INTRODUCTION
Barreswil\textsuperscript{1}, in 1848 observed that on the addition of hydrogen peroxide to an aqueous solution of chromic acid or to an acidified solution of dichromate/chromate, a deep blue compound was produced. This blue compound was found to be very unstable in water but more stable and soluble in ether. Thus it could be extracted with ether. Barreswil named it as blue perchromic acid or peroxy chromic acid in analogy with other peracids.

Grosvenor\textsuperscript{2} found that there were other oxygen containing solvents such as, ethyl acetate, ethyl valerate, amyl valerate, amyl chloride, amyl butyrate, amyl formate and amyl acetate in which the blue compound could be extracted. He further observed that solvents such as benzene, aniline, toluene, nitrobenzene, chloroform, carbon tetra-chloride, carbon disulphide and petroleum did not dissolve the blue compound. Recently Sastri and Sunder\textsuperscript{3}, and Tuck and Walters\textsuperscript{4}, have used tri-n-butyl phosphate - cyclohexane mixtures as the solvent for the blue perchromic acid.

Schonbein\textsuperscript{5} prepared alkali chromates by the reaction of blue perchromic acid with alkali hydroxides. Aschoff\textsuperscript{6} observed that solutions of ferrous salts discharged the blue colour of the blue perchromic acid, while potassium hydroxide developed a pale blue colour in the non - aqueous layer and brownish violet colour in the
aqueous layer. Martinon\textsuperscript{7} found that the blue compound was
decomposed both in acid and alkaline media, with the
formation of chromic ions and chromates respectively.
Jorissen and Reicher\textsuperscript{8} studied the decomposition of blue
perchromic acid by oxalic acid.

Werther\textsuperscript{9} studied the inhibiting effect of
vanadates on the formation of blue perchromic acid and
found that the inhibiting action depended on the quantity
of vanadates.

Riechard\textsuperscript{10} observed that the action of vanadate
could be neutralised by adding sodium hydrophosphate or
hydroarsenate in a small amount. He further observed that
the tungstate, molybdate, phosphate and arsenate also
impart similar effect on the formation of blue compound
but to a lesser extent than vanadates.

A number of methods were employed by various
investigators to elucidate the nature and constitution of
the blue perchromic acid, and various formulae were assigned
to it. In order to have a clear understanding of the nature
and constitution of the blue peroxychromic acid, the
reactions and methods utilised on the subject may be
classified as under:

(1) Study of the nature of complexes formed from ethereal
blue perchromic acid and nitrogenous organic bases or
other basic substances.
(2) Study of catalytic decomposition of hydrogen peroxide by aqueous solution of chromic acid or by aqueous as well as acidified dichromate or chromate solutions.

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

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

(5) Physico-chemical studies: such as potentiometric measurements, conductometry, molecular weight determination, spectrophotometry, ultra-violet spectra, infra-red spectra, magnetic measurements and x-ray crystallography.

(6) Chemical kinetics:

STUDIES ON THE COMPLEXES OF ETHEREAL BLUE PEROXY CHROMIC ACID:

Complexes were prepared by the following two methods:

(1) The blue peroxychromic acid was prepared by interaction of chromic acid solution and hydrogen peroxide and was extracted with ether, washed with water and then treated with various organic nitrogenous bases. The complexes so formed were filtered, washed with organic solvents and dried.

(ii) A - The chromic acid solution was mixed with the excess of organic nitrogenous base, cooled below 0°C. and to this
mixture 30% hydrogen peroxide was added, coloured crystals or flakes were precipitated, filtered, washed with organic solvent and analysed.

(ii) B - Aqueous solutions of dichromate or chromate was mixed with alkalis, cooled below 0°C and then 30% hydrogen peroxide was added to this mixture. Red crystals were precipitated.

Wiede\textsuperscript{11} used the first method to prepare the complexes of blue peroxychroomic acid with organic nitrogenous bases and ammonia. He observed that when ethereal blue peroxychroomic acid was mixed with aqueous ammonia solution at low temperature, a greenish brown precipitate was formed. On recrystallisation in 30% ammonia solution, pale brown needle - shaped crystals were obtained which have the composition $\text{CrO}_4\cdot3\text{NH}_3$.

Wiede\textsuperscript{12} also prepared pyridine and aniline complexes of the composition $\text{PyHCrO}_5$ and $\text{AnHCrO}_5$ by treating the blue compound with pyridine and aniline respectively. Aniline complex was found to be more explosive than pyridine. He\textsuperscript{13} also prepared the complexes of piperidine, trimethylamine, quinoline and tetramethyl ammonium hydroxide by treating blue peroxychroomic acid with these bases. Wiede studied the composition of the these complexes and concluded that the blue peroxychroomic acid should have the formula $\text{HCrO}_5$. 
The second method was mainly used by Riesenfeld and co-workers\textsuperscript{14-16}, who prepared ammonium, sodium and potassium perchromates by the direct oxidation of the respective chromate solutions with hydrogen peroxide in alkaline solution below $O_2$. These red perchromates were regarded to be salts of the hypothetical acid $H_3CrO_8$. When acid medium was used, in preparing these compounds, then blue salts such as $KH_2CrO_7$ and $(NH_4)_2CrO_7$ were formed. The red salts were found to decompose in neutral or alkaline solution yielding chromates, whilst in acid solution, blue perchromate were formed which were instantaneously reduced to chromic salts.

