CITY OF LIVERPOOL

EDUCATION COMMITTEE

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FORM or CLASS U6 Sc.

SUBJECT Chemistry Practical.

GROUP I.

E° → Li

	abnormal I.E ↑	↓ reaction with water	↓ reaction with chlorine	↓ stability of $HCO_3^{\ominus}$ and $CO_3^{\ominus}$
Li				← no $HCO_3^{\ominus}$
Na				all form solid $HCO_3^{\ominus}$ that are ionic.
K				
Rb				
Cs				

E°:

$$\begin{tikzcd} M^{+}(aq) + e^- \arrow[r, "\Delta H"] & M(s) \arrow[d, "\cancel{\Delta H\ hyd}\ \Delta H\ sub."] \\ M^{+}(g) + e^- \arrow[u, "\Delta H\ hyd"'] & M(g) \arrow[l, "I.E"'] \end{tikzcd}$$

ΔH hyd. large for Li^+ ∴ swamps others and Li^+ is the largest ΔH – others tend to increase down group Li > K ≃ Rb > Cs > Na
↳ (High I.E for Na(g))

Reaction with Fluorides the U becomes much larger than for Cl ∴ stability is reversed.

Carbonates and $HCO_3^{\ominus}$ are alkaline in solⁿ
(Li_2CO_3 insoluble cf $MgCO_3$)

P.T.O.

eg $Na_2CO_3(s) \xrightarrow{H_2O} 2Na^+(aq) + CO_3^{2-}(aq)$

but: $CO_3^{2-}(aq) + 2H_2O \rightleftharpoons H_2CO_3 + 2OH^-$

∴ alkaline sol^n.

Similarly $NaHCO_3 \xrightarrow{H_2O} Na^\oplus + HCO_3^\ominus$

then $HCO_3^\ominus + H_2O \rightleftharpoons H_2CO_3 + OH^\ominus$

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hydrogen carbonates decompose on heating

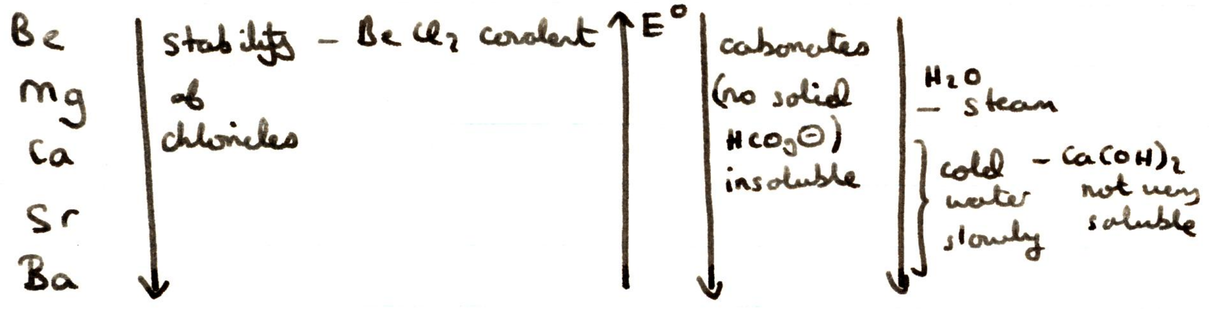
$2MHCO_3 \rightarrow M_2CO_3 + CO_2 + H_2O$

Carbonates are much more stable (except Li_2CO_3 cf $MgCO_3$) stability of both increases down group. $M_2CO_3 \rightarrow M_2O + CO_2$

requires heating

$O^{2-} < CO_3^{2-}$, so with small cation the lattice energy of M_2O is large compared to M_2CO_3 ∴ $U(Li_2CO_3) < U(Li_2O)$ ∴ Li_2CO_3 tends to decompose into Li_2O. This is less significant as the cation gets bigger, $U(Cs_2CO_3)$ is only just less than $U(Cs_2O)$ ∴ Cs_2CO_3 stable to a high temp.

GROUP II



Not as reactive as group I. ~~chlorides~~ Do not react as strongly with chlorides. All ions are heavily hydrated. Be^{2+} only exists as BeF_2 or $Be(H_2O)_4^{2+}$ ie $BeSO_4.4H_2O$ all other Be compounds are covalent (cf $Al(H_2O)_6^{3+}$) acidic in sol^n ∴ displaces CO_2 from CO_3^{2-} and $BeCO_3$ does not exist.

