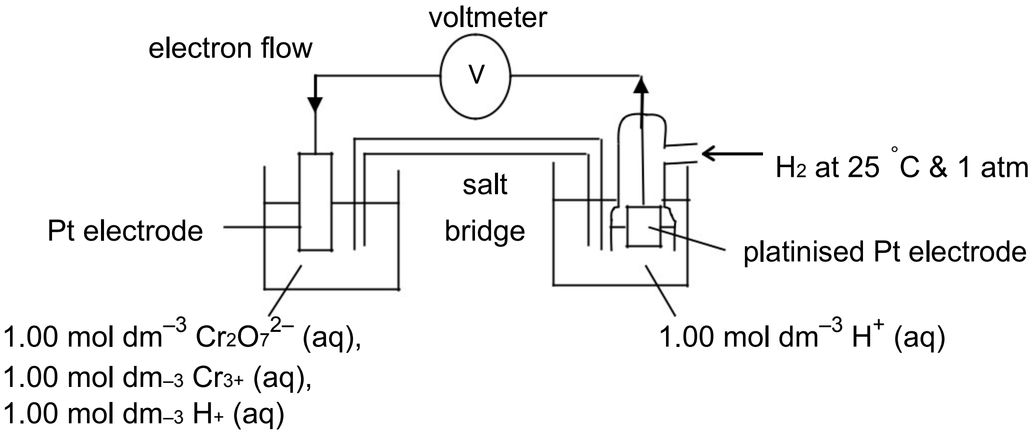
2012 H2 Chemistry Preliminary Examination Paper 3 Solutions

1 **(a)** **(i)** $4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \longrightarrow 2Fe_2O_3 + 8Na_2CrO_4 + 8CO_2$

a **=** 8**,** ***b*** **=** 7**,** ***c*** **=** 2**,** ***d*** **=** 8**,** ***e*** **=** 8

I Any dilute acid e.g. dilute H_2SO_4 or dilute HCl

(b)



correct components of each half–cell
direction of electron flow

(c) $Zn^{2+} + 2e \rightleftharpoons Zn$ –0.76 V

$Cr^{3+} + e \rightleftharpoons Cr^{2+}$ –0.41 V

Zn reduces Cr^{3+} to blue $Cr^{2+}(aq)$; $E^{\ominus}_{cell} = +0.35\ V > 0$,

$2H^+ + 2e \rightleftharpoons H_2$ 0.00 V

The acid present in the solution oxidises blue Cr^{2+} back to green Cr^{3+}; $E^{\ominus}_{cell} = +\ 0.41\ V$, producing H_2 gas.

(i) Mole ratio of CrO_x^{n-} : $Cr_2O_7^{2-}$ = 7.5×10^{-3} : 2.5×10^{-3} = 3 : 1

Thus, 3 mol of CrO_x^{n-} disproportionate to 1 mol of $Cr_2O_7^{2-}$ and 1 mol of

Cr^{3+} Let O.N. of Cr be y.

y – 3 = 2(6) –
2y y = 5

O.N. of Cr in the ion CrO_x^{n-} = +5

(e) **(i)** $Fe^{3+} + e \rightleftharpoons Fe^{2+}$ +0.77 V
$Cr^{3+} + e \rightleftharpoons Cr^{2+}$ –0.41 V

$E^{\ominus}_{cell} = +1.18\ V$

$Fe^{3+} + Cr^{2+} \longrightarrow Fe^{2+} + Cr^{3+}$

(ii) When cell discharges, iron half–cell becomes less positive and the chromium half–cell becomes more positive. Passage of current would stop. Membrane allows anions to pass through to maintain electrical neutrality in the two half–cells. (not allowing the positive ions to pass through, otherwise self–discharge or short circuit occurs) [2]

(iii) $E^{e}_{cell} = E^{e}_{red} - E^{e}_{ox}$
$1.59 = +0.40 - E^{e}_{anode}$
$E^{e}_{anode} = \underline{-1.19\ V}$

Anode: $Zn + 4OH^- \longrightarrow Zn(OH)_4^{2-} + 2e$
(or $Zn + 2OH^- \longrightarrow Zn(OH)_2 + 2e$)

(iv) Q = 0.8 x 1.9/65.4 x 2 x 96500 = 4486 C
Current = 4486 / (30 x 24 x 60 x 60) = 1.73×10^{-3} A

(v) ICB is expected to discharge faster as it involves simple electron transfer reactions, while energy is needed to break covalent bonds in O_2 (and H_2O) in the zinc–air battery.