Riesenfeld and co-workers (loc.cit) were of the view that hydrogen peroxide, oxidised alkaline solution of chromic acid to form reddish brown salts derived from the peracid $H_3CrO_8$ while the acidified solution of chromic acid gave blue salts derived from the acid $H_2CrO_7$. The salts of these two acids were interconvertible. On addition of an acid, the aqueous suspension of the red salt $(NH_4)_3CrO_8$ was converted into the blue salt $(NH_4)_2CrO_7$, with the evolution of oxygen. When an excess of pyridine was added to either of these salts, a compound $PyHCrO_5$ was obtained. When an excess of ammonia solution was added to an aqueous solution of either $(NH_4)_3CrO_8$ or $(NH_4)_2CrO_7$ or $PyHCrO_5$, the compound
CrO$_4$.3NH$_3$ was obtained. Riesenfeld and Wesch$^{17}$ determined the molecular weight of the triamine chromium tetraoxide by the cryoscopic method and assigned to it the molecular formula CrO$_4$.3NH$_3$.

Thus Riesenfeld$^{18}$, from his extensive investigations on blue and red perchromates, came to the conclusion that there were two classes of perchromates:
(i) the blue salts derived from penta acid, HCrO$_5$, and
(ii) red salts derived from octa acid, H$_3$CrO$_8$.

He determined the constitution of the respective salts of these acids by molecular weight and permanganate reduction equivalent determinations during the decomposition of these salts and assigned the following formulae to these acids:

Penta acid HCrO$_5$

Octa acid H$_3$CrO$_8$

(Blue)  

(Red)
Hofmann and Hiedlmair\textsuperscript{19} prepared an ammonium salt, CrO$_2$(O.O.NH$_4$)$_2$, of chromatodiper acid by the action of 30% hydrogen peroxide on a paste of chromic hydroxide and ammonium hydroxide at 0\degree C. This compound, having octahedral crystals of dark red colour, when dissolved in water or exposed to air, yielded ammonium chromate with the evolution of oxygen. On heating or moistening with concentrated sulphuric acid, it exploded but with dilute sulphuric acid or acetic acid it gave the blue acid. These workers\textsuperscript{20} also prepared the compounds CrO$_4$C$_2$H$_8$N$_2$.2H$_2$O and CrO$_4$C$_6$H$_{12}$N$_4$ of ethylene diamine hydrate and hexamethylene tetramine respectively and studied their properties.

Patten\textsuperscript{21} observed that chromic acid was reduced to chromous state and a higher oxide of hydrogen peroxide was produced when a saturated solution of acidified potassium dichromate is mixed with H$_2$O$_2$ (2%) at -16\degree C. The chromous state has been confirmed on the basis of production of chromous acetate if the ethereal blue perchromate is treated with sodium acetate. He was, therefore, of the opinion that chromium is present in chromous state in the blue perchromate and that no acid like HCrO$_5$ was produced.

Dougals G. Nicholson\textsuperscript{22} obtained a tancoloured precipitate by adding alcoholic ammonia solution to the blue peroxychromic acid. He studied the physical and chemical
properties of this compound and suggested the formula
CrO$_4$·3NH$_3$ for this compound.

Rai$^{23}$ prepared the complexes of blue perchromate
with pyridine, piperidine, quinoline and hexamethylenetetra-
amine by Wiede's method, and assigned to them R$_2$Cr(CrO$_5$),
R$_3$Cr(CrO$_5$), RCrO$_5$ and RCrO$_{12}$ formulae respectively. From
the studies of these complexes he confirmed the presence of
chromium(III) along with chromium(VI) in the blue peroxy
chromic acid. Further Rai and co-workers$^{24-26}$ prepared
various complexes of the ethereal blue peroxy chromic acid
with a number of organic nitrogenous bases such as 8-hydroxy
quinoline, strychnine, pyridine, quinoline and piperidine.
They studied the nature of these complexes and showed the
presence of Cr(III) along with Cr(VI) in the so called
blue peroxy chromic acid.

2. CATALYTIC STUDIES:

Berthelot$^{27}$ for the first time studied the
decomposition of hydrogen peroxide by adding to it an aqueous
solution of potassium dichromate and observed that a small
amount of the latter could decompose an unlimited amount
of the former without itself being affected. He$^{28}$ further
observed that unacidified solution of potassium dichromate
did not give a blue colour with hydrogen peroxide and
therefore acid was found to be necessary for the formation
of blue peroxy chromic acid.
Bach\textsuperscript{29}, while studying the action of chromic acid on hydrogen peroxide observed that in presence of sulphuric acid one molecule of chromic acid was used for every two molecules of hydrogen peroxide, but in the absence of an acid, an unstable brown adduct of hydrogen peroxide and chromic acid was formed, which decomposed spontaneously resulting in the formation of chromic acid and the whole of the peroxo oxygen of hydrogen peroxide was given off.

Spitalsky\textsuperscript{30-31} 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 hydrogen 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 hydrogen peroxide concentration and nearly independent of the chromic acid concentration. He further observed that there was a constant ratio between Cr(III) and Cr(VI) irrespective of the amount of hydrogen peroxide taken, provided that it was in considerable excess of chromic acid solution.
Riesenfeld\textsuperscript{32} studied the reaction between chromic acid and hydrogen peroxide and supported the view of Spitalsky that about 28\% of chromic acid was reduced to Cr(III) at the end of the reaction. He also observed that the oxygen evolved was always less than the theoretical quantity due to the formation of blue compound. He represented the reaction between chromic acid and hydrogen peroxide as:

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

Spitalsky\textsuperscript{33} and Riesenfeld\textsuperscript{34} observed independently that a mixture of chromate and dichromate solutions decomposed hydrogen peroxide catalytically. Robertson\textsuperscript{35} observed that the decomposition of hydrogen peroxide by a mixture of chromate and dichromate was promoted by manganese salts. Rubinshetin\textsuperscript{36} studied the effect of cadmium sulphate on the decomposition of hydrogen peroxide by potassium dichromate.