All carbonates are white insoluble solids, thermal stability increases down group. Hydrogencarbonates only exist in solution.

solubility of halides (and all compounds) depends on size of ions:

$$\begin{tikzcd}
MX(s) \arrow[rr] \arrow[dr, "-U"'] & & M^{2+}(aq) + X^{2-}(aq) \\
& M^{2+}(g) + X^{2-}(g) \arrow[ur, "\Delta H \text{ hyd.}"'] &
\end{tikzcd}$$

U is large for small ions ∴ tend to be insoluble if two small ions involved (U terms tend to be larger than ΔH hyd in this case). Two large ions have small ΔH hyd, not likely to be larger than U ∴ tend to be insoluble. One large one small has moderate U and ΔH hyd ∴ tend to be soluble.

Mg compounds ~~also~~ are sometimes covalent. Mg forms the only direct compounds with N_2 (like Li) eg Mg_3N_2, Li_3N.

GROUP III

B - non metal - all covalent
Al - metal

B has no metallic prop, no B_c^{3+}. no hydrated ionic salts. Forms Borides and hydrides TiB_2, B_nH_{n+4} B_nH_{n+6}. Al weak metal, Al^{3+} polarising formed in oxide and fluoride - rest covalent. $Al(H_2O)_6^{3+}$ acidic ∴ no carbonate. $Al(OH)_3(H_2O)_3$ is amphoteric. Al will form ionic crystaline salts of $Al(H_2O)_6^{3+}$ which is larger and more stable - hydrated nitrate and sulphate.

Boron halides are covalent and lewis acids. H_3N + BF_3 forms stable solid H_3NBF_3. B-O bond is strong, hydrolised by water $BCl_3 + 3H_2O \rightarrow 3HCl + H_3BO_3$

$B-F > B-O$ ∴ $4BF_3 + 3H_2O \longrightarrow 3HBF_4 + H_3BO_3$

$B(OH)_3$ acts as a lewis acid

$$B(OH)_3 + 2H_2O \rightarrow B(OH)_4^- + H_3O^{\oplus}$$

Prep. Boron halides by direct comb. not in H_2O. No dimers of halides - steric reasons.

Al^{3+} highly polaising ∴ only AlF_3 is ionic. $AlCl_3$ solid is pollymeric,

$$(AlCl_3)_2\,(s) \xrightarrow{200°C} Al_2Cl_6\,(g) \xrightarrow{600°C} AlCl_3\,(g)$$

Solid $AlCl_3$ is still a Lewis acid.

$$\underset{excess}{AlCl_3} + H_2O \rightarrow Al(OH)_3 + HCl$$

$$AlCl_3 + \underset{excess}{H_2O} \rightarrow Al(H_2O)_6^{3+}.\,3Cl^-$$

high ΔH hyd compensates for high I.E. Can crystalise $Al(H_2O)_6^{3+}.\,3Cl^-$. Not easy to convert anhyd ⇔ hydrated compounds

$$Al(H_2O)_6Cl_3 \xrightarrow{heat} Al(OH)_3 + 3HCl + 3H_2O$$

$$\downarrow Al_2O_3$$

Prepare anhyd. by direct comb. with dry Cl_2, passed over hot Al shavings using soda lime to prevent moisture and collect excess Cl_2. Hydrated salt has **no** Lewis acid properties.

$$Al(H_2O)_6^{3+}(aq) \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} [Al(H_2O)_5OH]^{2+}(aq) + H^+(aq)$$

$$[Al(H_2O)_5OH]^{2+} + OH^- \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} [Al(H_2O)_4(OH)_2]^+ + H_2O$$

$$[Al(H_2O)_4(OH)_2]^+ + OH^- \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} Al(H_2O)_3(OH)_3\downarrow + H_2O$$

white gelatinous.

