INTRODUCTION
Barreswil¹, in 1847 observed for the first time that when hydrogen peroxide was added to an acid solution of a chromate or dichromate a deep blue solution was produced. This substance was very unstable in water, more stable and soluble in ether and thus could be extracted with the latter from the aqueous layer. The blue substance was named as blue perchromic or peroxochromic acid in analogy with other peracids.

Griggi², substituted amyl alcohol, as a solvent for the blue substance in place of ether, in which it was found much more stable. Grosvenor³ found that there were other oxygen containing organic solvents such as, ethyl acetate and valerate, amyl valerate, amyl chloride, amyl butyrate, formate and acetate that dissolved the blue substance from the aqueous solution. It was further observed that the blue substance extracted with ethyl acetate was most stable, and he did not agree with Griggi's view (loc.cit.). He also observed that carbon-disulphide, benzene, light petroleum, terpentine, castor oil, bergamot oil, oil of winter green, paraffins, chloroform, carbontetrachloride, toluene, nitrobenzene and aniline did not dissolve it. Recently Sastri and Sunder⁴, and Tuck and Waters⁵ have used tri-butyl phosphate as the solvent for the so-called blue perchromate.

Schonbein⁶ prepared alkali chromates by reacting blue perchromic acid with alkali hydroxides. Aschoff⁷ observed that ferrous salts solutions discharged the blue colour of the ethereal blue perchromic acid, while potassium hydroxide developed
a pale blue colour in the non-aqueous layer and the aqueous layer acquired brownish violet colour. Martinon\textsuperscript{8} found that the blue perchromic acid was decomposed both in acidic and alkaline media. He further observed that whereas salts of chromic ions were formed in acidic medium, chromates were formed in an alkaline medium. Jorissen and Riecher\textsuperscript{9} studied the decomposition of blue perchromic acid by oxalic acid.

Werther\textsuperscript{10} studied the effect of adding vanadate in the formation of blue perchromic acid and found that the blue colour very much diminished as the quantity of vanadate was increased. Riehard\textsuperscript{11} observed that the action of vanadate could be counter balanced by adding sodium hydrophosphate or hydroarsenate in small quantities. He further observed that the presence of tungstate, molybdate, phosphate, and arsenate during the formation of blue perchromate also had the inhibiting action but to a lesser degree than vanadate.

This blue substance has been the subject of numerous investigations, and various formulae have been assigned to it. These modifications on its composition have followed in rapid succession. Some of them have been revolutionary in character. We will shortly see that many time-honoured concepts have given way to ideas arising from totally new and radically different interpretations. To have a clear understanding of the nature and constitution of this blue peroxychromic acid, the reactions
and different methods adopted for investigation on this subject, may be classified under the following five heads:

(1) Study of the catalytic decomposition of hydrogen peroxide by aqueous solution of chromic acid or by aqueous as well as acidified dichromate solutions.

(2) Study of the nature of the complexes formed from ethereal blue peroxychromic acid and nitrogenous organic bases or other basic substances.

(3) Study of the compounds formed by the reaction between ethereal blue peroxychromic acid and alkali and alkaline earth group metals.

(4) Study of the decomposition products obtained from the blue peroxychromic acid under different conditions.

(5) Physico-chemical studies: such as, potentiometric measurements, conductometry, molecular weight measurements, spectrophotometry, absorption spectra, ultraviolet spectra, infra-red spectra, magnetic measurements and X-ray crystallography.

(* 1 ) CATALYTIC STUDIES:

Berthelot\textsuperscript{12} studied for the first time the catalytic decomposition of hydrogen peroxide in presence of aqueous potassium dichromate solution and observed that a small amount of the latter could decompose an unlimited amount of the former without itself being affected. He\textsuperscript{13} further showed that aqueous solution of a dichromate did not give a blue colour with hydrogen peroxide and therefore, acid was found to be necessary for the formation of the
blue acid. Strong and weak acids gave different substances having
different colours. When hydrogen peroxide was added to a very
dilute, aqueous solution of potassium dichromate, a deep brown
colour developed and was supposed to be due to the formation of
chromium chromate.

Rai\textsuperscript{14} described that blue perchromic acid obtained by
the interaction between hydrogen peroxide and potassium dichromate
solution acidified with acetic acid differed from the one prepared
in presence of sulphuric acid.

Bach\textsuperscript{15} studied the decomposition of hydrogen peroxide
by the action of chromic acid solution on it and observed that in
presence of sulphuric acid one molecule of chromic acid was used
for every two molecules of hydrogen peroxide present. But in
the absence of an acid an intermediate brown, unstable adduct of
hydrogen peroxide and chromic acid was formed, which decomposed
spontaneously resulting in the formation of chromic acid and the
whole of peroxy oxygen of hydrogen peroxide was given off.

Riesenfeld, Kutsch and Ohl\textsuperscript{16} studied the reaction
between an aqueous solution of potassium dichromate acidified with
sulphuric acid and hydrogen peroxide and observed that the amount
of oxygen evolved depended on the mode of reaction, whether hydrogen
peroxide was added to an acidified solution of dichromate or
vice versa, the oxygen evolved was always less than the theoretical
quantity. They, therefore, concluded that the blue colour produced
during the reaction was due to perchromic acids, $\text{H}_2\text{CrO}_8$ and $\text{H}_3\text{CrO}_7$
as well as anhydride $\text{CrO}_4$. 
Spitalsky\textsuperscript{17} made an extensive study of the catalytic decomposition of hydrogen peroxide by chromic acid solution and found that the velocity of decomposition of hydrogen peroxide depended on the ratio of hydrogen peroxide to chromic acid. When the peroxide was present in considerable excess, the rate of decomposition was found approximately proportional to the chromic acid concentration. After the reaction it was found that about 28\% of the chromic acid had been reduced to Cr(III), and this proportion was independent of the initial peroxide concentration and nearly independent of the chromic acid concentration. He\textsuperscript{18} further observed that there was a constant ratio between Cr(III) and Cr(IV) irrespective of the amount of hydrogen peroxide taken provided that it was in considerable excess of chromic acid solution.