Thus, the observations made in this direction reveal the fact that about 28\% of total Cr(VI) is always reduced to Cr(III). Inspite of such a clear indication of the fixed ratio of Cr(III) and Cr(VI) obtained after the reaction between hydrogen peroxide and chromic acid, no use had been made to elucidate the nature and the constitution of the blue compound.
3. Study of the various compounds formed by the action of alkali and alkaline earth group metals on ethereal blue perchromic acid:

Haussermann\textsuperscript{37} prepared reddish brown crystals of sodium perchromate, $\text{Na}_6\text{Cr}_2\text{O}_7\cdot15\text{H}_2\text{O}$, by adding sodium peroxide to a thin paste of chromium hydroxide and water at $10^\circ$ to $12^\circ\text{C}$.

Horace, Bayers and Reid\textsuperscript{38} prepared various perchromates by adding metallic potassium, sodium, lithium, magnesium, barium, calcium and zinc to the ethereal blue perchromic acid at $-30^\circ\text{C}$. The potassium salt of blue perchromate was found to be a purplish black compound having the composition $\text{KCrO}_4$ or $\text{K}_2\text{Cr}_2\text{O}_7$. It was found very unstable and rapidly decomposed giving potassium dichromate with the evolution of oxygen. They, therefore, concluded that ethereal blue peroxy chromic acid contained $\text{H}_2\text{Cr}_2\text{O}_8$ 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{39} obtained red calcium perchromate by treating an alkaline suspension of chromic hydroxide with 30% hydrogen peroxide. They assigned to it the formula $\text{Ca}_3\text{Cr}_2\text{O}_7\cdot12\text{H}_2\text{O}$ and suggested the presence of Cr(III).
in this compound to be linked to peroxide group. Martínez and Porter\textsuperscript{40} however, disagreed with this view and proposed the following structure for this compound:

\[
\begin{array}{c}
\text{Ca} \\
\text{Ca} \\
\text{Ca} \\
\end{array} \quad 10\, \text{H}_2\text{O}
\]

This alternative structure was supported due to its resemblance with Na\textsubscript{6}Cr\textsubscript{2}O\textsubscript{15} nH\textsubscript{2}O, which gave calcium perchromate on adding calcium chloride solution to it. This structure was further supported by the fact that calcium perchromate on thermal decomposition yielded calcium chromate.

Rosenheim, Hakki and Krause\textsuperscript{41} obtained lithium, sodium and potassium perchromates of the composition Li\textsubscript{6}Cr\textsubscript{2}O\textsubscript{13} and Li\textsubscript{6}Cr\textsubscript{2}O\textsubscript{15}, Na\textsubscript{6}Cr\textsubscript{2}O\textsubscript{15} nH\textsubscript{2}O and K\textsubscript{6}Cr\textsubscript{2}O\textsubscript{16} nH\textsubscript{2}O respectively by the interaction of corresponding chromates with 30\% hydrogen peroxide under varying conditions of preparation.
Martinez$^{42}$ obtained $K_3CrO_8$ by treating potassium hydroxide and chromic acid in boiled distilled water solution with hydrogen peroxide in a close system. Martinez and co-workers$^{43-45}$ prepared red peroxo chromates of magnesium and sodium or potassium of the composition $K_2Mg_2Cr_2O_{16}15H_2O$ and $Na_2Mg_2Cr_2O_{16}16H_2O$ by adding magnesium nitrate dissolved in 30% hydrogen peroxide to the aqueous solution of corresponding chromates at $-10^\circ C$.

Bogdanov, Pentrova and Minaev$^{46}$ obtained dark brown crystals of a new compound $CaCrO_6\cdot nH_2O$ by adding freshly prepared $CaCrO_4$ to 55% hydrogen peroxide at $-80^\circ C$, followed by an addition of ethyl alcohol.

It may be easily seen that the perchromates have been prepared by the two methods:

(i) by taking a solution of chromic acid, chromate or dichromate in alkaline medium to which 30% hydrogen peroxide is added at temperature below $0^\circ C$. and

(ii) by taking the chromic acid or acidified dichromate and adding hydrogen peroxide to it and after extracting the blue compound, it is treated with alkali salts. The first method always gave red perchromates besides other types of compounds whereas blue perchromates (salts of blue compound) were obtained by the second method. The red perchromates yielded chromates while blue perchromates gave dichromates after decomposition.
4. Study of the decomposition products obtained under different conditions:

Moissan\textsuperscript{47} for the first time attempted to isolate the blue compound by carefully evaporating the excess of the solvent at -20\degree and got a blue oily liquid, very unstable, to which he assigned the formula CrO$_3$H$_2$O$_2$. Rai\textsuperscript{48} observed that on further concentration it decomposed to chromium chromate with a hissing sound.

Schwarz and Giese\textsuperscript{49} prepared the pyridine complex of blue perchromic acid by Wiede's method. They decomposed it in dilute acids, treated the pyridine complex with aqueous potassium permanganate and measured the amount of oxygen evolved in the presence of solid silver oxide. They calculated the amount of oxygen set free per atom of chromium and suggested the mechanism of the reaction\textsuperscript{50}. They found $3\text{CrO}_5 \rightleftharpoons 4\text{KMnO}_4$ or $\text{CrO}_5 \rightleftharpoons \frac{4}{3} \text{KMnO}_4$ that is, 4 equivalents of potassium permanganate (since $\text{KMnO}_4/3$ is the equivalent weight of $\text{KMnO}_4$). Thus they concluded that the blue peroxy chromic acid is not a true acid but a peroxide CrO$_5$.