$Al(H_2O)_3(OH)_3$ is amphoteric

$Al(H_2O)_3(OH)_3 + OH^- \rightarrow Al(H_2O)_2(OH)_4^{\ominus}$

no further reaction due to neg. charges.

c.f $Cr(H_2O)_6^{3+}$

GROUP IV

carbon	non metal	ox. 4	inert pair effect. ↓
Silicon		ox. 4	
Ge	- metalloid	ox. 4 (some 2)	
Sn	metals.	ox. 4 = ox. 2	
Pb		ox. 2 (some 4)	

M^{4+} unfavourable ∴ covalent { PbF_4, SnF_4 ionic)

all are sp^3 hybridised - carbon only 4 bonds rest can hybridise more, & double bonds are less favourable down group - only C really.

Cl atoms too large for $SiCl_6^{2-}$

Carbon – diamond inert, graphite attacked by ox. agents eg HNO_3 conc. H_2SO_4. Combines directly with a few elements F_2, O_2, S, Cl_2 slowly under forcing conditions.

Silicon – unreactive, when powdered reacts with some metals eg Mg and halogens.

$2Mg + Si \rightarrow Mg_2Si \xrightarrow{H_2O} SiH_4$ inflamable.

Stable to all acids except HF

$Si + 6HF \rightarrow H_2SiF_6 + 2H_2$

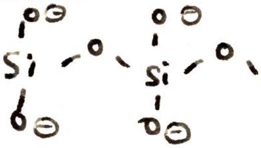
strong SiF bonds formed.

Will react with alkalis

$Si + 2OH^- + H_2O \rightarrow SiO_3^{2-} + 2H_2\uparrow$

$\downarrow$

macromollecular -



Ge – similar to Si, reacts with $HNO_3 \rightarrow GeO_2$.

Sn – mainly metallic, not very reactive. Direct reactions with O_2, S and halogens (ox. agents) give Sn (IV)

$Sn + \underset{\text{ox. agent}}{HNO_3} \longrightarrow \underset{\text{white ppt.}}{SnO_2 \cdot x\,H_2O}$

With none ox acids eg HCl Sn(II) favoured.

Pb - mainly Pb(II) with O_2, halogens (except F_2)

$$2Pb + O_2 \rightarrow 2PbO$$

$$6PbO + \underset{excess}{O_2} \xrightarrow{450°C} Pb_3O_4$$ dilead (II) lead (IV) oxide.

PbO_2 cannot be formed directly. No reaction with H_2SO_4 or cold dil. HCl, $PbCl_2$ only soluble in hot H_2O. With hot conc. $HNO_3 \rightarrow$ Pb(II) nitrate + oxides of nitrogen. $Pb + 2OH^- + 2H_2O \rightarrow Pb(OH)_4^{2-} + H_2\uparrow$

Halides.

C - all are tetravalent and made by direct comb.

$C-F > C-O > C-Cl > C-Br > C-I$ ∴ $\leq Cl$ thermodynamically unstable to water, CCl_4 is stable to water however as the reaction has a high E_A (in order to react the H_2O would have to donate into the prohibitively high 3s of carbon S_N2 mechanism). Will hydrolise slowly if boiled with OH^-. CF_4 is inert.

Si - all tetrahalides formed by direct combination. all are easily hydrolised, retaining strong Si-F bond

$3SiF_4 + 3H_2O \rightarrow 2H_2SiF_6 + H_2SiO_3$

SiF_6^{2-} ion

others violently : $SiCl_4 + 3H_2O \rightarrow HCl + H_2SiO_3$

$(SiO_2 . H_2O)$

Ge - 4 tetrahalides similar to SiX_4 ; $GeCl_2$ exists but is easily disproportionated

$$2GeCl_2 \xrightarrow[75^\circ C]{} GeCl_4 + Ge$$

dibromide , ~~diiode~~ diiodide exist , flourine is too strong as ox. agent.

Sn - all four di- and four tetra-halides are known. Under ox. conditions (ie with X_2) tetrahalides form directly. SnF_4 white crystaline solid , others are covalent and violently hydrolised. SnI_4 - heat Sn with I_2 in CCl_4 reflux for several days. $SnCl_4$ fuming liquid, forms $[Sn(H_2O)_4{}^{4+} . 4Cl^- . H_2O]$ when water added cf. $Al(H_2O)_6{}^{3+} . 3Cl^-$.

