CHAPTER II

EXPERIMENTAL DATA AND SUMMARY OF RESULTS

OF

REACTION BETWEEN GLYCOLIC ACID AND CHROMIC ACID

IN AQUEOUS MEDIUM
II - A

METHODS OF MEASUREMENTS

Materials:

Chromic acid solution was prepared by dissolving an appropriate amount of CrO₃ (R.D.H.) in distilled water and standardized iodometrically. Glycolic acid (Riedel) was diluted with distilled water and then standardized with a standard sodium hydroxide solution. All other chemicals used were either R.D.H. 'AnalalR' or R.Merck 'pro-analysis' reagents.

Unless otherwise stated, Pyrex glasswares were used throughout these investigations. Tightly stoppered flasks were used for keeping reactants, reaction mixtures etc. Distilled water was used as medium of reaction throughout the course of these investigations.

Kinetic Measurements:

Disappearance of chromic acid was followed by the usual iodometric method.

90ml. of aqueous solution containing appropriate concentration of glycolic acid and other substances were kept in a Pyrex flask. An aqueous solution of chromic acid of suitable concentration was taken in another flask. Both the flasks were kept in a thermostat, maintained at the proper
temperature and was kept constant with a precision of ± 0.1°C. Sufficient time was allowed for the solutions to attain the temperature of the thermostat. 10ml. solution of chromic acid was then added to the glycolic acid solution and mixed thoroughly. The time of starting of reaction was taken as the instant at which half of 10ml. chromic acid solution was just discharged into the glycolic acid solution. This instant has been referred to as 'zero time' in the following pages. 10ml. of this reaction mixture was withdrawn, by means of a pipette, each time at different known intervals of time and the reaction was arrested by discharging this in a solution containing potassium iodide and sulphuric acid of required strength. The liberated iodine was titrated against a standard solution of hypo and the chromic acid content in it was calculated.

In tables of kinetic data, 't' is the time in minutes, (a-x) the volume of hypo (in ml.), required to titrate the liberated iodine (as the normality of hypo is not required in the calculations of first order rate constants, it has not been given). The first order rate constants are calculated from the expression

\[ k_1 = \frac{2.303}{t} \log \frac{a}{(a-x)} \]

where 'a' is the zero time concentration and \( k_1 \) is the pseudo-first order rate constant.
At the beginning of reaction, a slight variation is observed, in calculated values of pseudo-first order rate constants for consumption of chromic acid and these are slightly less at the beginning of reaction and become constant after some time. Hence zero order rate equation was also tried for calculating rate constants but these values of zero order rate constants were found to vary much with the variation in concentration of chromic acid. However, the first order rate constants for different concentrations of chromic acid (glycolic acid concentration and temperature being same) are seen to be fairly constant. The times for half change in chromic acid concentration, for different concentrations of chromic acid, are, also, fairly constant (given later in chapter II-B). Hence first order rate constants are only considered. Further, since the values of rate constants are slightly less at the beginning of reaction and become constant after some time, the lower values are not considered for average.

Kinetic measurements were made at 25, 35 and 45°C. Temperature coefficients $k_{35}/k_{25}$ and $k_{45}/k_{35}$ were calculated. Kinetic data for all reaction mixtures were measured at these three temperatures and hence rate constants calculated. For sake of brevity, illustrative kinetic data for a few reaction mixtures at 25°C are only given. The concentrations of reactants and other substances mentioned in tables are over-all concentrations in the reaction mixtures.
pH Measurements:

For measuring the pH of a redox system the glass electrode is the only suitable electrode. A Phillips PR 9400 pH Meter was used for the pH measurements.

The glass and the calomel electrodes were kept immersed in water at 25°C in a thermostat. The reactants were mixed at 25°C in the usual manner and the reaction mixture was immediately transferred to an empty beaker placed in the thermostat. The electrodes were then immersed in it and the pH value of the reaction mixture noted.

Conductivity Measurements:

Some conductivity measurements, using a Doran Conductivity Bridge and a W.T.W. Oscillator, were also made.
DETERMINATION OF THE TOTAL ORDER OF REACTION BETWEEN
GLYCOLIC ACID AND CHROMIC ACID IN AQUEOUS MEDIUM

The author followed the Ostwald's isolation method for determining the order of reaction. This method is particularly useful in studying the reaction of high molecularity. Soubert and Carstens\(^1\) used this method to study various chromic acid oxidations. Dhar\(^2\) also applied this method to study the various catalysed reactions.

**Determination of the order of reaction with respect to chromic acid:**

The order of reaction with respect to chromic acid was determined by method of integration using the first order rate expression described in chapter II-A and was also confirmed by using Noyes equation\(^3\). Concentration of glycolic acid was kept much higher than that of chromic acid and the rates of reaction were measured at 25, 35 and 45\(^\circ\)C.

The following table gives the kinetic data for one of the reaction mixtures.
# Table 1

<table>
<thead>
<tr>
<th>Temperature 25°C</th>
<th>Glycolic acid 0.30 N</th>
<th>Chromic acid 0.0100 N</th>
</tr>
</thead>
<tbody>
<tr>
<td>t</td>
<td>(a-x)</td>
<td>$k_1$ (min.$^{-1}$)</td>
</tr>
<tr>
<td>0</td>
<td>17.05</td>
<td>-</td>
</tr>
<tr>
<td>45</td>
<td>15.55</td>
<td>0.002045</td>
</tr>
<tr>
<td>90</td>
<td>14.00</td>
<td>0.002191</td>
</tr>
<tr>
<td>135</td>
<td>12.65</td>
<td>0.002213</td>
</tr>
<tr>
<td>180</td>
<td>10.80</td>
<td>0.002538</td>
</tr>
<tr>
<td>225</td>
<td>9.25</td>
<td>0.002717</td>
</tr>
<tr>
<td>270</td>
<td>8.15</td>
<td>0.002757</td>
</tr>
<tr>
<td>315</td>
<td>7.05</td>
<td>0.002795</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td>0.002702</td>
</tr>
</tbody>
</table>

The kinetics of reaction was also studied by varying the concentration of chromic acid.

# Table 2

<table>
<thead>
<tr>
<th>Temperature 25°C</th>
<th>Glycolic acid 0.30 N</th>
<th>Chromic acid 0.0075 N</th>
</tr>
</thead>
<tbody>
<tr>
<td>t</td>
<td>(a-x)</td>
<td>$k_1$ (min.$^{-1}$)</td>
</tr>
<tr>
<td>0</td>
<td>12.90</td>
<td>-</td>
</tr>
<tr>
<td>93</td>
<td>10.70</td>
<td>0.002011</td>
</tr>
<tr>
<td>135</td>
<td>9.60</td>
<td>0.002188</td>
</tr>
<tr>
<td>180</td>
<td>8.50</td>
<td>0.002317</td>
</tr>
<tr>
<td>225</td>
<td>7.50</td>
<td>0.002409</td>
</tr>
<tr>
<td>270</td>
<td>6.55</td>
<td>0.002452</td>
</tr>
<tr>
<td>315</td>
<td>5.90</td>
<td>0.002482</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td>0.002415</td>
</tr>
</tbody>
</table>
TABLE 3
Temperature 25°C

<table>
<thead>
<tr>
<th></th>
<th>Glycolic acid 0.30 N</th>
<th>Chromic acid 0.0050 N</th>
</tr>
</thead>
<tbody>
<tr>
<td>t</td>
<td>(a-x)</td>
<td>k₁ (min⁻¹)</td>
</tr>
<tr>
<td>0</td>
<td>12.90</td>
<td>-</td>
</tr>
<tr>
<td>45</td>
<td>11.75</td>
<td>0.002078</td>
</tr>
<tr>
<td>90</td>
<td>10.35</td>
<td>0.002180</td>
</tr>
<tr>
<td>135</td>
<td>9.55</td>
<td>0.002228</td>
</tr>
<tr>
<td>180</td>
<td>8.50</td>
<td>0.002313</td>
</tr>
<tr>
<td>225</td>
<td>7.65</td>
<td>0.002320</td>
</tr>
<tr>
<td>270</td>
<td>6.75</td>
<td>0.002400</td>
</tr>
<tr>
<td>315</td>
<td>6.00</td>
<td>0.002412</td>
</tr>
<tr>
<td>Average</td>
<td>0.002336</td>
<td></td>
</tr>
</tbody>
</table>

The rate constants of all these reaction mixtures at 25, 35 and 45°C are recorded in Table 4.

