Problem 2 *(16% of total)*	Question	2.1	2.2	2.3	2.4	2.5	2.6	2.7	2.8	2.9	Total
	Points	1	9	3	3	1	1	1	3	1	23

Problem 2: Onsens…

By Dillion Lim and Ranen Yong, Singapore

Authors' Note: *It is* ***highly recommended*** *for different members of the team to work on different parts of the problem at the same time. The problem has been structured such that individual parts can largely be done independent of each other, except for the ending.*

Fig. 2.1: rymh's quirky obsession with onsens

Rymh received an unknown package in his mail. Despite the risk of getting Anthrax from frustrated ACOT participants, he believed that it was the Japanese onsen concentrate, *Yunomoto*, that he ordered from a Yahoo! auction on Buyee. So he rips the package open — fortunately, there's no Anthrax in there.

When preparing the bath for the first time, rymh accidentally spilled a few drops onto his fingers. The concentrate turned out to be pretty corrosive, as rymh found out the hard way (it stung his fingers).

Curious, rymh decided to search up the ingredients list to figure out the ingredient responsible for the concentrate's corrosive properties. However, a quick google search in Japanese brings up only two active ingredients in the product:

■有効成分
多硫化態硫黄･酸化カルシウム

■ **Active ingredients**
Polysulfide sulfur/calcium oxide

**Powered by Google Translate.*

Rymh figures that the mixture cannot just be made from these two ingredients alone, and decides to conduct some tests on it to ascertain the identity of other ingredients in there. Of course, "polysulfide sulfur" also sounds very suspicious, so he decides to determine the *actual* sulfur-containing compounds present in the concentrate.

Introduction: Strange Smells and White Powder

Before even beginning proper tests to figure out the identity (or identities) of any compounds present, he first decided to enjoy a good, long, soak in the bathtub. Of course, he added a capful of *Yunomoto* to the bathtub, as per the directions stated on the packaging. There was a faint but familiarly unpleasant smell, but he paid it no mind and went ahead. *After all, since it's one of the highest-rated bath additives in Japan, it's probably still safe to use, right?*

When the concentrate was added to the tub, it formed a slightly murky yellowish-green solution. Interestingly, rymh noted that the yellowish-green colour faded, and a white precipitate formed over time.

2.1 **What** is the identity of the compound most likely responsible for the 'faint but familiarly unpleasant smell'?

H_2S **[1]**

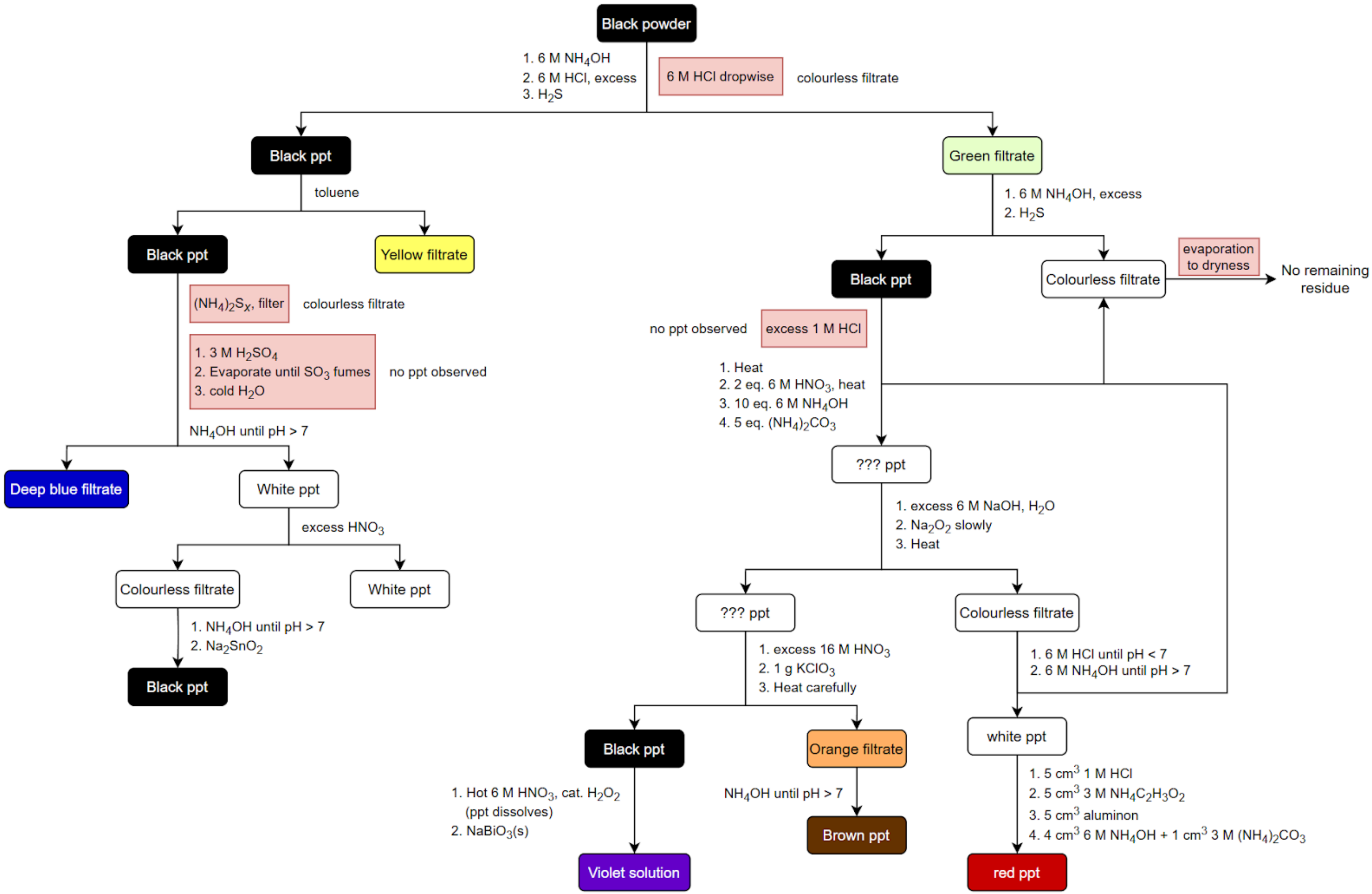
Before stepping into the bath, rymh decided to scoop a sufficiently large sample of the now-white and murky solution. He poured the mixture over a large coffee filter, and left it alone while he enjoyed the nice bath.