Di-halides are ionic decreasing $SnF_2 - SnI_2$. all stable. Sn^{2+} will ~~reduces~~ reduce Fe^{3+} to Fe^{2+}

SnX_3^- and SnX_4^{2-} formed from SnX_2 + excess X^-

Prep with HX - reducing conditions

$$Sn + 2HX_{(aq)} \rightarrow SnX_2 + H_2\uparrow$$

Pb – Only PbF_4, $PbCl_4$ rest are Pb(II). ~~made by direct~~ [illegible] $PbCl_4$ unstable yellow fuming liquid

PbF_4 made by direct comb. Cl_2 not strong enough ox. agent ∴

$$PbCl_2 + \underset{\text{conc HCl}}{2Cl^-(aq)} \rightarrow PbCl_4^{2-}(aq)$$

ox. $$PbCl_4^{2-}(aq) + Cl_2 \rightarrow PbCl_6^{2-}(aq)$$

$$2NH_4^+ + PbCl_6^{2-} \rightarrow (NH_4)_2PbCl_6 \downarrow$$

dry cond. $$(NH_4)_2PbCl_6 + \underset{\text{conc.}}{H_2SO_4} \rightarrow (NH_4)_2SO_4 + 2HCl\uparrow + PbCl_4(l).$$

$PbCl_4$ [illegible] rapidly hydolised.

All dihalides exist – all ionic PbI_2 yellow, rest are white. Low sol in cold, high in hot H_2O. Dissolve in excess ~~H~~ X^- to form PbX_4^{2-}

Oxides

C – CO, CO_2 CO only stable C(II) compound

$$\underset{\text{Na salt}}{HCO_2H} \xrightarrow[\text{conc. } H_2SO_4]{} CO \quad \text{or} \quad (CO_2H)_2 \xrightarrow[H_2SO_4]{\text{conc.}} CO_2\uparrow + CO\uparrow$$

CO insoluble in water, classed neutral. CO_2 can act as ox. agent [eg with Mg] CO as reducing (blast furnace).

CO acts as a ligand (Fe, Ni) will combine directly with halogens or sulphur

Si – SiO_2 covalent macromolecular c.f diamond, SiO_2 empirical formula, insoluble found in rocks. Has some acidic properties

$$SiO_2 + 2NaOH \xrightarrow{\text{fuse}} \underset{\text{sodium silicate}}{Na_2SiO_3} + H_2O$$

Si prep: $SiO_2 + 2Mg \rightarrow 2MgO + Si$

Ge – similar to SiO_2, Ge prep $Ge \xrightarrow[HNO_3]{\text{conc}} GeO_2$

Sn – SnO_2 stable, SnO oxidised easily – reducing agent

$$Sn + O_2 \xrightarrow{\text{heat}} SnO_2 \text{ white solid}$$

$$Sn + \text{conc } HNO_3 \rightarrow SnO_2$$

$$\underset{\text{Tin (II) oxalate}}{SnC_2O_4} \xrightarrow[N_2]{\text{heat in}} \underset{\text{black}}{SnO} + CO + CO_2$$

both oxides are amphoteric

$$SnO_2 + H^+(aq) \rightarrow \underset{Sn(H_2O)_4^{\,4+}}{Sn^{4+}(aq)} + 2H_2O$$

$$2H_2O + SnO_2 + 2OH^- \rightarrow Sn(OH)_6^{\,2-}$$

$\{$ c.f $CO_3^{\,2-}$, $SiO_3^{\,2-}$, $GeO_3^{\,2-}$, $Pb(OH)_6^{\,2-}$ $\}$

$SnO + 2H^+(aq) \rightarrow Sn^{2+}(aq) + H_2O$

$H_2O + SnO + 2OH^- \rightarrow Sn(OH)_4^{2-}$

Pb — PbO - most stable

PbO_2 } quite stong ox. agents, easily reduced
Pb_3O_4 } to Pb (II)

Pb_3O_4 =

$2Pb + O_2 \xrightarrow{heat} PbO$

$6PbO + \underset{excess}{O_2} \xrightarrow{450} Pb_3O_4$

PbO - cf SnO - amphoteric

PbO_2 only react with HCl

$PbO_2 + 4HCl \rightarrow PbCl_2 + Cl_2 + 2H_2O$

with alkali if forced $\rightarrow Pb(OH)_6^{2-}$

$Pb_3O_4 + \underset{HNO_3}{4H^+(aq)} \rightarrow 2Pb^{2+}(aq) + 2H_2O + PbO_2\downarrow$.

