GENERAL DISCUSSION
The peroxides of chromium are probably better known and better characterized than those of any other transitional elements. Four different series of derivatives are known, formed under different conditions of pH, and solid members of each series have been prepared: They are:

1. The red tetraperoxy chromates (V), \( \frac{M}{3} [Cr(O_2)_4] \).
2. The violet diperoxy chromates (VI), \( M^+HCr(O_2)_2(O_2) \).
3. The derivatives of diperoxychromium (IV), \( \frac{2}{3} Cr(O_2)_2 \) and
4. The derivatives of blue chromium (VI) peroxide. This particular compound of chromium requires further investigations for the establishment of constitution and will be discussed in the account that follows:

The present thesis mainly deals with the studies on the nature and constitution of the blue chromium peroxide and its derivatives obtained by decomposing it under different conditions as well as by treating with organic nitrogenous bases.

A thorough survey of literature on the study of the nature and constitution of blue compound extracted either with ether or ethyl acetate reveals that the following three main formulae have been suggested by the different investigators for the so-called blue peroxy chromic acid or blue perchromate.

1. Spitalsky\(^1\), Riesenfeld\(^2\) and co-workers, and Wiede\(^3\) assigned to it the formula, \( HCrO_5 \) which dominated over the formulae

\[ M^* \] stands for monovalent atom. \( \ddot{D} \) represents one molecule of organic nitrogenous base.
H$_2$Cr$_2$O$_7$ and H$_2$Cr$_2$O$_5$ suggested by Barreswil$^4$ and Moisson$^5$ respectively. All the above workers supported the acidic behaviour of blue perchromate.

(ii) Schwarz and Giese$^6$ assumed it to be CrO$_5$ only and denied the acidic nature of the blue perchromate. This formula was supported by several workers, like Glasner and Steinberg$^7$, Bobtelsky et al$^8$, Evans$^9$, Tuck and Waters$^{10}$ and Stomberg$^{11}$.

Whereas (iii) Rai$^{12-16}$ gave altogether different formulae, Cr$_2$(Cr$_2$O$_{10}$)$_3$ and Cr(CrO$_8$) to this blue compound. He also regarded it neither an acid, HCrO$_5$(Loc. cit.) nor a peroxide, CrO$_5$(Loc. cit.), but a peroxy compound of chromium; chromium perchromate. These formulae were supported by Pillai$^{17}$, Rajput$^{18}$ and Jagmer$^{19}$. The view of Rai, that chromium was present in lower valency state than six in the peroxy chromates had also been suggested by Patten$^{20}$, Raynolds and Reedy$^{21}$, Laren and Helmholt$^{22}$ and Stomberg$^{23}$.

It is now evident that whereas the HCrO$_5$ and CrO$_5$ formulae differ regarding the presence or absence of hydrogen in the molecule, they agree at least at a more convincing point that only hexavalent chromium is present and have no room for the presence of trivalent chromium any where in the blue compound. The formulae Cr$_2$(Cr$_2$O$_{10}$)$_3$ and Cr(CrO$_8$) on the other hand suggest the presence of Cr(III) along with the Cr(VI) in the molecule of the blue compound.
In view of the complexity of the problem and contradictory formulae suggested regarding the blue compound I thought it worth while to under-take a systematic study of the nature of the so-called blue perchromic acid and to see as to which of the above formulae is correct. In the account that follows each formulae is described in turn, after which an attempt has been made to discuss the suitability of the above two formulae, \( \text{CrO}_5 \) and \( \text{Cr}_2(\text{Cr}_2\text{O}_7) \) or \( \text{CrCrO}_8 \). On the basis of the conclusion drawn from the above a formula is suggested for the blue compound extracted with ether or ethyl acetate prepared with phthalic acid.

The first method is employed in arriving at the constitution of the blue perchromate prepared by adding 6% hydrogen peroxide to a mixture of aqueous solutions of phthalic acid and potassium dichromate and comparing its chemical properties with the one prepared by adding sulphuric acid instead of phthalic acid. The various ratios of their oxidation values as well as of the various decomposition products have been determined and explained by taking one by one the above formulae as the formula of the blue compound.

**Investigations with the Blue Compound Prepared with Sulphuric Acid.**

It has been observed that the blue compound extracted either with ether or ethyl acetate liberates iodine from aqueous potassium iodide solution in two stages (vide chapters 1 and 4). The liberated iodine is titrated against the standard sodium
thiosulphate solution to a yellow end point and this on addition of dilute sulphuric acid liberates a further quantity of iodine, which is again titrated with the same sodium thiosulphate solution to the characteristic green end point using starch solution as an indicator. The ratios obtained between these two oxidation states are found to be within 0.55 and 0.66. If we consider \( \text{Cr}_2(\text{Cr}_2\text{O}_{10})_3 \) and \( \text{CrCrO}_8 \) formulae for blue compound, the mechanism involved in the two-stage titration was suggested by Rai as under:

1. **Accepting Rai's formulae for blue compound:**
   
   (i) In case of \( \text{Cr}_2(\text{Cr}_2\text{O}_{10})_3 \) formula:
   
   1st stage: \( \text{Cr}_2(\text{Cr}_2\text{O}_{10})_3 + \text{aq.KI} \rightarrow \text{Cr}_2(\text{Cr}_2\text{O}_8)_3 + 6 \text{I}_2 \) (b)
   2nd stage: \( \text{Cr}_2(\text{Cr}_2\text{O}_8)_3 + \text{dil.} \text{H}_2\text{SO}_4 \rightarrow 4\text{Cr}_2\text{O}_3 + 12 \text{H}_2\text{O} \) (c)

   Ratio: \( B : c = 6 : 12 \) or \( 0.5 : 1 \)

   and (ii) In case of \( \text{CrCrO}_8 \) formula:

   1st stage: \( 4\text{CrCrO}_8 \rightarrow \text{Cr}_2(\text{Cr}_2\text{O}_8)_3 + 8 \text{I}_2 \) (b)
   2nd stage: \( \text{Cr}_2(\text{Cr}_2\text{O}_8)_3 \rightarrow 4\text{Cr}_2\text{O}_3 + 12 \text{H}_2\text{O} \) (c)

   Ratio: \( B : c = 8 : 12 \) or \( 0.66 : 1 \)

   Thus the ratio of available oxygen from equation (b) and (c) is between 0.5 to 0.66 which is in close agreement with the experimental values recorded in columns (f) of the tables 1.13 to 1.18.

2. **Accepting Schwarz's formula for blue compound:**

   When titrated in two stages, \( \text{CrO}_5 \) will behave as:
(148)

1st stage: \[8\text{CrO}_5 \xrightarrow{\text{aq.} \text{Kl}} 8\text{CrO}_3 + 16 \cdot 0\] (b)

2nd stage: \[8\text{CrO}_3 \xrightarrow{\text{dilH}_2\text{SO}_4} 4\text{Cr}_2\text{O}_3 + 12 \cdot 0\] (c)

Ratio: \[b : c, \ 16 : 12 \text{ or } 1.33 : 1.\]

The value 1.33 : 1 does not agree with the experimental value, and hence the validity of Rai's formulae is confirmed from the above observations.

Here the present author is not considering Riesenfeld's and Wiede's formula HCrO₅ as the formula for blue compound, as it has already been overshadowed by CrO₅, Schwarz's formula. Therefore, the present struggle is between CrO₅ and Cr₂(Cr₂O₁₀)₃ or CrCrO₄ formulae for existence.

**Investigations with the various decomposition products of ethereal Blue compound:**

The above formulae are also examined by studying the oxidising powers of various decomposition products and comparing with the theoretical values calculated from each of the formulae.

(a) **Water decomposition product:**

**(1)** In case of Rai's formulae: like persulphuric acid, which gives sulphuric acid, the compound having formula, like Cr₂(Cr₂O₁₀)₃ can be understood to give Cr₂(Cr₂O₇)₃, Cr₂(CrO₄)₃ and CrCrO₄ compounds after decomposition in water, the open and the closed bottles respectively.

**(1)** In case of Cr₂(Cr₂O₁₀)₃ formula:

It has been shown by Rai²⁵ that the water decomposition
product of ethereal blue compound is chromium dichromate.

\[
\text{Cr}_2(\text{Cr}_2\text{O}_7)_3 + \text{water} \rightarrow \text{Cr}_2(\text{Cr}_2\text{O}_7)_3 + 9.0
\]

in presence of acid it behaves as:

\[
\text{Cr}_2(\text{Cr}_2\text{O}_7)_3 + \text{dil. H}_2\text{SO}_4 \rightarrow 4\text{Cr}_2\text{O}_3 \\
9.0 \quad \text{(d)}
\]

When this is oxidised in an alkaline solution (NaOH) with 30% hydrogen peroxide, following reaction will occur:

\[
\text{Cr}_2(\text{Cr}_2\text{O}_7)_3 + 16 \text{NaOH} + 2\text{H}_2\text{O}_2 \rightarrow 8 \text{Na}_2\text{CrO}_4 + 11 \text{H}_2\text{O} \\
\text{in presence of acid,}
\]

\[
8\text{Na}_2\text{CrO}_4 \rightarrow 8\text{Na}_2\text{O} + 4\text{Cr}_2\text{O}_3 + 12.0
\quad \text{(e)}
\]

(ii) \(\text{CrCrO}_8\) Formula:

\[
4\text{CrCrO}_8 + \text{water} \rightarrow \text{Cr}_2(\text{Cr}_2\text{O}_7)_3 + 11.0
\]

other reactions are the same as in the case of (i) formula.

(2) In case of \(\text{CrO}_5\):

Formation of \(\text{Cr}_2(\text{Cr}_2\text{O}_7)_3\) is difficult to explain with \(\text{CrO}_5\) formula for blue compound. But as it is formed, it may be assumed to have formed in the following manner:

\[
8 \text{CrO}_5 + \text{water} \rightarrow \text{Cr}_2(\text{Cr}_2\text{O}_7)_3 + 19.0
\]

other reactions are the same as explained in case of formula (i).

(b) Open bottle decomposition products:

The formation of \(\text{Cr(III)}\) chromate can be explained as:

(i) In case of \(\text{Cr}_2(\text{Cr}_2\text{O}_7)_3\) formula:

\[
5\text{Cr}_2(\text{Cr}_2\text{O}_7)_3 \rightarrow \text{open bottle} \rightarrow 8\text{Cr}_2(\text{CrO}_4)_3 + 54.0
\]

in presence of acid,

\[
2\text{Cr}_2(\text{CrO}_4)_3 \rightarrow \text{acid} \rightarrow 5\text{Cr}_2\text{O}_3 + 9.0
\quad \text{(d)}
\]
This when oxidised with 30% \( \text{H}_2\text{O}_2 \) in NaOH solution will give:

\[
2\text{Cr}_2(\text{CrO}_4)_3 + 20\text{NaOH} + 6\text{H}_2\text{O}_2 \rightarrow 10\text{Na}_2\text{CrO}_4 + 16 \text{H}_2\text{O}
\]
in presence of acid,

\[
10 \text{Na}_2\text{CrO}_4 \rightarrow 10 \text{Na}_2\text{O} + 5\text{Cr}_2\text{O}_3 + 15 \cdot 0 \quad (e)
\]

(ii) In case of CrCrO\(_8\) formula: The formation of Chromium (III) chromate can be explained as:

\[
5\text{CrCrO}_8 \xrightarrow{\text{openbottle}} 2\text{Cr}_2(\text{CrO}_4)_3 + 16 \cdot 0
\]
other reactions are the same as in case of (i) formula.

(iii) In case of CrO\(_5\) formula: The formation of Chromium (III) chromate may be shown as:

\[
10\text{CrO}_5 \xrightarrow{\text{Open bottle}} 2\text{Cr}_2(\text{CrO}_4)_3 + 26 \cdot 0
\]
for other reactions see formula (i) as they are the same.

c) Closed bottle decomposition products:

The formation of chromium (II) chromate can be explained from each of the formulae as:

(i) In case of \( \text{Cr}_2(\text{Cr}_2\text{O}_7)_3 \) formula:

\[
\text{Cr}_2(\text{Cr}_2\text{O}_7)_3 \xrightarrow{\text{closed bottle}} 4\text{CrCrO}_4 + 14 \cdot 0
\]
in presence of acid:

\[
2\text{CrCrO}_4 + 3\text{H}_2\text{SO}_4 \rightarrow \text{Cr}_2(\text{SO}_4)_3 + 3\text{H}_2\text{CrO}_4 + \text{H}_2
\]
and

\[
2\text{H}_2\text{CrO}_4 \rightarrow 2\text{H}_2\text{O} + \text{Cr}_2\text{O}_3 + 3 \cdot 0 \quad (d)
\]
This when oxidised with 30% \( \text{H}_2\text{O}_2 \) in NaOH solution forming sodium chromate:

\[
2\text{CrCrO}_4 + 8\text{NaOH} \rightarrow 4\text{Na}_2\text{CrO}_4 + 4\text{H}_2\text{O}
\]
in presence of acid,

\[
4\text{Na}_2\text{CrO}_4 \rightarrow 4\text{Na}_2\text{O} + 2\text{Cr}_2\text{O}_3 + 6 \cdot 0 \quad (e)
\]
(11) In case of CrCrO₈ formula:

\[ \text{CrCrO}_8 \xrightarrow{\text{closed}} \text{CrCrO}_4 + 4 \cdot 0 \]

Other reactions are the same as given in case of (1) formula.

(iii) In case of CrO₅ formula:

In this case to check the results formation of chromium (II) chromate may be explained as follows:

\[ 2\text{CrO}_5 \xrightarrow{\text{closed}} \text{CrCrO}_4 + 6 \cdot 0 \]

Other reactions will be the same as given in case of (1) formula.