TABLE 4
Rate Constants
Glycolic acid 0.30 N

<table>
<thead>
<tr>
<th>No.</th>
<th>Concentration of chromic acid (N)</th>
<th>k₁ (min⁻¹)</th>
<th>25°C</th>
<th>35°C</th>
<th>45°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0.0100</td>
<td>0.002702</td>
<td>0.004718</td>
<td>0.008520</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>0.0075</td>
<td>0.002415</td>
<td>0.004598</td>
<td>0.007971</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0.0050</td>
<td>0.002336</td>
<td>0.004290</td>
<td>0.007491</td>
<td></td>
</tr>
</tbody>
</table>

The same aspect was also studied with a second concentration of glycolic acid (0.40 N).
TABLE 5
Temperature 25°C

<table>
<thead>
<tr>
<th>Glycolic acid 0.40 N</th>
<th>Chromic acid 0.0100 N</th>
</tr>
</thead>
<tbody>
<tr>
<td>t</td>
<td>(a-x)</td>
</tr>
<tr>
<td>0</td>
<td>17.05</td>
</tr>
<tr>
<td>40</td>
<td>15.05</td>
</tr>
<tr>
<td>75</td>
<td>13.20</td>
</tr>
<tr>
<td>110</td>
<td>11.25</td>
</tr>
<tr>
<td>145</td>
<td>9.40</td>
</tr>
<tr>
<td>180</td>
<td>7.90</td>
</tr>
<tr>
<td>215</td>
<td>6.50</td>
</tr>
</tbody>
</table>

Average 0.004315

The rates of all the reaction mixtures containing 0.40 N glycolic acid at the three temperatures, are compiled in Table 6.

TABLE 6
Rate Constants

<table>
<thead>
<tr>
<th>Glycolic acid 0.40 N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration of chromic acid (N)</td>
</tr>
<tr>
<td>No.</td>
</tr>
<tr>
<td>-----</td>
</tr>
<tr>
<td>1</td>
</tr>
<tr>
<td>2</td>
</tr>
<tr>
<td>3</td>
</tr>
</tbody>
</table>
The time for half change, \( t_{0.5} \), is defined as the time required for one half of a given reactant to be used up. The time for half change depends on the initial concentration of reactants in a way which is fixed by the order of reaction.

By substituting \((a-x) = a/2\) in the rate expression for first order reactions, the expression is reduced to

\[
t_{0.5} = \log \frac{2}{k_1}.
\]

Thus \( t_{0.5} \) for first order reactions is independent of the initial concentration 'a'.

The time for half change in the concentration of chromic acid for various reaction mixtures were obtained from plots of \( t \) versus \((a-x)\) and the values are tabulated in tables 7 and 8.

### TABLE 7
**Time for half change**

<table>
<thead>
<tr>
<th>No.</th>
<th>Concentration of chromic acid (N)</th>
<th>( t_{0.5} ) (in minutes)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>25⁰C</td>
</tr>
<tr>
<td>1</td>
<td>0.0100</td>
<td>254.0</td>
</tr>
<tr>
<td>2</td>
<td>0.0075</td>
<td>270.0</td>
</tr>
<tr>
<td>3</td>
<td>0.0050</td>
<td>280.0</td>
</tr>
</tbody>
</table>
### TABLE 2

Time for half change
Glycolic acid 0.40 N

<table>
<thead>
<tr>
<th>No.</th>
<th>Concentration of chromic acid (N)</th>
<th>t₀.₅ (in minutes)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>25⁰</td>
</tr>
<tr>
<td>1</td>
<td>0.0100</td>
<td>167.0</td>
</tr>
<tr>
<td>2</td>
<td>0.0075</td>
<td>179.0</td>
</tr>
<tr>
<td>3</td>
<td>0.0050</td>
<td>177.0</td>
</tr>
</tbody>
</table>

A perusal of tables 7 and 8 shows that at a constant temperature and a constant concentration of glycolic acid, the time for half change is fairly constant and is not dependent on the initial concentrations of chromic acid. This points to the first order nature of the reaction with respect to chromic acid.

Noyes equation³ for calculation of order of reaction is

\[
n = 1 + \frac{\log t_{0.5} - \log t_{0.5}'}{\log a - \log a'}
\]

where \( n \) is the order of reaction, \( t_{0.5} \) and \( t_{0.5}' \) are the times for half change when \( a \) and \( a' \) are the initial concentration of the reactant in two different runs, all other conditions being same.

Values of the order of reaction with respect to chromic acid calculated by using Noyes equation from the values
of times for half change given in table 7 are tabulated below:

**TABLE 9**

<table>
<thead>
<tr>
<th></th>
<th>25°</th>
<th>35°</th>
<th>45°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>From S.No. 1 &amp; 2 (table 7) 1.21</td>
<td>1.07</td>
<td></td>
<td>1.00</td>
</tr>
<tr>
<td>From S.No. 1 &amp; 3 (table 7) 1.14</td>
<td>1.07</td>
<td></td>
<td>1.08</td>
</tr>
<tr>
<td>From S.No. 2 &amp; 3 (table 7) 1.00</td>
<td>1.17</td>
<td></td>
<td>1.32</td>
</tr>
</tbody>
</table>

Thus the order of reaction with respect to chromic acid is one.

**Determination of order of reaction with respect to glycolic acid**:

The order of reaction with respect to glycolic acid was determined by using following formula:

\[
\text{Order with respect to glycolic acid} = \frac{\log \frac{k_2}{k_1}}{\log \frac{C_2}{C_1}}
\]

where \( k_1 \) and \( k_2 \) are the rate constants with \( C_1 \) and \( C_2 \) as the initial concentrations of glycolic acid. Chromic acid concentration was kept constant in both the cases.

Rate constants for all the reaction mixtures with different concentrations of glycolic acid and keeping chromic acid concentration constant at the three temperatures are given in table 10.
Temperature coefficients from tables 4 and 6 are summarised in table 12.

**TABLE 12**

**Temperature Coefficients**

<table>
<thead>
<tr>
<th>No.</th>
<th>Concentration of Chromic acid (N)</th>
<th>Concentration of Glycolic acid (N)</th>
<th>(k_{35}/k_{25})</th>
<th>(k_{45}/k_{35})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0075</td>
<td>0.30</td>
<td>1.92</td>
<td>1.73</td>
</tr>
<tr>
<td>2</td>
<td>0.0075</td>
<td>0.40</td>
<td>1.92</td>
<td>1.72</td>
</tr>
<tr>
<td>3</td>
<td>0.0050</td>
<td>0.30</td>
<td>1.85</td>
<td>1.74</td>
</tr>
<tr>
<td>4</td>
<td>0.0050</td>
<td>0.40</td>
<td>1.92</td>
<td>1.74</td>
</tr>
</tbody>
</table>

**Summary of Results:**

It is apparent from the foregoing study that the reaction between glycolic acid and chromic acid in aqueous medium is first order with respect to chromic acid. Calculations from table 10 show that the order with respect to glycolic acid approaches two. Thus the total order of reaction is three.

The values of temperature coefficients are about 1.80 with higher concentrations of chromic acid (table 11), while these with lower concentrations of chromic acid is about 1.90 between temperatures 25 and 35°C and about 1.74 between temperatures 35 and 45°C (table 12).
II - C

ASCERTAINMENT OF THE HOMOGENEOUS NATURE OF THE REACTION BETWEEN GLYCOLIC ACID AND CHROMIC ACID

In order to ascertain that the reaction between glycolic acid and chromic acid in aqueous medium is homogeneous, reaction rates were measured in various conical flasks made of different types of glass and also in presence of glass powder. Initial concentrations of glycolic acid and chromic acid in all these were kept same.

The values of reaction rates at 25, 35 and 45°C in different containers is given in following table.

<table>
<thead>
<tr>
<th>No.</th>
<th>Container</th>
<th>Glycolic acid 0.30 N</th>
<th>Chromic acid 0.010 N</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$k_1$ (min.$^{-1}$)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>25</td>
<td>35</td>
</tr>
<tr>
<td>1</td>
<td>Pyrex glass</td>
<td>0.002702</td>
<td>0.004718</td>
</tr>
<tr>
<td>2</td>
<td>Skyrex glass</td>
<td>0.002745</td>
<td>0.004776</td>
</tr>
<tr>
<td>3</td>
<td>Borosil glass</td>
<td>0.002732</td>
<td>0.004743</td>
</tr>
<tr>
<td>4</td>
<td>Glass powder</td>
<td>0.002782</td>
<td>0.004792</td>
</tr>
</tbody>
</table>

Temperature coefficients for the above reaction mixtures are recorded in table 14.
TABLE 14

Temperature Coefficients

<table>
<thead>
<tr>
<th>No.</th>
<th>Container</th>
<th>$k_{35}/k_{25}$</th>
<th>$k_{45}/k_{35}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Pyrex glass</td>
<td>1.75</td>
<td>1.80</td>
</tr>
<tr>
<td>2.</td>
<td>Skyrex glass</td>
<td>1.74</td>
<td>1.79</td>
</tr>
<tr>
<td>3.</td>
<td>Borosil glass</td>
<td>1.74</td>
<td>1.78</td>
</tr>
<tr>
<td>4.</td>
<td>Glass powder</td>
<td>1.74</td>
<td>1.79</td>
</tr>
</tbody>
</table>

Summary of Results:

It is obvious from the above observations that the rate constants and temperature coefficients are independent of the nature of the container. Addition of glass powder which greatly increases the area of the glass surface has no effect on them.