Riesenfeld\textsuperscript{19} represented the reaction between hydrogen peroxide and chromic acid as:

\[ 4\text{H}_2\text{Cr}_2\text{O}_7 + 7\text{H}_2\text{O}_2 \rightarrow \text{Cr}_2(\text{Cr}_2\text{O}_7)_3 + 11\text{H}_2\text{O} + 5\text{O}_2 \]

Thus his observations were in agreement with Spitalsky's view (Loc. cit.) that about 28\% of the chromic acid was reduced to Cr(III).

Spitalsky\textsuperscript{20} and Riesenfeld\textsuperscript{21} observed separately that a mixture of chromate and dichromate solutions decomposed the hydrogen peroxide catalytically. Robertson\textsuperscript{22} studied the effect of manganese salts and Rubinschetin\textsuperscript{23} that of cadmium sulphate on the decomposition of hydrogen peroxide by potassium dichromate solution.
Bancroft and Murphy\textsuperscript{24} suggested on the basis of e.m.f.

studies of catalytic decomposition of hydrogen peroxide that

chromium had valency not higher than six in blue peroxychromic acid

Rumr\textsuperscript{25} studied the reaction between hydrogen peroxide

and acidified chromate or dichromate solution extracted with

organic solvent by Job's continuous variation method and assigned

$\text{H}_2\text{CrO}_6$ formula to the blue compound.

No definite clue about the nature and constitution of

the blue compound can be withdrawn from the above studies except

that: the blue compound is formed by the action of hydrogen

peroxide on chromic acid or acidified dichromate or chromate

solutions, which can be extracted with many organic solvents.

(2) **STUDIES ON COMPLEXES OF ETHEREAL BLUE PEROXYCHROMIC ACID**

Complexes were prepared and studied by the following

two methods.

(1) The blue peroxychromic acid was prepared first by the

interaction of chromic acid and hydrogen peroxide, extracted with

ether, separated, washed with water and then treated with various

organic nitrogenous bases. The complexes formed were filtered,

washed and dried.

(11) (A) The chromic acid solution was mixed with excess of

organic bases, cooled below $0^\circ\text{C}$ and to this mixture $30\%$ hydrogen

peroxide was added. Coloured crystals or flakes were precipitated,

filtered, washed with organic solvents and analysed.
(B) Aqueous solution of dichromate or chromate was mixed with alkalies, it was cooled below 0°C and then 30% hydrogen peroxide was added to it. Red crystals were precipitated.

(1) Wiede\textsuperscript{26} used the first method to prepare the complexes of blue peroxychromic acid with organic nitrogenous bases. He obtained greenish-brown precipitate after treating ethereal blue perchromic acid with aqueous ammonia at low temperature. This when recrystallised in 10% warm ammonia solution, gave pal-brown needles, corresponding to the formula CrO\textsubscript{4}.3NH\textsubscript{3}, which were separated on cooling. He further observed that if instead of ammonia solution alkalies were employed the corresponding chromates were formed. He also prepared pyridine and aniline complexes of the compositions, Py.HCrO\textsubscript{5} and An.HCrO\textsubscript{5} by treating ethereal blue compound with pyridine and aniline respectively. Aniline complex was found more explosive than pyridine complex. Wiede\textsuperscript{27} prepared NH\textsubscript{4}CrO\textsubscript{5}+H\textsubscript{2}O\textsubscript{2} by the action of ammonia under certain conditions on an ethereal solution of perchromic acid. This compound was a violet-black coloured crystalline powder. When exposed to air it turned completely into ammonium dichromate. Ammonia converted the substance into the compound of chromium tetraoxide and ammonia. He investigated in detail the action of barium chloride, lead acetate, silver nitrate, ferric chloride, ferrous sulphate, potassium permanganate etc., on this compound.

Wiede\textsuperscript{28} prepared various complexes by the interaction between organic bases and ethereal blue perchromic acid. The bases
employed were quinoline, piperidine, trimethylamine and tetramethyl ammonium hydroxide. He also studied their properties and concluded that the blue peroxychromic acid should have a formula $\text{HCrO}_5$.

(ii) The second method was mainly used by Riesenfeld and his co-workers. Hofmann and Hiendlmaier obtained an ammonium salt, $\text{CrO}_2(0.0.\text{NH}_4)_2$, of chromatodiper acid by the action of hydrogen peroxide on a mixture of chromic hydroxide and ammonium hydroxide at $0^\circ\text{C}$. They suggested that it could also be prepared by oxidising an aqueous solution of ammonium dichromate with hydrogen peroxide in presence of ammonia. This compound having octahedral crystals of dark-red colour was found to be highly explosive when heated, hammered or moistened with a drop of concentrated sulphuric acid. The above salt gave blue peroxychromic acid when heated with dilute sulphuric and acetic acids.

The same workers prepared brown crystals of the complex, $\text{CrO}_4(\text{NH}_3)_3$ having the properties of those of an amine by adding 30% of hydrogen peroxide to a solution of 10% aqueous ammonium hydroxide saturated (at $0^\circ\text{C}$) with crystallised ammonium dichromate. They also prepared the compounds of $\text{CrO}_4\text{C}_2\text{H}_8\text{N}_2\cdot2\text{H}_2\text{O}$ and $\text{CrO}_4\text{C}_6\text{H}_{12}\text{N}_4$ of ethylenediamine hydrate and hexamethylene tetramine respectively, in a similar way as described above and studied their properties.

Riesenfeld and co-workers prepared various perchromates and attempted to study the constitution of perchromic acids with
the help of these compounds. They\textsuperscript{32} prepared ammonium, sodium, and potassium perchromates by the direct oxidation of respective chromate solutions with hydrogen peroxide in alkaline solution below 0°C. These red or reddish-brown perchromates were regarded to be salts of hypothetical acid $\text{H}_3\text{CrO}_8$. When acid medium was used, however, in preparing these compounds, blue salts such as $\text{KH}_2\text{CrO}_7$ and $(\text{NH}_4)_2\text{CrO}_7$ were formed. The red salts were found to decompose in neutral or alkaline solutions yielding chromate, whilst in acid solution, blue perchromates were formed which were instantly reduced to chromic salts.