Schwarz and Giese also determined the molecular weight of pyridine complex by cryoscopic method in benzene and confirmed the unimolecular structure PyCrO$_5$.

Schwarz and Giese\textsuperscript{51} studied the degradation of the alkali perchromates and suggested three formulae for blue
potassium perchromates, $\text{KH}_2\text{CrO}_7$, $\text{KCrO}_5\cdot 2\text{H}_2\text{O}$ and $\text{KCrO}_6\cdot \text{H}_2\text{O}$. They represented the blue and red perchromates as double molecules $\text{K}_2\text{Cr}_2\text{O}_7$ and $\text{K}_6\text{Cr}_6\text{O}_{16}$ respectively containing hexavalent chromium with a number of peroxide linkages.

Schwarz and Elstner\textsuperscript{52} obtained $\text{CrO}_5\text{MeO}_2$ by the action of chromic acid and concentrated hydrogen peroxide in $\text{Me}_2\text{O}$ at sufficient low temperature. They disagreed with Riesenfeld (loc. cit) on the formation of the compound like $\text{H}_3\text{CrO}_6\cdot 2\text{H}_2\text{O}$ and proposed $\text{CrO}_5$ as a formula for the blue compound. They\textsuperscript{53}, further, attempted to prepare it directly from $\text{CrO}_2\text{Cl}_2$ and hydrogen peroxide, which gave an equilibrium mixture like:

$$\text{CrO}_2\text{Cl}_2 + 2\text{H}_2\text{O}_2 \rightarrow \text{CrO}_5 + \text{H}_2\text{O} + 2\text{HCl}.$$ 

Rai\textsuperscript{54} studied the nature and properties of pyridine and piperidine complexes of blue perchromate and suggested $\text{RCrO}_2\cdot 0.5$ or $\text{R}_2\text{Cr}_2\cdot 0.5$ formula for pyridine and $\text{R}_1\text{CrO}_2\cdot 2.5$ or $\text{R}_3\text{Cr}_2\cdot 0.5$ formula for piperidine complexes. He studied the quinoline and hexamethylene tetramine complexes also.

Pillai and Rai\textsuperscript{55} studied the 8-hydroxy quinoline, quinoline and strychnine complexes of blue perchromate, preparing them by Wiede's method and suggested $\text{R}_2\text{Cr(CrO}_10$, 
$R_4\text{Cr}_2(\text{Cr}_2\text{O}_{20})$ or $R_4\text{Cr}_2(\text{CrO}_{10})_2$ formula for quinoline and 8-hydroxy-quinoline complexes and $R_2\text{Cr(CrO}_8$ for the strychnine complex.

Rai and Prakash\textsuperscript{56} observed that the ethereal blue perchromate furnished $\text{Cr}_2(\text{Cr}_2\text{O}_7)_3$ on decomposition in contact with water and on this basis they suggested that the blue perchromate contained Cr(III) along with Cr(VI). Rai proposed $\text{Cr}_2(\text{Cr}_2\text{O}_{10})_3$ as a formula for the blue perchromate. Rai\textsuperscript{57} further showed that this formula was in equilibrium with another labile form in presence of excess of hydrogen peroxide.

$$\text{Cr}_2(\text{Cr}_2\text{O}_{10})_3 + 2 \text{H}_2\text{O}_2 \longrightarrow 4\text{CrO}_8 + 2\text{H}_2\text{O}$$

Pillai and Rai\textsuperscript{58} extracted the blue perchromate in ethyl acetate and they noted that the ethyl acetate extracted blue perchromate decomposed in contact with water to yield a compound of the formula $\text{Cr}_2(\text{Cr}_2\text{O}_8)_3$. In analogy with perdisulphate, this compound has been named as chromium peroxydichromate by these workers. Recently Dayal Singh and Rai\textsuperscript{59} have carried out a critical study of the nature of the water decomposition products of ethereal as well as ethyl acetate extracted blue perchromate. They observed that the two decomposition products are in fact the mixtures of both $\text{Cr}_2(\text{Cr}_2\text{O}_7)_3$ and $\text{Cr}_2(\text{Cr}_2\text{O}_8)_3$, the proportion of these compounds being dependent upon the volume of water used to
decompose a given volume of the blue perchromate. This
dependence on the volume of water has been in turn found
to be due to the pH value of the medium. Using buffers
solutions of various pH, these workers have shown that when
buffer solutions of pH range 5.5 - 7.0 are used, both ethereal
as well as ethyl acetate extracted blue perchromate give
\( \text{Cr}_2(\text{Cr}_2\text{O}_7)_3 \) as the decomposition product. The peroxy nature
of this compound has been established by Dayal Singh who
has studied the kinetics of the reaction of this compound with
sulphuric acid and potassium iodide respectively.

Rai and Rajput\(^{59}\) studied the water decomposition
product of ethereal blue perchromate with the help of ion
exchange resins and found that \( \text{Cr(III)} \) and \( \text{Cr(VI)} \) was present
in the ratio 1:3 in the water decomposition product. Thus
they supported Rai's formula \( \text{Cr}_2(\text{Cr}_2\text{O}_7)_3 \), for the water
decomposition product of the ethereal blue perchromate. Rai
and Rajput (loc.cit.) had also studied the open and the closed
bottle decomposition products of ethereal blue perchromate
with ion exchange resins. The ratio of \( \text{Cr(III)} \) and \( \text{Cr(VI)} \)
were found to be 2:3 in the case of the open bottle and
1:1 in the case of the closed bottle decomposition products.