As already mentioned in chapter I that several reactions actually proceed on the walls of reaction vessels. Examples of such reactions are formation of quaternary ammonium salts, oxidation of oxalic acid by potassium persulphate, reaction between malic acid and potassium peroxidisulphate, etc.

The criterion of homogeneous reaction as given by Hinshelwood is that the rate of reaction is independent of
the area of the surface of the container and that of a heterogeneous reaction is that the velocity of reaction, for the container of the same material and volume, is directly proportional to the internal area of the container.

The above results clearly meet the definition of homogeneous nature of the reaction. The flasks of different glasses had different internal area. Even the presence of glass powder did not alter the rate of reaction. Hence the reaction between glycolic acid and chromic acid in aqueous solution is of homogeneous nature.
II - D

EFFECT OF SULPHURIC ACID

It was first ascertained by preliminary investigations that there is no reaction between sulphuric acid and chromic acid in the concentration range of study. Sneathlase and others have reported the decomposition of chromic acid by sulphuric acid. Hence selection of those ranges of concentrations, in which sulphuric acid did not react with chromic acid was necessary. It was also ascertained that there is no interaction between glycolic acid and sulphuric acid within the concentration range selected for investigations.

100ml. of an aqueous solution containing 0.0100 N chromic acid and 2.50 N sulphuric acid was prepared. 10ml. of this solution was titrated immediately iodometrically with hypo solution. The remaining solution was kept for 48 hours and then again 10ml. of this solution was withdrawn and titrated with the same hypo. Observations are recorded in the following table.

<table>
<thead>
<tr>
<th>TABLE 15</th>
</tr>
</thead>
<tbody>
<tr>
<td>10ml. of the solution at the beginning.</td>
</tr>
<tr>
<td>10ml. of the solution after 48 hours</td>
</tr>
</tbody>
</table>

It is thus evident that no interaction takes place between chromic acid and sulphuric acid in the maximum of
FIG. 1  EFFECT OF SULPHURI ACID ON THE RATE OF REACTION BETWEEN
GLYCOLIC ACID & CHROMIC ACID AT 25°C

Mls of 4N Sulphuric acid in 100 mls of reaction mixture

Glycolic acid 0.300n
Chromic acid 0.010n
concentration range used in these investigations.

100 ml. of an aqueous solution containing 0.40 N glycolic acid and 2.50 N sulphuric acid was prepared. 10 ml. of this was diluted to 250 ml. 10 ml. of this diluted solution was titrated with a standard sodium hydroxide solution to the phenolphthalein end point. The remaining of the original solution was kept for 48 hours and 10 ml. of this was diluted again to 250 ml. 10 ml. of this diluted solution was then titrated with the same sodium hydroxide solution as before. Observations are recorded in the following table.

**TABLE 16**

| 10 ml. of diluted solution at the beginning | = | 13.20 ml. of sodium hydroxide solution |
| 10 ml. of diluted solution after 48 hours | = | 13.20 ml. of same sodium hydroxide solution |

From table 16 it is apparent, that there is no interaction between glycolic acid and sulphuric acid in the concentration range of study.

In order to study the effect of sulphuric acid, various reaction mixtures were prepared, in which concentrations of glycolic acid and chromic acid were kept constant at 0.30 N and 0.010 N respectively, while that of sulphuric acid was varied from 0.00 to 2.40 N, by addition of calculated quantities of 4 N sulphuric acid solution.
The rate constants of these reaction mixtures at the three temperatures are recorded in table 17.

**TABLE 17**

**Rate Constants**

<table>
<thead>
<tr>
<th>No.</th>
<th>Concentration of sulphuric acid (N)</th>
<th>Glycolic acid 0.30 N</th>
<th>Chromic acid 0.010 N</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$k_1$ (min.$^{-1}$)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>25°C</td>
<td>35°C</td>
</tr>
<tr>
<td>1</td>
<td>0.00</td>
<td>0.002702</td>
<td>0.004718</td>
</tr>
<tr>
<td>2</td>
<td>0.04</td>
<td>0.004935</td>
<td>0.008463</td>
</tr>
<tr>
<td>3</td>
<td>0.08</td>
<td>0.007164</td>
<td>0.01201</td>
</tr>
<tr>
<td>4</td>
<td>0.16</td>
<td>0.01314</td>
<td>0.02037</td>
</tr>
<tr>
<td>5</td>
<td>0.24</td>
<td>0.01629</td>
<td>0.02447</td>
</tr>
<tr>
<td>6</td>
<td>0.32</td>
<td>0.01950</td>
<td>0.02624</td>
</tr>
<tr>
<td>7</td>
<td>0.40</td>
<td>0.02097</td>
<td>0.03088</td>
</tr>
<tr>
<td>8</td>
<td>0.80</td>
<td>0.02428</td>
<td>0.03489</td>
</tr>
<tr>
<td>9</td>
<td>1.20</td>
<td>0.02437</td>
<td>0.03512</td>
</tr>
<tr>
<td>10</td>
<td>1.60</td>
<td>0.02448</td>
<td>0.03533</td>
</tr>
<tr>
<td>11</td>
<td>2.40</td>
<td>0.02506</td>
<td>0.03545</td>
</tr>
</tbody>
</table>

Fig. 1 shows the variation of rate of reaction with the concentration of sulphuric acid.

Temperature coefficients for the above values of rate constants were calculated and are recorded in table 18.
<table>
<thead>
<tr>
<th>No.</th>
<th>Concentration of sulphuric acid (N)</th>
<th>$k_{35}/k_{25}$</th>
<th>$k_{45}/k_{35}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.00</td>
<td>1.75</td>
<td>1.50</td>
</tr>
<tr>
<td>2</td>
<td>0.04</td>
<td>1.72</td>
<td>1.78</td>
</tr>
<tr>
<td>3</td>
<td>0.08</td>
<td>1.67</td>
<td>1.67</td>
</tr>
<tr>
<td>4</td>
<td>0.16</td>
<td>1.55</td>
<td>1.60</td>
</tr>
<tr>
<td>5</td>
<td>0.24</td>
<td>1.50</td>
<td>1.56</td>
</tr>
<tr>
<td>6</td>
<td>0.32</td>
<td>1.48</td>
<td>1.53</td>
</tr>
<tr>
<td>7</td>
<td>0.40</td>
<td>1.47</td>
<td>1.52</td>
</tr>
<tr>
<td>8</td>
<td>0.80</td>
<td>1.44</td>
<td>1.45</td>
</tr>
<tr>
<td>9</td>
<td>1.20</td>
<td>1.43</td>
<td>1.45</td>
</tr>
<tr>
<td>10</td>
<td>1.60</td>
<td>1.43</td>
<td>1.44</td>
</tr>
<tr>
<td>11</td>
<td>2.40</td>
<td>1.43</td>
<td>1.45</td>
</tr>
</tbody>
</table>

The pH values of the above reaction mixtures are given in the next table.

<table>
<thead>
<tr>
<th>No.</th>
<th>Concentration of sulphuric acid (N)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.00</td>
<td>2.10</td>
</tr>
<tr>
<td>2</td>
<td>0.04</td>
<td>1.70</td>
</tr>
<tr>
<td>3</td>
<td>0.08</td>
<td>1.50</td>
</tr>
<tr>
<td>4</td>
<td>0.16</td>
<td>1.30</td>
</tr>
<tr>
<td>5</td>
<td>0.24</td>
<td>1.20</td>
</tr>
<tr>
<td>6</td>
<td>0.32</td>
<td>1.10</td>
</tr>
<tr>
<td>7</td>
<td>0.40</td>
<td>1.05</td>
</tr>
<tr>
<td>8</td>
<td>0.80</td>
<td>0.85</td>
</tr>
<tr>
<td>9</td>
<td>1.20</td>
<td>0.75</td>
</tr>
<tr>
<td>10</td>
<td>1.60</td>
<td>0.70</td>
</tr>
<tr>
<td>11</td>
<td>2.40</td>
<td>0.60</td>
</tr>
</tbody>
</table>
The effect of sulphuric acid was also studied with a second concentration of glycolic acid (0.40 N). Concentrations of chromic acid and sulphuric acid were kept same as before and the rate constants were measured at 25 and 35°C. The rate constants of all these reaction mixtures are tabulated below.