Riesenfeld, Katsch, Ohl and Wohlers\textsuperscript{33,34} further studied the nature of above salts and generalised when oxidised by hydrogen peroxide in alkaline medium, chromic acid formed reddish-brown salts of the acid $\text{H}_3\text{CrO}_8$ and in acidic medium, blue salts of the acid $\text{H}_3\text{CrO}_7$. These authors further noticed that two types of salts, corresponding to two acids $\text{H}_3\text{CrO}_8$ and $\text{H}_3\text{CrO}_7$ were interconvertible. On addition of an acid the aqueous suspension of the red salts $(\text{NH}_4)_3\text{CrO}_8$ was converted to a blue salt, $(\text{NH}_4)_2\text{H}_2\text{CrO}_7$ with the evolution of oxygen. When an excess of pyridine was added, to either of these salts a compound of the formula, PyHCrO$_5$ was formed. When an excess of ammonia solution was added to an aqueous solution of either $(\text{NH}_4)_3\text{CrO}_8$ or $(\text{NH}_4)_2\text{H}_2\text{CrO}_7$ or PyHCrO$_5$, the compound CrO$_4$.3NH$_3$ was obtained.

Riesenfeld and Wesch\textsuperscript{35} determined the molecular weight of triamine chromium tetraoxide by the cryoscopic method and the values obtained were found to agree with the formula $(\text{NH}_3)_3\text{CrO}_4$ and
assigned the structures as:

\[
\begin{array}{c}
\text{H}_3\text{N} \\
\text{H}_3\text{N} \\
\text{H}_3\text{N}
\end{array}
\begin{array}{c}
\text{Cr} \\
\text{(O)} \\
\text{O}_2
\end{array}
\]

in support of this formula dieyano-monoamine derivative intermediate between tricyano compound of \((\text{NH}_3)_3\text{CrO}_4\) were prepared and presented as:

\[
\text{K}_2\begin{array}{c}
\text{CN} \\
\text{CN} \\
\text{H}_3\text{N}
\end{array}
\begin{array}{c}
\text{Cr} \\
\text{(OH)}_2 \\
0.\text{(OH)}_2
\end{array}\text{ K}_3\begin{array}{c}
\text{CN} \\
\text{CN} \\
\text{CN}
\end{array}
\begin{array}{c}
\text{Cr} \\
\text{(O)} \\
\text{O}_2
\end{array}
\]

Riesenfeld\textsuperscript{36} from his extensive researches on blue and red perchromates came to the conclusion that there were two classes of perchromates, (i) The blue salts derived from penta acid, \(\text{HCrO}_5\), and (ii) The red salts derived from octa acid, \(\text{H}_3\text{CrO}_8\). He determined the constitution of the respective salts of these acids from (i) molecular weight and (ii) permanganate reduction equivalent determinations during the decomposition of these salts, and assigned the following formulae to these acids:

\[
\begin{array}{c}
\text{Penta-acid}, \text{HCrO}_5 \\
\text{Octa-acid}, \text{H}_3\text{CrO}_8
\end{array}
\begin{array}{c}
\text{O}_2\equiv\text{Cr} \\
\text{0.OH}
\end{array}\begin{array}{c}
\text{O}_2\equiv\text{Cr} \\
\text{0.OH}
\end{array}
\]

\(\text{Blue}\) \hspace{1cm} \(\text{Red}\)

Riesenfeld and Mau\textsuperscript{37} further observed that when red potassium or sodium perchromate was decomposed by means of any
acid, the formation of blue perchromic acid occurred only when water was also present, otherwise anhydrous acids decomposed the red salts to chromic salts only. They, therefore, concluded that red perchromates must be considered as anhydrous salts of the blue perchromic acid, their constitution being $\text{Cr}(0.0\text{M})_3^{0}$ whilst that of the acid being $(\text{OH})_4\text{Cr}(0.0\text{H})_3$, that is, $\text{H}_3\text{CrO}_8.2\text{H}_2\text{O}$. The water was considered as water of crystallisation, since blue colour resulted only when water was also present along with perchromates and free acid.

Patten observed that chromic acid was reduced to chromous state and a higher oxide of hydrogen was produced when a saturated solution of potassium dichromate was treated with $2\%$ hydrogen peroxide at $-16^\circ$ C. He obtained chromous acetate by adding sodium acetate to ethereal blue perchromate. He was, therefore, of the opinion that chromium was present in chromous state in the blue perchromate and no acid, like $\text{HCrO}_5$ was produced.

Rai and Pillai and Rai prepared various complexes of ethereal blue perchromate with pyridine, piperidine, quinoline, hexamethylene tetramine, 8-hydroxyquinoline and strychnine, and studied their properties and showed the presence of $\text{Cr}(\text{III})$ along with $\text{Cr}(\text{VI})$ in the blue perchromate.

Thus, we see from the survey of the observations carried out by both the schools, Riesenfeld and his co-workers, and Wiede that blue peroxychromic acid is $\text{HCrO}_5$ in which there is only one Cr atom and that too hexavalent and there is a relationship between
blue and red perchromates analogous to an acid with its anhydride. Rai and his co-workers restricted their studies to blue perchromate and did not try to co-relate red and blue perchromates with each other and showed the presence of Cr(III) along with Cr(VI) in the blue perchromic acid.

(3) STUDY OF THE VARIOUS COMPOUNDS FORMED BY THE ACTION OF ALKALI AND ALKALINE EARTH GROUP METALS ON ETHERAL BLUE PERCHROMIC ACID.

Haüssermann\textsuperscript{41} obtained reddish-brown crystals of sodium perchromate of the formula $\text{Na}_6\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ by adding $\text{Na}_2\text{O}_2$ to a thin paste of Cr(0H)$_3$ and water at 10 to 120\textdegree C. He did not observe an intermediate compound of characteristic blue colour when the crystals were decomposed with dilute sulphuric acid.

Horace, Byers and Emmet Räid\textsuperscript{42} prepared various perchromates by adding metallic potassium, sodium, lithium, magnesium, calcium, barium and zinc to the ethereal blue peroxy chromic acid and found that hydrogen was evolved with the production of coloured precipitates. In the case of potassium, the compound was found to have the composition $\text{KCrO}_4$ or $\text{K}_2\text{Cr}_2\text{O}_7$. Similar formulae were obtained for compounds of other metals. They, therefore, concluded that ethereal blue perchromic acid contained $\text{H}_2\text{Cr}_2\text{O}_7$, but when the solution was prepared in excess of hydrogen peroxide, probability of the formation of a more highly oxidised compound was suggested.