5. Physico - Chemical Methods:

(i) Conductivity measurements: This method was used for
the first time by Spitalsky and Kobosev\(^{60}\) to study the
reaction between chromic acid and hydrogen peroxide. They
observed that during the reaction the conductivity at first decreased sharply to a value which remained approximately constant during the major part of the reaction and then returned to its initial value as the reaction approached completion. From the nature of the curve so obtained, they were of the opinion that two intermediate compounds were reversibly formed during the course of reaction which required no hydrogen ion for their formation, while a third compound, which was more stable, required H\(^+\) ions for its formation. They assigned KH\(_5\)Cr\(_4\)O\(_{18}\) as the formula for this third compound.

Kobosev and Galbraich\(^{61}\) again performed the above study at 56\(^0\) and found that the first order of the reaction suggested by above workers changed to second order on the basis of the entropy and thermal data. They proposed the formation of Cr\(_2\)O\(_9\)\(^-\) ion contrary to the formation of KH\(_5\)Cr\(_4\)O\(_{18}\) during the reaction between hydrogen peroxide and acidified dichromate solution.

Pillai\(^{62}\) studied the decomposition of ethereal as well as ethyl acetate extracted blue perchromate over water by conductivity measurements. He obtained three breaks in the curve in the case of ethereal blue perchromate corresponding to three compounds Cr\(_2\)(Cr\(_2\)O\(_9\))\(_3\), Cr\(_2\)(Cr\(_2\)O\(_8\))\(_3\) and Cr\(_3\)(Cr\(_2\)O\(_7\))\(_3\) and two breaks in ethyl acetate case corresponding
to two compounds $\text{Cr}_2(\text{Cr}_2\text{O}_9)_3$ and $\text{Cr}_2(\text{Cr}_2\text{O}_9)_3$. Singh and Rai observed that $\text{Cr}_2(\text{Cr}_2\text{O}_9)_3$ oxidized organic compounds and got reduced to $\text{Cr(III)}$ by mineral acids.

(ii) Molecular weight determination:

Riesenfeld determined the molecular weight of potassium salt $K_3\text{CrO}_4$ in aqueous solutions by cryoscopic method. The values obtained were 68.41, 81.11, 61.55 and 78.72 and these were in approximate agreement with the theoretical value of 74.3. The variation in the values might be accounted for by the decomposition of the salt in aqueous solution.

The values, obtained for the molecular weight of the red ammonium salt $(\text{NH}_4)_3\text{CrO}_4$ in 0.3 N ammonia solution, were much greater than the theoretical value due to the lesser dissociation of this salt than that of potassium salt. The results were in agreement with the formula $(\text{NH}_4)_6\text{Cr}_2\text{O}_16$ which would have the molecular weight 67, if complete dissociation could be assumed.

Schwarz and Giese (loc. cit) determined the molecular weight of pyridine complex of the blue peroxo chromic acid by freezing - point - method in $\text{C}_6\text{H}_6\text{PF}_5\text{NO}_2$, $\text{CHBrO}_3$ or in pyridine and confirmed the unimolecular structure. But Rai (loc. cit) observed that if pyridine complex
was dissolved in pyridine or any organic solvent, it started decomposing. Therefore, the formula determined by this above method for blue peroxy chromic acid could not be relied upon.

(iii) Spectrophotometric Studies :-

(a) Absorption spectrophotometry : - Rumpf\textsuperscript{66} supported the formula CrO\textsubscript{5} for the blue compound by measuring the absorption of light by an equimolar mixture of the solution of hydrogen peroxide and potassium dichromate at equal intervals of time, the pH being maintained below 4.

Bobtelsky, Glasner and Bobtelsky-Chaikin\textsuperscript{67} used the spectrophotometric method along with pH measurements in the study of the reaction between chromic acid and hydrogen peroxide solution. They suggested that two types of perchromates were formed during the reaction, one blue at pH 4 and other violet beyond pH 4, thus confirming the view of Spitalsky and Kobosev (loc.cit). They also were of the opinion that there was an equilibrium between the two perchromates and that no hydrogen ions was required for the conversion of the blue in violet.

Glasner\textsuperscript{68} repeated the above reaction and confirmed the formation of blue and violet compounds. He concluded that in the above reaction one molecule of chromic acid reacted with one and a half molecule of hydrogen peroxide to give one molecule of the blue compound as suggested by
Riesenfeld, Glasner and Steinberg attempted to arrive at the composition of the blue peroxo chromic acid by measuring the optical density during the reaction between chromic acid and hydrogen peroxide by taking chromic acid, acidified dichromate and chromate and adding varying amounts of hydrogen peroxide to them. In the case of chromic acid and acidified dichromate solution the ratio, \( \frac{H_2O_2}{CrO_3} \), was found to be 1.5:1, whereas in the other case it was 2:1, but in solutions weaker in acids the ratio changed to 4:1.

(b) Infra-red spectrophotometry: Evans measured the infra-red spectra of the pyridine and 1:10 phenanthroline complexes of the blue peroxo chromic acid and also of the pyridine nitrate, \( PyHNO_3 \) and \( (AgPy)NO_3 \) in nujol or hexachloro butadien by infra-red spectrophotometry over a region of 2 - 15 \( \mu \) 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 chromium(III) in the complex.

Griffith measured the infra-red spectra of the anhydrous potassium salt of violet diperoxy chromate and confirmed the presence of -OH groups and found one hydrogen atom per molecule. He also suggested that the number of peroxy groups per chromium was the same both in the violet
salt and chromium pentaoxide. He assigned the formula 
\[ \text{K} \left[ \text{Cr} \left( \text{O}_2 \right)_2 \text{H} \right] \] 
to the violet diperoxy chromate on the basis of the above observations.