After finishing his bath, he came back to the filtration setup and discovered that the mixture separated into a colourless filtrate and a white residue. He washed the white residue with deionized water and left it to dry for a full day.

Part 1: Elucidation Fun

By the following day, the white residue had dried into a white powder. Knowing that Ca^{2+} was present in the sample, he decided to separate it out before performing further tests, which he thankfully managed to do (with the help of some black magic).

Upon strong heating, the white powder turned black, and there was a notable loss in mass. To determine the identity of the ions present in the sample, he then performed a series of tests as shown on the next page.



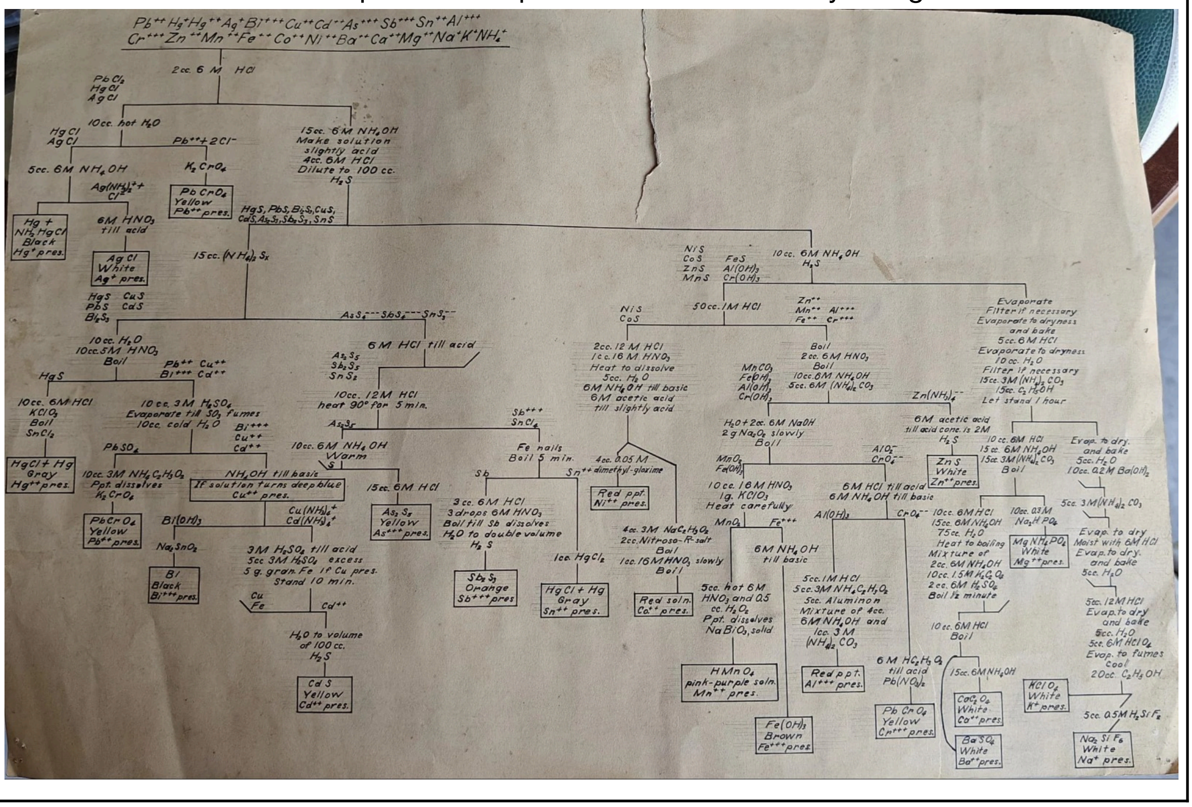
Black powder
1. 6 M NH_4OH
2. 6 M HCl, excess
3. H_2S
6 M HCl dropwise
colourless filtrate
Black ppt
toluene
Black ppt
Yellow filtrate
$(NH_4)_2S_x$, filter
colourless filtrate
1. 3 M H_2SO_4
2. Evaporate until SO_3 fumes
3. cold H_2O
no ppt observed
NH_4OH until pH > 7
Deep blue filtrate
White ppt
excess HNO_3
Colourless filtrate
White ppt
1. NH_4OH until pH > 7
2. Na_2SnO_2
Black ppt
Green filtrate
1. 6 M NH_4OH, excess
2. H_2S
Black ppt
Colourless filtrate
evaporation to dryness
No remaining residue
no ppt observed
excess 1 M HCl
1. Heat
2. 2 eq. 6 M HNO_3, heat
3. 10 eq. 6 M NH_4OH
4. 5 eq. $(NH_4)_2CO_3$
??? ppt
1. excess 6 M NaOH, H_2O
2. Na_2O_2 slowly
3. Heat
??? ppt
Colourless filtrate
1. excess 16 M HNO_3
2. 1 g $KClO_3$
3. Heat carefully