2.38 g 

50.1g CS_2

~~boiled~~
$\Delta T = 0.48\ °C$

$C(CS_2) - 29.6\ K\ mol^{-1}\ 100g^{-1}$ timer

3 moles 0 moles

$(1 - 3\alpha)$ α

$N^{3-} + 3H_2O \rightarrow NH_3 + 3OH^-$

strong base.

$2Al + 2OH^- + 6H_2O \rightarrow 2Al(OH)_4^- + 3H_2\uparrow$

$Be + 2OH^- + 2H_2O \rightarrow H_2\uparrow + Be(OH)_4^{2-}$

~~Li > Rb > Cs > K > Na~~

Li > K ≈ Rb > Cs > Na - E°

$\longleftarrow$ -ve

$2MHCO_3(s) \xrightarrow{heat} M_2CO_3(s) + CO_2\uparrow + H_2O(l)$

$U \propto \dfrac{n z_+ z_-}{(r_+) + (r_-)}$

z_+ charge on cation

r_+ radius of cation

n = no. of ions per formula.

~~$U(MCO_3)$ [illegible] $U(M_2CO_3)$~~

Ca$(OH)_2$ not very soluble.

$Be^{2+}(aq) + CO_3^{2-}(aq) + H_2O \rightarrow Be(OH)_2 + CO_2\uparrow$

$MgCO_3$ easily decomposed

$Be(H_2O)_4SO_4 \rightarrow$ crystaline white

$BCl_3 + 3H_2O \rightarrow 3HCl + H_3BO_3$

$4BF_3 + 3H_2O \rightarrow 3HBF_4 + H_3BO_3$

Fluorboric acid — orthoboric acid

$B(OH)_3 + 2H_2O \rightarrow B(OH)_4^- + H_3O^+$

↑ not hydrated — Lewis acid

$AlCl_3 + 3H_2O \rightarrow Al(OH)_3 + HCl$

excess — ↑ not ~~hydrolise~~ hydrated

$AlCl_3 + 6H_2O \rightarrow Al(H_2O)_6^{3+}.3Cl^-$

excess

$Al(H_2O)_6Cl_3 \xrightarrow{heat} Al(OH)_3 + 3HCl + 3H_2O$

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grey (α) Sn $\xrightleftharpoons[13^\circ C]{}$ white β $\xrightleftharpoons[161^\circ C]{}$ γ tin $\xrightleftharpoons[232^\circ C]{}$ liquid

grey (α) Sn: non metallic, covalent, macromollecular, low density

white β: metallic, high density

Si, Ge, Sn, Pb } $M + 2OH^- + H_2O \rightarrow MO_3^{2-} + 2H_2\uparrow$

a) prepare CF_4 directly

~~S~~ $CS_2 + 3Cl_2 \rightarrow CCl_4 + S_2Cl_2$

all 4 Si halides prep. directly.

hydolise in the same way as BF_4, BCl_4.

Sn → $Sn + 2X_2 \rightarrow SnX_4$

$Sn + 2HX \rightarrow SnX_2 + H_2\uparrow$

hydrolises like Al ie forms $Sn(H_2O)_4^{4+}$: $4Cl$

$\cdot H_2O$

$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O$

pure

$4NH_3 + 5O_2 \xrightarrow{Pt} 4NO + 6H_2O$

$PCl_3 + Cl_2 \underset{heat}{\overset{ice}{\rightleftharpoons}} PCl_5$

$NCl_3 + 3H_2O \underset{SN2}{\rightarrow} NH_3 + 3HOCl$

$Cl_3N: \curvearrowright H-OH$

Eng: $F > O > Cl \sim N > Br > I > C > H$

$X^- + H_2SO_4 \Rightarrow HX\uparrow + HSO_4^-$

for Cl react give Br_2, I_2 as H_2SO_4 ox agent, for Cl_2 use $MnO_4^{\ominus}$

$B + H_2O \rightleftharpoons BH^+ + OH^-$

$$K_b = \frac{[BH^+][OH^-]}{[B]} \qquad [H_2O] = K$$

Should not ox. of toluene by MnO_4^- be carried out in $H^{\oplus}$ not $OH^{\ominus}$ in ~~ord~~ order to get

Is $Fe(OH)_2$ (aq) ~~$Fe(H_2O)_4(OH)_2$~~

or $Fe(H_2O)_6^{2+}$ $2OH^-$?