**TABLE 20**

**Rate Constants**

<table>
<thead>
<tr>
<th>Glycolic acid 0.40 N</th>
<th>Chromic acid 0.010 N</th>
</tr>
</thead>
<tbody>
<tr>
<td>No.</td>
<td>Concentration of sulphuric acid (N)</td>
</tr>
<tr>
<td>-----</td>
<td>---------------------------------</td>
</tr>
<tr>
<td>1</td>
<td>0.00</td>
</tr>
<tr>
<td>2</td>
<td>0.04</td>
</tr>
<tr>
<td>3</td>
<td>0.08</td>
</tr>
<tr>
<td>4</td>
<td>0.16</td>
</tr>
<tr>
<td>5</td>
<td>0.24</td>
</tr>
<tr>
<td>6</td>
<td>0.32</td>
</tr>
<tr>
<td>7</td>
<td>0.40</td>
</tr>
<tr>
<td>8</td>
<td>0.80</td>
</tr>
<tr>
<td>9</td>
<td>1.20</td>
</tr>
<tr>
<td>10</td>
<td>1.60</td>
</tr>
<tr>
<td>11</td>
<td>2.40</td>
</tr>
</tbody>
</table>

The temperature coefficients and the pH values of the above reaction mixtures are recorded in table 21.
<table>
<thead>
<tr>
<th>No.</th>
<th>Concentration of sulphuric acid (N)</th>
<th>k₃₅/k₂₅</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.00</td>
<td>1.74</td>
<td>2.05</td>
</tr>
<tr>
<td>2</td>
<td>0.04</td>
<td>1.73</td>
<td>1.80</td>
</tr>
<tr>
<td>3</td>
<td>0.08</td>
<td>1.71</td>
<td>1.55</td>
</tr>
<tr>
<td>4</td>
<td>0.16</td>
<td>1.60</td>
<td>1.40</td>
</tr>
<tr>
<td>5</td>
<td>0.24</td>
<td>1.59</td>
<td>1.25</td>
</tr>
<tr>
<td>6</td>
<td>0.32</td>
<td>1.55</td>
<td>1.15</td>
</tr>
<tr>
<td>7</td>
<td>0.40</td>
<td>1.55</td>
<td>1.05</td>
</tr>
<tr>
<td>8</td>
<td>0.80</td>
<td>1.51</td>
<td>0.90</td>
</tr>
<tr>
<td>9</td>
<td>1.20</td>
<td>1.43</td>
<td>0.70</td>
</tr>
<tr>
<td>10</td>
<td>1.60</td>
<td>1.42</td>
<td>0.65</td>
</tr>
<tr>
<td>11</td>
<td>2.40</td>
<td>1.42</td>
<td>0.35</td>
</tr>
</tbody>
</table>

**Summary of Results:**

It was observed from the kinetic data of the reaction mixtures that the order of reaction with respect to chromic acid is not affected by the presence of sulphuric acid and remains one. A glance at Table 17 and Fig. 1 clearly brings out the fact that sulphuric acid has a great catalytic effect on the rate of reaction between glycolic acid
and chromic acid. With increasing concentrations of sulphuric acid the rate of reaction is first increased, but at higher concentrations of sulphuric acid further increase in the acid concentration does not have any effect on the rate of reaction and it becomes constant. Same effect of sulphuric acid persists at higher temperatures.

From table 20 it is clear that the effect of sulphuric acid on the reaction rate with the higher concentration of glycolic acid is similar to that with lower concentration.

The values of temperature coefficients are seen to decrease slightly with the increasing concentrations of sulphuric acid (tables 18 & 21).

The pH values of the reaction mixtures also decrease with increase in sulphuric acid contents (tables 19 and 21).
II - n

EFFECT OF HYDROCHLORIC ACID

Though no interaction between glycolic acid and hydrochloric acid has been reported in the literature, hence it was thought desirable to ascertain that there is no reaction between the two acids in the selected range of study. Similarly it was also ascertained that no reaction takes place between chromic acid and hydrochloric acid at the conditions at which these investigations were made.

100 ml. of an aqueous solution containing 2.00 N hydrochloric acid and 0.40 N glycolic acid was prepared. 5 ml. of this solution was diluted to make 100 ml. solution. 10 ml of this diluted solution was titrated against a standard sodium hydroxide solution to the phenolphthalein end point. Rest of the original solution was kept for 48 hours and 5 ml of this was again diluted to 100 ml. 10 ml of this diluted solution was titrated with the same sodium hydroxide solution as before. Observations are recorded in the following table.

<table>
<thead>
<tr>
<th>TABLE 22</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 ml of the diluted solution at the beginning</td>
</tr>
<tr>
<td>10 ml of the diluted solution after 48 hours</td>
</tr>
</tbody>
</table>
FIG. 2 - EFFECT OF HYDROCHLORIC ACID ON THE RATE OF REACTION BETWEEN GLYCOLIC ACID & CHROMIC ACID AT 25°C

Glycolic acid 0.300 N
Chromic acid 0.010 N

M Ls of 4 N Hydrochloric acid in 100 mls of reaction mixture
100 ml of an aqueous solution containing 2.00 N hydrochloric acid and 0.010 N chromic acid was prepared. 10 ml of this solution was titrated immediately with a standard hypo solution iodometrically. After 48 hours 10 ml of the solution was again withdrawn and titrated with the same hypo solution. Observations are recorded in table 23.

**TABLE 23**

10 ml of the solution at the beginning = 12.50 ml of hypo solution.

10 ml of the same solution after 48 hours = 12.50 ml of same hypo solution.

To study the effect of hydrochloric acid the concentrations of glycolic acid and chromic acid were maintained at 0.30 N and 0.010 N respectively, while that of hydrochloric acid was varied from 0.00 N to 1.60 N.

The rate constants of all reaction mixtures at 25, 35 and 45°C are tabulated in table 24.
### TABLE 24

**Rate Constants**

<table>
<thead>
<tr>
<th>No.</th>
<th>Concentration of hydrochloric acid (N)</th>
<th>Glycolic acid 0.30 N</th>
<th>Chromic acid 0.010 N</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>25</td>
<td>35</td>
</tr>
<tr>
<td>1</td>
<td>0.00</td>
<td>0.002702</td>
<td>0.004718</td>
</tr>
<tr>
<td>2</td>
<td>0.04</td>
<td>0.005976</td>
<td>0.01058</td>
</tr>
<tr>
<td>3</td>
<td>0.08</td>
<td>0.01014</td>
<td>0.01800</td>
</tr>
<tr>
<td>4</td>
<td>0.16</td>
<td>0.01796</td>
<td>0.03053</td>
</tr>
<tr>
<td>5</td>
<td>0.24</td>
<td>0.02333</td>
<td>0.03783</td>
</tr>
<tr>
<td>6</td>
<td>0.32</td>
<td>0.02492</td>
<td>0.04048</td>
</tr>
<tr>
<td>7</td>
<td>0.40</td>
<td>0.02453</td>
<td>0.03793</td>
</tr>
<tr>
<td>8</td>
<td>0.56</td>
<td>0.01794</td>
<td>0.02655</td>
</tr>
<tr>
<td>9</td>
<td>0.80</td>
<td>0.01196</td>
<td>0.01756</td>
</tr>
<tr>
<td>10</td>
<td>1.20</td>
<td>0.005634</td>
<td>0.008179</td>
</tr>
<tr>
<td>11</td>
<td>1.60</td>
<td>0.003312</td>
<td>0.004776</td>
</tr>
</tbody>
</table>

The variation of the rate constant with increase in concentration of hydrochloric acid is shown in Fig. 2.

The temperature coefficients of all the above reaction mixtures are recorded in the table 25.

### TABLE 25

**Temperature coefficients**

<table>
<thead>
<tr>
<th>No.</th>
<th>Concentration of hydrochloric acid (N)</th>
<th>Glycolic acid 0.30 N</th>
<th>Chromic acid 0.010 N</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>k₃₅/k₂₅</td>
<td>k₄₅/k₃₅</td>
</tr>
<tr>
<td>1</td>
<td>0.00</td>
<td>1.75</td>
<td>1.80</td>
</tr>
<tr>
<td>2</td>
<td>0.04</td>
<td>1.76</td>
<td>1.79</td>
</tr>
<tr>
<td>3</td>
<td>0.08</td>
<td>1.76</td>
<td>1.65</td>
</tr>
<tr>
<td>4</td>
<td>0.16</td>
<td>1.70</td>
<td>1.64</td>
</tr>
<tr>
<td>5</td>
<td>0.24</td>
<td>1.62</td>
<td>1.55</td>
</tr>
<tr>
<td>6</td>
<td>0.32</td>
<td>1.61</td>
<td>1.50</td>
</tr>
<tr>
<td>7</td>
<td>0.40</td>
<td>1.54</td>
<td>1.50</td>
</tr>
<tr>
<td>8</td>
<td>0.56</td>
<td>1.48</td>
<td>1.46</td>
</tr>
<tr>
<td>9</td>
<td>0.80</td>
<td>1.47</td>
<td>1.45</td>
</tr>
<tr>
<td>10</td>
<td>1.20</td>
<td>1.45</td>
<td>1.42</td>
</tr>
<tr>
<td>11</td>
<td>1.60</td>
<td>1.44</td>
<td>1.41</td>
</tr>
</tbody>
</table>
The pH values of all the reaction mixtures at 25°C are tabulated in table 26.