<table>
<thead>
<tr>
<th>Formula</th>
<th>Ratios</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>decomposition product</td>
</tr>
<tr>
<td>b c : d</td>
<td>b c : e</td>
</tr>
<tr>
<td>Cr₂(Cr₂O₁₀)₃</td>
<td>2.0 : 1</td>
</tr>
<tr>
<td>CrCrO₈</td>
<td>2.22 : 1</td>
</tr>
<tr>
<td>CrO₅</td>
<td>3.11 : 1</td>
</tr>
<tr>
<td>Experimental value</td>
<td>Between 2.11 : 1 to 2.15 : 1</td>
</tr>
</tbody>
</table>

Open bottle decomposition product:

<table>
<thead>
<tr>
<th>Formula</th>
<th>Ratios</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr₂(Cr₂O₁₀)₃</td>
<td>2.50 : 1</td>
</tr>
<tr>
<td>CrCrO₈</td>
<td>2.77 : 1</td>
</tr>
<tr>
<td>CrO₅</td>
<td>3.28 : 1</td>
</tr>
<tr>
<td>Experimental value</td>
<td>Between 2.56 : 1 to 2.77 : 1</td>
</tr>
</tbody>
</table>
Closed bottle decomposition product.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Ratio 1:1</th>
<th>Ratio 1:2</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Cr}_2(\text{Cr}<em>2\text{O}</em>{10})_3$</td>
<td>3.0 : 1</td>
<td>1.5 : 1</td>
</tr>
<tr>
<td>$\text{CrCr}_2\text{O}_8$</td>
<td>3.33 : 1</td>
<td>1.66 : 1</td>
</tr>
<tr>
<td>$\text{Cr}_2\text{O}_5$</td>
<td>4.66 : 1</td>
<td>2.33 : 1</td>
</tr>
</tbody>
</table>

Experimental value

Between 2.98 : 1 to 3.14 : 1
Between 1.54 : 1 to 1.66 : 1

It is thus evident from the comparison of experimental values for different ratios obtained under varying conditions of decomposition of blue perchromate recorded in Chapter I, tables 1.13 to 1.18 and Chapter III, tables 3.1 to 3.3 with those calculated from different formulae of the decomposition products, that $\text{Cr}_2(\text{Cr}_2\text{O}_{10})_3$ and $\text{CrCr}_2\text{O}_8$, and not $\text{Cr}_2\text{O}_5$ should be the formulae for ethereal blue perchromate.

Let us now discuss as to how far Rai's formulae (loc.cit.) for the blue compound embrace the experimental observations recorded in tables 1.13 to 1.18 and 3.1 to 3.3 for the various decomposition products.

Rai and Prakash (loc.cit.) observed that the ethereal blue compound on decomposition in water yields, $\text{Cr}_2(\text{Cr}_2\text{O}_7)_3$ and when this water decomposition product is oxidised with hydrogen peroxide in presence of N NaOH solution it is converted to chromate and gives eight molecules of sodium chromate.

The above observations with water decomposition product are further confirmed here by carrying out the gravimetric
estimations of unexchanged and exchanged ingredients with the help of ion-exchange resins and chromium has been estimated in the basic as well as in the acidic parts before and after oxidation. The ratio between Cr(III) and Cr(VI) has been found to be 1 : 3 (vide Chapter III, table 3.1, columns h & j) confirming Cr₂(Cr₂O₇)₃ formula for water decomposition product.

If the water decomposition product of the blue compound is CrO₅ as suggested by Schwarz and Giese²⁶, then since chromium in it is already in the hexavalent state, there should not be any change in its oxidising powers before and after oxidation with hydrogen peroxide in N. NaOH and the ratio e/d (tables 1.13 and 1.16) should have been unity and the question of estimating gravimetrically, exchanged and unexchanged ingredients of Chromium in the basic as well as in the acidic parts does not arise. But the ratios obtained in table 3.1 columns g and h or j are 1 : 1.33 and 1 : 3 respectively. This is one of the greatest objections to the formula, CrO₅ for the blue compound.

It can easily be seen that when ethereal blue compound is decomposed in an open bottle the values in columns (d) and (e) tables 1.14 and 1.17 are approximately in the ratio of 1 : 1.5 (column h). The values in column (d) are due to the liberation of iodine from the decomposition product, acidified with dilute sulphuric acid, which probably should be the chromate. As shown in column (e) table 1.14 there is an increase in the oxidation
value of the open bottle decomposition product after its oxidation. Hence Cr(III) must also be present in the decomposition product, which on oxidation is further converted to Cr(VI). And since this increase in the oxidation values is in the ratio 2 : 3, the number of chromium atoms in the basic and the acidic parts must be in the ratio 2 : 3. This ratio of Cr(III) and Cr(VI) in the basic as well as acidic parts has been confirmed by gravimetric study, of the open bottle decomposition product, unexchanged and exchanged by ion-exchange resins before and after oxidation, vide table 3.2, columns h & j.

On this basis the formula of the open-bottle decomposition product may be taken as \( \text{Cr}_2(\text{CrO}_4)_3 \). The various ratios determined experimentally and recorded in the table 1.14 and 3.2 are in close agreement with the formula, \( \text{Cr}_9(\text{CrO}_4)_3 \).

Further, it is very interesting to note that when ethereal blue compound is allowed to decompose in the tightly closed bottle, without the presence of any foreign substance, the chromate formed is different from that obtained in case of open bottle decomposition product, as the values shown in column (d) table 1.14 are quite different from those shown in column (d) of table 1.15.

The oxidation power (column d) after oxidation with \( \text{H}_2\text{O}_2 \) and \( \text{NaOH} \) becomes double (column e), indicating thereby the presence of chromium in the equal amounts in the basic as well as in the
acidic parts of the decomposition product. The various ratios recorded in table 1.15 are also in close agreement with above observations. This leads us to assume that the product here is CrCrO₄. This type of compound has also been reported by Vanquelin²⁷. This compound has also been confirmed gravimetrically by estimating chromium in the ingredients, exchanged by ion-exchange resins, before and after oxidation, as well as in the unexchanged products. The ratio 1:1 has been found out between Cr(III) and Cr(VI) vide tables 3.3.

Thus the formula, CrO₅ suggested by Schwarz and Giese fails to explain any of the observations recorded in chapters I & II.

INVESTIGATIONS WITH THE DECOMPOSITION PRODUCTS OF BLUE COMPOUND EXTRACTED WITH ETHYL ACETATE:

(A) Water decomposition product:

(1) In case of Cr₂(Cr₂O₁₀)₃ formula: The formation of Cr₂(Cr₂O₈)₃ can easily be shown from Cr₂(Cr₂O₁₀)₃ formula. It has been shown by Pillai and Rai²⁸ that water decomposition product of the blue compound extracted with ethyl acetate is chromium peroxydichromate Cr₂(Cr₂O₈)₃.

\[
\text{Cr}_2(\text{Cr}_2\text{O}_{10})_3 \xrightarrow{\text{water}} \text{Cr}_2(\text{Cr}_2\text{O}_8)_3 + 6.0
\]

in presence of dilute sulphuric acid.

\[
\text{Cr}_2(\text{Cr}_2\text{O}_8)_3 + 12 \text{H}_2\text{SO}_4 \rightarrow 4\text{Cr}_2(\text{SO}_4)_3 + 12\text{H}_2\text{O} + 12.0 -(d)
\]
(11) In case of $\text{CrCrO}_8$ formula: Accepting this formula for blue compound, the water decomposition product is explained as:

$$4\text{CrCrO}_8 \xrightarrow{\text{water}} \text{Cr}_2(\text{Cr}_2\text{O}_8)_3 + 8.0 \quad (d''')$$
in presence of acid behaves as formula (i).

(iii) In case of $\text{CrO}_5$ formula: In this case for checking the results it may be assumed to take place as follows:

$$8\text{CrO}_5 \xrightarrow{} \text{Cr}_2(\text{Cr}_2\text{O}_8)_3 + 16.0 \quad (d'''')$$

Other reactions with acids, before and after oxidation are the same as described in case of water decomposition product of ethereal blue compound.

(B) Open and closed bottle decomposition products:

In this case it is to be noted that the oxidising powers of the open and the closed bottle decomposition products of blue perchromate extracted with ethyl acetate are the same; vide tables 1.17 and 1.18, thereby showing the formation of only one compound corresponds to the formula, $\text{Cr}_4(\text{Cr}_2\text{O}_4)_3$. Its formation and oxidising powers before and after oxidation will, therefore, be the same as given in case of open-bottle decomposition products of ethereal blue compound. Here only $B+C : d$ ratio of water decomposition is calculated on the basis of various formulae while other ratios $e : d$, $e : c$ and $B+C : e$ of water, open and closed bottle decomposition products are the same as in case of ethereal blue compound.

<table>
<thead>
<tr>
<th>Formulae</th>
<th>$b+c : d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Cr}_2(\text{Cr}_2\text{O}_10)_3$</td>
<td>1.5 : 1</td>
</tr>
<tr>
<td>$\text{CrCrO}_8$</td>
<td>1.66 : 1</td>
</tr>
<tr>
<td>$\text{CrO}_5$</td>
<td>2.33 : 1</td>
</tr>
</tbody>
</table>
and the experimental value recorded in tables 1.16 to 1.18 is between 1.49 : 1 and 1.63 : 1, which is in close agreement with Rai's formulae, \( \text{Cr}_2(\text{Cr}_2\text{O}_{10})_3 \) and \( \text{CrCrO}_8 \) even for blue compound extracted with ethyl acetate whereas formula \( \text{CrO}_5 \) is unable to explain any ratio recorded in tables 1.16 to 1.18.

The presence of \( \text{Cr(III)} \) along with \( \text{Cr(VI)} \) in the formula \( \text{Cr}_2(\text{Cr}_2\text{O}_{10})_3 \), suggested by Rai (loc. cit.) is not new but it will not be out of place to mention here the observations of Riesenfeld\(^{29}\) and Spitalsky\(^ {30} \). Riesenfeld observed that during the reaction between chromic acid and hydrogen peroxide about 28% \( \text{Cr(VI)} \) was reduced to \( \text{Cr(III)} \) state. This was further supported by the observations of Spitalsky\(^ {31} \). He found that there was a constant ratio between \( \text{Cr(III)} \) and \( \text{Cr(VI)} \) irrespective of the amount of hydrogen peroxide taken provided that it was in considerable excess to chromic acid solution. Riesenfeld\(^ {32} \) had gone to the extent of showing the formation of \( \text{Cr}_2(\text{Cr}_2\text{O}_{7})_3 \) in the reaction between hydrogen peroxide and chromic acid solutions.

No further work was done till 1949. In this year, however, Rai\(^ {33} \) could not get observations explained by accepting Schwarz's formula, \( \text{CrO}_5 \) for blueperchromate. Thus he proposed, on the basis of his observations, \( \text{Cr}_2(\text{Cr}_2\text{O}_{10})_3 \) and \( \text{CrCrO}_8 \) formulae for ethereal blue compound.

The blue compound prepared with sulphuric acid has been used as a reference and properties of blue compound prepared with phthalic acid have been explained with its help.
When the blue perchromat is prepared with phthalic acid, phthalate ions are found in the decomposition products of this blue compound. This shows that phthalate ions are involved in the composition of blue compound as otherwise it is difficult to find them in the decomposition products. Phthalic acid is almost insoluble in ether and hence its entry through this medium is difficult to agree to. Moreover, the blue compound obtained from the reaction mixture, containing ether and phthalic acid along with other reactants is washed several times with ice-cold distilled water which further minimises the above possibility.

We will now discuss as to which of the formulae, CrO₅, Cr₂(CrO₃)₃ and CrCrO₃ favors to accommodate phthalate ion without violating the valency rules. In the formula, CrO₅ there is only one hexavalent chromium which is so much over strained by the presence of two peroxy oxygen groups and one oxygen atom, CrO(O₂)₂ that it will be least interested to accommodate a negatively bivalent ion. But even if we accept only CrO₅ formula for the blue compound, it fails to explain the various ratios recorded in tables 1.12 to 1.18. Again, CrO₅ formula is a neutral molecule as was supposed by Schwarz and others (loc.cit.) and hence its association with negatively bivalent ion (phthalate) is out of question. But even if we accept that phthalate ion associates itself with it, it will be CrO₅Ph⁻². As now it is negatively bivalent ion; it will go in ether as a salt of some cation present
in the reaction mixture. But in this case Cr(III) salt can not be assumed as in that case Schwarz's formula (CrO₅) would become analogous to that of Rai's formula by taking Cr₂O₁₀⁻² anion instead of CrO₅. There is also no evidence in this case as it forms salts with K⁺ and H⁺. Moreover any such presumption does not prove fruitful.

Let us now consider how far Cr₂(Cr₂O₁₀)₃ formula is bent upon to accommodate foreign ion; say phthalate ion to prove the experimental observations recorded in tables 1.1 to 1.12. This formula as it is called Chromium (III) perchromate contains two Cr(III) along with six Cr(VI). The trivalent chromium can easily form a complex with a strong complexing anion like phthalate ion. In this case the position of phthalate ion can be expected to be safe from the valency point of view as well as from other complexing Cr₂O₁₀⁻² anions, as both of them are separately linked with two Cr(III) ions.

Riesenfeld (loc.cit.), Spitalsky (loc.cit.) and Rai (loc.cit.) suggested simultaneous oxidation and reduction of Cr₂O₇⁻² anions during the reaction between acidified dichromate solution and hydrogen peroxide, giving Cr₂O₁₀⁻² complex anions and Cr(III) cations respectively. For the formation of blue compound extracted with ether with ether or ethyl acetate, Rai has suggested the following mechanism:

\[ 3\text{Cr}_2\text{O}_7^{-2} + 9\text{H}_2\text{O}_2 \rightarrow 3\text{Cr}_2\text{O}_{10}^{-2} + 9\text{H}_2\text{O} \]
\[ \text{Cr}_2\text{O}_7^{-2} + 14\text{H}^+ \rightarrow 2\text{Cr(III)} + 7\text{H}_2\text{O} \]
as the Cr(III) is freshly generated and is a powerful complex forming ion, it coordinates with three \( \text{Cr}_2\text{O}_{10}^{2-} \) ions to give a complex anion, \( [\text{Cr}(\text{Cr}_2\text{O}_{10})_3]^{-3} \) and then this complex anion combines with Cr(III) ion to give \( \text{Cr}[\text{Cr}(\text{Cr}_2\text{O}_{10})_3] \) blue complex. This can be represented by the following structure:

\[
3\text{Cr}_2\text{O}_{10}^{2-} + \text{Cr}(\text{III}) \rightarrow [\text{Cr}(\text{Cr}_2\text{O}_{10})_3]^{-3}
\]

Blue Compound.

But if instead of sulphuric acid, phthalic acid is taken it gives two protons and a phthalate ion. The \( \text{H}^+ \) ions supplied by phthalic acid is consumed in the reduction of \( \text{Cr}_2\text{O}_7^{2-} \) ions to Cr(III) ions by hydrogen peroxide. The freshly generated Cr(III) ions are to coordinate with two types of anions i.e., \( \text{(Cr}_2\text{O}_{10})^{-2} \) and \( \text{(phthalate)}^{-2} \), but not with free phthalic acid, as it has to supply \( \text{H}^+ \) ions for the reduction of \( \text{Cr}_2\text{O}_7^{2-} \) to Cr(III) during the formation of blue compound in the reacting system.

