Redox Equilibria

① Find the emfs of the following cells:

a) $Al_{(s)} | Al^{3+}_{(aq)} || Cd^{2+}_{(aq)} | Cd_{(s)}$
b) $Ag_{(s)} | Ag^{+}_{(aq)} || Cu^{2+}_{(aq)} | Cu_{(s)}$
c) $Pt_{(s)} | Fe^{2+}_{(aq)}, Fe^{3+}_{(aq)} || Cl_{2(g)}, 2Cl^{-}_{(aq)} | Pt_{(s)}$

$E^{\ominus}_{cell} = E^{\ominus}_{RHand} - E^{\ominus}_{LHand}$

Values ($E^{\ominus}$)
$Al^{3+}/Al = -1.66$ volts
$Cd^{2+}/Cd = -0.40$ volts
$Ag^{+}/Ag = +0.80$ volts
$Cu^{2+}/Cu = +0.34$ volts
$Fe^{3+}/Fe^{2+} = +0.77$ volts
$Cl_2/2Cl^{-} = +1.36$ volts

a) $-0.40 - (-1.66) = +1.26$ volts
b) $+0.34 - (+0.80) = -0.46$ volts
c) $+1.36 - (+0.77) = +0.59$ volts.

② Calculate the unknown $E^{\ominus}$ values from $E^{\ominus}_{cell}$ and the $E^{\ominus}$ given values below:

a) Cr^{3+}/Cr if $E^{\ominus}_{cell} = -0.49$ volts for $Ni_{(s)} | Ni^{2+}_{(aq)} || Cr^{3+}_{(aq)} | Cr_{(s)}$
b) V^{3+}/V^{2+} if $E^{\ominus}_{cell} = -2.11$ volts for $Pt_{(s)} | V^{2+}_{(aq)}, V^{3+}_{(aq)} || Mg^{2+}_{(aq)} | Mg_{(s)}$
c) Mn^{2+}/Mn if $E^{\ominus}_{cell} = +0.79$ volts for $Mn_{(s)} | Mn^{2+}_{(aq)} || Cd^{2+}_{(aq)} | Cd_{(s)}$

$E^{\ominus}_{cell} = E^{\ominus}_{RHand} - E^{\ominus}_{LHand}$

Values ($E^{\ominus}$)
$Ni^{2+}/Ni = -0.25$ volts
$Mg^{2+}/Mg = -2.37$ volts
$Cd^{2+}/Cd = -0.40$ volts

a) $-0.49 = ? - (-0.25) = -0.74$ volts
b) $-2.11 = -2.37 - ? = -0.26$ volts
c) $+0.79 = -0.40 - ? = -1.19$ volts

③ Which of the following reactions are feasible?

a) $3Co^{2+}(aq) + 2Al(s) \rightarrow 3Co(s) + 2Al^{3+}(aq)$

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

c) $2Br^{-}(aq) + Cl_2(g) \rightarrow Br_2(l) + 2Cl^{-}(aq)$

$E^{\ominus}cell = R\,Hand - L\,Hand$

a) $Co^{2+}(aq) + 2e^{-} \rightleftharpoons Co(s)$ $E^{\ominus} = -0.28$ volts

$Al^{3+}(aq) + 3e^{-} \rightleftharpoons Al(s)$ $E^{\ominus} = -1.66$ volts

(feasible) $E^{\ominus}cell = -0.28 - (-1.66) = \underline{+1.38 \text{ volts}}$

b) $Na^{+}(aq) + e^{-} \rightleftharpoons Na(s)$ $E^{\ominus} = -2.71$ volts

$Mg^{2+}(aq) + 2e^{-} \rightleftharpoons Mg(s)$ $E^{\ominus} = -2.37$ volts

(Not feasible) $E^{\ominus}cell = -2.71 - (-2.37) = -0.34$ volts

c) $Br_2(l) + 2e^{-} \rightleftharpoons 2Br^{-}(aq)$ $E^{\ominus} = +1.07$ volts

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

(feasible) $E^{\ominus}cell = +1.36 - (+1.07) = +0.29$ volts

Values ($E^{\ominus}$)
$Al^{3+}/Al = -1.66$ volts
$Co^{2+}/Co = -0.28$ volts
$Na^{+}/Na = -2.71$ volts
$Mg^{2+}/Mg = -2.37$ volts
$Br_2/2Br^{-} = +1.07$ volts
$Cl_2/2Cl^{-} = +1.36$ volts
$Fe^{3+}/Fe^{2+} = +0.77$ volts

④ Potassium Manganate(VII) solution acidified with dilute sulphuric acid, and potassium dichromate (VI) solution acidified with dilute sulphuric acid are both oxidising agents. Are either, or both, strong enough to oxidise chloride ions to chlorine?

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

$MnO_4^{-} + 8H^{+}(aq) + 5e^{-} \rightleftharpoons Mn^{2+}(aq) + 4H_2O(l)$ $E^{\ominus} = +1.51$ volts

$Cr_2O_7^{2-}(aq) + 14H^{+}(aq) + 6e^{-} \rightleftharpoons 2Cr^{3+}(aq) + 7H_2O(l)$ $E^{\ominus} = +1.33$ volts

MnO_4^{-} - feasible as less negative so itself will be reduced!

$Cr_2O_7^{2-}$ Not feasible as more negative so will reduce chlorine to Cl^{-}!

BUT! ∵ often acidified by more than 1 mol dm^{-3} HCl ∴ not standard conditions and in reality will work!

(5) Water can be oxidised to oxygen according to the equation

$$2H_2O \longrightarrow O_2 + 4H^+_{(aq)} + 4e^-$$

Given the following $E^\ominus$ values, what can you use to oxidise water in this way?

$MnO_4^-{}_{(aq)} + 8H^+_{(aq)} + 5e^- \rightleftharpoons Mn^{2+}_{(aq)} + 4H_2O_{(l)}$	$E^\ominus = +1.51$ volts
$Cl_2 + 2e^- \rightleftharpoons 2Cl^-_{(aq)}$	$E^\ominus = +1.36$ volts
$Cr_2O_7^{2-}{}_{(aq)} + 14H^+_{(aq)} + 6e^- \rightleftharpoons 2Cr^{3+}_{(aq)} + 7H_2O_{(l)}$	$E^\ominus = +1.33$ volts
$O_{2\,(g)} + 4H^+_{(aq)} + 4e^- \rightleftharpoons 2H_2O_{(l)}$	$E^\ominus = +1.23$ volts
$Br_{2(l)} + 2e^- \rightleftharpoons Br^{2-}{}_{(aq)}$	$E^\ominus = +1.07$ volts

All of them except Bromine! (Bromine is the better reducer).

<u>BUT!</u> = Not true as $Cr_2O_7^{2-}$ never oxidises water to oxygen. This is because EA is too high!