Raynolds and Reedy\textsuperscript{43} noticed that a solution of red
perchromic acid was obtained when freshly precipitated \( \text{Cr(OH)}_3 \) was acted upon by 30% hydrogen peroxide at \( 0^\circ \). They prepared calcium perchromate of the composition \( \text{Ca}_3\text{Cr}_2\text{O}_7\cdot12\text{H}_2\text{O} \) as a buff powder which exploded at \( 100^\circ \). The aqueous solution of calcium perchromate on acidification gave rise to blue perchromic acid. They also suggested the presence of \text{Cr(III)} in the above compound to be linked to peroxide groups. Martínez and Porter \(^4\) however, disagreed to this and proposed the following structure:

\[
\begin{align*}
\text{Ca} & \quad \text{O} \\
\quad & \quad \text{O} \\
\text{O} & \quad \text{0} \\
\quad & \quad \text{Cr} \quad \text{=\text{0}} \\
\quad & \quad \text{O} \\
\text{Ca} & \quad \text{O} \\
\quad & \quad \text{O} \\
\quad & \quad \text{Cr} \quad \text{=\text{0}} \\
\end{align*}
\]

\( 0.10 \text{H}_2\text{O} \)

This alternative structure was supported on the basis of its resemblance with \( \text{Na}_6\text{Cr}_2\text{O}_{15} \cdot n\text{H}_2\text{O} \), which gave calcium perchromate on adding calcium chloride solution to it. This structure was further supported by the fact that the calcium perchromate on thermal decomposition yielded calcium chromate.

Rosenheim, Hakki and Krause\(^4\) prepared potassium and sodium perchromates of the compositions \( \text{K}_6\text{Cr}_2\text{O}_{16} \cdot n\text{H}_2\text{O} \) and \( \text{Na}_6\text{Cr}_2\text{O}_{15} \cdot n\text{H}_2\text{O} \) by the interaction of corresponding chromates with 30% hydrogen peroxide at \( 0^\circ \). They also obtained lithium perchromates \( \text{Li}_6\text{Cr}_2\text{O}_{13} \) and \( \text{Li}_6\text{Cr}_2\text{O}_{15} \) under varying conditions of preparation.

Martínez\(^4\) prepared pure carbonate free \( \text{K}_3\text{CrO}_8 \) by
treating KOH, chromic acid and boiled distilled water with hydrogen peroxide in a closed system.

Martinez, Rodrigenez and Brito\textsuperscript{47} prepared red peroxy chromates of Mg and Na or K of the compositions $K_2Mg_2Cr_2O_7\cdot15H_2O$ and $Na_2Mg_2Cr_2O_7\cdot16H_2O$ by adding Mg(NO$_3$)$_2$ dissolved in 30\% hydrogen peroxide to the aqueous solution of corresponding chromates at $-10^\circ$.

Martinez and Roca Adell\textsuperscript{48,49} studied the preparation and properties of the red peroxychromates of magnesium of the empirical formula Mg$_3$Cr$_2$O$_7\cdot26H_2O$ and also of calcium, barium and strontium and their double salts with alkali peroxychromates. Pure strontium and barium peroxychromates could not be prepared owing to the insolvability of their chromates.

Recently, Russian authors, Bogdanov, Petrova and Minaev\textsuperscript{50} obtained dark brown crystals of a new compound CaCrO$_6\cdot nH_2O$ by adding freshly prepared CaCrO$_4$ to 55\% hydrogen peroxide at $-30^\circ$ followed by the addition of ethyl alcohol.

Besides these compounds, Joyner and Wilmarth\textsuperscript{51} suggested on the basis of oxygen exchange studies that a peroxy cation of chromium might be formed as an intermediate in the action of peroxide on solutions of Cr(II).

Fujioka and Cady\textsuperscript{52} found a blue-green peroxychromic derivative to be formed by the reaction between chromic acid and hydrogen peroxide in trifluoro acetic acid but nothing was further known about it.
Thus it is seen that peroxychromates have been prepared by the two methods: (i) By taking a solution of chromic acid, chromate or dichromate in alkaline media and adding to it a 30% hydrogen peroxide solution, and (ii) by taking chromic hydroxide in alkaline medium and adding the same 30% hydrogen peroxide solution. The first method always gave red perchromates besides other types of compounds, whereas the second method gave mainly the blue perchromates. The red perchromates decomposed to give chromates whereas the blue perchromates yielded dichromate after decomposition. Since both of these perchromates are prepared in a similar way by taking Cr(VI) and adding hydrogen peroxide in alkaline medium, therefore, earlier workers have created a great confusion by comparing the nature, properties and constitutions of the red perchromates with the blue one. Whereas Rai and his co-workers (loc. cit.) restricted their studies to the blue perchromates only, prepared by adding 6% hydrogen peroxide to chromic acid solution or acidified dichromate solution in presence of organic solvents.

(4) STUDY OF THE DECOMPOSITION PRODUCTS OBTAINED FROM THE BLUE PERCHROMIC ACID UNDER DIFFERENT CONDITIONS:

Moissan53 was the first who tried to isolate the blue compound by careful evaporation of the excess of solvent at -20° and could get nothing except a blue oily liquid, very unstable and highly soluble in ether. He assigned CrO₃·2H₂O₂ formula to this oily liquid. Rai54 observed that on further concentration it decomposed to chromium dichromate with a hissing sound.
Schwarz and Giese\textsuperscript{55} studied the decomposition products of the pyridine complex of ethereal blue perchromic acid to elucidate the nature and constitution of blue perchromic acid. They prepared pyridine complex by Wiede's method (loc. cit.)\textsuperscript{59} decomposed it in dilute acids, treated the pyridine complex with aqueous potassium permanganate and measured the oxygen evolved from the ethereal blue peroxychromic acid in presence of silver oxide. They then calculated the amount of oxygen set free per atom of chromium and gave the mechanism for the reactions \textsuperscript{56} (Emeleus, H.J. and Anderson, J.S., "Modern aspects of Inorganic Chemistry" page 426, Routledge and Kegan Paul, 1959). They found $3\text{CrO}_5 \equiv 4\text{KMnO}_4$; therefore, $\text{CrO}_5 \equiv 4/3 \text{KMnO}_4$. They, thus, considered peroxychromic acid to be not a true acid but a peroxide $\text{CrO}_5\cdot O \equiv \text{Cr(O}_2\text{)}_2$. They also determined the molecular weight of the pyridine complex by cryoscopic method in benzene, nitrobenzene or pyridine and confirmed the unimolecular structure, $\text{PyCrO}_5$.