The presence of \( \text{(Cr}_2\text{O}_{10})^{-2} \) has been confirmed iodometrically whereas that of the \( \text{(phthalate)}^{-2} \) has been confirmed by fluorescence test. The presence of phthalate ions is also confirmed when water decomposition product of ethereal blue compound prepared with phthalic acid is exchanged with the help of ion-exchange resins. The effluent from anion exchangers and elutriant from cation
exchangers, both give the fluorescein test of phthalic acid. This proves that the phthalate ions are coordinated with Cr(III) i.e., cationic chromium and not with chromium in the anionic state. The coordination of phthalate ions with cationic chromium in the composition of blue compound is also supported by relatively low concentration of blue compound prepared with phthalic acid than with sulphuric acid. In the former case some of the Cr(III) ions might have coordinated individually with two or more phthalate ions to give anions of the form $[\text{Cr(Phth)}_{2}]^{-1}$ or $[\text{Cr(Phth)}_{3}]^{-3}$ and therefore will not be able to coordinate with negatively charged $(\text{Cr}_{2}O_{10})^{-2}$. These anions may, therefore, combine with other cations such as potassium or any other cation present in the solution, thus, giving less quantity of blue perchromate.

If it is accepted that phthalate ions are involved in the composition of blue perchromate extracted with ether or ethyl acetate the following three complexes of the formulae:

(a) $(\text{CrPhth})_{2}\text{Cr}_{2}O_{10}$ ;
(b) $\text{Cr}_{2}\text{Phth}(\text{Cr}_{2}O_{10})_{2}$ and
(c) $(\text{CrPhth})_{3}\left[\text{Cr}(\text{Cr}_{2}O_{10})_{3}\right]$ are possible to be formed during the preparation of the blue compound in presence of phthalic acid.

Each of the above formulae will be discussed in detail now.

**Formation of Blue Compound in Presence of Phthalic Acid:**

Rai (loc.cit.) suggested simultaneous oxidation and reduction of $\text{Cr}_{2}O_{7}^{-2}$ ions during the reaction between acidified dichromate and hydrogen peroxide giving $(\text{Cr}_{2}O_{10})^{-2}$ and Cr(III) respectively. When a mixture of aqueous solutions of potassium
dichromate and phthalic acid is treated with hydrogen peroxide, the following reactions may be expected to occur:

(1) Oxidation of \( \text{Cr}_2\text{O}_7^{2-} \) to \( \text{Cr}_2\text{O}_{10}^{3-} \):

\[
3\text{H}_2\text{Cr}_2\text{O}_7 + 9 \text{H}_2\text{O}_2 \rightarrow 3\text{Cr}_2\text{O}_{10}^{3-} + 6\text{H}^+ + 9\text{H}_2\text{O} \quad (i)
\]

(2) Reduction of \( \text{Cr}_2\text{O}_7^{2-} \) to \( \text{Cr(III)} \):

\[
\text{H}_2\text{Cr}_2\text{O}_7 + 3 \text{H}_2\text{O}_2 \rightarrow \text{Cr}_2\text{O}_3 + 4\text{H}_2\text{O} + 6.0 \quad (ii)
\]

\( \text{H}^+ \) ions from reaction (i) will combine with \( \text{Cr}_2\text{O}_3 \) then:

\[
\text{Cr}_2\text{O}_3 + 6 \text{H}^+ \rightarrow 2\text{Cr}^{3+} + 3\text{H}_2\text{O}
\]

as the \( \text{H}^+ \) ions, furnished by phthalic acid in aqueous solution are used up during the reduction of \( \text{Cr}_2\text{O}_3 \) to \( \text{Cr(III)} \) by hydrogen peroxide. This proves that phthalate ions but not phthalic acid molecules are coordinated with \( \text{Cr(III)} \) in the complexes.

(3) As the \( \text{Cr(III)} \) ions are freshly generated and are powerful complex forming ions, are to accommodate two types of anions, \( (\text{Cr}_2\text{O}_{10})^{2-} \) and \( (\text{Phth})^{2-} \), (Phth. represents the phthalate ion). It seems that there is a competition between phthalate ions and \( \text{Cr}_2\text{O}_{10}^{2-} \) ions for \( \text{Cr(III)} \) ions to form blue compound.

It will be needful to mention here the work of Rai\(^{34}\), and Gautam\(^{35}\). They prepared blue compound with hydrofluoric acid and also with lactic acid separately, and observed that a stage is reached during the preparation of blue compound when it does not form at all. At this stage it appears that \( \text{Cr}_2\text{O}_{10}^{2-} \) ions do not get the opportunity to coordinate either with \( \text{Cr(III)} \) or any other
complex cation of Cr(III) with HF₂⁻ in the former case and a complex cation of Cr(III) with lactate ion in the later case.

The blue compound prepared with phthalic acid may have one of the following probable formulae:

(A) \(2\text{Cr(III)} + 2\text{Phth}^2_- + 2\text{Cr}_2\text{O}_{10}^- \rightarrow (\text{CrPhth})_2\text{Cr}_2\text{O}_{10}\)

(B) \(2\text{Cr(III)} + \text{Phth}^2_- + 2\text{Cr}_2\text{O}_{10}^- \rightarrow \text{Cr}_2\text{Phth(Cr}_2\text{O}_{10})_2\)

(C) \(4\text{Cr(III)} + 3\text{Phth}^2_+ + 2\text{Cr}_2\text{O}_{10}^- \rightarrow (\text{CrPhth})_3\left[\text{Cr(Cr}_2\text{O}_{10})_3\right]\)

It has already been seen that compounds having formulae \(\text{CrCrO}_8\) and \(\text{Cr}[\text{Cr}_2\text{O}_{10}]_3\) (loc. cit.) behave in the same manner as the blue compound when prepared with sulphuric acid. The formulae mentioned above for the blue compound prepared with phthalic acid, individually should be in agreement with the experimental observations recorded in the various tables of Chapters I to VIII. If it is so, this will prove the appropriateness of the above formulae to be regarded individually as the formula for blue compound. Each of the above formulae are described in turn and compared with the experimental observations to decide which of the formulae confirms the nature and structure of blue compound. (A) In case of \((\text{CrPhth})_2\text{Cr}_2\text{O}_{10}\) formula: The structure is proposed as:

![Diagram of the proposed structure]
(1) When titrated in two stages: iodometrically, it behaves as:

Ist stage: $\text{(CrPhth)}_2\text{Cr}_2\text{O}_{10}^{\text{aq,II}} \rightarrow (\text{CrPhth})_2\text{Cr}_2\text{O}_7 + 3.0$ (b)

IIInd stage: $\text{(CrPhth)}_2\text{Cr}_2\text{O}_7^{\text{dil. acid}} \rightarrow (\text{CrPhth})_2\text{O} + \text{Cr}_2\text{O}_3 + 3.0$ (c)

the ratio $b : c = 1 : 1$, same as determined experimentally
vide tables 1.1 to 1.12.

(2) Water decomposition product: It decomposes in water as follows:

$\text{(CrPhth)}_2\text{Cr}_2\text{O}_{10} \rightarrow (\text{CrPhth})_2\text{Cr}_2\text{O}_6 + 4.0$

and in presence of dilute sulphuric acid it gives,

$\text{(CrPhth)}_2\text{Cr}_2\text{O}_6 \rightarrow (\text{CrPhth})_2\text{O} + \text{Cr}_2\text{O}_3 + 2.0$ (d)

the ratio $b + c : d = 6 : 2$ or $3 : 1$, it agrees with the experimental values vide tables 1.1, 1.4 and 1.7.

After oxidation: The water decomposition product when oxidised with 30% $\text{H}_2\text{O}_2$ in N. $\text{NaOH}$ solution it forms:

$(\text{CrPhth})_2\text{Cr}_2\text{O}_6 + 4\text{NaOH} + \text{H}_2\text{O}_2 \rightarrow (\text{CrPhth})_2\text{O} + 2\text{Na}_2\text{CrO}_4 + 3\text{H}_2\text{O}$

and in presence of dilute sulphuric acid, this oxidised product gives:

$(\text{CrPhth})_2\text{O} + 2\text{Na}_2\text{CrO}_4 \rightarrow (\text{CrPhth})_2\text{O} + 2\text{Na}_2\text{O} + \text{Cr}_2\text{O}_3 + 3.0$ (e)

It appears that even on oxidation with 30% $\text{H}_2\text{O}_2$ in strongly alkaline medium the complex is not destroyed.

**Ratios:**

<table>
<thead>
<tr>
<th>Calculated from the formula</th>
<th>Experimental values</th>
</tr>
</thead>
<tbody>
<tr>
<td>$b + c : e = 6 : 3$ or $2 : 1$</td>
<td>$1.75 : 1$</td>
</tr>
<tr>
<td>$e : d = 3 : 2$ or $1.5 : 1$</td>
<td>$1.71 : 1$</td>
</tr>
<tr>
<td>$e : c = 3 : 3$ or $1 : 1$</td>
<td>$1.16 : 1$</td>
</tr>
</tbody>
</table>
These ratios except \( b : c \) and \( b + c : d \) of the oxidising powers as calculated theoretically from the \((A)\) formula do not agree with the experimental values (vide tables 1.1, 1.7 & 1.10).

If it is accepted that the complex is destroyed during oxidation with 30% hydrogen peroxide in alkaline medium then,

\[
(\text{CrPhth})_2\text{Cr}_2\text{O}_7\text{Na}_2\text{O} + 6\text{H}_2\text{O}_2 \rightarrow 2\text{PhthNa}_2 + 4\text{Na}_2\text{CrO}_4 + 12\text{H}_2\text{O}.
\]

and in presence of dilute sulphuric acid it gives:

\[
4\text{Na}_2\text{CrO}_4 \rightarrow 4\text{Na}_2\text{O} + 2\text{Cr}_2\text{O}_3 + 6.0 \quad (e')
\]

Now various ratios are as under:

\[
b + c : e' = 6 : 6 \text{ or } 1 : 1 ; \ e' : d = 6 : 2 \text{ or } 3 : 1 ; \text{ and } e' : c = 6 : 3 \text{ or } 2 : 1 \text{ as calculated theoretically.}
\]

These ratios are either very low or very high as compared with the experimental values. Therefore, it is altogether unacceptable that the complex is destroyed during oxidation under these conditions.

(3) **Open bottle decomposition product:** It decomposes under open bottle conditions as follows:

\[
(\text{CrPhth})_2\text{Cr}_2\text{O}_10 \rightarrow (\text{CrPhth})_2\text{O} + \text{CrCr}_2\text{O}_4 + 5.0
\]

and in presence of dilute sulphuric acid it gives,

\[
(\text{CrPhth})_2\text{O} + \text{CrCr}_2\text{O}_4 \rightarrow (\text{CrPhth})_2\text{O} + \text{Cr}_2\text{O}_3 + 0 \quad (d)
\]

The ratio \( b + c : d = 6 : 1 \) \( \text{or} \) does not agree with the experimental value,\(5.1:1\) (Tables 1.2, 1.5, 1.8 and 1.11).

**After oxidation:** When treated with 30% hydrogen peroxide in a strongly alkaline medium, this product behaves as:

\[
(\text{CrPhth})_2\text{O} + \text{CrCr}_2\text{O}_4 + 4\text{NaOH} + 2\text{H}_2\text{O}_2 \rightarrow (\text{CrPhth})_2\text{O} + 2\text{Na}_2\text{CrO}_4 + 4\text{H}_2\text{O}
\]
and in presence of dilute sulphuric acid it gives,

\[
\text{(CrPhth)}_2O + 2\text{Na}_2\text{CrO}_4 \rightarrow \text{(CrPhth)}_2O + 2\text{Na}_2O + \text{Cr}_2\text{O}_3 + 3\text{O} \ (e)
\]

**Ratios**: Calculated from the formula. | Experimental values.
---|---
\(b\) : \(c\) : \(e\) = 6 : 3 or 2 : 1 | 1.71 : 1
\(e\) : \(d\) = 3 : 1 | 3 : 1
\(e\) : \(c\) = 3 : 3 or 1 : 1 | 1.16 : 1

All these ratios except \(e\) : \(d\) do not agree with the experimental values (vide tables 1.8 & 1.11). It seems here also that the complex does not destroy during oxidation with 30% hydrogen peroxide in strongly alkaline medium, on the grounds discussed earlier in case of water decomposition product.

(3) **Closed bottle decomposition product**:

From the various ratios recorded in the tables of Chapter I, it appears that the same compound is formed as in case of open-bottle decomposition product. Therefore no further explanation is required.

It is evident from the comparison of the various ratios of the oxidising powers of the different decomposition products of ethereal blue compound having \((\text{CrPhth})_2\text{Cr}_2\text{O}_{10}\) formula that the values determined experimentally do not agree with the values calculated from formula. They are either higher or lower than those determined experimentally. The \(\text{Cr(III)} : \text{Cr(VI)}\) ratio is 1 : 1.5 as determined (vide table 2.3) gravimetrically in the basic and acidic parts of the exchanged ingredients with the help of ion exchange resins, from the water decomposition product, which is not possible from this formula.
because in this case Cr(III) : Cr(VI) as calculated theoretically is 1 : 1. This also goes against the formula. Hence the complex having the formula, (CrPhth)_2Cr_2O_10 is altogether unacceptable.

(B) In case of Cr_2Phth(Cr_2O_10)_2 formula: The structure is proposed as:

\[
\begin{align*}
&\text{O} \\
C &- O \quad \text{Cr} = \text{Cr}_2\text{O}_{10} \\
C &- O \quad \text{Cr} = \text{Cr}_2\text{O}_{10}
\end{align*}
\]

(1) When titrated in two stages: iodometrically, it behaves as:

1st stage: \[
\text{Cr}_2\text{Phth}(\text{Cr}_2\text{O}_{10})_2 \xrightarrow{\text{aq.KI}} \text{Cr}_2\text{Phth}(\text{Cr}_2\text{O}_7)_2 + 6.0 \quad (b)
\]

2nd Stage: \[
\text{Cr}_2\text{Phth}(\text{Cr}_2\text{O}_7)_2 \xrightarrow{\text{dil.acid}} (\text{Cr}_2\text{Phth})_2\text{O}_2 + 2\text{Cr}_2\text{O}_3 + 6.0 \quad (c)
\]

The ratio \( b : c = 1 : 1 \), same as determined experimentally vide tables 1.1 to 1.12, column f.