(vi) Zn–air battery has higher energy density as it uses air as the oxidising agent, unlike the heavier oxidising agent, MnO_2, used in the alkaline battery. Thus, more zinc can be packed within a cell of similar weight.

2 **(a)** **(i)** It is the amount of energy evolved when 1 mole of solid ionic compound is formed from its constituent gaseous ions at 298 K and 1 atm.

(ii) **I**: As the cationic radius increases down the group, inter–ionic distance increases

OR state that L.E. a $\frac{q^+q^-}{r^+ + r^-}$ and cationic radius (r_+) increases down the group.
Thus, the strength of electrostatic forces of attraction between the M^{2+} and SO_4^{2-} ions decreases. Hence, the magnitude of L.E. decreases.

II: D$H_{hydration}$ of the cation a $\frac{q^+}{r_+}$ $\frac{q^+}{r^+}$
As the cationic radius increases down the group,
OR the charge density of the cation decreases.

Thus, the strength of ion–dipole interactions formed between M^{2+} and water molecules decreases and hence D$H_{hydration}$ becomes less exothermic.

(iii) D$H_{solution}$ = – L.E. + D$H_{hydration}$ of M^{2+} + D$H_{hydration}$ of anion

For Group II sulfates, the decrease in |L.E| is less than that of |D$H_{hydration}$ of M^{2+}|. Thus, D$H_{solution}$ becomes more positive down the group and solubility decreases

For Group II hydroxides, size of the OH^- anion is much smaller than that of the SO_4^{2-} anion. The decrease in |L.E| is more than that of |DH_{hyd} of M^{2+}|. Thus, D$H_{solution}$ becomes more negative down the group and solubility increases.

OR
The size of the cation is much smaller than that of the anion (SO_4^{2-}), thus the decrease in |L.E| is less significant than the decrease in the |D$H_{hydration}$|.

Conversely, the size of the OH^- anion is much smaller than that of the SO_4^{2-} anion, thus the decrease in |L.E| is more significant than the decrease in the $|DH_{\text{hydration}}|$.

(b) **(i)** For Hg_2SO_4, min. $[SO_4^{2-}] = 7.4 \times 10^{-7} / (0.1/2)^2 = 2.96 \times 10^{-4}$ mol dm^{-3}
For $CaSO_4$, min. $[SO_4^{2-}] = 2.4 \times 10^{-5} / (0.1/2) = 4.80 \times 10^{-4}$ mol dm^{-3}

(ii) Since min. $[SO_4^{2-}]$ required to precipitate first trace of Hg_2SO_4 is lower, Hg_2SO_4 will be precipitated first.