Schwarz and Giese\textsuperscript{57} suggested three formulae for blue potassium perchromates: $\text{KH}_2\text{CrO}_7$, $\text{KCrO}_5\cdot 2\text{H}_2\text{O}$ and $\text{KCrO}_6\cdot \text{H}_2\text{O}$, based on the degradation of alkali perchromate. They showed that thallium perchromate was $\text{TlCrO}_6$ and hence the corresponding potassium salt $\text{KCrO}_6\cdot \text{H}_2\text{O}$ was correct and proposed the formulae for the blue and red perchromates and represented them as double molecules, $\text{K}_2\text{Cr}_2\text{O}_{12}$ and $\text{K}_2\text{Cr}_2\text{O}_{16}$ respectively containing hexavalent chromium with numerous peroxide linkages.

Resenfeld\textsuperscript{58} contradicted the view of Schwarz and Giese...
regarding the preparation of pyridine complex by his method and suggested careful cooling during preparation. The compound \( \text{CrO}_5 \cdot \text{C}_5 \text{H}_5 \text{N} \) prepared in this way and that prepared by Schwarz differed only slightly in the rate of decomposition and behaviour towards acids and alkalis, which he assumed to be due to stereoisomerism.

Schwarz and Elstner\(^6\) prepared \( \text{CrO}_5 \cdot \text{Me}_2 \text{O} \) by the interaction of \( \text{CrO}_3 \) and concentrated hydrogen peroxide in \( \text{Me}_2 \text{O} \) at \(-50^\circ\), by careful evaporation of the excess of solvent, the crystals which were originally mistaken for the free acid \( \text{H}_3 \text{CrO}_8 \) by Reisenfeld and Max (loc. cit.) and confirmed the formula \( \text{CrO}_5 \) for blue compound. They further attempted to prepare it directly from \( \text{CrO}_2 \text{Cl}_2 \) and \( \text{H}_2 \text{O}_2 \) which gave an equilibrium mixture that retained some chromyl chloride and from which no definite compound was isolated\(^6\):

\[
\text{CrO}_2 \text{Cl}_2 + 2 \text{H}_2 \text{O}_2 \xrightleftharpoons{} \text{Cr}(0) \left( \text{O}_2 \right)_2 + \text{H}_2 \text{O} + 2 \text{HCl}
\]

Rai\(^6\) studied the decomposition products of pyridine and piperidine complexes of the blue perchromate and suggested \( \text{RCrO}_2 \cdot 5 \) or \( \text{R}_2 \text{Cr}_2 \text{O}_5 \) for pyridine and \( \text{R}_{1,5} \text{CrO}_2 \cdot 5 \) or \( \text{R}_3 \text{Cr}_2 \text{O}_5 \) formulae for piperidine complexes. He also studied (loc. cit.) the quinoline and hexamethyltetramine complexes.

Pillai and Rai\(^6\) studied the 8-hydroxyquinoline, quinoline and strychnine complexes of the blue perchromate, preparing them by Wiede's method (loc. cit.) and suggested \( \text{R}_2 \text{Cr} \left( \text{CrO}_1 \right)_2 \cdot 10 \), \( \text{R}_2 \text{Cr}_2 \left( \text{Cr}_2 \text{O}_2 \right)_2 \) or \( \text{R}_4 \text{Cr}_2 \left( \text{CrO}_1 \right) \cdot 2 \) formulae for the
quinoline and 8-hydroxyquinoline complexes and $R_2Cr(\text{CrO}_3)$ for strychnine complex.

Rai and Prakash\textsuperscript{64} had shown that the blue perchromate furnished $Cr_2(\text{Cr}_2O_7)_3$ on decomposition in water and on this basis, Rai suggested that the blue perchromate contained Cr(III) and proposed $Cr_2(\text{Cr}_2O_{10})_3$ formula for the blue peroxychromic acid. Rai\textsuperscript{65} further showed that this formula was in equilibrium with another labile form in presence of excess of $H_2O_2$.

$$Cr_2(\text{Cr}_2O_{10})_3 + 2H_2O_2 \rightleftharpoons 4Cr\text{CrO}_3 + 2H_2O$$

Rillai and Rai\textsuperscript{66} studied the decomposition of blue compound extracted with ethyl acetate in water and found that it furnished $Cr_2(\text{Cr}_2O_7)_3$ and not $Cr_2(\text{Cr}_2O_8)_3$ as found in case of ether. This behaviour of blue compound was attributed to the greater stability in ethyl acetate.

Rai and Rajput\textsuperscript{67} studied the water decomposition product of ethereal blue perchromate exchanged with the help of ion exchange resins. Cationic and anionic chromium was separated, estimated volumetrically oxidised and unoxidised by titrating against standard sodium thiosulphate solution. The ratio of Cr(III) : Cr(VI) i.e., 1 : 3 had been found. This supported Rai's formula (loc. cit.), $Cr_2(\text{Cr}_2O_7)_3$ for water decomposition product.

Rai and Rajput\textsuperscript{68} further studied tightly corked bottle and open bottle decomposition products of ethereal blue perchromate, exchanged by ion exchange resions. Cationic and anionic ingredients had been separated, estimated after oxidation and before oxidation.
iodometrically. The ratios of Cr(III) and Cr(VI) had been calculated and found 1 : 1 for corked bottle and 2 : 3 in case of open bottle decomposition products.

The decomposition of the blue perchromic acid had been the subject of some unconvincing kinetic studies. One series of experiments made by Gnadniger\(^6\) had led to the conclusion that the rate of decomposition in aqueous solution, like the rate of formation, was independent of the concentration of \(H_2O_2\), was first order in \(CrO_5\), and at a given concentration of \(H_2O_2\) and of dichromate was first order in sulphuric acid. Prakash and Rai\(^7\) found that in organic solvents, the decomposition was unimolecular with rate constants at 10\(^{\circ}\) and 20\(^{\circ}\) of 0.002125 and 0.005273 sec, respectively.