(2) Water decomposition product: It decomposes in water as follows:

\[
\text{Cr}_2\text{Phth}(\text{Cr}_2\text{O}_{10})_2 \rightarrow \text{Cr}_2\text{Phth}(\text{Cr}_2\text{O}_6)_2 + 8.0
\]

and in presence of dilute sulphuric acid it gives:

\[
\text{Cr}_2\text{Phth}(\text{Cr}_2\text{O}_6)_2 \rightarrow (\text{Cr}_2\text{Phth})_2\text{O}_2 + 2\text{Cr}_2\text{O}_3 + 4.0 \quad (d)
\]

the ratio \( b + c : d = 12 : 4 \) or \( 3 : 1 \), it agrees with the experimental values (vide tables 1.1, 1.4, 1.7 and 1.10; column g).

After oxidation: When oxidised with 30% hydrogen peroxide in strongly alkaline medium it forms:

\[
\text{Cr}_2\text{Phth}(\text{Cr}_2\text{O}_6)_2 + 8\text{NaOH} + 2\text{H}_2\text{O}_2 \rightarrow (\text{Cr}_2\text{Phth})_2\text{O}_2 + 4\text{Na}_2\text{Cr}_4\text{O}_4 + 6\text{H}_2\text{O}
\]
and in presence of dilute sulphuric acid, this oxidised product gives:

\[ (\text{Cr}_2\text{Phth})_0 + 4\text{Na}_2\text{CrO}_4 \rightarrow (\text{Cr}_2\text{Phth})_0 + 4\text{Na}_2\text{O} + 2\text{Cr}_2\text{O}_3 + 6 \cdot 0 \]  

(e)

It appears that even on oxidation with 30% hydrogen peroxide in strongly alkaline medium the complex is not destroyed.

Ratios:

- Calculated from the formula:
  - \( b+c : e = 12 : 6 \text{ or } 2 : 1 \)
  - \( e : c = 6 : 6 \text{ or } 1 : 1 \)
  - \( e : d = 6 : 4 \text{ or } 1.5 : 1 \)

- Experimental values:
  - \( 1.75 : 1 \)
  - \( 1.16 : 1 \)
  - \( 1.71 : 1 \)

All these ratios calculated theoretically from the formula are the same as in the case of \( (A) \) formula. Hence it is ruled out on the grounds discussed earlier in the case of \( (A) \) formula.

(3) Open and closed bottle decomposition products: As the same complexes are formed under the open and tightly closed conditions the blue compound having the formula \( \text{Cr}_2\text{Phth(Cr}_2\text{O}_{10})_2 \) decomposes as follows:

\[ \text{Cr}_2\text{Phth(Cr}_2\text{O}_{10})_2 \rightarrow (\text{Cr}_2\text{Phth})_0 + 2\text{Cr}_2\text{O}_4 + 10 \cdot 0 \]

and in presence of dilute sulphuric acid it gives:

\[ (\text{Cr}_2\text{Phth})_0 + 2\text{Cr}_2\text{O}_4 \rightarrow (\text{Cr}_2\text{Phth})_0 + 2\text{Cr}_2\text{O}_3 + 2 \cdot 0 \]  

(d)

the ratio, \( b+c : d = 12 : 2 \text{ or } 6 : 1 \); it does not agree with the experimental value which is \( 5.1 : 1 \) (tables 1.2, 1.3, 1.5, 1.6, 1.8 & 1.9).

After oxidation: When treated with 30% hydrogen peroxide in excess of sodium hydroxide solution, this product behaves as follows
(169)

$$(\text{Cr}_2\text{Phth})_2 \text{O}_2 + 2\text{CrCl}_4 + 8\text{NaOH} + 4\text{H}_2\text{O}_2 \rightarrow (\text{Cr}_2\text{Phth})_2 \text{O}_2 + 4\text{Na}_2\text{CrO}_4 + 8\text{H}_2\text{O}$$

and in presence of dilute sulphuric acid it gives:

$$(\text{Cr}_2\text{Phth})_2 \text{O}_2 + 4\text{Na}_2\text{CrO}_4 \rightarrow (\text{Cr}_2\text{Phth})_2 \text{O}_2 + 4\text{Na}_2\text{O} + 2\text{Cr}_2\text{O}_3 + 6.0 \ (e)$$

**Ratios**

<table>
<thead>
<tr>
<th>Calculated from the formula</th>
<th>Experimental values</th>
</tr>
</thead>
<tbody>
<tr>
<td>$b:c : e = 12 : 6$ or $2 : 1$</td>
<td>$1.71 : 1$</td>
</tr>
<tr>
<td>$e : d = 6 : 2$ or $3 : 1$</td>
<td>$3 : 1$</td>
</tr>
<tr>
<td>$e : c = 6 : 6$ or $1 : 1$</td>
<td>$1.16 : 1$</td>
</tr>
</tbody>
</table>

All these ratios calculated theoretically from the formula, $(\text{Cr}_2\text{Phth}(\text{Cr}_2\text{O}_{10})_2$ are the same as in the case of (A) formula and the $\text{Cr(III)} : \text{Cr(VI)}$ as calculated from the formula is $1 : 2$, against $1 : 1.5$ determined gravimetrically (table 2.3). Hence the complex having the formula $\text{Cr}_2\text{Phth}(\text{Cr}_2\text{O}_{10})_2$ is altogether unacceptable on the grounds which have been discussed earlier in the case of (A) formula and therefore it requires no further explanation.

(C) In case of $(\text{CrPhth})_3\left[\text{Cr(Cr}_2\text{O}_{10})_3\right]$ formula: The structure is proposed as:

\[
(\text{CrPhth})_3
\]

1. When titrated in two stages: iodometrically, it behaves as:
   1st stage: $2(\text{CrPhth})_3[\text{Cr} (\text{Cr}_2\text{O}_{10})_3]$ $\rightarrow$ $2(\text{CrPhth})_3[\text{Cr} (\text{Cr}_2\text{O}_7)_3]$ $+ 18.0$ (b)
   2nd stage: $2(\text{crPhth})_3[\text{Cr}(\text{Cr}_2\text{O}_7)_3]$ $\rightarrow$ $3(\text{crPhth})_2\text{Cr}_2\text{O}_3 + 18.0$ (c)

the ratio $b : c = 1 : 1$ same as determined experimentally vide
tables 1.1 to 1.12, column f.

(2) Water decomposition product: The compound having the formula, \((\text{CrPhth})_3[\text{Cr}(\text{Cr}_2\text{O}_{10})_3]\) decomposes in water as follows:

\[
2(\text{CrPhth})_3 [\text{Cr}(\text{Cr}_2\text{O}_{10})_3] \rightarrow 2(\text{CrPhth})_3 [\text{Cr}(\text{Cr}_2\text{O}_6)_3] + 24.0
\]

and in presence of dilute sulphuric acid it gives:

\[
2(\text{CrPhth})_3 [\text{Cr}(\text{Cr}_2\text{O}_6)_3] \rightarrow 3(\text{CrPhth})_2\text{O} + 7\text{Cr}_2\text{O}_3 + 12.0
\]  (d)

The ratio \(b+c : d = 36 : 12\) or \(3 : 1\), it agrees with the experimental values (vide tables 1.1, 1.4 1.7 and 1.10, column g).

After oxidation: When oxidised with 30% hydrogen peroxide in strongly alkaline solution it forms:

\[
2(\text{CrPhth})_3 [\text{Cr}(\text{Cr}_2\text{O}_6)_3] + 28\text{NaOH} + 9\text{H}_2\text{O}_2 \rightarrow 3(\text{CrPhth})_2\text{O} + 14\text{Na}_2\text{CrO}_4 + 23\text{H}_2\text{O}
\]

and in presence of dilute sulphuric acid, this oxidised product gives:

\[
3(\text{CrPhth})_2\text{O} + 14\text{Na}_2\text{CrO}_4 \rightarrow 3(\text{CrPhth})_2\text{O} + 14\text{Na}_2\text{O} + 7\text{Cr}_2\text{O}_3 + 21.0
\]  (e)

It appears that even on oxidation with 30% hydrogen peroxide in strongly alkaline medium the complex is not destroyed. In case it destroys it will give 20 molecules of \(\text{Na}_2\text{CrO}_4\) which will give 30 oxygen atoms per two molecules of the complex in presence of dilute sulphuric acid. The excess of available oxygen (30 atoms) will give either lower or higher values of the ratios than those determined experimentally. Thus, it goes against the experimental observations. Hence it can not be accepted that it destroys after oxidation by 30% hydrogen peroxide in strongly alkaline medium.
Ratios: Calculated from the formula Experimental values.

\[ \begin{align*}
  \text{b+c : e} &= 36 : 21 \text{ or } 1.75 : 1 \quad 1.70 \text{ to } 1.78 : 1 \\
  \text{e : c} &= 21 : 18 \text{ or } 1.16 : 1 \quad 1.10 \text{ to } 1.17 : 1 \\
  \text{e : d} &= 21 : 12 \text{ or } 1.71 : 1 \\
  & \quad 1.70 \text{ to } 1.76 : 1
\end{align*} \]

All these ratios including \( b : c \) and \( b+c : d \) calculated from the formula of the complex are in close agreement with the experimental values (vide tables 1.1, 1.4, 1.7 and 1.10, columns f, g, h, i & j).

The \( \text{Cr(III)} : \text{Cr(VI)} \) as calculated from the formula of water decomposition product of the complex is 1 : 1.5. This value is the same as determined gravimetrically in the basic and acidic part of the exchanged ingredients separated with the help of ion exchange resins, from the water decomposition product of the blue compound (vide table 2.3, columns c & e).

It can be inferred from the above observations that only the formula \((\text{CrPhth})_3[\text{Cr(Cr}_2\text{O}_6)_3]\) is valid for the water decomposition product of ethereal blue perchromate prepared with phthalic acid. More arguments in favour of the complex of formula, \((\text{CrPhth})_3[\text{Cr(Cr}_2\text{O}_6)_3]\) will be presented later on.

(3) Open and closed bottle decomposition products: As the same complexes are formed under the open and the tightly closed bottle conditions the blue compound of the formula, \((\text{CrPhth})_3[\text{Cr(Cr}_2\text{O}_6\text{)}_3]\) decomposes as follows:

\[ 2(\text{CrPhth})_3[\text{Cr(Cr}_2\text{O}_6\text{)}_3] \rightarrow 3(\text{CrPhth})_2\text{O} + 7\text{CrO}_4 + 29.0 \]
and in presence of dilute sulphuric acid it gives:

\[3(\text{CrPhth})_2O + 7\text{Cr}_2\text{O}_3 \rightarrow 3(\text{CrPhth})_2O + 7\text{Cr}_2\text{O}_5 + 7 \cdot 0\]  

(d)

the ratio b+c : d = 36:7 or 51:1, it also agrees with the experimental values (vide tables 1.2, 1.3, 1.5, 1.6, 1.8 & 1.9).

After oxidation: When oxidised with 30% hydrogen peroxide in strongly alkaline medium it forms:

\[3(\text{CrPhth})_2O + 7\text{Cr}_2\text{O}_3 + 28\text{NaOH} + 9\text{H}_2\text{O}_2 \rightarrow 3(\text{CrPhth})_2O + 14\text{Na}_2\text{Cr}_4 + 23\text{H}_2\text{O}\]

and in presence of dilute sulphuric acid, this product gives:

\[3(\text{CrPhth})_2O + 14\text{Na}_2\text{Cr}_4 \rightarrow 3(\text{CrPhth})_2O + 14\text{Na}_2O + 7\text{Cr}_2\text{O}_5 + 21 \cdot 0\]  

(e)

It appears in this case also that even on oxidation with 30% hydrogen peroxide in strongly alkaline medium the complex is not destroyed and behaves similarly as the complex of water decomposition product after oxidation. Since it consumes the same amount of sodium thiosulphate as in case of water decomposition product after oxidation; the compounds formed after oxidation in both the cases are the same having the same formula.

**Ratios:** Calculated from the formula | Experimental values.
---|---
\[b+c : e = 36 : 21 \text{ or } 1.71 : 1\] | 1.70 to 1.74 : 1
\[e : d = 21 : 7 \text{ or } 3 : 1\] | 2.94 to 3.08 : 1
\[e : c = 21 : 18 \text{ or } 1.16 : 1\] | 1.10 to 1.19 : 1

All these ratios including \(b : c\) and \(b+c : d\), calculated from the formula of the complex are in a very close agreement with the experimental values (vide tables 1.2, 1.3, 1.5, 1.6, 1.8 & 1.9; columns f, g, h, i and j).
THE VARIOUS RATIOS OF THE OXIDISING POWERS OF BLUE PERCHROMATE AND ITS DECOMPOSITION PRODUCTS AS CALCULATED FROM THE POSSIBLE FORMULAE OF THE COMPLEX.

<table>
<thead>
<tr>
<th>VALUES CALCULATED FROM THE FORMULA</th>
<th>EXPERIMENTAL VALUES</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) (\text{(CrPhth)}_2\text{Cr}<em>2\text{O}</em>{10})</td>
<td>(b) (\text{Cr}_2\text{Phth(Cr}<em>2\text{O}</em>{10})_2)</td>
</tr>
</tbody>
</table>

(1) Water decomposition

<table>
<thead>
<tr>
<th>Product</th>
<th>(i)</th>
<th>(ii)</th>
<th>(iii)</th>
<th>(iv)</th>
<th>(v)</th>
<th>(vi)</th>
</tr>
</thead>
<tbody>
<tr>
<td>b : c</td>
<td>1 : 1</td>
<td>3 : 1</td>
<td>1.5 : 1</td>
<td>1 : 1</td>
<td>2 : 1</td>
<td>1 : 2</td>
</tr>
<tr>
<td>e : d</td>
<td>1.5 : 1</td>
<td>3 : 1</td>
<td>1.75 : 1</td>
<td>1.66 : 1</td>
<td>1.71 : 1</td>
<td>1.5 : 1</td>
</tr>
<tr>
<td>e : c</td>
<td>1 : 1</td>
<td>3 : 1</td>
<td>1.75 : 1</td>
<td>1.66 : 1</td>
<td>1.71 : 1</td>
<td>1.5 : 1</td>
</tr>
<tr>
<td>b + c : e = 2 : 1</td>
<td>6 : 1</td>
<td>5.1 : 1</td>
<td>4.90 to 5.28 : 1</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(2) Open & closed bottle decomposition products.