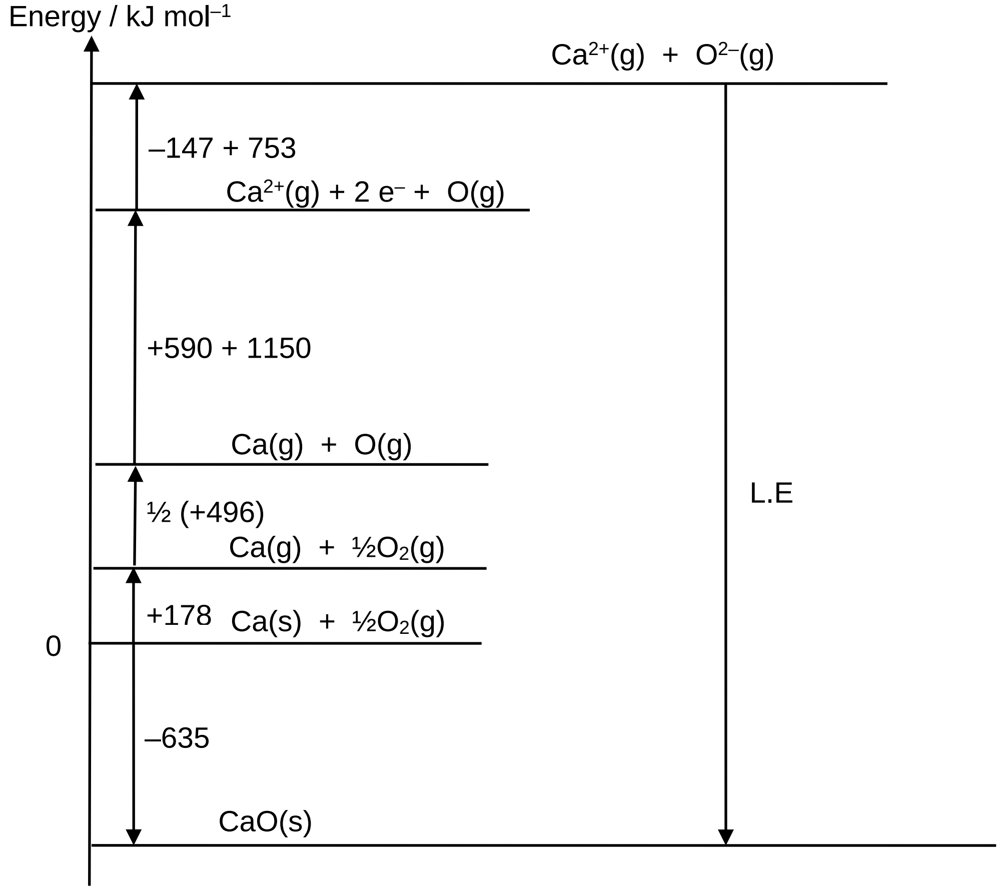
When max. Hg_2SO_4 is precipitated, i.e. when first trace of $CaSO_4$ appears,
$[SO_4^{2-}]_{\text{in solution}} = 4.80 \times 10^{-4}$ mol dm^{-3}
\ $[Hg^+]_{\text{in solution}} = [7.4 \times 10^{-7} / (4.80 \times 10^{-4})]^{1/2} = 0.0393$ mol dm^{-3}

n(Hg^+) in 50 cm^3 solution = 0.0393 x 50/1000 = 1.97 x 10^{-3} mol
n(Hg^+) precipitated = 0.1 x 25.0/1000 – 1.97 x 10^{-3} = 5.30 x 10^{-4} mol

$$2Hg^+ + SO_4^{2-} \longrightarrow Hg_2SO_4$$

n(Hg_2SO_4) precipitated = ½ x n(Hg^+) precipitated = ½ x 5.30 x 10^{-4} = 2.65 x 10^{-4} mol
Max. mass of Hg_2SO_4 precipitated = 2.65 x 10^{-4} x (2 x 201 + 32.1 + 4 x 16.0) = 0.132 g

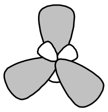
(c) **(i)**



L.E of CaO = –(– 147 + 753 + 590 + 1150 + ½ (496) + 178) + (–635)
= <u>– 3410</u> kJ mol^{-1} (3 s.f.)

(ii) magnitude of the L.E. of Ca_3N_2 should be larger than that of CaO due to a larger charge on N^{3-}
OR due to more ionic attractions between 5 mol of ions in 1 mol of Ca_3N_2 than between 2 mol of ions in 1 mol of CaO.

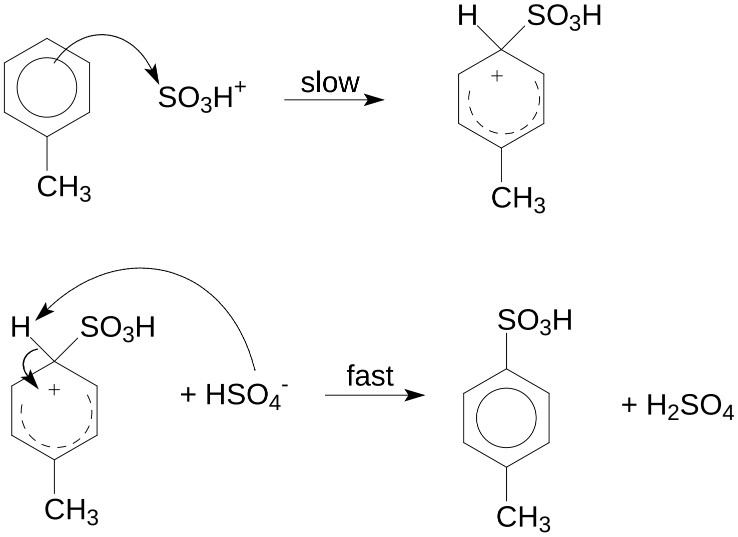
3 **(a)** **(i)**



sp² hybrid orbitals

(ii) $H_2SO_4 + SO_3 \longrightarrow HSO_4^- + HSO_3^+$

(iii) Electrophilic substitution [1]



correct arrow movement
correct carbocation intermediate and regeneration of catalyst