1. 6 M HCl until pH < 7
2. 6 M NH_4OH until pH > 7
Black ppt
Orange filtrate
white ppt
1. Hot 6 M HNO_3, cat. H_2O_2 (ppt dissolves)
2. $NaBiO_3$(s)
NH_4OH until pH > 7
1. 5 cm^3 1 M HCl
2. 5 cm^3 3 M $NH_4C_2H_3O_2$
3. 5 cm^3 aluminon
4. 4 cm^3 6 M NH_4OH + 1 cm^3 3 M $(NH_4)_2CO_3$
Violet solution
Brown ppt
red ppt

He determined that the heated black powder consisted of a relatively inert macromolecule and 5 other cations of different elements, one of which is Bi^{3+}.

2.2 **<u>Determine</u>** the identities of the 4 remaining cations present in the black solid, explaining your reasoning clearly. **<u>What</u>** is the most likely identity of the macromolecule present?
[Hint: Don't overthink about why the pre-heated powder is white.]

[1] for determining the absence of Pb^{2+}, Hg^{+} or Ag^{+} (stating just one will suffice).
[1] for determining presence of Cu^{2+}.
[1] for determining the absence of Ba^{2+}, Zn^{2+} or Mg^{2+} (stating just one will suffice).
[2] for determining the presence of Fe^{3+}.
[1] for determining the presence of Al^{3+}.
[2] for determining the presence of Mn^{2+}.
[1] for stating that the macromolecule present is likely SiO_2.

<u>Note:</u>
The entire scheme was adapted from a post on Reddit about a year ago:



2.3 **<u>State</u>** a possible reason for the presence of the yellow filtrate in the scheme, and **<u>cite</u>** a piece of evidence from the scheme to support your reasoning. **<u>Write</u>** down the relevant equation(s) responsible for its formation.