<table>
<thead>
<tr>
<th>No.</th>
<th>Glycolic acid 0.30 N</th>
<th>Chromic acid 0.010 N</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Concentration of hydrochloric acid (N)</td>
<td>pH</td>
</tr>
<tr>
<td>1</td>
<td>0.00</td>
<td>2.10</td>
</tr>
<tr>
<td>2</td>
<td>0.04</td>
<td>1.50</td>
</tr>
<tr>
<td>3</td>
<td>0.08</td>
<td>1.30</td>
</tr>
<tr>
<td>4</td>
<td>0.16</td>
<td>1.10</td>
</tr>
<tr>
<td>5</td>
<td>0.24</td>
<td>1.00</td>
</tr>
<tr>
<td>6</td>
<td>0.32</td>
<td>0.90</td>
</tr>
<tr>
<td>7</td>
<td>0.40</td>
<td>0.80</td>
</tr>
<tr>
<td>8</td>
<td>0.56</td>
<td>0.70</td>
</tr>
<tr>
<td>9</td>
<td>0.80</td>
<td>0.55</td>
</tr>
<tr>
<td>10</td>
<td>1.20</td>
<td>0.40</td>
</tr>
<tr>
<td>11</td>
<td>1.60</td>
<td>0.25</td>
</tr>
</tbody>
</table>

The effect of hydrochloric acid was also studied with the second concentration of glycolic acid.

The rate constants of all the reaction mixtures with second concentration of glycolic acid is given in the next table.
### TABLE 27
Rate Constants

<table>
<thead>
<tr>
<th>No.</th>
<th>Concentration of hydrochloric acid (N)</th>
<th>$k_1$ (min.⁻¹) 25°C</th>
<th>$k_1$ (min.⁻¹) 35°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.00</td>
<td>0.004515</td>
<td>0.007321</td>
</tr>
<tr>
<td>2</td>
<td>0.04</td>
<td>0.007868</td>
<td>0.01375</td>
</tr>
<tr>
<td>3</td>
<td>0.08</td>
<td>0.01207</td>
<td>0.02131</td>
</tr>
<tr>
<td>4</td>
<td>0.16</td>
<td>0.01870</td>
<td>0.03288</td>
</tr>
<tr>
<td>5</td>
<td>0.24</td>
<td>0.02499</td>
<td>0.03855</td>
</tr>
<tr>
<td>6</td>
<td>0.32</td>
<td>0.03582</td>
<td>0.04121</td>
</tr>
<tr>
<td>7</td>
<td>0.40</td>
<td>0.02508</td>
<td>0.03835</td>
</tr>
<tr>
<td>8</td>
<td>0.56</td>
<td>0.01883</td>
<td>0.02657</td>
</tr>
<tr>
<td>9</td>
<td>0.80</td>
<td>0.01265</td>
<td>0.01874</td>
</tr>
<tr>
<td>10</td>
<td>1.20</td>
<td>0.008579</td>
<td>0.009607</td>
</tr>
<tr>
<td>11</td>
<td>1.60</td>
<td>0.004252</td>
<td>0.008267</td>
</tr>
</tbody>
</table>

The temperature coefficients and the pH values at 25°C of reaction mixtures are given in Table 28.

### TABLE 28
Temperature Coefficients & pH values

<table>
<thead>
<tr>
<th>No.</th>
<th>Concentration of hydrochloric acid (N)</th>
<th>$k_{35}/k_{25}$</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.00</td>
<td>1.74</td>
<td>2.05</td>
</tr>
<tr>
<td>2</td>
<td>0.04</td>
<td>1.75</td>
<td>1.48</td>
</tr>
<tr>
<td>3</td>
<td>0.08</td>
<td>1.76</td>
<td>1.55</td>
</tr>
<tr>
<td>4</td>
<td>0.16</td>
<td>1.76</td>
<td>1.15</td>
</tr>
<tr>
<td>5</td>
<td>0.24</td>
<td>1.66</td>
<td>1.00</td>
</tr>
<tr>
<td>6</td>
<td>0.32</td>
<td>1.64</td>
<td>0.90</td>
</tr>
<tr>
<td>7</td>
<td>0.40</td>
<td>1.61</td>
<td>0.80</td>
</tr>
<tr>
<td>8</td>
<td>0.56</td>
<td>1.51</td>
<td>0.65</td>
</tr>
<tr>
<td>9</td>
<td>0.80</td>
<td>1.49</td>
<td>0.55</td>
</tr>
<tr>
<td>10</td>
<td>1.20</td>
<td>1.46</td>
<td>0.55</td>
</tr>
<tr>
<td>11</td>
<td>1.60</td>
<td>1.45</td>
<td>0.28</td>
</tr>
</tbody>
</table>
Summary of Results:

It is well known that hydrochloric acid is oxidised by chromic acid. Hence it was necessary to ascertain that there is no interaction between hydrochloric acid and chromic acid under the conditions of these investigations. Preliminary investigations on pages 59 and 60 show clearly that hydrochloric acid does not react with either chromic acid or glycolic acid at the maximum of concentrations used in these investigations.

It is observed from the kinetic data of reaction mixtures that order of reaction with respect to chromic acid does not change in presence of hydrochloric acid and remains one.

A perusal of table 24 shows that the rate constant of the reaction is markedly affected by the catalytic activity of hydrochloric acid. Rate constant at first increases with increase in concentration of hydrochloric acid up to a concentration of 0.33 N and further increase in concentration of acid causes a decrease in the rate of reaction. Thus the lower concentrations of hydrochloric acid has an accelerating effect, while at higher concentrations the reaction rate is retarded. The same behaviour is observed at higher temperatures.
The values of temperature coefficients decrease slightly with the increasing concentrations of hydrochloric acid (table 25).

Tables 27 and 28 show the similar behaviour of hydrochloric acid with the second concentration of glycolic acid.

The pH values of the reaction mixtures (table 26 and 28) decrease, as is natural, with the increasing concentration of hydrochloric acid.
EFFECT OF o-PHOSPHORIC ACID

Preliminary experiments are first conducted to make sure that there is no interaction between o-phosphoric acid and chromic acid within the concentration range of study. This was done by the same method as was followed in case of sulphuric acid and hydrochloric acid. Results are recorded in the following table.

**TABLE 29**

10 ml of solution containing 2.00 N o-phosphoric acid and 0.010 N chromic acid  = 14.30 ml of hypo solution

10 ml of the above solution after 48 hours  = 14.30 ml of same hypo solution

It may be mentioned here that o-phosphoric acid solution was standardised by titrating it with a standard sodium hydroxide solution, using a mixture of α-naphtholphthalein and phenolphthalein as an indicator.

In order to study the effect of o-phosphoric acid various reaction mixtures were prepared as usual and their kinetic data was measured at 25, 35 and 45°C.

Rate constants of all reaction mixtures are recorded in table 30.
FIG. 3. EFFECT OF PHOSPHORIC ACID ON THE RATE OF REACTION BETWEEN GLYCOLIC ACID & CHROMIC ACID AT 25°C

GLYCOLIC ACID 0.300N
CHROMIC ACID 0.010N

Mls of 5N Phosphoric acid in 100mls of reaction mixture
<table>
<thead>
<tr>
<th>No.</th>
<th>Concentration of o-phosphoric acid (N)</th>
<th>Glycolic acid 0.30 N</th>
<th>Chromic acid 0.010 N</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>k₁ (min⁻¹) 25</td>
<td>k₁ (min⁻¹) 35</td>
</tr>
<tr>
<td>1</td>
<td>0.00</td>
<td>0.004202</td>
<td>0.004718</td>
</tr>
<tr>
<td>2</td>
<td>0.05</td>
<td>0.004283</td>
<td>0.004867</td>
</tr>
<tr>
<td>3</td>
<td>0.10</td>
<td>0.0053127</td>
<td>0.0059527</td>
</tr>
<tr>
<td>4</td>
<td>0.25</td>
<td>0.003727</td>
<td>0.004296</td>
</tr>
<tr>
<td>5</td>
<td>0.50</td>
<td>0.005560</td>
<td>0.0061790</td>
</tr>
<tr>
<td>6</td>
<td>0.75</td>
<td>0.003486</td>
<td>0.0040327</td>
</tr>
<tr>
<td>7</td>
<td>1.00</td>
<td>0.003704</td>
<td>0.0042535</td>
</tr>
<tr>
<td>8</td>
<td>1.50</td>
<td>0.002459</td>
<td>0.003002</td>
</tr>
<tr>
<td>9</td>
<td>2.00</td>
<td>0.002094</td>
<td>0.0026021</td>
</tr>
</tbody>
</table>

Fig. 3 shows the variation of rate constant with increase in concentration of o-phosphoric acid.

Temperature coefficients of all the reaction mixtures are recorded in Table 31.

<table>
<thead>
<tr>
<th>No.</th>
<th>Concentration of o-phosphoric acid (N)</th>
<th>k₃₅/k₂₅</th>
<th>k₄₅/k₃₅</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.00</td>
<td>1.75</td>
<td>1.60</td>
</tr>
<tr>
<td>2</td>
<td>0.05</td>
<td>1.76</td>
<td>1.75</td>
</tr>
<tr>
<td>3</td>
<td>0.10</td>
<td>1.76</td>
<td>1.75</td>
</tr>
<tr>
<td>4</td>
<td>0.25</td>
<td>1.69</td>
<td>1.69</td>
</tr>
<tr>
<td>5</td>
<td>0.50</td>
<td>1.63</td>
<td>1.62</td>
</tr>
<tr>
<td>6</td>
<td>0.75</td>
<td>1.56</td>
<td>1.60</td>
</tr>
<tr>
<td>7</td>
<td>1.00</td>
<td>1.54</td>
<td>1.59</td>
</tr>
<tr>
<td>8</td>
<td>1.50</td>
<td>1.56</td>
<td>1.54</td>
</tr>
<tr>
<td>9</td>
<td>2.00</td>
<td>1.51</td>
<td>1.51</td>
</tr>
</tbody>
</table>
The values of pH of the above reaction mixtures are tabulated in table 32.