(c) Ultra-Violet Spectra:

Fergusson, Wilkins and Young\textsuperscript{73} studied the pyridine and 1:10 phenanthroline complexes of the blue perchromate by this method and found that in the pyridine derivative, the chromium atom was in a sense six-coordinated, but the ligands form a pentagonal pyramid, so that there was a vacant co-ordination position, axial to the unique oxygen atom. But they observed that the ultra-violet spectrum of 1:10 phenanthroline was rather different. Pyridine compound showed two peaks at \( \sim 5800 \) and 7000\( \text{A}^0 \) while phenanthroline gave two bands of about this intensity but at \( \sim 6300 \) and 8300\( \text{A}^0 \). They further suggested that 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 Matsumo\textsuperscript{74} measured the ultra-violet spectrum of \( 3\text{NH}_2\text{Cr}(\text{O}_2)_2 \) complex and contradicted the formulae suggested by Hofmann and Hiedlmaier, and Riesenfeld, Kutsch and Ohl (loc.cit) for the derivative of diperoxy chromium and also that the compound was polymorphic and existed in two isomeric forms.
4. Magnetic Measurements:

Tjabbes\textsuperscript{75} determined the magnetic susceptibility of K\textsubscript{3}CrO\textsubscript{4} and found it to be paramagnetic, having a magnetic moment of 1.8 Bohr magnetons. On this basis, he concluded that chromium in red perchromate was quinquevalent. Klemm and Werth\textsuperscript{76} measured the magnetic moment of the red and blue perchromates of potassium. They found the magnetic moment of the red salt to be 1.8 B.M. and thus supported the view of Tjabbes. In the blue salt of potassium, chromium was found to be slightly paramagnetic showing the hexavelency of chromium in it.

Bhatnagar, Prakash and Hamid\textsuperscript{77} and Ferguson and Wilkins (loc. cit.) measured the magnetic susceptibility of CrO\textsubscript{4} 3 NH\textsubscript{3} and found it to be 2.8 B.M. The paramagnetic moment of the compound was in agreement with the presence of two unpaired electrons associated with Cr(IV).

Rai\textsuperscript{78} measured the magnetic moment of the ethereal and ethyl acetate extracted blue perchromate washed and unwashed and found it to be paramagnetic.

Pillai\textsuperscript{79} observed the values 3.8 B.M. and 3.88 B.M. for the quinoline and 8-hydroxy quinoline complexes of blue perchromate and suggested the presence of Cr(III) in these complexes. Strychnine complex of blue perchromate was found to be feebly paramagnetic.
Singh\textsuperscript{80} studied the magnetic susceptibility of complexes of isoquinoline and 8-hydroxy quinoline with ethereal blue perchromate prepared with sulphuric acid and phthalic acid respectively. On the basis of his results, he confirmed the presence of Cr(III) in the blue perchromate.

5. X-Ray Crystallography :-

Stomberg and Brosset\textsuperscript{81} studied the single crystal of potassium salt of tetraperoxy chromate \( M_3 \left[ Cr(O_2)\right] \) by X-ray crystallography and showed that chromium atom was surrounded by four equivalent peroxy groups, in an arrangement that could be described as a distorted dodecahedron of oxygen atoms. The molecular orbital calculations were made by Swalen and Ibers\textsuperscript{82} and they assigned the unpaired electron to a 'B', orbital of chromium. The 0-0 distance of 1.40Å, was rather less than 1.49Å found in alkali metal peroxides (Abrahams and Kalnajs)\textsuperscript{83}, perhaps because the electrons, which in free oxide were in antibonding \( \pi \) orbitals, were partly delocalised in the complex in to orbitals of chromium.

Stomberg\textsuperscript{84}, Pedersen and Pedersen\textsuperscript{85} studied the pyridine complex of blue chromium perchromate by X-ray crystallography and confirmed the formula \( p_1Cr(O)(O_2)\)\textsubscript{2} for this complex.
McLaren and Helmholtz determined the crystal structure of triamino chromium tetraoxide, $3\text{NH}_3\cdot\text{Cr(O}_2\text{)}_2$, and showed that in the crystal, the chromium atom might be described as seven co-ordinated with a roughly T-shaped arrangement of nitrogen atoms around it; the peroxy groups laid with the O-O axes in the plane of the downstroke of the T, so that these groups 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 superoxide of Cr(II).

6. Kinetics:

As in the present investigation the kinetics of formation and decomposition of blue perchromate in non-aqueous medium, has also been studied, it will not be out of place to discuss the fundamental of the subject here.

Kinetics is a part of the science of motion. In physics it means the science which deals with motion of bodies and effect of forces on motion, whereas in Chemistry kinetics deals with the rate of chemical reactions with all factors such as concentration of reactants, temperature and medium etc. which influence the rate of reaction and with the explanation of the rate in terms of the reaction
mechanism. Thus kinetics may be called chemical dynamics. Chemical reactions where the equilibrium is eventually reached, are dealt with in chemical thermodynamics. Thermodynamics is concerned only with the initial and final states of the system, whereas reaction path and the time required for the chemical change are of no importance. Kinetics is concerned fundamentally with the details of the process whereby a system gets from one state to another and also with the time required for the transition. Thus thermodynamics will tell with precision the extent of reaction, but only kinetics will give the idea of the rate of reaction.