The yellow filtrate is dissolved elemental sulfur:

$$2\,Fe^{3+} + 3\,H_2S \rightarrow Fe_2S_3 + 3\,H^+$$
$$Fe_2S_3 + 3\,HCl \rightarrow 2\,FeCl_2 + 2\,H_2S + S \text{ **OR** } Fe_2S_3 \rightarrow 2\,FeS + S$$

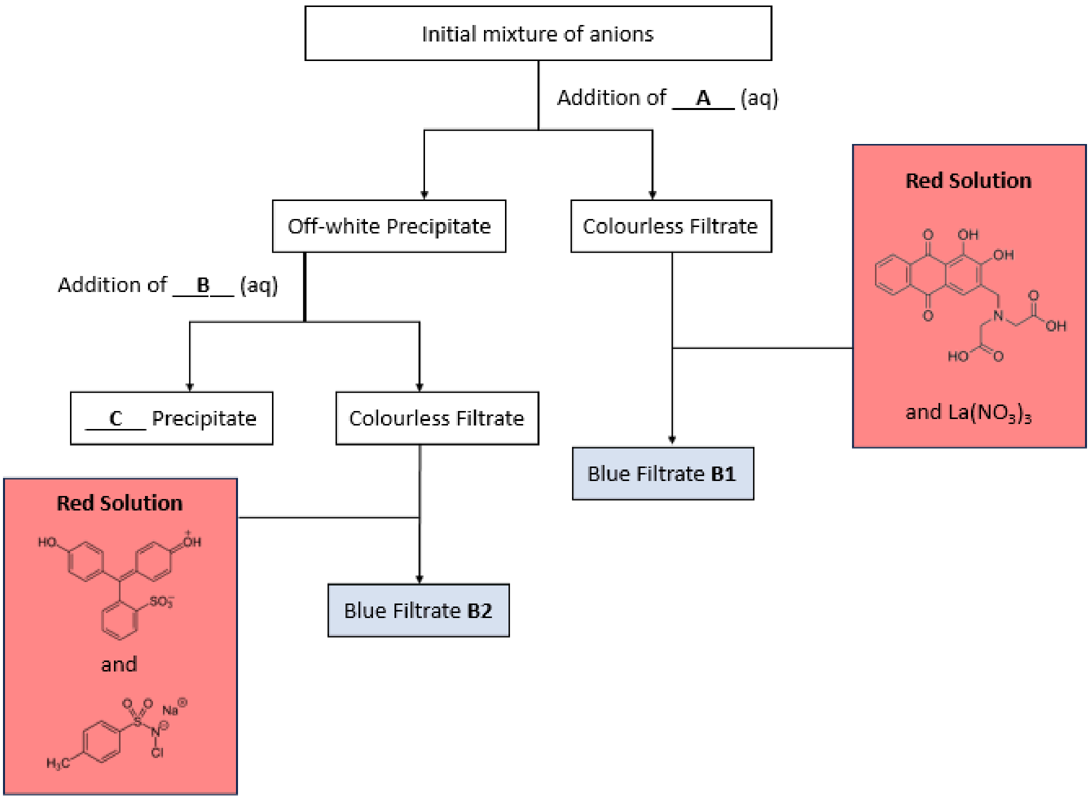
Fe^{3+} reacts with the bubbled H_2S to form Fe_2S_3, which decomposes at room temperature to give FeS and elemental sulfur. **OR** Fe^{3+} reacts with the bubbled H_2S to form Fe_2S_3, which decomposes with the excess HCl to give $FeCl_2$, H_2S and elemental sulfur.

This is further evidenced by the fact that the filtrate is green, which is characteristic of Fe^{2+} (note: FeS is soluble in acids).

[1] for identifying that the yellow filtrate is elemental sulfur.
[1] for either decomposition reaction given (both are likely to occur).
[1] for stating the correct supporting evidence.

Part 2: More elucidation fun

It is known that onsens should probably contain bromide, iodide and fluoride anions. So, rymh proceeded to confirm their presence using the scheme below.



2.4 If it is known that Br^-, I^- and F^- are all present in the initial mixture, **fill in the blanks** for **A**, **B** and **C** respectively.

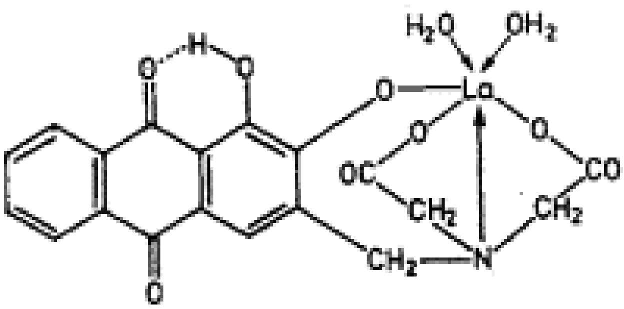
A: $AgNO_3$

B: (concentrated) NH_3
C: Yellow / AgI

[1] for each correct answer (Total: [3]).
*Note: stating that **B** is concentrated is not required for full credit to be awarded. However, do note that the dissolution of AgBr in concentrated NH_3 is similar to the formation of Tollens' reagent through dissolution of AgCl in dilute NH_3.*