<table>
<thead>
<tr>
<th>Product</th>
<th>(i)</th>
<th>(ii)</th>
<th>(iii)</th>
<th>(iv)</th>
</tr>
</thead>
<tbody>
<tr>
<td>b : c</td>
<td>6 : 1</td>
<td>3 : 1</td>
<td>1 : 1</td>
<td>2 : 1</td>
</tr>
<tr>
<td>e : d</td>
<td>3 : 1</td>
<td>1 : 1</td>
<td>1.71 : 1</td>
<td>1.69 to 1.75 : 1</td>
</tr>
<tr>
<td>e : c</td>
<td>1 : 1</td>
<td>1.66 : 1</td>
<td>1.71 : 1</td>
<td>1.69 to 1.75 : 1</td>
</tr>
<tr>
<td>b + c : e = 2 : 1</td>
<td>5.1 : 1</td>
<td>4.90 to 5.28 : 1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

As we have already discussed earlier and is also evident from the comparison of the above ratios of the oxidising powers of the different decomposition products of ethereal blue compound, the complexes having the formulae \(\text{(CrPhth)}_2\text{Cr}_2\text{O}_{10}\) and \(\text{Cr}_2\text{Phth(Cr}_2\text{O}_{10})_2\) are not blue perchromate but the complex of the formula \(\text{(CrPhth)}_3\left[\text{Cr(Cr}_2\text{O}_{10})_3\right]\) is to be regarded as the blue perchromate prepared with phthalic acid.
Is is also very interesting to note that the value of e : c is 1.0 as calculated from formulae, \((\text{CrPhth})_2\text{Cr}_2\text{O}_{10}\) and \(\text{Cr}_2\text{Phth}(\text{Cr}_2\text{O}_{10})_2\) of the complexes of blue compound prepared with phthalic acid. It indicates that the IIInd stage titre value is equal to the titre values of the oxidised decomposition products. Contrary to this, the observed value of e : c lies between 1.16 & 1.20 (vide tables 1.7 to 1.12) showing thereby that the decomposition products consume from 1.16 to 1.20 times more the volume of thiosulphate solution than what is consumed by the IIInd stage reaction products.

It can be easily explained from the formula, \((\text{CrPhth})_3 [\text{Cr} (\text{Cr}_2\text{O}_{10})_3]\) of the blue compound prepared with phthalic acid as that the IIInd stage reaction product is \((\text{CrPhth})_3 [\text{Cr} (\text{Cr}_2\text{O}_{7})_3]\) and water decomposition product is \((\text{CrPhth})_3 [\text{Cr} (\text{Cr}_2\text{O}_6)_3]\) both having one Cr(III) coordinated with six Cr(VI) in each case. During the process of oxidation of water decomposition product only Cr(III) gets oxidised to Cr(VI) and the number of total Cr(VI) in the oxidised products becomes seven. Thus, the value of e : c 7 : 6 or 1.16 is the same as observed experimentally. Hence the most probable formula of the complex is \((\text{CrPhth})_3 [\text{Cr} (\text{Cr}_2\text{O}_{10})_3]\).

The various ratios of the oxidising powers of water decomposition product of ethereal blue compound prepared with phthalic acid can only be explained when chromium is accepted to be in the pentavalent state in these products. The stabilisation of pentavalent chromium due to complex formation in these cases is
Not new. Several such cases are known where pentavalent chromium is stabilized due to complex formation.\textsuperscript{37}

There are certain values in the columns f, g, h, i & j of tables 1.1 to 1.6 which are either the same or slightly higher than those obtained when blue perchromate is prepared with sulphuric acid (vide tables 1.13 to 1.15). It indicates that when N/15 phthalic acid is used in small amounts i.e., less than 150 ml., only very few phthalate ions contribute to the formation of blue compound and a mixture of two complexes, \(\text{Cr}^2_2(\text{Cr}_2\text{O}_10)_3\) and \((\text{CrPhth})_3[\text{Cr}(\text{Cr}_2\text{O}_10)^3]\) is obtained in which the latter is in traces, explaining slightly higher values than that of the blue compound prepared with sulphuric acid. As the amount of phthalic acid is increased gradually the quantity of the complex, \((\text{CrPhth})_3[\text{Cr}(\text{Cr}_2\text{O}_10)^3]\) increases and of \(\text{Cr}_2(\text{Cr}_2\text{O}_10)_3\), complex decreases in the mixture. When 150 ml. of phthalic acid is used the latter complex does not form at all but only \((\text{CrPhth})_3[\text{Cr}(\text{Cr}_2\text{O}_10)^3]\) complex is formed and so a maximum constant value of the ratio b : c is 1.0, where there is no further increase, whatever amount of phthalic acid may be used for the preparation of blue compound. From this it appears that the complex forming capacity of \(\text{Cr}_2\text{O}_10^2\) and phthalate\(^\text{2+}\) ions is the same.

It is again very interesting to note that unlike the blue compound prepared with sulphuric acid, if the amount of the same concentration of hydrogen peroxide is varied during the preparation...
of blue compound in presence of phthalic acid, the concentration of the blue compound decrease as the amount of hydrogen peroxide increases, thereby causing no change in the ratios (vide tables 1.7 to 1.12). It can be explained that large amount of hydrogen peroxide will increase Cr(III) in the solution and hence its removal either in the form of complex anion \((\text{CrPhth}_2)^-\) or \((\text{CrPhth}_3)^-\). This results in shortage of \((\text{CrPhth}_3)^+\) cation and hence the low concentration of blue compound.

The formula, \([\text{Cr(Cr}_2\text{O}_1\text{O}_3)^3]\) for blue compound prepared with phthalic acid is further confirmed from the mechanism of the formation of blue compound suggested by Rai (loc. cit.). When a mixture of aqueous solution of potassium dichromate and phthalic acid is treated with hydrogen peroxide, the following reactions may be expected to occur:

(i) Oxidation of \(\text{Cr}_2\text{O}_7^{2-}\) to \(\text{Cr}_2\text{O}_10^{2-}\):

\[
3\text{H}_2\text{Cr}_2\text{O}_7 + 3 \text{H}_2\text{O}_2 \rightarrow 3\text{Cr}_2\text{O}_10^{2-} + 6\text{H}^+ + 9 \text{H}_2\text{O} \quad (1)
\]

(ii) Reduction of \(\text{Cr}_2\text{O}_7^{2-}\) to \(\text{Cr}_2\text{O}_3\) and then to \(\text{Cr}(\text{III})\):

\[
\text{H}_2\text{Cr}_2\text{O}_7 + 3 \text{H}_2\text{O}_2 \rightarrow \text{Cr}_2\text{O}_3 + 4 \text{H}_2\text{O} + 6 \cdot \text{O} \\
\text{Cr}_2\text{O}_3 + 6 \text{H}^+ \rightarrow 2\text{Cr}(\text{III}) + 3 \text{H}_2\text{O} \quad (2)
\]

(iii) As the \(\text{Cr(III)}\) is freshly generated and is a powerful complex forming ion, it coordinates with three \(\text{Cr}_2\text{O}_10^{2-}\) ions to form a complex anion \([\text{Cr(Cr}_2\text{O}_1\text{O}_3)^3]^-\) and also with phthalate ions to form complex cation \((\text{CrPhth}_3)^+\). Both complex anion and cation combine together resulting in the formation of the complex, \((\text{CrPhth}_3)^+\text{Cr(Cr}_2\text{O}_1\text{O}_3)^3\)
as follows. The complex is blue and soluble in ether. Ether molecules coordinate with the blue complex and stabilize it. The ether-extracted blue compound prepared with phthalic acid may be kept at $0^\circ$C for about a week or 150 to 160 hours.

\[
\text{Cr(III)} + 3 \text{Cr}_2\text{O}_{10}^{-2} \rightarrow \begin{bmatrix}
\text{Cr}_2\text{O}_{10}^{-2} & \text{Cr}_2\text{O}_{10}^{-2} \\
\text{Cr} & \text{Cr}_2\text{O}_{10}^{-2} \\
\text{Cr}_2\text{O}_{10}^{-2} & \text{Cr}_2\text{O}_{10}^{-2}
\end{bmatrix}^{-3}
\]

Complex anion

\[
3\text{Cr(III)} + 3 \text{Phth}^{-2} \rightarrow 3(\text{CrPhth})^+ 
\]

Complex cation.

\[
3(\text{CrPhth})^+ + [\text{Cr}(\text{Cr}_2\text{O}_{10})_{3}]^{-3} \rightarrow (\text{CrPhth})_3 
\]

Blue complex.

When excess of phthalic acid is used, the volume of hydrogen peroxide is varied, the complex cation (CrPhth$^+$) coordinates with the excess of phthalate$^{-2}$ ions forming complex anions, (CrPhth$_2$)$^-$ or (CrPhth$_3$)$^{-3}$ which does not combine with Cr$_2$O$_{10}$$^{-2}$ hence low concentration results.

The formula, (CrPhth)$_3[\text{Cr(}\text{Cr}_2\text{O}_{10}$$^3$] for blue perchromate prepared with phthalic acid has further been confirmed by carrying out the study of water decomposition product with the help of ion-exchange resins (vide Chapter II). As discussed earlier that
the water decomposition product of ethereal blue perchromate prepared
with phthalic acid is \((\text{CrPhth})_3 \left[\text{Cr}(\text{Cr}_2\text{O}_6)_3\right]\). The ratio between
the titre values of water decomposition product before and after
oxidation with 30% hydrogen peroxide in N \(\text{NaOH}\) solution is
1 : 1.75 (vide table 2.1, column\(^{11}\)).

It is very interesting to note from the study of water
decomposition product of blue perchromate prepared with phthalic
acid that the titre values entered in columns 'a' and 'c' or 'd'
(vide table 2.1) of the same decomposition product before and
after exchanging are different. It appears that the anionic chromium
of the unexchanged product after exchanging has changed to \(\text{Cr(VI)}\).
Had it been the same in the unexchanged and exchanged ingredients
the ratio a : c or a : d would have 1 : 1, as in case of water
decomposition product of the blue perchromate prepared with sulphuric
acid. Further, it can be explained as follows:

Unexchanged water decomposition product is:

\[
2(\text{CrPhth})_3 \left[\text{Cr}(\text{Cr}_2\text{O}_6)_3\right] \xrightarrow{\text{dil. acid}} 3(\text{CrPhth})_2\text{O} + 7\text{Cr}_2\text{O}_3 + 12.0 \quad (a)
\]

Exchanged with cation exchangers: the effluent is:

\[
2\text{H}_3 \left[\text{Cr}(\text{Cr}_2\text{O}_7)_3\right] \xrightarrow{\text{dil. acid}} 3\text{H}_2\text{O} + 7\text{Cr}_2\text{O}_3 + 18.0 \quad (c),(d)
\]

The ratio, a : c = 12 : 18 or 0.66 : 1, same as determined experi-
mentally vide table 2.1.

Elutriant from cation exchangers is:

\[
6(\text{CrPhth}) + 2\text{CrA}_3 \xrightarrow{\text{after oxidation}} 3(\text{CrPhth})_2\text{O} + 2\text{Na}_2\text{CrO}_4 + 12\text{NaA} \]

and when treated with dilute sulphuric acid gives:
\[
2\text{Na}_2\text{Cr}_4\text{O}_7 \rightarrow 2\text{Na}_2\text{O} + \text{Cr}_2\text{O}_3 + 3\cdot 0 \quad (e)
\]

Ratios: \( a : d = 12 : 18 \) or \( 0.66 : 1 \); \( c : e = 18 : 3 \) or \( 6 : 1 \).

They are in close agreement with the experimental values.

The chromium in the basic and acidic ingredients, (effluent and elutriant) separated with the help of ion exchange resins from water decomposition product has also been estimated gravimetrically and the ratio between \( \text{Cr(V)} \) or \( \text{Cr(VI)} \) and \( \text{Cr(III)} \) is found to be \( 1.5 : 1 \) (vide table 2.3). This is the same as calculated from the formula \( (\text{CrPhth})_3\left[\text{Cr}_2\text{O}_6\right]_3 \).

Thus, observations noted in tables 2.1 to 2.3 further lead to conclude that water decomposition product is \( (\text{CrPhth})_3[\text{Cr}_2\text{O}_6]_3 \) complex; hence the probable formula of blue perchromate prepared with phthalic acid is \( (\text{CrPhth})_3[\text{Cr}_2\text{O}_{10}]_3 \).

The water, open and closed decomposition products of ethereal blue compound prepared with sulphuric acid have been studied (vide Chapter III) with and without the application of ion-exchange resins. It is evident from the various ratios of tables 3.1, 3.2 and 3.3 that the amounts of chromium in the cationic and anionic portions of the water, the open and the closed - bottle decomposition products are present in the ratios of \( 1 : 3 \), \( 2 : 3 \) and \( 1 : 1 \) respectively. Hence the formula of the compound for water decomposition product is \( \text{Cr}_2(\text{Cr}_2\text{O}_7)_3 \) whereas \( \text{Cr}_2(\text{CrO}_4)_3 \) and \( \text{CrCrO}_4 \) for the compounds of the open and the closed bottle decomposition products, as suggested by Rai (loc.cit.).
Schwarz and Giese (loc. cit.) extended the most authentic evidence in favour of \( \text{CrO}_5 \) formula by decomposing ethereal blue compound in presence of silver oxide, chromic acid is obtained.

\[
\text{CrO}_5 + \text{Ag}_2\text{O} \rightarrow \text{CrO}_3 + 2.0
\]

Meneghini, Hans and Lyden observed that silver oxide is capable of oxidising trivalent chromium to hexavalent state. They have further suggested that besides qualitative utility, this behaviour of silver oxide can be used for quantitative estimation of trivalent chromium.

The author repeated the above experiment of Schwarz and Giese taking consideration of the above references and found (vide Chapter IV) that chromic acid is formed if blue perchromate prepared with sulphuric acid is decomposed in presence of silver oxide.

It is evident from the above study that during the decomposition of blue perchromate in presence of silver oxide, trivalent chromium originally present in the blue compound gets oxidised. It seems that Schwarz and Giese somehow missed the reference of the work of Meneghini, Hans and Lyden and ignored the role of \( \text{Ag}_2\text{O} \) as an oxidising agent.

In the case of blue compound prepared with phthalic acid, the titre value of water decomposition product of this blue compound is the same whether it is decomposed in presence or in absence of silver oxide (vide table 4.4, columns c and e). It seems that
silver oxide is a mild oxidising agent and weak alkali, therefore, it is incapable of oxidising trivalent chromium already present in the complex anion and cation of the blue compound.

