference between the two E values decreases (no longer under standard conditions; see below) until eventually *equilibrium* is reached and the EMF (voltage) of the cell is zero.

The Standard Hydrogen Electrode

- it is not possible to measure the potential (E, voltage) of a single half-cell.
- one can only measure the potential *difference* between two ½ cells
- the ½ cell that is chosen as the standard is the standard hydrogen electrode, which is given a SRP of exactly zero.

$$2H^+ + 2e^- \Leftrightarrow H_2 \qquad E = 0.00V$$

direction of electron flow

+0.00V   0.76V   -0.76V

cathode   anode

Pt   Zn

$\leftarrow + \quad - \rightarrow$

$H_2(g)$ salt bridge

1.0molL^{-1} 1.0molL^{-1}
H^+(aq) Zn^{2+}(aq)

Standard Conditions

- solutions have a concentration of $1.00 mol L^{-1}$

- gases have a pressure of $101.3 kPa$ ($1.00 atm$)

- temperature of $25^{o}C$

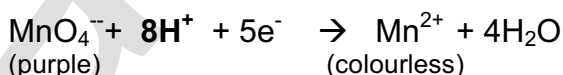# Limitations of Standard Reduction Potentials

- only apply under standard conditions

- the can be used as an indicator of feasibility of reactions, but give no indication of rate of reaction.

REDOX TITRATIONS

quantitative reaction between an oxidant and a reductant

oxidants	reductants
MnO_4^-/H^+	**Fe^{2+}**
$Cr_2O_7^{2-}/H^+$	**$C_2O_4^{2-}$**
	$H_2C_2O_4$ (HOOCCOOH)

- reductants in **bold** above can be used as primary standards. The two oxidants can not be used as primary standards as they are not available in high purity, and are also unstable once made up into aqueous solutions.

- permanganate and dichromate need to be acidified because of their ½ equations;

$$Cr_2O_7^{2-} + \mathbf{14H^+} + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$
(orange)   (green)

$$MnO_4^- + \mathbf{8H^+} + 5e^- \rightarrow Mn^{2+} + 4H_2O$$
(purple)   (colourless)

- H_2SO_4 used as source of H^+ because……..

- the NO_3^- ions in nitric acid can also act as an oxidant

- the Cl^- ions in HCl can be oxidized to Cl_2 by MnO_4^-

- no indicators required because reactions are 'self-indicating' with their own colour changes

ELECTROLYTIC CELLS

These are the opposite process to an glavanic cell.

Galvanic ells convert chemical energy into electrical energy.

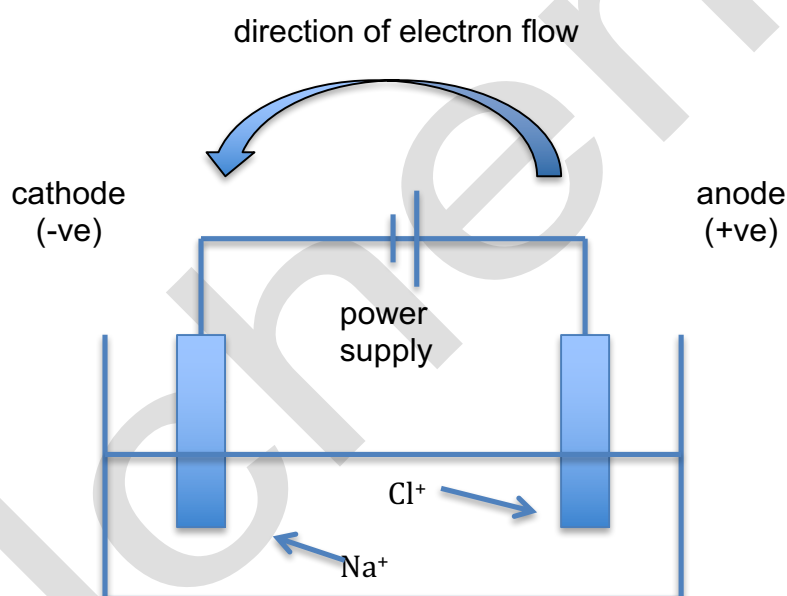Electrolytic cells convert electrical energy into chemical energy.

The electrolysis of molten salts is performed with inert (usually graphite or platinum) electrodes and an external power supply.

At the –ve cathode, reduction occurs (reduction of positive metal ions to the metallic element)

At the +ve anode, oxidation occurs (oxidation of negative non-metal ions to the non-metallic element)

Note that the polarities of the two electrodes are the opposite to galvanic cells, but the process occurring at each electrode remains the same (n.b, 'RAC", **r**eduction **a**t **c**athode)
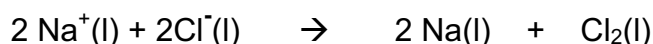
e.g the electrolysis of molten sodium chloride

direction of electron flow

cathode
(-ve)

power
supply

anode
(+ve)

Cl^+

Na^+

cathode reaction $\qquad$ $Na^+(l) + e^- \quad \rightarrow \quad Na(l)$

anode reaction $\qquad$ $2Cl^-(l) \quad \rightarrow \quad Cl_2(l) \quad + \quad 2e^-$

overall reaction $\qquad$ $2\ Na^+(l) + 2Cl^-(l) \quad \rightarrow \quad 2\ Na(l) \quad + \quad Cl_2(l)$

The characteristics of the anode and cathode in galvanic and electrolytic cells can be summarized as follows

	GALVANIC CELLS		ELECTROLYTIC CELLS	
	Polarity	Process	Polarity	Process
Anode	-ve	oxidation	+ve	oxidation
Cathode	+ve	reduction	-ve	reduction