**PHYSICO-CHEMICAL METHODS:**

Following are various physical methods, which have been used for the study of the nature and constitution of the blue perchromates.

1. Potentiometric measurements
2. Conductivity measurements.
3. Determination of molecular weight.
4. Spectrophotometric studies: (a) Absorption spectra (b) Infra-red spectra
(c) Ultraviolet spectra
5. Magnetic measurements
6. X-ray crystallography.

1. **Potentiometric measurements**:

Riveng\(^7\) studied the formation of persalts with hydrogen peroxide by potentiometric and colorimetric measurements, but no definite conclusion regarding the exact valency of the element was drawn.
(2) **Conductivity Measurements**

Spitalsky and Kobosev\(^72\) were the first to study the reaction between \(\text{H}_2\text{O}_2\) and chromic acid by the conductivity method. They observed that during the reaction between chromic acid or acidified dichromate solution and hydrogen peroxide the conductivity at first decreased sharply to a value which approximately remained constant during the major part of the reaction and then returned to its initial value as the reaction neared completion. The nature of the curves obtained from conductivity measurements led to the hypothesis that during the course of the reaction two intermediate compounds were reversibly formed which required no \(\text{H}^+\) for their formation and possessed relatively small affinity constant, while third compound which was more stable required \(\text{H}^+\) for its formation.

Kobozev and Galbreich\(^73\) repeated the above study at 56\(^\circ\) and noticed that the first order of the reaction suggested by Spitalsky and Kobosev changed to second order on the basis of entropy and thermal data. They suggested the formation of \(\text{Cr}_2\text{O}_9^{2-}\) ion contrary to the formation of \(\text{KH}_5\text{Cr}_4\text{O}_{18}\) during the reaction between \(\text{H}_2\text{O}_2\) and acidified dichromate solution.

Fergusson, Wilkins and Young\(^74\) found the very small value of the conductivity of pyridine complex of blue perchromic acid in dimethyl formamide, and proved that the compound was a molecular donor - acceptor complex.

Pillai\(^76\) studied the nature of decomposition of the blue perchromic acid in contact with water by conductivity
measurements. In case of ethereal blue perchromate three distinct breaks, corresponding to three compounds, \(\text{Cr}_2(\text{Cr}_2\text{O}_7)_3\), \(\text{Cr}_2(\text{Cr}_2\text{O}_8)_3\) and \(\text{Cr}_2(\text{Cr}_2\text{O}_7)_3\), were located. Similarly, he observed two breaks corresponding to two compounds, \(\text{Cr}_2(\text{Cr}_2\text{O}_9)_3\) and \(\text{Cr}_2(\text{Cr}_2\text{O}_8)_3\), in the conductivity curve in case of the decomposition of blue acid extracted with ethyl acetate in water. The peroxo nature of peroxo dichromate, \(\text{Cr}_2(\text{Cr}_2\text{O}_8)_3\), was confirmed by Jagmer Singh\(^7\). He oxidised organic compounds and got \(\text{Cr(III)}\) in presence of mineral acid.\(^7\)

(3) **Determination of Molecular Weight:**

Riesenfeld\(^7\) determined the molecular weight of potassium salt, \(\text{K}_3\text{Cr}_2\text{O}_8\) in water by cryoscopic method and obtained the values: 81.31, 68.41, 78.70 and 61.55 experimentally. The observed values agreed with the theoretical value 74.3. As the values differed very much among themselves, this variation in values might be possible if the compound had decomposed to some extent in aqueous solution. In the case of red ammonium salt \((\text{NH}_4)_3\text{CrO}_8\) molecular weight was found to be 129. 98 as against the theoretical value 58.5. The experimental values differed very much from the theoretical value and accounted for double formula of the compound. The double formula was also suggested by Martinez and Adell, and Raynold and Reed (loc. cit.). Riesenfeld (Loc. cit) also suggested \(C_5H_5N.H\text{CrO}_5\) formula for the pyridine complex on the basis of its molecular weight, which he found to be 220 and 208 in benzene solution. These values were much nearer to the theoretical value 212.
Schwarz and Giese (loc. cit.) determined the molecular weight of the pyridine compound of the blue perchromic acid by means of freezing point method in benzene, nitrobenzene, tribromomethane or pyridine and confirmed the unimolecular structure.

Rai (loc. cit.) observed that in most of the organic solvents, the pyridine compound started decomposing and hence the results obtained by the above workers could not be relied. Rai and Rajput (loc. cit.) also attempted to determine the molecular weight of the isoquinoline complex in benzene but the results were very erratic due to decomposition.

(4) Spectrophotometric studies:

(a) Absorption spectrophotometry: Mme. P. Rumpf\textsuperscript{80} supported the formula \( \text{CrO}_5 \) for the blue compound by measuring at equal intervals of time the absorption of light by an equimolar mixture of solutions of hydrogen peroxide and potassium dichromate, the pH being maintained below 4. She also observed that the maximum concentration of the blue compound was obtained when \( \text{CrO}_3/\text{H}_2\text{O}_2 \) ratio was 1 : 0.5.

Bobtelsky, Glasner and Bobtelsky-Chaikin\textsuperscript{81} used the spectrophotometric method along with pH measurements in the study of the reaction between chromic acid and hydrogen peroxide solutions. They confirmed the earlier view of Spitalsky and Kobosev (loc. cit.) that the two types of perchromates were formed during the course of reaction, one blue at pH 4 and the other violet beyond pH 4.
They also were of the opinion that there was an equilibrium between the two perchromates, and that no hydrogen ion was needed for the conversion of the violet form from the blue.

Glasner$^{82}$ repeated the above reaction and confirmed the formation of blue and violet compounds. As suggested by Riesenfeld and Wiede, Glasner came to the conclusion that in the above reaction one molecule of chromic acid reacted with one and half molecule of peroxide to give one molecule of blue compound.