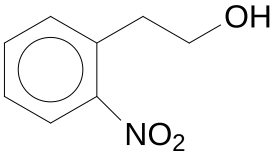
(iv) The lone pair of electrons on N atom is delocalised into the benzene ring. This further intensifies the negative charge on the sulfonate anion, making it less stable.

(v) Add aqueous bromine to each compound.
Observation: orange solution of bromine turns colourless and a white precipitate is formed for 4–aminobenzenesulfonic acid. Bromine solution remains orange and no precipitate formed for 4–methylbenzenesulfonic acid

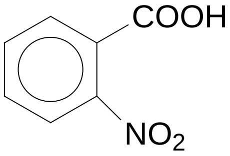
OR
Heat each compound with $KMnO_4$ in dilute H_2SO_4.
Observation: purple $KMnO_4$ turns colourless for 4–methylbenzenesulfonic acid. $KMnO_4$ remains purple for 4–aminobenzenesulfonic acid.

OR
Add cold HC*l* / H_2SO_4
Observation: 4–aminobenzenesulfonic acid dissolves in HC*l* but 4–methylbenzenesulfonic gives two immiscible layers.

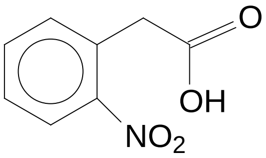
(c) **(i)**



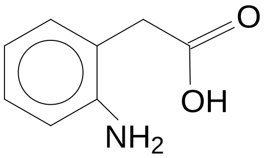
K



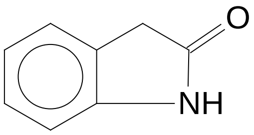
L



M



N



O

Reaction	**Type of reaction**	**Deduction**
Treating compound **K**, $C_8H_9NO_3$, with hot acidified potassium manganate(VII) gives compound **L**, $C_7H_5NO_4$.	oxidation	loss of 1 C Þ side–chain oxidation occurred.
L produces effervescence with sodium hydrogen carbonate.	acid–base reaction	Carboxylic acid group in **L** reacted with sodium hydrogen carbonate. **L** contains carboxylic acid group, –COOH.
Heating compound **K** under reflux with acidified potassium dichromate(VI) gives compound **M**, $C_8H_7NO_4$.	oxidation	gain in 1 O, loss of 2 H Þ 1^o alcohol in **K** is oxidised to –COOH in **M**.
Compound **M** is treated with tin and concentrated hydrochloric acid, followed careful neutralisation, compound **N**, $C_8H_9NO_2$ is obtained.	reduction	$–NO_2$ group in **M** is reduced to $–NH_2$ group in **N**.

1 mole of compound **N** reacts with 2 moles of aqueous bromine.	electrophilic substitution	**N** is a phenylamine. -Br is substituted at positions 2, 4 or 2, 6 w.r.t the $–NH_2$ group
Treatment of compound **N** with anhydrous phosphorus pentachloride produces compound **O**, C_8H_7NO.	**N** is first converted to acyl chloride, by PCl_5 via nucleophilic substitution. The acyl chloride formed then undergoes intra–molecular condensation with the $–NH_2$ group to form a cyclic amide **O.**	The $–CH_2COOH$ group must be adjacent to the $–NH_2$ group in **N** to enable ring formation/formation of a cyclic amide

(ii) Compound **N** will dissolve in the aqueous layer while compound **O** will remain in the organic layer. The basic $–NH_2$ group in compound **N** will react with cold dilute HCl to give an ionic product which can form strong ion–dipole interactions with water molecules.

Compound **O** is neutral and does not react with cold dilute HCl, hence remains in the organic layer.

4 (a) (i) *Complex ion* consists of a central metal ion or atom surrounded by ligands via dative bonds.