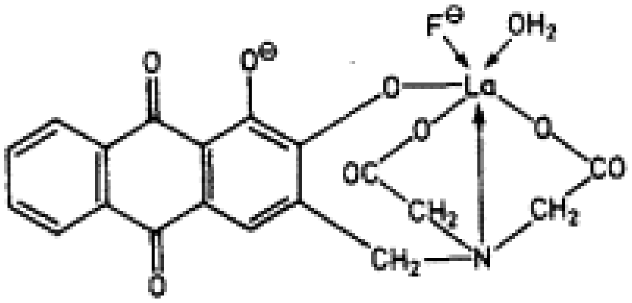
To arrive at blue filtrate **B1**, the colourless filtrate was mixed with a red solution comprising alizarin complexone and $La(NO_3)_3$.

2.5 <u>**Suggest**</u> the product formed (yielding the red solution) when alizarin complexone and $La(NO_3)_3$ is mixed together.



[1] for the correct answer (accept other plausible structures).

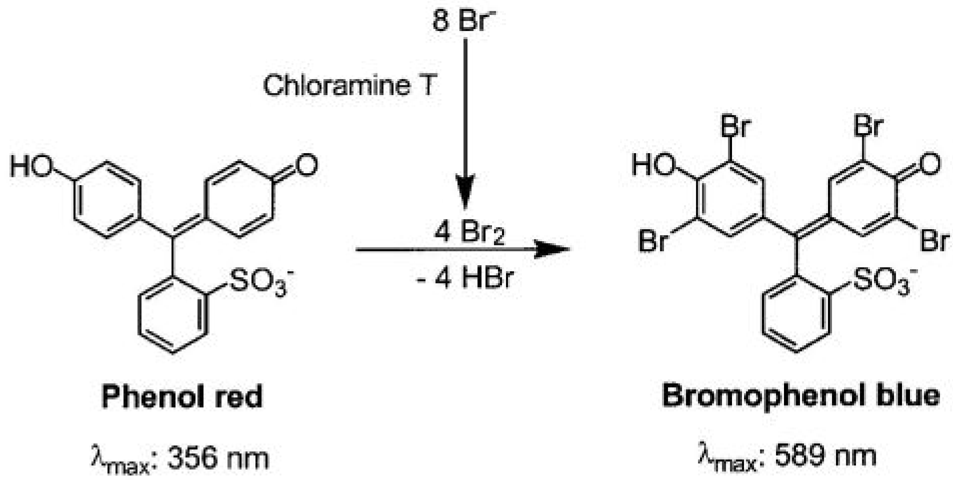
2.6 Hence, <u>**suggest**</u> the identity of the blue filtrate **B1**, given that a **single** ligand exchange occurred.



[1] for the correct answer (accept other plausible structures).

To arrive at blue filtrate **B2**, the colourless filtrate was mixed with a red solution comprising phenol red and chloramine-T.

2.7 <u>**Suggest**</u> the product formed when chloramine-T reacts with the colourless filtrate.



[1] for the correct answer (bromophenol blue).

2.8 Hence, **draw** the mechanism for the formation of the blue filtrate **B2**.

Mechanism is a simple electrophilic aromatic substitution. Note that the quinone branch and the phenol substituent are tautomers.

[3] for the correct mechanism drawn.

It is known from the research done by Serbulea and Payyappallimana (2012) that the composition of onsens are:

Name of the substance	Quantity / kg
Lithium (Li^{+}) ions	1 mg
Strontium (Sr^{2+}) ions	10 mg
Barium (Ba^{2+}) ions	5 mg
Iron ($Fe^{2+/3+}$) ions	10 mg
Manganese (Mn^{2+}) ions	10 mg
Bromide (Br^{-}) ions	5 mg
Iodide (I^{-}) ions	1 mg
Fluoride (F^{-}) ions	2 mg

2.9 Based on the information above, **suggest** whether the onsen bath additives accurately represent the composition of a real onsen.

Since Mn^{2+}, Fe^{3+}, Br^-, I^- and F^- are all present, the onsen bath additives do accurately represent the composition of a real onsen.

[1] for correct conclusion drawn.

Epilogue

After this adventure, rymh was slightly addicted to Onsen bath salts. He then notices that when adding Onsen balt salts to water, some white precipitate forms. He then aspires to investigate the white precipitate known as 湯の花 (Yunohana), typically found in Onsens, in more detail. To continue with his adventures, see Bronze Tier, Team Round, Problem 2! For a slightly buffed version of this question, see Gold Tier, Team Round, Problem 3!