<table>
<thead>
<tr>
<th>No.</th>
<th>Concentration of o-phosphoric acid (N)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.00</td>
<td>2.10</td>
</tr>
<tr>
<td>2</td>
<td>0.05</td>
<td>2.00</td>
</tr>
<tr>
<td>3</td>
<td>0.10</td>
<td>1.90</td>
</tr>
<tr>
<td>4</td>
<td>0.25</td>
<td>1.80</td>
</tr>
<tr>
<td>5</td>
<td>0.50</td>
<td>1.65</td>
</tr>
<tr>
<td>6</td>
<td>0.75</td>
<td>1.55</td>
</tr>
<tr>
<td>7</td>
<td>1.00</td>
<td>1.50</td>
</tr>
<tr>
<td>8</td>
<td>1.50</td>
<td>1.40</td>
</tr>
<tr>
<td>9</td>
<td>2.00</td>
<td>1.30</td>
</tr>
</tbody>
</table>

The effect of o-phosphoric acid was also studied with glycolic acid concentration 0.40 N. Concentration of chromic acid was kept at 0.010 N and that of o-phosphoric acid was varied as before from 0.00 to 2.00 N.

Rate constants for all reaction mixtures at 25 and 35°C are recorded in table 33.
### TABLE 33
**Rate Constants**

<table>
<thead>
<tr>
<th>No.</th>
<th>Concentration of o-phosphoric acid (N)</th>
<th>k₁ (min⁻¹) 25°C</th>
<th>k₁ (min⁻¹) 35°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.00</td>
<td>0.004315</td>
<td>0.007821</td>
</tr>
<tr>
<td>2</td>
<td>0.05</td>
<td>0.004327</td>
<td>0.008744</td>
</tr>
<tr>
<td>3</td>
<td>0.10</td>
<td>0.004604</td>
<td>0.008310</td>
</tr>
<tr>
<td>4</td>
<td>0.25</td>
<td>0.004751</td>
<td>0.008555</td>
</tr>
<tr>
<td>5</td>
<td>0.50</td>
<td>0.004530</td>
<td>0.007700</td>
</tr>
<tr>
<td>6</td>
<td>0.75</td>
<td>0.003984</td>
<td>0.006899</td>
</tr>
<tr>
<td>7</td>
<td>1.00</td>
<td>0.003576</td>
<td>0.006064</td>
</tr>
<tr>
<td>8</td>
<td>1.50</td>
<td>0.002916</td>
<td>0.004887</td>
</tr>
<tr>
<td>9</td>
<td>2.00</td>
<td>0.002412</td>
<td>0.003803</td>
</tr>
</tbody>
</table>

The temperature coefficients and the pH values of the above are recorded in the next table.

### TABLE 34
**Temperature coefficients & pH values**

<table>
<thead>
<tr>
<th>No.</th>
<th>Concentration of o-phosphoric acid (N)</th>
<th>k₃5/k₂5</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.00</td>
<td>1.74</td>
<td>2.05</td>
</tr>
<tr>
<td>2</td>
<td>0.05</td>
<td>1.80</td>
<td>2.00</td>
</tr>
<tr>
<td>3</td>
<td>0.10</td>
<td>1.80</td>
<td>1.90</td>
</tr>
<tr>
<td>4</td>
<td>0.25</td>
<td>1.80</td>
<td>1.80</td>
</tr>
<tr>
<td>5</td>
<td>0.50</td>
<td>1.70</td>
<td>1.65</td>
</tr>
<tr>
<td>6</td>
<td>0.75</td>
<td>1.69</td>
<td>1.55</td>
</tr>
<tr>
<td>7</td>
<td>1.00</td>
<td>1.69</td>
<td>1.50</td>
</tr>
<tr>
<td>8</td>
<td>1.50</td>
<td>1.61</td>
<td>1.40</td>
</tr>
<tr>
<td>9</td>
<td>2.00</td>
<td>1.58</td>
<td>1.30</td>
</tr>
</tbody>
</table>
Summary of Results:

Oxidation of diphenylmethane and diphenyl methanol, with improved yield, to benzophenone could be achieved by using a mixture of chromic acid and phosphoric acid. Riley has reported the oxidation of carbon by chromic acid in presence of phosphoric acid. Hence it was made sure that there is no reaction between phosphoric acid and chromic acid in the selected range of study. Observations in table 29 confirm this.

The kinetic data of the reaction mixtures show that the order of reaction with respect to chromic acid is not altered by the presence of o-phosphoric acid. Similar to the effect of hydrochloric acid, increasing concentrations of o-phosphoric acid first increases the rate of reaction up to 0.31 N concentration and with further increase in o-phosphoric acid concentration the reaction rate is decreased (table 30).

Temperature coefficients is seen to decrease slightly with increasing concentrations of o-phosphoric acid (table 31). The same effect is observed at higher temperatures.

Effect of o-phosphoric acid on the rate of reaction with higher concentration of glycolic acid is similar to that with lower concentration of glycolic acid (table 33,34).

The pH values of the reaction mixtures decrease with increasing o-phosphoric acid concentration (table 33,34).
EFFECT OF ACETIC ACID

The author has found that in the selected range of concentrations, the effect due to acetic acid, on the rate of reaction between glycolic acid and chromic acid in aqueous medium, is not appreciable. Hence the author has studied the effect of acetic acid taking very high concentrations.

It was, of course, first ascertained by usual preliminary experiments that there is no reaction between acetic acid and chromic acid. The results are recorded in the following table.

\[
\text{TABLE 35}
\]

| 10 ml of the solution containing | \equiv 12.60 ml of hypo solution. |
| 0.010 N chromic acid and 6.00 N acetic acid | |
| 10 ml of the same solution after 48 hours | \equiv 12.60 ml of same hypo solution. |

The effect of acetic acid was investigated at the three temperatures, with glycolic acid and chromic acid concentrations at 0.30 N and 0.010 N respectively while acetic acid concentration was varied from 0.00 to 6.00 N.

The rate constants for all reaction mixtures are recorded in table 36.
FIG. 4 EFFECT OF ACETIC ACID ON THE RATE OF REACTION BETWEEN GLYCOLIC ACID & CHROMIC ACID AT 25°C

Mls of 1N Acetic acid in 100mls of reaction mixture
### TABLE 36
Rate Constants

<table>
<thead>
<tr>
<th>No.</th>
<th>Glycolic acid 0.30 N</th>
<th>Chromic acid 0.010 N</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Concentration of acetic acid (N)</td>
<td>k₁ (min⁻¹)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>25</td>
</tr>
<tr>
<td>1</td>
<td>0.20</td>
<td>0.002702</td>
</tr>
<tr>
<td>2</td>
<td>0.50</td>
<td>0.002828</td>
</tr>
<tr>
<td>3</td>
<td>1.00</td>
<td>0.003978</td>
</tr>
<tr>
<td>4</td>
<td>2.00</td>
<td>0.003298</td>
</tr>
<tr>
<td>5</td>
<td>3.00</td>
<td>0.003461</td>
</tr>
<tr>
<td>6</td>
<td>4.00</td>
<td>0.003724</td>
</tr>
<tr>
<td>7</td>
<td>5.00</td>
<td>0.004127</td>
</tr>
<tr>
<td>8</td>
<td>6.00</td>
<td>0.004378</td>
</tr>
</tbody>
</table>

Fig. 4 shows the variation of rate constant with increasing concentrations of acetic acid.

Temperature coefficients for the above are recorded in the following table.

### TABLE 37
Temperature Coefficients

<table>
<thead>
<tr>
<th>No.</th>
<th>Glycolic acid 0.30 N</th>
<th>Chromic acid 0.010 N</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Concentration of acetic acid (N)</td>
<td>k₃₅/k₂₅</td>
</tr>
<tr>
<td>1</td>
<td>0.00</td>
<td>1.75</td>
</tr>
<tr>
<td>2</td>
<td>0.50</td>
<td>1.75</td>
</tr>
<tr>
<td>3</td>
<td>1.00</td>
<td>1.77</td>
</tr>
<tr>
<td>4</td>
<td>2.00</td>
<td>1.75</td>
</tr>
<tr>
<td>5</td>
<td>3.00</td>
<td>1.78</td>
</tr>
<tr>
<td>6</td>
<td>4.00</td>
<td>1.80</td>
</tr>
<tr>
<td>7</td>
<td>5.00</td>
<td>1.80</td>
</tr>
<tr>
<td>8</td>
<td>6.00</td>
<td>1.77</td>
</tr>
</tbody>
</table>
The pH values of the reaction mixtures at 25°C are given in next table.