(ii) In the presence of ligands,

- the partially–filled 3d orbitals are split into two levels (non–degenerate) with a small energy gap
- energy is absorbed from the visible light region when an electron promotes from a lower level d orbital to a vacant higher energy d orbital, i.e. d–d transition,
- colour of the complex T is the complement of the colour absorbed.

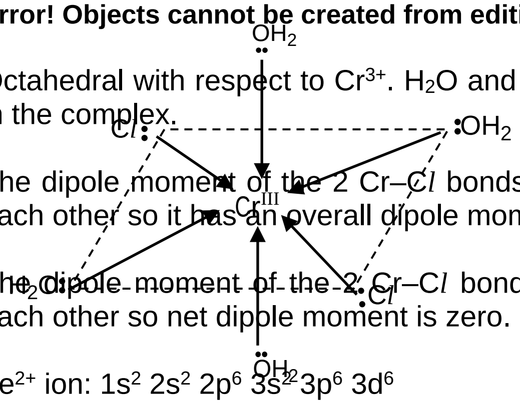
(iii) Number of moles of free $Cl^–$ per mole of complex = 2 x number of moles of $PbCl_2$ precipitated per mole of complex

T: 1.5 mol of $PbCl_2$ precipitated
=> 3 moles of free $Cl^–$ per mole of complex
=> cation is $[Cr(H_2O)_6]^{3+}$

U: 1 mol of $PbCl_2$ precipitated
=> 2 moles of free $Cl^–$ per mole of complex and 1 mole of $Cl^–$ as ligand per mole of complex
=> cation is $[Cr(H_2O)_5Cl]^{2+}$

V: 0.5 mol of $PbCl_2$ precipitated
=> 1 mole of free $Cl^–$ per mole of complex and 2 moles of $Cl^–$ as ligand per mole of complex
=> cation is $[Cr(H_2O)_4Cl_2]^+$

(iv) **Error! Objects cannot be created from editing field codes.**

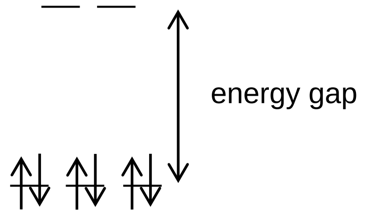


Octahedral with respect to Cr^{3+}. H_2O and Cl^- ligands are dative bonded to the Cr(III) atom in the complex.

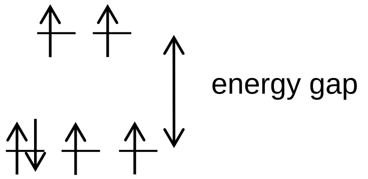
(v) The dipole moment of the 2 Cr–Cl bonds which are on the same side in **V** do not cancel each other so it has an overall dipole moment.

The dipole moment of the 2 Cr–Cl bonds which are on opposite sides in **W** cancel out each other so net dipole moment is zero.

(b) **(i)** Fe^{2+} ion: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6$



low spin state



high spin state

(ii) CN^- will cause a larger energy gap E between its d–orbitals

In the presence of CN^- ligands, the relative paramagnetism is lower. This means that electrons are paired up and arranged in a low spin state. Hence, the energy gap is larger.

(iii) In the presence of water ligands, the electrons of Fe^{2+}(aq) and Fe^{3+}(aq) are arranged in a high spin state
where there are 4 unpaired electrons in the d–orbitals of Fe^{2+}(aq)
and 5 unpaired electrons in the d–orbitals of Fe^{3+}(aq).

Hence the relative paramagnetism of the Fe^{2+}(aq) and Fe^{3+}(aq) ions is 4 : 5.

(c) **(i)**

$$K_{stab} = \frac{[Fe(SCN)(H_2O)_5^{2+}]}{[Fe(H_2O)_6^{3+}][SCN^-]}$$

units: **$mol^{-1}\ dm^3$**

(ii) Since K_{stab} for the complex formed by CN^- and Fe^{3+} ions (1×10^{34}) is much larger than that by SCN^- and Fe^{3+} ions (9×10^2). $[Fe(CN)_6]^{3-}$ is more stable than $[Fe(SCN)(H_2O)_5]^{2+}$, hence the predominant complex formed is **$[Fe(CN)_6]^{3-}$**.