Glasner and Steinberg$^{84}$ attempted to arrive at the composition of blue perchromic acid by measuring the optical density during the reaction between chromic acid and hydrogen peroxide or by taking acidified with sulphuric acid and hydrochloric acid, perchloric acid, $\text{K}_2\text{Cr}_2\text{O}_7$ and $\text{K}_2\text{CrO}_4$ and varying quantities of $\text{H}_2\text{O}_2$. In the case of chromic acid and acidified solutions of dichromate the ratio, $\text{H}_2\text{O}_2/\text{Cr}_2\text{O}_7$ was found to be 1.5 : 1, whereas in other cases it was 2 : 1, but in solutions weaker in acids the ratio moved to 4 : 1.

(b) Infra-red spectrophotometry: Evans$^{85}$ measured the infra-red spectra of the pyridine and 1 : 10 phenanthroline complexes and also of the pyridinium nitrate, PyHNO$_3$ and (AgPy)NO$_3$ in Nujol or hexachlorobutadiene over a region of 2 - 15 µ and could not get any peak corresponding to either N - H or OH groups but obtained similar spectra as those given by pyridine or (AgPy)NO$_3$ complex. The (AgPy)NO$_3$ infra-red spectra showed that in the corresponding
chromium complex pyridine had coordinated with Cr(III) in the complex.

The composition of violet diperoxy chromates was long believed to be represented by the formula $M^+\text{CrO}_6$; usually with the one molecule of water of crystallization as suggested by Schwarz. Griffith measured the infra-red spectra of the anhydrous potassium salt of violet diperoxy chromates and found one hydrogen atom per molecule and the presence of -OH groups, was also confirmed by the infra-red spectra. It was also established that the number of peroxy groups per chromium was the same in the violet salts and in the chromium pentaoxide. The violet diperoxy chromate was formulated as $K[\text{Cr}(O)_2(O_2)H]$ by the above measurements.

(c) Ultra-violet spectra:

Fergusson, Wilkins and Young studied the pyridine and 1:10 phenanthroline complexes of the blue compound by ultraviolet spectra, and found that in the pyridine derivative, the chromium atom was in a sense six-coordinated, but the ligands form a pentagonal pyramide, so that there was what might be called a vacant coordination position axial to the unique oxygen atom. In the adducts of bidentate diamines, this position might well be filled. But they observed that the ultraviolet spectrum of 1:10 phenanthroline was rather different. Pyridine compound showed two peaks at $\sim 5800$ and $7000 \text{ A}$ ($\epsilon \sim 500$), while phenanthroline gave two bands of about this intensity but at $\sim 6300$ and $8300\text{ A}$.
They further suggested that the infra-red bands assigned to modes of the peroxy groups in the spectra of the two compounds in the NaCl region, however, were at very similar frequencies.

Shibata and Matsuno measured the ultraviolet spectrum of \(3\text{NH}_3\cdot\text{Cr(O}_2\text{)}_2\) complex and contradicted the formulae suggested by Hofmann and Hiendemaier, and Riesenfeld, Kutsch and Ohl (loc. cit. for the derivative of diperoxychromium and also that the compound was polymorphic and existed in two isomeric forms.

(5) Magnetic measurements:

Tjabbes, Klemm and Werth measured the magnetic susceptibility of the red tetra peroxichromate, and found it to be 1.30 B.M., in accordance with the potassium salt, \(K_3[Cr(O_2)_4]\). The formula implied the presence of chromium (V). Rodriguez Rios, and Horrau determined the magnetic susceptibility of \(Mg_2K_2Cr_2O_7\). The values had shown that the compound really contained the tetraperoxy chromate (V) ion.

Klemm and Werth, Fergusson and Wilkins, and Griffith measured the magnetic susceptibility of pyridine complex of blue perchromate. The small and probably temperature independent paramagnetic susceptibility \((\mu = 0.4 - 0.8 \text{ B.M.})\) was consistent with presence of Cr(VI). Similarly Fergusson and Wilkins got the small and probably temperature independent paramagnetism \((\mu \sim 0.6 \text{ B.M.})\) associated with Cr (VI) in violet diperoxy chromates, \(M[Cr(O_2)(O_2)_2H]\).
Bhatnagar, Prakash and Hamid\textsuperscript{93}, and Fergusson and Wilkins (loc. cit.) measured the magnetic susceptibility of Cr(\textsubscript{2}O\textsubscript{2})\textsubscript{2}.3NH\textsubscript{3}, derivative of diperoxy chromium, and found it to be 2.8 B.M. The paramagnetic moment of the compound was consistent with the presence of the two unpaired electrons associated with chromium (IV).

Raj\textsuperscript{94}, measured the magnetic moment of the ethereal and ethyl acetate extracted blue perchromates, washed and unwashed and found it to be paramagnetic in nature.

Pillai\textsuperscript{95} found values of 3.8 and 3.88 B.M. for the quinoline and 8-hydroxy quinoline complexes of blue perchromate, and suggested the presence of Cr(III). Strychnine complex of blue perchromic acid was found to be feebly paramagnetic.

(6) \textbf{X-Ray Crystallography}:

Stomberg and Brosset\textsuperscript{96} studied the single crystal of potassium salt of tetrperoxy chromate (V), M\textsubscript{3} [Cr(\textsubscript{2}O\textsubscript{2})\textsubscript{4}] 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{97} using parameters derived from the g-values; the unpaired electron was assigned to a \textit{B} orbital of chromium. The O - O distance of 1.40Å was rather less than the 1.49 Å found in alkali metal peroxides (Abrahams and Kalnajs)\textsuperscript{98}, perhaps because electrons that in the
free peroxide were in antibonding π orbitals were partly delocalized in the complex into orbitals of chromium.

Two X-ray studies of the pyridine complex of blue chromium perchromate were made by Stomberg and Pedersen and Pedersen. They found that the chromium atom, the two peroxo 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 Py·Cr(0)(O₂)₂.

McLaren and Helmholtz determined the crystal structure of triamino chromium tetraoxide 3NH₃·Cr(O₂)₂ and shown that in the crystal, the Cr atom might be described as seven coordinated with a roughly T-shaped arrangement of nitrogen atoms around it; the peroxo groups laid with the O - O axes in the plane of the downstroke of the T, so that they and one nitrogen atom form an irregular plane pentagon around the Cr atom.