An industrial chemist is interested in chemical kinetics so as to work out optimum conditions with a view to obtaining maximum yield in a process. A pure chemist, on the other hand, takes help of the chemical kinetics for working out the mechanism of reactions. From a physical chemist's point of view, mechanism of a reaction is understood to mean all the individuals collisional or other elementary process involving atoms, radicals, ions or molecules, that take place simultaneously or consecutively in producing the observed overall reaction. This definition, however, is incomplete and it can be seen from the following two reactions that the mechanism can not be predicted from the overall reaction alone.
(1) \( H_2 + I_2 = 2HI \)

(11) \( H_2 + Br_2 = 2HBr \)

The stoichiometry of both the reactions is similar but their mechanisms are altogether different. The reaction between hydrogen and iodine takes place at bimolecular collisions involving a single molecule of each kind. The reaction between hydrogen and bromine was studied by Bodenstein and Lind in 1906. They concluded that it was not possible to give simple rate expression for this reaction. The empirical rate expression given by them is,

\[
\frac{d(\text{HBr})}{dt} = \frac{k [H_2] [Br_2]}{1 + k'[\text{HBr}]}/[Br_2]
\]

where \( k' = \frac{1}{10} \) and \( k \propto e^{-40200/RT} \)

The form of the rate expression given above was explained later by Christiansen(1919), Herzfeld (1919) and Polanyi (1920) in terms of the following mechanism.

\[
\begin{array}{c}
\text{Br}_2 \xrightarrow{k_1} 2\text{Br} \\
\text{Br} + H_2 \xrightarrow{k_2} \text{HBr} + H \\
\text{H} + \text{Br}_2 \xrightarrow{k_3} \text{HBr} + \text{Br} \\
\text{H} + \text{HBr} \xrightarrow{k_4} \text{H}_2 + \text{Br} \\
2\text{Br} \xrightarrow{k_5} \text{Br}_2
\end{array}
\]
The modern concept of reaction mechanism includes not only a knowledge of all the individual steps in overall reaction, but also a detailed stereochemical picture of each step as it occurs. This implies a knowledge not only of the composition of the activated complex in terms of the various atoms or molecules of reactants, but also of the geometry of the activated complex in terms of interatomic distances and angles. The importance of this aspect is realised in cases such as the hydrolysis of organic halides leading to inversion of the original configuration, retention of configuration or a mixture of the two.

Whereas kinetics is very useful in determining the individual steps of a reaction, but it is limited in furnishing stereochemical details. Hence it is essential to invoke the aid of other methods in obtaining information about stereochemical aspects of the reaction. It will be appreciated that such methods are bound to be incomplete in themselves, but these can be used in combination with the kinetic evidence. The most important among these methods are given below.

(1) Identification of reaction products:

The importance of identifying the products of reaction is not only in fixing the stoichiometry of the reaction, but also in elucidating the mechanism of the
reaction. For example, in the alkaline hydrolysis of an ester, such as ethyl acetate, the formation of alcohol and an acetate ion indicates the reaction of a hydroxide ion with an ester molecule by breaking one C - O bond.

\[
\text{CH}_3\text{C} = \text{O} + \text{C}_2\text{H}_5\text{OH} \rightarrow \text{CH}_3\text{C} - \text{O} - + \text{C}_2\text{H}_5\text{OH}
\]

(2) Stereochemical Evidence :-

By examining the stereochemistry of the reactants and products of a chemical reaction, invaluable information concerning the intimate details of a mechanism can be obtained. If an optically active alcohol, R - R' - CH₂OH, is used instead of ethyl alcohol to prepare an ester and if on hydrolysis of the ester, the original alcohol can be recovered without racemization or without inversion, it can easily be inferred that in the formation of the ester as well as in its hydrolysis the C - O bond involved is one in which oxygen atom of the alcohol remains unchanged.

(3) Use of Isotopes :-

If in the alkaline hydrolysis of ethyl acetate, the alkali used is enriched with $^{18}O$, then it is found that heavy oxygen is present in the acetate ion rather than in the alcohol. This shows that the carbon - oxygen bond
which is broken is \( C - O\text{C}_2\text{H}_5 \). The increased production of isotopes of the more common elements has led to an increasing application of this technique in studying reactions where mechanisms are not easily determined by other methods.

(4) Detection of short-lived intermediates:

This method is chiefly applied to reactions involving free atoms or radicals which are extremely reactive and hence short-lived. This can be done by adding substances like NO or \( I_2 \) to the reaction mixture which trap the radicals as stable compound or by observing some specific physical or chemical property such as mass spectrogram, absorption spectrum or removal of metallic mirrors. A recent and very powerful tool for the study of free radicals is electron paramagnetic resonance (E.P.R) which measures directly the concentration of radicals and also supplies specific information about their structure.

(5) Refinements of kinetic methods:

These include the study of effect of substituents on the rate of a given reaction, or the effect of changing the solvent, ionic strength etc.

The rate expression: The reaction rate at a fixed temperature is a function of the concentration of some or all of the
various components of the system, but usually of only the reactants. If the concentration of a product affects the rate, this effect is called either autoinhibition or autocatalysis. If a substance, neither a reactant nor a product, affects the rate it is called an inhibitor, retarder, sensitizer or a catalyst depending on the nature of the effect. The functional relation between rate and concentration is called a rate expression. In general it is not possible to predict the rate expression for a given reaction by just knowing the stoichiometric equation.