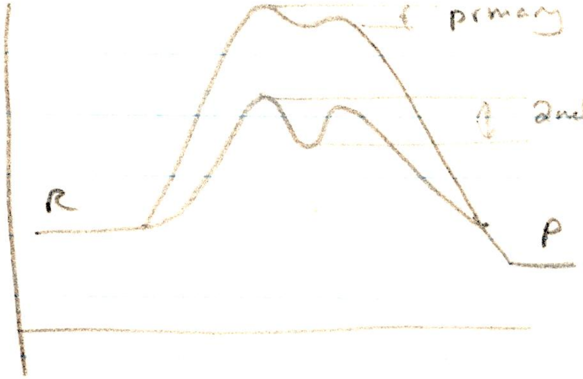
~~If latter then surely [$Cr(H_2O)_4(OH)_2$~~

Is there a $Fe(H_2O)_4(OH)_2$?

$Cu(H_2O)_6^{2+} \xrightarrow{\text{excess } NH_3} [Cu(NH_3)_4(H_2O)_2]^{2+}$?

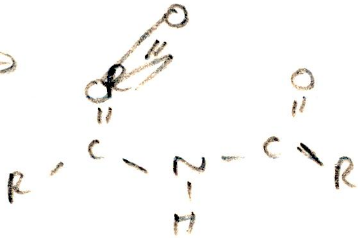
If $CrCl_3 . 6H_2O$ is deliquescent what does it form?

Is not greater stability of 2nd ary carbonium ions reflected in bigger trough near ~~high~~ lower peak



Cannot aldehydes and Ketones be protonated like alcohols and carboxylic acids?

With excess $RCOCl + NH_3 \rightarrow$



Will all acid derivatives condense with $X-NH_2$?

What is different about acid chlorides + aldehydes + ketones?

Are the reactions of secondary + tertiary amines common to aliphatic + aromatic amines.

$NH_4Cl \rightarrow NH_4^{\oplus} + Cl^{\ominus}$

$NH_3 + H_2O \rightarrow NH_4^{\oplus} + Cl^{\ominus}$

$NH_4^{\oplus} + \overset{H_3O^{\oplus}}{\cancel{H^{\oplus}}}_{(aq)} \rightarrow NH_3 + \cancel{H_2O}\ H_2\uparrow$

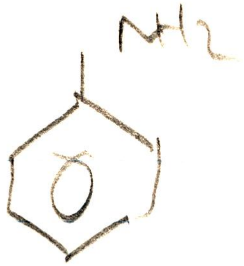
$NH_3 + + OH^{-} \rightarrow NH_3^{\ominus} + H_2O$

$NH_4^{\oplus} + H^{+} \rightarrow NH_3 + H_2O$

~~$NH_3 + OH^{-} \rightarrow$~~

$NH_3 + H^{+} \rightarrow NH_4^{+}$

$NH_4^{+} + OH^{-} \rightarrow NH_3 + H_2O$



+ { HOBr
HBr
Br_2

C 6
Si 14

+ CH_3CH_2OH

KCr_2O_7

↓

C - $1s^2\ 2s^2\ 2p^2$
Si - $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^2$

~~$CO_3^{2-} + H_2O \rightarrow H_2CO_3 + \ominus_2$~~

$Na^+(aq) + CO_3^{2+}(aq) + H_2O \rightleftharpoons H^+_{aq}\ OH^-_{aq}$

$Na^+(aq) + CO_3$

$NaCH_3CO_2 \rightleftharpoons Na^+ + CH_3CO_2^{\ominus}$

$CH_3CO_2H \rightleftharpoons H^+ + CH_3CO_2^{\ominus}$

$H^+ + CH_3CO_2^{\ominus} \rightarrow HCO.$

$OH^- + CH_3CO_2H \rightarrow CO$

0·8

$MnO_4^- + 5e^- + 8H$

~~Br^-~~

$Br_2 + H_2$ $Br_2 + H_2O$

$HOBr + HBr$

$NaCr_2O_7$

Before you cross the road,

STOP, LOOK AND LISTEN

every time.