<table>
<thead>
<tr>
<th>Glycolic acid 0.30 N</th>
<th>Chromic acid 0.010N</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>No.</strong></td>
<td><strong>Concentration of acetic acid (N)</strong></td>
</tr>
<tr>
<td>1</td>
<td>0.00</td>
</tr>
<tr>
<td>2</td>
<td>0.50</td>
</tr>
<tr>
<td>3</td>
<td>1.00</td>
</tr>
<tr>
<td>4</td>
<td>2.00</td>
</tr>
<tr>
<td>5</td>
<td>3.00</td>
</tr>
<tr>
<td>6</td>
<td>4.00</td>
</tr>
<tr>
<td>7</td>
<td>5.00</td>
</tr>
<tr>
<td>8</td>
<td>6.00</td>
</tr>
</tbody>
</table>

Effect of acetic acid was also investigated taking the second concentration of glycolic acid. The rate constants at 25 and 35°C of the various reaction mixtures are recorded in table 59.

<table>
<thead>
<tr>
<th>Glycolic acid 0.40 N</th>
<th>Chromic acid 0.010 N</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>No.</strong></td>
<td><strong>Concentration of acetic acid (N)</strong></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0.00</td>
</tr>
<tr>
<td>2</td>
<td>0.50</td>
</tr>
<tr>
<td>3</td>
<td>1.00</td>
</tr>
<tr>
<td>4</td>
<td>2.00</td>
</tr>
<tr>
<td>5</td>
<td>3.00</td>
</tr>
<tr>
<td>6</td>
<td>4.00</td>
</tr>
<tr>
<td>7</td>
<td>5.00</td>
</tr>
<tr>
<td>8</td>
<td>6.00</td>
</tr>
</tbody>
</table>
The values of temperature coefficients and pH are tabulated below.

**TABLE 40**

**Temperature coefficients & pH values**

<table>
<thead>
<tr>
<th>No.</th>
<th>Concentration of acetic acid (N)</th>
<th>k35/k25</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.00</td>
<td>1.74</td>
<td>2.05</td>
</tr>
<tr>
<td>2</td>
<td>0.50</td>
<td>1.73</td>
<td>1.95</td>
</tr>
<tr>
<td>3</td>
<td>1.00</td>
<td>1.76</td>
<td>1.95</td>
</tr>
<tr>
<td>4</td>
<td>2.00</td>
<td>1.73</td>
<td>1.90</td>
</tr>
<tr>
<td>5</td>
<td>3.00</td>
<td>1.77</td>
<td>1.85</td>
</tr>
<tr>
<td>6</td>
<td>4.00</td>
<td>1.73</td>
<td>1.75</td>
</tr>
<tr>
<td>7</td>
<td>5.00</td>
<td>1.72</td>
<td>1.70</td>
</tr>
<tr>
<td>8</td>
<td>6.00</td>
<td>1.70</td>
<td>1.65</td>
</tr>
</tbody>
</table>

**Summary of Results:**

Table 35 shows that there is no interaction between chromic acid and acetic acid at the maximum of concentration used in studying the effect of acetic acid on the reaction between glycolic acid and chromic acid.

The order of reaction with respect to chromic acid remains one and is not altered by the presence of acetic acid. A perusal of the table 36 and Fig. 4 shows that the rate of reaction is linearly increased by increasing concentrations of acetic acid. The same is also true at higher temperatures (table 39).

The value of temperature coefficients are not affected by the presence of acetic acid. The values of pH are seen to decrease slightly with increase in acetic acid concentration.
SALT EFFECT

It has been stated earlier that the author has planned to study the effect of sulphates and chlorides of lithium, sodium and potassium on the rate of reaction between glycolic acid and chromic acid in aqueous medium. During these investigations the author has observed that while the sulphates of these alkali metals have some effect on the reaction rate, the chlorides of these metals does not appreciably affect the rate of reaction. This has been verified by studying the effect at different temperatures, by varying the concentration of glycolic acid and using high concentrations of the alkali chlorides. However, the sulphates and chlorides in presence of their corresponding acids, affect the reaction rate considerably.

The work presented in the following pages deals with the effect of sulphates of lithium, sodium and potassium. The effect of chlorides being not appreciable is not dealt with. Effect of sulphates of lithium, sodium and potassium, in presence of sulphuric acid and of chlorides of these metals in presence of hydrochloric acid is also given.

Similarly the effect of manganese sulphate alone and also in presence of sulphuric, hydrochloric, o-phosphoric and acetic acids on the rate of reaction is also presented.
II - H

EFFECT OF LITHIUM SULPHATE

Lithium sulphate solution was standardised against a standard barium chloride solution using rhodizonic acid as an indicator\textsuperscript{12}.

In these investigations, various reaction mixtures were prepared with the concentrations of glycolic acid and chromic acid, 0.30 N and 0.010 N respectively and that of lithium sulphate was varied from 0.00 to 1.60 N.

The values of the rate constants obtained for the reaction mixtures are recorded in the table below.

<table>
<thead>
<tr>
<th>TABLE 41</th>
<th>Rate Constants</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glycolic acid 0.30 N</td>
<td>Chromic acid 0.010 N</td>
</tr>
<tr>
<td>No.</td>
<td>Concentration of lithium sulphate (N)</td>
</tr>
<tr>
<td>------</td>
<td>--------------------------------</td>
</tr>
<tr>
<td>1</td>
<td>0.00</td>
</tr>
<tr>
<td>2</td>
<td>0.06</td>
</tr>
<tr>
<td>3</td>
<td>0.20</td>
</tr>
<tr>
<td>4</td>
<td>0.40</td>
</tr>
<tr>
<td>5</td>
<td>0.60</td>
</tr>
<tr>
<td>6</td>
<td>1.00</td>
</tr>
<tr>
<td>7</td>
<td>1.60</td>
</tr>
</tbody>
</table>

The variation of the rate of the reaction with increasing concentrations of lithium sulphate is shown in Fig. 5.
FIG. 5 EFFECT OF LITHIUM SULPHATE ON RATE OF REACTION BETWEEN GLYCOLIC ACID AND CHROMIC ACID AT 25°C

GLYCOLIC ACID 0.300 N
CHROMIC ACID 0.010 N

MIS OF 4N Li_2 SO_4 SOLUTION IN 100 MIS OF REACTION MIXTURE
The values of temperature coefficients for the above are recorded in table 42.

**Table 42**

**Temperature Coefficients**

<table>
<thead>
<tr>
<th>No.</th>
<th>Concentration of lithium sulphate (N)</th>
<th>$k_{35}/k_{25}$</th>
<th>$k_{45}/k_{35}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.00</td>
<td>1.75</td>
<td>1.80</td>
</tr>
<tr>
<td>2</td>
<td>0.08</td>
<td>1.80</td>
<td>1.78</td>
</tr>
<tr>
<td>3</td>
<td>0.20</td>
<td>1.81</td>
<td>1.75</td>
</tr>
<tr>
<td>4</td>
<td>0.40</td>
<td>1.79</td>
<td>1.73</td>
</tr>
<tr>
<td>5</td>
<td>0.60</td>
<td>1.79</td>
<td>1.73</td>
</tr>
<tr>
<td>6</td>
<td>1.00</td>
<td>1.73</td>
<td>1.73</td>
</tr>
<tr>
<td>7</td>
<td>1.60</td>
<td>1.69</td>
<td></td>
</tr>
</tbody>
</table>

The pH values of the above reaction mixtures is given in table 43.

**Table 43**

**pH Values**

<table>
<thead>
<tr>
<th>No.</th>
<th>Concentration of lithium sulphate (N)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.00</td>
<td>2.10</td>
</tr>
<tr>
<td>2</td>
<td>0.08</td>
<td>2.20</td>
</tr>
<tr>
<td>3</td>
<td>0.20</td>
<td>2.40</td>
</tr>
<tr>
<td>4</td>
<td>0.40</td>
<td>2.45</td>
</tr>
<tr>
<td>5</td>
<td>0.60</td>
<td>2.45</td>
</tr>
<tr>
<td>6</td>
<td>1.00</td>
<td>2.50</td>
</tr>
<tr>
<td>7</td>
<td>1.60</td>
<td>2.55</td>
</tr>
</tbody>
</table>
Effect of lithium sulphate with the second concentration of glycolic acid at 25 and 35°C has also been studied.