In case of open and closed bottle decomposition products (obtained in presence of silver oxide) of ethereal blue compound prepared with phthalic acid, the titre values are of such a type (vide tables 4.5 & 4.6) that no definite inference can be drawn about the nature of the compounds formed under these conditions. Hence they require further intensive study to arrive at a definite conclusion.

Further it is very interesting to note that when the solutions of the above decomposition products obtained by treating with hydrochloric acid and removing the precipitated AgCl are oxidised with hydrogen peroxide in strongly alkaline medium the titre values are the same as obtained in the case of the oxidised decomposition product in the absence of silver oxide (vide tables 4.4 to 4.6, column 'f').

From the above observations it can easily be inferred that the blue compound prepared with sulphuric acid and phthalic acid, contain chromium of lower valency state along with hexavalency state.

Rai41,42 observed that blue perchromate prepared with sulphuric acid decomposes differently under different conditions i.e., in water, open and closed and in sodium hydroxide solution producing different decomposition products, Cr$_2$(Cr$_2$O$_7$)$_3$, Cr$_2$(CrO$_4$)$_3$.
CrCrO₄ and Na₂CrO₄ respectively.

Further, Rai⁴ from the decomposition of ethereal blue peroxycromate in water, NaOH, KOH and NH₄OH solutions has concluded that blue perchromate contains trivalent as well as hexavalent chromium. A similar study of its pyridine complex has led to the same conclusion.

Taking into consideration the above references, author repeated the above experiments of Rai and found that the titre values of the water decomposition products of ether and ethyl acetate extracted blue perchromate increased on oxidising the water decomposition products with hydrogen peroxide in sodium hydroxide solution.

But on decomposing ether and ethyl acetate extracted blue perchromate in alkalies (i.e., in NaOH, KOH, and NH₄OH solutions) there was no increase in the titre values of the decomposition products even after further oxidising the same with hydrogen peroxide (cf. columns d, e & f of tables 5.1 & 5.2).

In the light of the behaviour of blue perchromate in water after decomposition it is concluded that blue perchromate has trivalent as well as hexavalent chromium, and as blue perchromate is a peroxo compound it liberates peroxy oxygen in alkaline medium which converts Cr(III) originally present in the blue perchromate to hexavalent chromium, hence no increase in the titre values even after oxidising the same with hydrogen peroxide. Thus, the
observations made by Rai are confirmed.

Further, author tried to correlate the reactions between the ethereal blue perchromate prepared with phthalic acid and alkali hydroxides with its constitution. The observations carried out, vide chapter - V and the various ratios showed that the behaviour of blue perchromate prepared with phthalic acid is the same as that prepared with sulphuric acid. Similarly, by taking the formulae, \( (\text{CrPhth})_3[\text{Cr}(\text{Cr}_2\text{O}_{10})_3] \) for blue perchromate and \( (\text{CrPhth})_3[\text{Cr}(\text{Cr}_2\text{O}_6)_3] \) for water decomposition product, the various ratios (vide tables 5.3 and 5.4) are explained as follows:

When blue compound is titrated iodometrically it behaves as:

\[
2(\text{CrPhth})_3[\text{Cr}(\text{Cr}_2\text{O}_{10})_3]_{\text{aq.KI}} \rightarrow 3(\text{CrPhth})_2\text{O} + 7\text{Cr}_2\text{O}_3 + 36.0 \quad (a)
\]

In alkaline medium it seems to decompose as:

\[
2(\text{CrPhth})_3[\text{Cr}(\text{Cr}_2\text{O}_{10})_3] + 28\text{NaOH} \rightarrow 3(\text{CrPhth})_2\text{O} + 14\text{Na}_2\text{CrO}_4 + 12\text{H}_2\text{O} + 15.0
\]

and in presence of dilute sulphuric acid, this alkali decomposition product gives 2I oxygen atoms, same as water decomposition product after oxidation.

\[
14\text{Na}_2\text{CrO}_4_{\text{dil.acid.}} \rightarrow 12\text{Na}_2\text{O} + 7\text{Cr}_2\text{O}_3 + 21.0 \quad (b)
\]

The blue compound decomposes in water as follows:

\[
2(\text{CrPhth})_3[\text{Cr}(\text{Cr}_2\text{O}_{10})_3] \rightarrow 2(\text{CrPhth})_3[\text{Cr}(\text{Cr}_2\text{O}_6)_3] + 24.0
\]

and in presence of dilute sulphuric acid, it gives:

\[
2(\text{CrPhth})_3[\text{Cr}(\text{Cr}_2\text{O}_6)_3] \rightarrow 3(\text{CrPhth})_2\text{O} + 7\text{Cr}_2\text{O}_3 + 12.0 \quad (b)
\]

Water decomposition product when oxidised with 30% hydrogen peroxide...
in strongly alkaline medium, it forms:

\[ 2(Cr\text{Phth})_3 \left[ Cr(\text{Cr}_2O_3)_3 \right] \cdot 28\text{NaOH} + 9\text{H}_2\text{O}_2 \rightarrow 3(Cr\text{Phth})_2\text{O} + 14\text{Na}_2\text{CrO}_4 + 23\text{H}_2\text{O} \]

and in presence of dilute sulphuric acid it behaves as alkali decomposition product and gives,

\[ 14\text{Na}_2\text{CrO}_4 \xrightarrow{\text{acid.}} 14\text{Na}_2\text{O} + 7\text{Cr}_2\text{O}_3 + 2\text{H}_2\text{O} \] (c)

Calculated values are as:

**Water decomposition product.**

<table>
<thead>
<tr>
<th>a : b : c</th>
<th>Calculated</th>
<th>Experimental values</th>
</tr>
</thead>
<tbody>
<tr>
<td>36 : 12 : 3 : 1</td>
<td>1.75 : 1</td>
<td>1.71 : 1</td>
</tr>
<tr>
<td>36 : 21 : 1.71 : 1</td>
<td></td>
<td>1.76 : 1</td>
</tr>
<tr>
<td>21 : 12 : 1.75 : 1</td>
<td></td>
<td>1.73 : 1</td>
</tr>
</tbody>
</table>

**Alkali decomposition product.**

<table>
<thead>
<tr>
<th>a : b : c</th>
<th>Calculated</th>
<th>Experimental values</th>
</tr>
</thead>
<tbody>
<tr>
<td>36 : 21 : 1.71 : 1</td>
<td>1.76 : 1</td>
<td></td>
</tr>
<tr>
<td>36 : 21 : 1.71 : 1</td>
<td>1.76 : 1</td>
<td></td>
</tr>
<tr>
<td>21 : 21 : 1 : 1</td>
<td>1 : 1</td>
<td></td>
</tr>
</tbody>
</table>

The calculated values are in close agreement with the experimental values.

Thus, it is evident from the above study that blue perchromate prepared with phthalic as well as sulphuric acid contains \((Cr(\text{III})\) along with \(Cr(\text{VI})\).

To further substantiate the above verdict, pH studies have been made of water in contact with blue perchromates prepared with phthalic acid as well as with sulphuric acid. The water decomposition products of both the blue perchromates have also been studied at varying dilutions. The open and closed bottle
decomposition products are insoluble in water and therefore are to be dissolved in dilute mineral acid to prepare their solution. The presence of acid foils p\(H\) measurements of these decomposition products.

Hartford\(^{44}\) observed that except for a small variation with temperature in dilute solutions, the effect of temperature, purity of acid and water on the p\(H\) of aqueous \(\text{CrO}_3\) is negligible. Further he suggested that p\(H\) of chromic acid is affected to a very small extent on dilution. On the contrary, when p\(H\) of water decomposition product is measured at different dilutions (vide table 6.2) it varies showing thereby that water decomposition products are not chromic acid solutions but \(\text{Cr}_2(\text{Cr}_2\text{O}_7)_3\).

The variation in p\(H\) of conductivity water during the decomposition of different samples of blue perchromates found between 6.85 to 3.3 (vide table 6.1) clearly shows that they are chromium salts in solution and not chromic acid. Had the products formed during this decomposition been chromic acid (on the basis of \(\text{CrO}_5\) formula of Schwarz) the p\(H\) of water would have attained a much smaller value, contrary to the experimental observations.

Uemura and Sueda\(^{45}\) observed that chromium complexes like amines or chlorine substituted amines have p\(H\) in the range of 3-4 at \(1/300\) to \(1/500\) mole concentration. It is, therefore, not surprising if the compounds formed during the decomposition of
blue perchromates in water have pH between 3.3 to 3.45. The pH measurements explicitly show the expedience of the $\text{Cr}_2\text{(Cr}_2\text{O}_10)_3$ formula over $\text{CrO}_5$ for blue perchromate extracted with ether, or ethyl acetate.

A comparative study of complexes formed from the ethereal blue perchromate prepared with sulphuric acid as well as with phthalic acid, and organic nitrogenous bases such as isoquinoline and 8-hydroxyquinoline, have been worked out (vide chapter VII) with a view to arrive at a definite conclusion regarding the nature and constitution of ethereal blue perchromate.

It is worthwhile to note that isoquinoline complexes of blue perchromate prepared with sulphuric acid and phthalic acid are not stable, decompose and pass through various stages of decomposition states depending upon temperature. Here only two states of both complexes are obtained under varying conditions of temperature such as (1) undecomposed and (2) decomposed.

The isoquinoline complexes are stable at temperature below 20° C, and this state is named as undecomposed state, whereas the decomposed state of complexes is obtained on allowing the complexes for self decomposition at temperatures 20° C and above. (In the present case decomposed state is obtained by decomposing the complexes at 35° C.)
The undecomposed complexes are bright, dark-violet coloured and light scales or flakes, readily soluble in hot water, but slowly in cold water. They are also soluble in 2N sulphuric acid as well as in sodium hydroxide solution. The decomposed complexes are brownish amorphous solid, readily soluble in N sodium hydroxide solution and insoluble in water (hot and cold) and in 2N sulphuric acid.

The empirical formula for undecomposed isoquinoline complex of blue perchromate prepared with sulphuric acid, determined on the basis of percentage composition of various constituents present in the complex (vide table 7.4) is found to be $\textit{RCrO}_6$ (R stands for one molecule of the base).

It is evident from the study of water decomposition product of the complex that the titre values of water decomposition product as such (vide table 7.2, column 'b') and of the oxidised water decomposition product (vide column 'd') are in the ratio of 3 : 5 or 1 : 1.60 (approximately). This clearly shows that chromium is present in acidic as well as in basic parts of complex, but in the ratio of 1.5 : 1 respectively. On the other hand, when the complex is decomposed in sodium hydroxide solution, the titre values of the decomposition product before and after oxidation are the same as shown in columns 'b' and 'd' (table 7.3), thereby proving that the Cr(III) originally present in the complex along with Cr(VI) in the ratio 1 : 1.5 appears to have oxidised to Cr(VI) by peroxidic
oxygen in the presence of sodium hydroxide solution. Hence, the same titre values are obtained before and after oxidation of the sodium hydroxide decomposition product.

Therefore, considering the above data and the chemical properties of undecomposed isoquinoline complex of blue perchromate prepared with sulphuric acid, the probable molecular formula may be written as \( R_{2.5}Cr_{2.5}O_{15} \) or \( R_{2.5}Cr(Cr_{1.5}O_{15}) \) or \( R_5Cr_2(CrO_{10})_3 \) or \( R_5Cr_5O_{30} \).

In the case of decomposed isoquinoline complex of blue perchromate prepared with sulphuric acid, the empirical formula is determined on the basis of percentage composition of elements (vide table 7.6) of the complex and is found to be \( RCrO_5 \).

The complex is found to be soluble in sodium hydroxide solution and therefore its oxidising power is determined in this medium. It has been found from the study of alkali decomposition product of the decomposed isoquinoline complex that the titre values of the complex solution (vide table 7.5, column No. 1) are approximately the same as the titre values of the filtrate solution obtained after precipitating \( Cr(III) \) as \( Cr(OH)_3 \) from the above alkali decomposition product of the complex (column No. 3). Similarly the titre values of the oxidised decomposition product of the complex are approximately double the values of unoxidised
decomposition product (vide table 7.5, column No. 2). This clearly shows that chromium is present in the acidic as well as in the basic parts of the complex in equal proportions. This is further confirmed from the fact when the complex as such is ignited, the percentage of total chromium thus obtained is double the percentage of chromium obtained by igniting \( \text{Cr(OH)}_3 \), precipitated from the solution of the same amount of complex dissolved in sodium hydroxide solution (vide tables 7.5 and 7.6).

Therefore, considering the above data and the chemical properties of the complex, the probable molecular formula may be written as \( R_2\text{Cr(CrO}_{10} \).

It can be easily inferred from the percentage of constituent elements (table 7.14) of the 8-hydroxyquinoline complex of blue perchromate prepared with sulphuric acid that the empirical formula of the complex is \( \text{RCrO}_5 \).

It is evident from the study of the complex in sodium hydroxide solution that the titre values of the complex in N. sodium hydroxide solution (vide table 7.13) are approximately the same as the titre values of the filtrate solution obtained after precipitating \( \text{Cr(III)} \) as \( \text{Cr(OH)}_3 \) by boiling the above solution of the complex in sodium hydroxide. Similarly the titre values of the oxidised solution of complex are approximately double the values of unoxidised solution of the complex in sodium hydroxide (vide
table 7.13, columns 1 or 3 and 2). This clearly shows that chromium is present in the acidic as well as in the basic parts of the complex in equal proportions. This is further confirmed from the fact that when the complex as such is ignited, the percentage of total chromium thus obtained is double in percentage of chromium obtained on igniting Cr(OH)$_3$, precipitated from the solution of the complex in sodium hydroxide, by boiling (vide tables 7.13 and 7.14).

Therefore, considering the above data and the oxidising powers of the complex in sodium hydroxide solution, the probable molecular formula may be written as, R$_2$Cr(CrO$_{10}$).

The author could not estimate percentage of phthalate ions in the complexes due to non-availability of fluorimeter; and suggested some probable molecular formulae for the isoquinoline and 8-hydroxyquinoline complex of blue perchromate prepared with phthalic acid on the following basis: (i) Their oxidising powers in sulphuric acid, water and sodium hydroxide solution, (ii) the estimations of nitrogen, total chromium as well as chromium in the basic part; and (iii) comparing the results with the similar complexes of bases with blue perchromate prepared with sulphuric acid.

Therefore, author feels that these tentative formulae for these complexes need further corroborration by direct estimation of phthalate ion.
In the case of undecomposed isoquinoline complex of blue perchromate prepared with phthalic acid, the empirical formula (not considering the presence of phthalate ion) is determined on the basis of percentages of chromium, nitrogen and oxygen only (vide table 7.10) and is found to be $\text{RCrO}_{8.4}$.