(d) $S_2O_8^{2-}$(aq) + $2e^-$ **Error! Objects cannot be created from editing field codes.** $2SO_4^{2-}$ (aq)
$E^{\ominus}$ = +2.01V
Fe^{3+}(aq) + e^- **Error! Objects cannot be created from editing field codes.** Fe^{2+}(aq)
$E^{\ominus}$ = +0.77V
I_2(aq) + $2e^-$ **Error! Objects cannot be created from editing field codes.** $2I^-$ (aq)
$E^{\ominus}$ = +0.54V

Step 1: Formation of intermediate

$2Fe^{3+}(aq) + 2I^{-}(aq) \longrightarrow 2Fe^{2+}(aq) + I_2(aq)$ $\quad E^{\ominus}_{cell} = +0.23V$

Step 2: Regeneration of the catalyst

$2Fe^{2+}(aq) + S_2O_8^{2-}(aq) \longrightarrow 2Fe^{3+}(aq) + 2SO_4^{2-}(aq)$ $\quad E^{\ominus}_{cell} = +1.24V$

5 **(a)** **(i)** Since a fixed volume of thiosulfate is used in each experiment, rate can be measured by the time taken for fixed amount of iodine liberated, i.e. rate α 1/t.

(ii) So that $[H_2O_2]$ and $[H^+]$ are kept effectively constant and will not affect the rate of reaction / rate is only affected by the concentration of $[I^-]$.

(iii) evaluate (1/t)
labelled axes: y–axis – (1/t); x–axis – $[I^-]$
best–fit straight line drawn through the origin
correctly plotted points

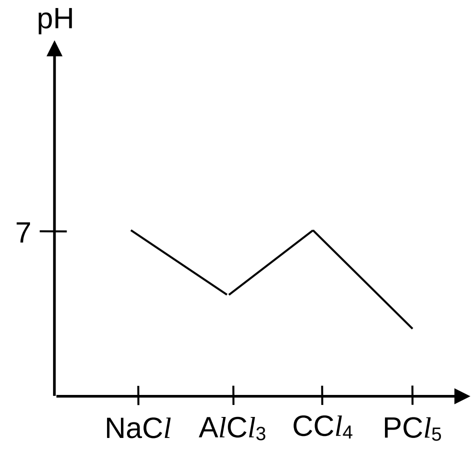
Rate α $[I^-]^{n} [H_2O_2]^{y} [H^+]^{z}$

Since rate α 1/t and $[H_2O_2]$ and $[H^+]$ are effectively constant, 1/t α $[I^-]^n$.

Since a straight line which passes through the origin is obtained when (1/t) is plotted against $[I^-]$, ***n*** = 1.

(iv) 1. It is a multi–step mechanism.
2. H^+ is not involved in the rate–determining step.
3. 1 (mol) of I^- and 1 (mol) of H_2O_2 are involved in the rate–determining step.

(b) **(i)**



(ii) PCl_5 undergoes hydrolysis in water but not CCl_4.

CCl_4 has no vacant low–lying (energetically accessible) d–orbitals to accept the lone pair of electrons from the water molecules. Therefore, it will not undergo hydrolysis.

OR

PCl_5 has vacant low–lying 3d–orbitals to accept the lone pair of electrons from the water molecules. Hence, it will undergo hydrolysis to give H_3PO_4 and HCl, resulting in an acidic solution.

$PCl_5 + 4H_2O \longrightarrow H_3PO_4 + 5HCl$

(c) Steamy / white fumes of HCl observed for KCl, violet / purple fumes of I_2 observed for KI.

$KCl + H_2SO_4 \longrightarrow KHSO_4 + HCl$

$KI + H_2SO_4 \longrightarrow HI + KHSO_4$
$8HI + H_2SO_4 \longrightarrow 4I_2 + H_2S + 4H_2O$

I^- being a stronger reducing agent (than Cl^-) will reduce H_2SO_4 to H_2S / itself oxidised to I_2.

(d) **(i)** Bottle **Z**
$Cl_2 + X^- \longrightarrow 2Cl^- + X_2$ where X = Br or I

(ii) Knowing that bottle **X** and **Y** is either KBr or KI, add hexane to the two brown mixtures obtained, separately.

If the organic layer is purple, bottle contains KI.
If the organic layer is red–brown, bottle contains KBr.