The O - O distance of 1.31 Å was some 0.18 Å less than in the peroxide ion, so the compound was described as a superoxide of Cr(II).

Thus, the view of the existing literature on the blue compound revealed that the different aspects of this compound under different conditions had been studied by numerous investigators who suggested various formulae giving totally new and radically different interpretations. The unstable nature of this compound
made its study difficult, and no definite formula was assigned to it which could be challenged.

Barreswil (loc. cit.) was the first to name the blue compound as the blue perchromic or peroxychromic acid and assigned a chemical formula $\text{Cr}_2\text{O}_7\cdot\text{H}_2\text{O}$ or $\text{H}_2\text{Cr}_2\text{O}_8$.

Brodie$^{102}$ from his experiments inferred that when chromic acid was in excess during the reaction between chromic acid and hydrogen peroxide, 6 gram atoms of oxygen were evolved per two molecules of chromic acid whereas with excess of hydrogen peroxide 9 gram atoms of oxygen were evolved. Martino$^{103}$ observed that deepest blue colouration was developed only of the ratio of hydrogen peroxide and chromic acid was 4:2. According to him the blue perchromic acid should be represented as $\text{H}_4\text{Cr}_2\text{O}_7$.

Riesenfeld et. al., (loc. cit.) recognised three series of perchromates which could be distinguished by their colours as: blue, red and violet, which might be represented by the typical formulae, $\text{PyHCrO}_5$, $\text{K}_3\text{CrO}_6$ and $\text{KH}_2\text{CrO}_7$ respectively. Riesenfeld and co-workers and Wiede (loc. cit.) agreed that the ethereal blue perchromic acid was $\text{HCrO}_5$. Riesenfeld was also of the opinion that the blue peroxychromates were compounds of hepta valent chromium.

Glasner (loc. cit.) spectrophotometrically supported the formula $\text{HCrO}_5$ and showed that 3 molecules of hydrogen peroxide reacted with 2 molecules of chromic acid to give one molecule of
blue perchromic acid as presented by Riesenfeld and Wiede. He also regarded it as monoperoxy chromic acid, HCr(0)\textsubscript{3}(O)\textsubscript{2}. After some times he with Steinberg made an extensive study of the above formula, HCrO\textsubscript{5} of the blue compound spectrophotometrically. The conclusion from an earlier work that the blue compound was the monoperoxy acid, was abandoned.

Schwarz and Giese (loc. cit.) questioned the hepta valency of chromium in the formula, HCrO\textsubscript{5}. They subsequently showed that the contents of the peroxidic oxygen were higher than had been found by Riesenfeld (loc. cit.). The blue compound and the pyridine derivative were given the formula Cr(0)(O)\textsubscript{2}\textsubscript{2} and Py(0)(O)\textsubscript{2}\textsubscript{2} respectively, on the basis of its reaction with dilute sulphuric acid, with silver oxide and also with neutral KMnO\textsubscript{4} (of which four equivalents were consumed per molecule of pyridine complex). This formula implied that the chromium atom was in the (formal) +6 state. The physico-chemical studies made by Evans, Glasner and Steinberg by spectrophotometric methods, by Fergusson, Wilkins and Young, and Griffith (loc. cit.) by magnetic measurements and Pederson and Stomberg by X-ray crystallography, supported the CrO\textsubscript{5} formula of blue perchromic acid as suggested by Schwarz and Giese.

Recently, Rai (loc. cit.) supported by Pillai & Rai, Rajput and Rai, and Singh and Rai (loc. cit.) suggested that blue perchromate was neither an acid, HCrO\textsubscript{5} or H\textsubscript{2}CrO\textsubscript{5} nor a peroxide CrO\textsubscript{5} but was a complex of Cr(III) having two formulae in equilibrium:

\[
\text{Cr}_2\text{Cr}_2\text{O}_{10} + \text{H}_2\text{O} \rightleftharpoons 4 \text{CrCrO}_3 + 2\text{H}_2\text{O}
\]
Besides Rai and co-workers, Patten (loc. cit.), Reynolds and Reedy (loc. cit.), McLaren and Helmboltz (loc. cit.), and Bohm and Stomberg (loc. cit.) also suggested the presence of chromium with lower valency state than six.

In view of the complexity of the problem and contradictory results obtained as shown in the above discussion I thought it worthwhile to undertake a systematic study of the nature of the so-called blue peroxochromic acid by chemical and physico-chemical methods. An attempt has been made to throw more light on the constitution of blue perchromates, prepared with phthalic acid as well as with sulphuric acid.

The present thesis embodies the following chapters of studies on the above subject:

I Studies on:
(i) Ethereal blue perchromate prepared with phthalic acid.
(ii) Ethereal blue perchromate prepared with sulphuric acid.
(iii) Ethyl acetate extracted blue perchromate prepared with sulphuric acid.

II The quantitative studies on the decomposition products of: ethereal blue perchromate prepared with phthalic acid, exchanged with the help of ion-exchange resins.

III The gravimetric study of decomposition products of ethereal blue perchromate prepared with sulphuric acid, with and without the application of ion-exchange resins.

IV Studies on the decomposition products of ethereal blue perchromate prepared with phthalic acid as well as with sulphuric acid obtained in presence of silver oxide.

V A comparative study of the decomposition of blue perchromates:
(i) prepared with phthalic acid in alkalies; and
(ii) prepared with sulphuric acid in alkalies.
VI  Study of pH of blue perchromates prepared with phthalic acid and sulphuric acid:
   (i) During decomposition in water at definite time intervals.
   (ii) Of water decomposition product at different dilutions.

VII A comparative study of complexes of isoquinoline and 8-hydroxy quinoline with ethereal blue perchromate:
   (i) Prepared with phthalic acid.
   (ii) Prepared with sulphuric acid.

VIII Magnetic susceptibility measurements of complexes of isoquinoline and 8-hydroxy quinoline with ethereal blue perchromate:
   (i) Prepared with phthalic acid.
   (ii) Prepared with sulphuric acid.

The results of investigations have been discussed in "General Discussion".
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<td>Ph.D. Thesis, Saugar University, 1963, On &quot;Studies on the so-called blue peroxy chromic acid&quot; Chapter VI.</td>
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