The study of water decomposition product of the complex indicates that the titre values of water decomposition products before and after oxidation are in the ratio 1 : 1.6 (approximately) as shown in columns 'b' and 'd' or 'c' and 'e' of table 7.8. This clearly shows that chromium is present in the basic and in the acidic parts of the complex, in the ratio 1 : 1.5. Further, the titre values of alkali decomposition product solution of the complex before and after oxidation are same (vide table 7.9). Thereby proving that Cr(III) originally present in the complex has oxidised to Cr(VI) by peroxydic oxygen in sodium hydroxide solution. Therefore, considering the above the complex may be written as $\text{R}_{2.5}\text{Cr(Cr}_{1.5}\text{O}_{21})$ or $\text{R}_5\text{Cr}_2\text{(Cr}_{14}\text{O}_{3})_3$ or $\text{R}_5\text{Cr}_{5.42}$.

From the study of oxidising powers the complexes in 2N sulphuric acid, it has been found that one gram of isoquinoline complex of blue perchromate prepared with phthalic acid consumes approximately the same volume of standard thiosulphate solution as isoquinoline complex of blue perchromate prepared with sulphuric acid (cf. tables 7.1 and 7.7) or slightly less. Similarly,
solutions of water and alkali decomposition products of iso-
quinoline complexes of blue perchromate prepared with phthalic
acid as well as with sulphuric acid consume approximately the same
volume of thiosulphate solution (cf. tables 7.2, 7.3, 7.8 and 7.9).

On comparing the two probable molecular formulae, $R_5Cr_5O_{30}$
and $R_5Cr_5O_{42}$ for undecomposed isoquinoline complexes of blue
perchromate prepared with sulphuric acid and phthalic acid they
are found to have the same numbers of chromium atoms and isoquinoline
molecules but different percentage composition of chromium and
nitrogen, as determined experimentally in both the complexes (cf.
tables 7.10 and 7.4). Similarly, their oxidising powers as
determined in water, sulphuric acid ($2N$) and sodium hydroxide ($N$)
solutions are the same. Therefore, they may have the same number
of oxygen atoms but the percentage of oxygen in the complexes may
be different. Further, the complex gives the characteristic
fluorescein test of phthalic acid, thereby, showing the presence of
phthalate ions in the complex. Moreover, it has already been shown
earlier (vide Chapter I) that only one phthalate ion coordinates
with one trivalent chromium.

Therefore, considering the above data, the presence of
phthalate ion and the chemical properties of the complex, the
probable molecular formula may be written as Phth$_x$ $R_5Cr_5O_{30}$. This
formula fits very well, as it confirms experimentally determined
percentages of elements like chromium, nitrogen and oxygen
in the complex.

It can be easily seen from tables 7.12 and 7.16 that the empirical formula for the complexes of decomposed isoquinoline and 8-hydroxyquinoline complexes of blue perchromate prepared with phthalic acid corresponds to RCrO$_{10}$ where R stands for one molecule of the base employed.

These complexes are found to be soluble in sodium hydroxide solution and therefore, their oxidising powers are determined in terms of standard sodium thiosulphate solution in this medium (vide tables 7.11 and 7.15). It has been found from the study of alkali decomposition products of both the complexes that the titre values of the complexes solutions (column No. 1 in each case) are approximately the same as the titre values of the filtrate solution obtained after precipitating Cr(III) as Cr(OH)$_3$ from the alkali decomposition products of the complexes (column No. 3). Similarly, the titre values of the oxidised decomposition products of the complexes are approximately double the volumes of unoxidised decomposition products (column No. 2 of both tables). This clearly shows that chromium is present in the acidic as well as in the basic parts of the complexes in equal proportions. This is further confirmed from the fact when the complexes as such are ignited the percentage of total chromium is double the percentage of total chromium obtained by igniting Cr(OH)$_3$, precipitated from the solution of the same amounts of complexes dissolved in sodium.
hydroxide solution (vide tables 7.11 and 7.15). This behaviour of complexes is similar to the behaviour of the same complexes formed from blue perchromate prepared with sulphuric acid and having the probable molecular formula, \( R_2CrCrO_{10} \). The decomposition products of the complexes of blue perchromate prepared with phthalic acid also give characteristic fluorescein test of phthalic acid whereas the same complexes of blue perchromate prepared with sulphuric acid do not respond to this test. This confirms the presence of phthalate ions in these complexes.

Therefore, from the above data and the oxidising powers of the complexes determined in sodium hydroxide solution, the probable molecular formula for both the complexes may be written as \( R_2Cr(CrO_{20}) \). But this molecular formula can not be accepted as the formula for the complexes on the following grounds.

The probable molecular formula, \( R_2Cr(CrO_{20}) \) represents the peroxy nature of the complexes. Had they been the peroxy compounds they would not have given two different titre values in sodium hydroxide solution before and after oxidation. Since peroxy oxygen oxidises chromium of lower valency state to Cr(VI) in alkaline medium. Further this formula lacks phthalate ions, hence the question of fluorescein test does not arise. Therefore, on the above grounds this formula can not be accepted as the probable molecular formula of the complexes.
The complexes (isoquinoline and 8-hydroxyquinoline) of blue perchromate prepared with phthalic acid show the similar behaviour in sodium hydroxide. Solution as the same complexes obtained from blue perchromate prepared with sulphuric acid. In case if we accept a formula having the same numbers of oxygen atoms Cr atoms and also the organic bases molecules along with one phthalation such as Phth._R2Cr(CrO10)3; it should behave as the complexes behave in sodium hydroxide. Thus we see that this molecular formula fits very well and represents the behaviour of complexes in sodium hydroxide solution and also explains experimentally determined percentages of chromium and nitrogen. This also represents the fluorescein test given by the complexes. Hence both the complexes of blue perchromate prepared with phthalic acid may be represented by the probable molecular formula Phth._R2Cr(CrO10)3 where R stands for one molecule of isoquinoline and also one molecule of 8-hydroxyquinoline.

It is quite evident from what has been observed in this chapter that though the complexes are prepared in the same way, not only their empirical formulae, but also their physical and chemical properties are found to be different. The isoquinoline complexes of ethereal blue perchromate prepared with phthalic acid as well as with sulphuric acid are not stable and decompose and pass through various stages depending upon temperature, reaching the stage (unde decomposed) where their molecular formulae are Phth._R2Cr2(CrO10)3 and
$\text{Phth.} \text{R}_5 \text{Cr}_2 (\text{CrO}_{10})_3$ respectively. There is also a stage (decomposed) when their molecular formulae are $\text{R}_2 \text{Cr}(\text{CrO}_{10})$ and $\text{Phth.} \text{R}_2 \text{Cr}(\text{CrO}_{10})$. The undecomposed isoquinoline complexes are quite different in their physical and chemical properties from the decomposed complexes. The 8-hydroxy quinoline complexes of ethereal blue perchromate prepared with sulphuric acid as well as with phthalic acid have their properties more similar to decomposed isoquinoline complexes, rather than those of undecomposed isoquinoline complexes. The 8-hydroxyquinoline complexes are also represented by molecular formulae, $\text{R}_2 \text{Cr}(\text{CrO}_{10})$ and $\text{Phth.} \text{R}_2 \text{Cr}(\text{CrO}_{10})$, similar to those of decomposed isoquinoline complexes of blue perchromates.

Thus, we see that the empirical and molecular formulae, as well as the physical and chemical properties of the complexes are different, inspite of similar methods of preparations. It is, therefore, doubtful to arrive at the constitution of ethereal blue perchromate on the strength of the observations made with such complexes.

Further, the probable molecular formula, $\text{R}_5 \text{Cr}_2 (\text{CrO}_{10})_3$ for undecomposed isoquinoline complex of blue perchromate shows the similarity with the formula, $\text{Cr}_2 (\text{CrO}_{10})_3$ for blue perchromate prepared with sulphuric acid. Similarly, the probable molecular formulae, $\text{R}_2 \text{Cr}(\text{CrO}_{10})$ and $\text{R}_2 ^' \text{Cr} (\text{CrO}_{10})$ for decomposed isoquinoline and 8-hydroxyquinoline complexes of blue perchromate respectively, show the same amount of chromium in the basic as well as in the acidic parts. Thus they support the formula $\text{Cr}(\text{CrO}_8)$ for the blue compound.
Hence two formulae (1) \( \text{Cr}_2(\text{Cr}_2\text{O}_7)_3 \) and (2) \( \text{CrCrO}_8 \) may be suggested for blue perchromate. It is probable that there is lability between these two formulae depending upon the pH of the solution and the quantity of the hydrogen peroxide present and that the two forms are reversible and can exist side by side under certain conditions. The lability can be represented as:

\[
\text{Cr}_2(\text{Cr}_2\text{O}_7)_3 + 2\text{H}_2\text{O}_2 \rightarrow 4\text{Cr(\text{CrO}_8)} + 2\text{H}_2\text{O} \\
\text{or} \quad 4\text{Cr(\text{CrO}_8)} + 2\text{H}_2\text{O} \rightarrow \text{Cr}_2(\text{Cr}_2\text{O}_7)_3 + 2\text{H}_2\text{O}_2
\]

Spitalsky and Kobosev have also given a similar view that two such forms are obtained reversibly, the first one being formed at pH 4 and the second at a higher pH. No hydrogen ions are needed for the formation of the second compound. Bobtalsky et. al. have also mentioned the formation of two forms of perchromate, first the blue one and then the violet one, by spectrophotometric and pH measurements during the reaction between chromic acid and hydrogen peroxide. The above observation has been confirmed spectrophotometrically by Glasner and Steinberg and Evans.

An attempt will be made here to discuss the inter-convertibility of the two forms of the blue perchromate. It is to be mentioned here that Rai has suggested the following mechanism of the reaction in the formation of blue peroxychromic acid when hydrogen peroxide is added to chromic acid solution:

Since chromic acid solution is a mixture of \( \text{H}_2\text{CrO}_4 \) and
H₂Cr₂O₇, it contains CrO₄²⁻ and Cr₂O₇²⁻ ions. When hydrogen peroxide is added to a solution of chromic acid or an acidified solution of potassium dichromate it behaves as an oxidising as well as reducing agent in presence of an acid. Therefore, it oxidises Cr₂O₇⁻² to Cr₂O₇⁻²:

\[ \text{Cr}_2\text{O}_7^{-2} + 3 \text{H}_2\text{O}_2 \rightarrow \text{Cr}_2\text{O}_10^{-2} + 3\text{H}_2\text{O} \quad \text{and reduces Cr}_2\text{O}_7^{-2} \text{to Cr}(\text{III}), \]

\[ \text{Cr}_2\text{O}_7^{-2} + 14\text{H}^+ \rightarrow 2\text{Cr(III)} + 7\text{H}_2\text{O} . \]

Thus, the chromic ion, so generated, is powerful complex forming ion. It combines with Cr₂O₁₀⁻² ion to give complex anion, \([\text{Cr(Cr}_2\text{O}_10^{-2})_3]^{-3}\) as under:

\[ \text{Cr(III)} + 3(\text{Cr}_2\text{O}_10^{-2}) \rightarrow \left[ \begin{array}{c} \text{Cr}_2\text{O}_10 \\ \text{Cr}_2\text{O}_10 \end{array} \right]^{-3} \]

This complex anion again combines with Cr(III) ion to form \(\text{Cr[Cr(Cr}_2\text{O}_10^{-2})_3]\). This can be represented as follows:

\[ \text{Cr(III)} + \left[ \begin{array}{c} \text{Cr}_2\text{O}_10 \\ \text{Cr}_2\text{O}_10 \\ \text{Cr}_2\text{O}_10 \end{array} \right]^{-3} \rightarrow \text{Cr} \left[ \begin{array}{c} \text{Cr}_2\text{O}_10 \\ \text{Cr}_2\text{O}_10 \end{array} \right]^{-3} \]

This happens at pH 4.

The above structure has also been confirmed here by preparing ethereal blue perchromate in presence of phthalic acid (cf. page 160) and also by carrying out the gravimetric study of the water decomposition product exchanged and unexchanged with the help of ion exchange
Resins where chromium has been found in the cationic and anionic ingredients in the ratio 1 : 1.5 or 2 : 3 (cf. table 2.3). The same ratio has been observed in unde decomposed isoquinoline complexes (vide Chapter VII).

If more hydrogen peroxide is present in the system then the O₂ group further coordinates with

\[
\begin{array}{c}
\text{Cr} \\
\text{Cr} \\
\text{Cr}
\end{array}
\]

\[
\begin{array}{c}
\text{CrO}_2 \\
\text{CrO}_2 \\
\text{CrO}_2
\end{array}
\]

which combines with Cr(III) to form:

\[
\begin{array}{c}
\text{Cr}
\end{array}
\]

\[
\begin{array}{c}
\text{CrO}_2 \\
\text{CrO}_2 \\
\text{CrO}_2
\end{array}
\]

This latter compound is formed at a pH above 4.

If water is added to this compound during washing, it first changes to:

\[
\begin{array}{c}
\text{Cr}
\end{array}
\]

\[
\begin{array}{c}
\text{CrO}_2 \\
\text{CrO}_2 \\
\text{CrO}_2
\end{array}
\]

\[
\text{H}_2\text{O}
\]

\[
\begin{array}{c}
\text{Cr}
\end{array}
\]

\[
\begin{array}{c}
\text{CrO}_2 \\
\text{CrO}_2 \\
\text{CrO}_2
\end{array}
\]

It may be pointed out here that when the compound is left for decomposition under tightly corked conditions it dispropor tionates into 4Cr(CrO₄) (vide Chapter I). Now it is possible that at a higher pH:
which suggests equal amounts of chromium in the acidic as well as in the basic parts of the compound in the complexes obtained (vide chapter VII).

Thus, we see that the dimeric form of the ethereal blue perchromate is converted into the monomeric form above pH 4. Riesenfeld\textsuperscript{52}, Wiede\textsuperscript{53}, Schwarz and Giese\textsuperscript{54} and others have found that the blue perchromates are monomeric. All these earlier workers observed the monomeric form in the compounds that were prepared in basic solutions too. Naturally, under such conditions the dimeric form must have changed into the monomeric one; for, in acid or in the presence of water the dimeric form will exist, probably at a pH below 4 but above this it changes into the monomeric form. It also changes into monomeric form in the presence of excess of hydrogen peroxide. Moreover, the formula \( \text{CrO}_5 \) or \( \text{HCrO}_5 \) has been arrived at mostly on the basis of the empirical molecular weight and it is needless to mention that the structure of a compound can not be determined solely from this.