Molecularity and order of reaction:

In contrast to the order, the molecularity of a reaction is a whole number; it can not be zero or fractional. The molecularity of a reaction indicates the number of molecules, atoms or ions involved in a simple collisional reaction process, that is, in each act leading to a chemical reaction. Molecularity is a theoretical concept, whereas order is empirical. Thus the order of reaction indicates the number of atoms or molecules whose concentrations determine the velocity or kinetics of the process. However, in many cases molecularity and order may be equal, but the reverse of this statement is less often true.
The reaction rate is expressed in the form of a product of concentration terms raised to appropriate powers, for example,

\[-\frac{dc}{dt} = k c_1^{n_1} c_2^{n_2} c_3^{n_3} \quad \ldots\]

where \( k \) is the specific reaction velocity coefficient or velocity constant.

For such type of rate expressions the order of reaction, \( n \), is defined as,

\[ n = n_1 + n_2 + n_3 + \ldots \]

Each individual power is known as the order with respect to that component. If in a particular reaction, the concentration of a reactant is held constant throughout the reaction, its concentration can also be included in the constant \( k \) and the order with respect to this reactant is said to be zero. This is the situation obtaining in catalytic reactions in which the concentration of the catalyst remains constant. Also if the concentration of one of the reactants is in such a large excess that during the reaction there is only a small change in its concentration, the order with respect to this reactant is zero.

In the present investigation, order of reaction is calculated by using one of the following integrated forms of rate expressions:
\( (1) \quad \frac{dx}{dt} = k_0 \quad \text{or} \quad x = k_0 t + \text{constant} \)

since \( x = 0 \), when \( t = 0 \).

Therefore, \( x = k_0 t \) or \( k_0 = x/t \), for the zero order reaction.

\( (2) \quad k_1 = \frac{2.303}{t} \log \frac{a}{a-x} \), for a first order reaction.

\( (3) \quad k_2 = \frac{1}{t} \frac{x}{a (a-x)} \), for a second order reaction.

**KINETICS OF BLUE PERCHROMATE:**

Gnadinger\(^91\) studied the decomposition of blue perchromate in aqueous solution and found that like the rate of formation, the rate of decomposition was independent of the concentration of hydrogen peroxide, and was of the first order in blue perchromate and at a given concentration of hydrogen peroxide and potassium dichromate was of the first order in sulphuric acid.

Rai and Prakash\(^92\) studied the decomposition of blue compound in ether as well as in presence of varying amounts of different organic solvents such as benzene, toluene, ethyl acetate, amyl acetate, acetone, amyl alcohol etc. The decomposition was found to be of the first order and it was observed that the decomposition increases if any of the solvents mentioned above is added to the ethereal blue perchromate.
Evans (loc. cit) studied the reaction between aqueous methyl alcoholic solution of sodium chromate and hydrogen peroxide (100vol.) in presence of perchloric acid by low temperature spectrophotometry. He also studied by rapid spectrophotometry the reaction between acidified potassium dichromate solution and hydrogen peroxide in aqueous medium at $10^\circ$C and suggested the equilibrium in dilute aqueous solution as,

$$\text{HCrO}_4^- + 2\text{H}_2\text{O}_2 + \text{H}^+ \rightarrow \text{CrO}_5 + 3 \text{H}_2\text{O}$$

on the basis of these experiments, Evans supported the CrO$_5$ formula for the blue peroxy chromic acid.

Tuck and Walters$^{93}$ studied spectrophotometrically the rate of formation of blue peroxy chromic acid in tributyl phosphate - cyclohexane mixture and suggested the following mechanism,

$$\text{H}_2\text{Cr}_{2.7} + 4 \text{H}_2\text{O}_2 \rightarrow 2\text{CrO}_5 + 5\text{H}_2\text{O}$$

Thus they supported the view of Schwarz and Giese (loc. cit) that the blue peroxy chromic acid is CrO$_5$.

Recently Dhankher$^{94}$ studied the kinetics of decomposition of blue perchromate and suggested the formation of three types of blue perchromates. According to him the compounds formed are $\text{Cr}_2(\text{Cr}_2\text{O}_10)_3$, $\text{Cr}_2(\text{Cr}_2\text{O}_{10})_3$ and $\text{Cr}_2(\text{Cr}_2\text{O}_{10})_3$ at the molar ratios of $\text{O}_2$.
chromic acid and hydrogen peroxide equal to 1:1.50, 1:1.625 and 1:1.75 respectively.

Thus the review of the existing literature on blue perchromate reveals the fact that the views of the different investigators on the nature and constitution of blue perchromate appear to be divergent. Schwarz and Giese and others (loc.cit) were of the opinion that only hexavalent chromium is present in the blue perchromate. Riesenfeld and Spitalsky (loc.cit) observed that about 28% of chromic acid was reduced to chromium (III) after the reaction between chromic acid and hydrogen peroxide. Rai and co-workers (loc.cit) showed the presence of trivalent chromium along with hexavalent chromium in blue perchromate in the ratio 1:3.

Besides Rai and co-workers, Patten (loc.cit) Reynolds and Reddy (loc.cit), McLaren and Helmholtz (loc.cit) and Stomberg (loc.cit) also suggested the presence of chromium in lower valency state than six in the blue compound.

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 and the constitution of blue perchromate by chemical and physico-chemical methods.
REFERENCES


18. ibid., 41, 3536-52, (1908).
35. Robertson, A.C. Ibid., 74, 48, (1912).
Reidy, E. Ibid., 52, 1831, (1930).
57. Rai, R.C.
58. Pillai, C.V.P. and Rai, R.C.
60. Singh, S.D. and Rai, R.C.
64. Ibid., 42, 274, (1966).
73. Ibid., 3943, (1962).
     Werth, J.
     Prakash, B. and
     Hamid, A.
     Broseti, C.
     Ibers, J.A.
     Kalnajs.
     Pedersen, B.
     Helmholtz, G.
89. Holmberg, B., Ber., 45, 2997, (1912).
     Szabo, A.K.