From what has been observed in the Chapter VII, it is quite evident that to arrive at the constitution of ethereal blue perchromate with the help of complexes formed with organic bases is
not reliable. An attempt has, therefore, been made to arrive at the constitution of ethereal blue perchromate by studying its own nature and also the nature of various decomposition products and comparing with the nature of the blue perchromate prepared with phthalic acid and its own decomposition products and not by only the complexes formed by it.

The last method studied successfully in this thesis to decide the nature of the blue perchromate is the measurement of magnetic susceptibilities of the complexes, described in Chapter VII, i.e., the complexes formed from ethereal blue compound prepared with sulphuric acid as well as with phthalic acid by adding isoquinoline and 8-hydroxyquinoline.

The value of $\mu_B$ 3.98 and 3.64 Bohr magnetons (vide tables 8.1 and 8.2) have been measured for 8-hydroxyquinoline complexes formed from ethereal blue perchromate prepared with phthalic acid and sulphuric acid respectively. The value of 3.8 to 4.01 Bohr magnetons is one which is the theoretical value for any compound of trivalent chromium. Thus the value 3.64 B.M. measured experimentally is near about the theoretical value and hence both the above values determined experimentally, strongly support the view that these complexes do contain the trivalent chromium and the blue compound too must be having the Cr(III).

The little low values, 3.356 and 3.029 B.M., (vide tables 8.3 and 8.4) obtained in case of isoquinoline complexes, is not
surprising and may easily be understood from the formulae

\[ \text{Phth} \cdot R_5 \text{Cr} \left[ \text{Cr(CrO}_{10} \right)_3 \] and \( R_5 \text{Cr} \left[ \text{Cr(CrO}_{10} \right)_3 \] of the complexes
described earlier in chapter VII. In these formulae one of the
Cr(III) ions coordinates with three \( \text{CrO}_{10}^{-2} \) ions to give an unstable
complex anion \( \text{Cr(CrO}_{10} \right)_3^{-3} \) and this complex anion in turn combines
with complex cations, \( R_5 \text{Cr}^{+3} \) and \( \text{Phth} \cdot R_5 \text{Cr}^{+3} \) in
the case of complexes formed from blue perchlorate prepared with
sulphuric acid and phthalic acid respectively, as follows:

\[
\begin{align*}
\text{CrO}_{10}^{-3} & \quad \text{CrO}_{10}^{-3} \\
\text{Cr} & + R_5 \text{Cr}^{+3} \\
\text{CrO}_{10} & \rightarrow R_5 \text{Cr}
\end{align*}
\]

and

\[
\begin{align*}
\text{CrO}_{10}^{-3} & \quad \text{CrO}_{10}^{-3} \\
\text{Cr} & + (\text{Phth} \cdot R_5 \text{Cr})^{+3} \\
\text{CrO}_{10} & \rightarrow \text{Phth} R_5 \text{Cr}
\end{align*}
\]

The compounds, \( R_5 \text{Cr} \left[ \text{Cr(CrO}_{10} \right)_3 \] and \( \text{Phth} \cdot R_5 \text{Cr} \left[ \text{Cr(CrO}_{10} \right)_3 \]
so formed contain unstable complex anion \( \text{Cr(CrO}_{10} \right)_3^{-2} \) in each of
the two formulae. In the complex anion Cr(III) possesses large
amount of peroxo oxygen groups which quench the paramagnetism of
Cr(III) ion involved in the complex anion to a greater extent
whereas in the complex cations, \( R_5 \text{Cr}^{+3} \) and \( \text{Phth} \cdot R_5 \text{Cr}^{+3} \) to a very
little extent. Hence the experimental values of \( \mu B \) obtained in
this case can easily be explained.

Raf\textsuperscript{55}, R.C., obtained three values for \( \mu B \) for ethereal
blue perchromate. He observed that if ethereal blue perchromate is not washed, the value of $\mu B$ obtained is about 2.2 B.M. when it is washed and kept in refrigerator for about half an hour the value is found to be 3.88 and 4.01 which is lowered to 2.67 and 2.85 $\mu B$ on keeping the blue compound in the refrigerator for about ninety minutes. The variation in values from 2.3 to 4.01 B.M. for the structural changes that ethereal blue compound undergoes.

Klemm and Werth established the hexavalency of chromium in the peroxychromic acid by measuring the magnetic susceptibility of the complexes of blue perchromates. They found the blue perchromate to be diamagnetic.

Bhatnagar et al. observed a value of 2.94 B.M. for the magnetic moment of triamino chromium tetraoxide $\text{CrO}_4 \cdot 3\text{NH}_3$ obtained from ethereal blue perchromate. This also confirms the presence of chromium in lower valency state.

Glasner and Steinberg (loc.cit.) prepared the blue compound and found by the absorption method that the ratio in which hydrogen peroxide and chromic acid, and hydrogen peroxide and dichromate solutions combine were 1.5 : 1, whereas the ratio in which hydrogen peroxide and potassium chromate combine was 2 : 1; and since the latter result was in agreement with the formula $\text{CrO}_5$ they supported the view of Schwarz and Giese (loc.cit.) that the blue compound was $\text{CrO}_5$, overlooking the general practice of accepting the majority values, which in this case was 1.5 : 1.
The majority value of the ratio 1.5 : 1 can, however, be explained on the basis of the formula \( \text{Cr}_2(\text{Cr}_2\text{O}_{10})_3 \) for the blue compound. When chromic acid (\( H_2\text{Cr}_2\text{O}_7 \)) reacts with hydrogen peroxide, oxidation of \( \text{Cr}_2\text{O}_7^{2-} \) ion takes place together with its reduction in the presence of \( H^+ \). This can be represented as:

\[
3H_2\text{Cr}_2\text{O}_7 + 9H_2O_2 \rightarrow 3(\text{Cr}_2\text{O}_{10})^{2-} + 6H^+ + 9H_2O \quad (1)
\]

and

\[
H_2\text{Cr}_2\text{O}_7 + 3H_2O_2 \rightarrow \text{Cr}_2O_3 + 4H_2O + 6.0 \quad (2)
\]

Then the \( H^+ \) ions from the reaction (1) will combine with \( \text{Cr}_2O_3 \) to give \( 2\text{Cr}^{3+} \). This may be represented as:

\[
\text{Cr}_2O_3 + 6H^+ \rightarrow 2\text{Cr}^{3+} + 3H_2O
\]

and finally

\[
2\text{Cr}^{3+} + 3(\text{Cr}_2\text{O}_{10})^{2-} \rightarrow \text{Cr}_2(\text{Cr}_2\text{O}_{10})_3
\]

Thus, we see that ratio of combination of \( H_2O_2 \) and \( H_2\text{Cr}_2\text{O}_7 \) is 12 : 4 or \( H_2O_2/2\text{Cr}_2O_3 = 3 : 1 \) and hence \( H_2O_2/\text{Cr}_2O_3 = 1.5 : 1 \).

Similarly, in the case of the reaction between acidified potassium dichromate and hydrogen peroxide the reaction may be represented as:

\[
6K^+ + 3\text{Cr}_2O_7^{-2} + 9H_2O_2 \rightarrow 6K^+ + 3\text{Cr}_2O_{10}^{-2} + 9H_2O
\]

and

\[
2K^+ + \text{Cr}_2O_7^{-2} + 3H_2O_2 + 8H^+ \rightarrow 2K^+ + 2\text{Cr}^{3+} + 7H_2O + 6.0
\]

Then chromic ions and perchromate ions combine to give chromic perchromate as:

\[
2\text{Cr}^{3+} + 3\text{Cr}_2O_{10}^{-2} \rightarrow \text{Cr}_2(\text{Cr}_2O_{10})_3
\]
Rai (loc. cit.) suggested, as has already been shown by the present author earlier that \( \text{Cr}_2(\text{Cr}_2\text{O}_{10})_3 \) exists in the form of the complex \( \text{Cr}[\text{Cr}(\text{Cr}_2\text{O}_{10})_3] \).

In the above case also four molecules of potassium dichromate react with twelve molecules of hydrogen peroxide to give one molecule of \( \text{Cr}[\text{Cr}(\text{Cr}_2\text{O}_{10})_3] \). The ratio in which \( \text{H}_2\text{O}_2 \) reacts with potassium dichromate is 12 : 4 or 3 : 1, since one molecule of dichromate contains \( 2\text{CrO}_3 \); the ratio between hydrogen peroxide and \( \text{CrO}_3 \) will come out to be 1.5 : 1. With more of hydrogen peroxide, the blue compound changes to the violet form as under:

\[
\text{Cr} \left[ \begin{array}{c} \text{Cr}_2\text{O}_{10} \\ \text{Cr}_2\text{O}_{10} \end{array} \right] + 2\text{H}_2\text{O}_2 \rightarrow \text{Cr} \left[ \begin{array}{c} \text{Cr}_2\text{O}_{10} \\ \text{Cr}_2\text{O}_{10} \end{array} \right] + 2\text{H}_2\text{O}.
\]

(Blue)

Thus, corresponding to 4 molecules of dichromate 14 molecules of hydrogen peroxide are required to give the violet compound. Hence the ratio increases to \( 14\text{H}_2\text{O}_2 : 4\text{K}_2\text{Cr}_2\text{O}_7 \) or \( 14\text{H}_2\text{O}_2 : 8\text{CrO}_3 \), i.e., \( \frac{\text{H}_2\text{O}_2}{\text{CrO}_3} = 1.75 : 1 \), which is very near to 2 : 1. Evans (loc. cit.) has said that the results obtained are within 10% of the theoretical value; moreover, we have assumed that no reduction of \( \text{CrO}_3 \) by \( \text{H}_2\text{O}_2 \), further than that required for the formation of the blue compound takes place. Thus, both the ratios, 1.5 : 1 and 2 : 1 obtained by Glasner and Steinberg can be explained by the formula \( \text{Cr}_2(\text{Cr}_2\text{O}_{10})_3 \) for the blue compound.
Recently, X-ray crystallographic studies have been carried out to confirm the structure of red and blue perchromates, and their complexes.

Stomberg and Brosset\textsuperscript{58} studied the single crystal of potassium salt of tetraperoxy chromate, $K_3CrO_8$ obtained when an alkaline solution of $K_2CrO_4$ was treated with hydrogen peroxide at $0^\circ$ C. i.e., Hofman and Hiedlmaier method, by X-ray crystallography. It showed that the chromium atom was surrounded by four equivalent peroxy groups, in an arrangement that could be described as a distorted dodecahedron of oxygen atoms; the two Cr – O distances were significantly different. The molecular orbital calculations had been made by Swalen and Ibers\textsuperscript{59} using parameters derived from the $g$ values; the unpaired electron was assigned to a $B'$ orbital of chromium. The $O$ – $O$ distance of 1.40 $\text{Å}$ was rather less than the 1.49 $\text{Å}$ found in alkali metal peroxides; perhaps because electrons that in the free peroxide were in antibonding $\pi$ orbitals were partly delocalized in the complex into orbitals of chromium. Thus, they confirmed presence of $Cr(V)$ in the compound $K_3 Cr(0_2)_4$.

Two X-ray studies of pyridine complex, $PyCrO_5$ prepared by Hofman & Hiendlmaier method, were made by Stomberg, and Pedersen and Pedersen\textsuperscript{60}. They found that the chromium atom, the two peroxy groups, and the nitrogen atom of the pyridine molecule were all nearly coplanar, while the fifth oxygen laid above the chromium atom.
This confirmed the structure as $\text{Py.Cr}(0)(O_2)_{2}$ which is consistent with $\text{Cr(II)}$.

Stanberg further determined the crystal structure of $(\text{NH}_3)_3\text{CrO}_4$ compound, prepared by Hofmann and Hiendlmaier method i.e., by direct reaction of ammonium dichromate, aqueous ammonia and hydrogen peroxide, and showed that in this compound, $(\text{NH}_3)_3\text{Cr}(O_2)_{2}$ chromium was in quadrivalent state.

Regarding the inferences drawn from the X-ray studies mentioned above, the author would like to mention that the above workers have prepared red perchromates and have discussed the structure and constitution of blue perchromate. Here, it is very important to note that blue and red perchromates are prepared in two different ways, i.e., blue perchromate is prepared in acidic medium by hydrogen peroxide of any strength, the red perchromates are prepared in alkaline medium by 33% hydrogen peroxide at/or below $-10^\circ\text{C}$ (Hofmann & Hiendlmaier method). Therefore, they have different physical and chemical properties and also different constitution. Thus, when the compound is prepared by the method of red perchromate it should give the constitution of red perchromate. But if we discuss the constitution of blue perchromate by the experimental results obtained with red perchromate, in my opinion it is not justified.
McLaren and Helmholtz prepared $\text{Cr(O}_2\text{)}_2\cdot3\text{NH}_3$, triammonium tetraoxide, by the method of complexes of blue perchromate and determined the crystal structure. In the crystal, the chromium atom may be described as seven coordinated with a roughly T-shaped arrangement of nitrogen atoms round it; the peroxy groups lie with the 0 - 0 axes in the plane of the downstroke of the T, so that they and one nitrogen atom form an irregular plane pentagon around the chromium atom. The 0 - 0 distance of 1.31 Å is same 0.18 Å less than in the peroxide ion, so the compound was described as a superoxide of Cr(II).

In this context, it is worthwhile to note that the above workers have prepared $\text{Cr(O}_2\text{)}_2\cdot3\text{NH}_3$ complex by the method of complexes of blue perchromate and they have got the presence of Cr(II), which the authors have also been able to show the presence of CrCrO$_4$ where Cr(II) is present. Thus, even by the X-ray study of blue perchromate, the presence of Cr of lower valency state is proved.

Thus the work described in the various chapters of this thesis concerns itself mainly with a detailed study of blue perchromate prepared with phthalic acid as well as with sulphuric acid with a view to investigate its constitution. The discussion, therefore, may conveniently be concluded on the basis of experimental results recorded in the present thesis as well as by explaining the results of earlier workers that the blue perchromate prepared
with phthalic acid may be represented by the formula,

$$(\text{CrPhth})_3 \left[\text{Cr}(\text{Cr}_2\text{O}_{10})_3\right]$$

in analogy with Rai's formula,

$$\text{Cr}\left[\text{Cr}(\text{Cr}_2\text{O}_{10})_3\right]$$

for blue perchromate.