**TABLE 44**  
Rate Constants

<table>
<thead>
<tr>
<th>No.</th>
<th>Concentration of lithium sulphate (N)</th>
<th>Glycolic acid 0.40 N</th>
<th>Chromic acid 0.010 N</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.00</td>
<td>0.004315</td>
<td>0.007231</td>
</tr>
<tr>
<td>2</td>
<td>0.08</td>
<td>0.003613</td>
<td>0.006575</td>
</tr>
<tr>
<td>3</td>
<td>0.20</td>
<td>0.003514</td>
<td>0.006413</td>
</tr>
<tr>
<td>4</td>
<td>0.40</td>
<td>0.003500</td>
<td>0.006267</td>
</tr>
<tr>
<td>5</td>
<td>0.60</td>
<td>0.003572</td>
<td>0.006479</td>
</tr>
<tr>
<td>6</td>
<td>1.00</td>
<td>0.003904</td>
<td>0.007157</td>
</tr>
<tr>
<td>7</td>
<td>1.60</td>
<td>0.004272</td>
<td>0.007881</td>
</tr>
</tbody>
</table>

**Summary of Results:**

From the kinetic data it was seen that the order of reaction with respect to chromic acid is not affected by the presence of lithium sulphate and remains one.

Table 41 and fig.5 show that the rate of reaction is first decreased by increasing concentrations of lithium sulphate up to a lithium sulphate concentration 0.40 N and with further increase in concentration of lithium sulphate the effect is reversed. The same effect persists at higher temperatures.
The value of the temperature coefficients remains almost constant in presence of lithium sulphate (table 42).

Similar effects are observed with the second concentration of glycolic acid (table 44).

The values of pH of the reaction mixtures are increased slightly with increase in the lithium sulphate concentration.
II - I

EFFECT OF SODIUM SULPHATE

In order to investigate the effect of sodium sulphate on the reaction rate, the concentrations of glycolic acid and chromic acid were maintained at 0.30 N and 0.010 N respectively and that of sodium sulphate was varied from 0.00 to 0.60 N.

The rate constants for all reaction mixtures at the three temperatures are summarised in table 45.

**TABLE 45**

<table>
<thead>
<tr>
<th>No.</th>
<th>Concentration of sodium sulphate (N)</th>
<th>25</th>
<th>35</th>
<th>45°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.00</td>
<td>0.002702</td>
<td>0.004718</td>
<td>0.0068520</td>
</tr>
<tr>
<td>2</td>
<td>0.10</td>
<td>0.002228</td>
<td>0.003946</td>
<td>0.006713</td>
</tr>
<tr>
<td>3</td>
<td>0.20</td>
<td>0.002070</td>
<td>0.003556</td>
<td>0.006327</td>
</tr>
<tr>
<td>4</td>
<td>0.30</td>
<td>0.001913</td>
<td>0.003482</td>
<td>0.006106</td>
</tr>
<tr>
<td>5</td>
<td>0.40</td>
<td>0.001908</td>
<td>0.003357</td>
<td>0.005842</td>
</tr>
<tr>
<td>6</td>
<td>0.60</td>
<td>0.001858</td>
<td>0.003314</td>
<td>0.005801</td>
</tr>
</tbody>
</table>

Fig. 6 shows the variation of rate constants with the concentration of sodium sulphate.

The values of temperature coefficients and pH of the reaction mixtures are recorded in tables 46 and 47 respectively.
FIG. 6 EFFECT OF SODIUM SULPHATE ON THE RATE OF REACTION BETWEEN GLYCOLIC ACID & CHROMIC ACID AT 25°C

GLYCOLIC ACID 0.300N
CHROMIC ACID 0.010N

$k_1 \times 10^4$

MIS OF IN SODIUM SULPHATE SOLUTION IN 100 ml OF REACTION MIXTURE
### TABLE 46
**Temperature Coefficients**

<table>
<thead>
<tr>
<th>No.</th>
<th>Concentration of sodium sulphate (N)</th>
<th>$k_{35}/k_{25}$</th>
<th>$k_{45}/k_{35}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.00</td>
<td>1.75</td>
<td>1.80</td>
</tr>
<tr>
<td>2</td>
<td>0.10</td>
<td>1.77</td>
<td>1.70</td>
</tr>
<tr>
<td>3</td>
<td>0.20</td>
<td>1.72</td>
<td>1.78</td>
</tr>
<tr>
<td>4</td>
<td>0.30</td>
<td>1.77</td>
<td>1.77</td>
</tr>
<tr>
<td>5</td>
<td>0.40</td>
<td>1.76</td>
<td>1.74</td>
</tr>
<tr>
<td>6</td>
<td>0.60</td>
<td>1.76</td>
<td>1.75</td>
</tr>
</tbody>
</table>

### TABLE 47
**pH Values**

<table>
<thead>
<tr>
<th>No.</th>
<th>Concentration of sodium sulphate (N)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.00</td>
<td>2.10</td>
</tr>
<tr>
<td>2</td>
<td>0.10</td>
<td>2.30</td>
</tr>
<tr>
<td>3</td>
<td>0.20</td>
<td>2.40</td>
</tr>
<tr>
<td>4</td>
<td>0.30</td>
<td>2.45</td>
</tr>
<tr>
<td>5</td>
<td>0.40</td>
<td>2.50</td>
</tr>
<tr>
<td>6</td>
<td>0.60</td>
<td>2.55</td>
</tr>
</tbody>
</table>

The effect of sodium sulphate with the second concentration of glycolic acid (0.40 N) was also investigated. Concentrations of sodium sulphate and chromic acid were kept as before and the rate of reaction was determined at 25 and 35°C.
The rate constants for all reaction mixtures are given in the following table.

**Table 48**

<table>
<thead>
<tr>
<th>Rate Constants</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glycolic acid 0.40 N</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>No.</th>
<th>Concentration of sodium sulphate (N)</th>
<th>k₁ (min⁻¹) 25°C</th>
<th>k₁ (min⁻¹) 35°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.00</td>
<td>0.004315</td>
<td>0.007821</td>
</tr>
<tr>
<td>2</td>
<td>0.10</td>
<td>0.003990</td>
<td>0.006131</td>
</tr>
<tr>
<td>3</td>
<td>0.20</td>
<td>0.003365</td>
<td>0.005660</td>
</tr>
<tr>
<td>4</td>
<td>0.30</td>
<td>0.003220</td>
<td>0.005420</td>
</tr>
<tr>
<td>5</td>
<td>0.40</td>
<td>0.003132</td>
<td>0.005352</td>
</tr>
<tr>
<td>6</td>
<td>0.60</td>
<td>0.003045</td>
<td>0.005237</td>
</tr>
</tbody>
</table>

**Summary of Results:**

From the kinetic data of various reaction mixtures it was clear that the order of reaction with respect to chromic acid remains one.

The rate of reaction, however, is decreased continuously with the increasing concentrations of sodium sulphate (tables 45 and 48). Fig. 6 shows that the decrease in the rate constant is exponential in nature. Similar results are observed at higher temperatures (table 45 and 48).

The values of the temperature coefficients are not affected by the presence of sodium sulphate (table 46).

The pH values of the reaction mixtures is altered by addition of sodium sulphate and is increased slightly with increasing sodium sulphate concentration (table 47).
II - J

EFFECT OF POTASSIUM SULPHATE

In order to study the effect of potassium sulphate on the reaction, various reaction mixtures were taken in which the concentration of glycolic acid and chromic acid were kept constant at 0.30 N and 0.010 N respectively, while the concentration of potassium sulphate was varied from 0.00 to 0.60 N.

The rate constant of all the reaction mixtures at the three temperatures are recorded in Table 42.

<table>
<thead>
<tr>
<th>TABLE 42</th>
<th>Rate constants</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glycolic acid 0.30 N</td>
<td>Chromic acid 0.010 N</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>No.</th>
<th>Concentration of potassium sulphate (N)</th>
<th>$k_1$ (min$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>25$^\circ$</td>
</tr>
<tr>
<td>1</td>
<td>0.00</td>
<td>0.002702</td>
</tr>
<tr>
<td>2</td>
<td>0.10</td>
<td>0.002188</td>
</tr>
<tr>
<td>3</td>
<td>0.20</td>
<td>0.001958</td>
</tr>
<tr>
<td>4</td>
<td>0.30</td>
<td>0.001627</td>
</tr>
<tr>
<td>5</td>
<td>0.40</td>
<td>0.001730</td>
</tr>
<tr>
<td>6</td>
<td>0.60</td>
<td>0.001636</td>
</tr>
</tbody>
</table>

Fig. 7 shows a variation of rate constants with increasing concentrations of potassium sulphate.

The values of temperature coefficients for the above are recorded in Table 50.
FIG. 7  EFFECT OF POTASSIUM SULPHATE ON THE RATE OF REACTION BETWEEN GLYCOLIC ACID & CHROMIC ACID AT 25°C

\[ K_1 \times 10^{-4} \]

Mls of in Potassium sulphate in 100 mls of reaction mixture
TABLE 50
Temperature coefficients

<table>
<thead>
<tr>
<th>No.</th>
<th>Glycolic acid 0.30 N</th>
<th>Chromic acid 0.010 N</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Concentration of potassium sulphate (N)</td>
<td>k_{35}/k_{25}</td>
</tr>
<tr>
<td>1</td>
<td>0.00</td>
<td>1.75</td>
</tr>
<tr>
<td>2</td>
<td>0.10</td>
<td>1.80</td>
</tr>
<tr>
<td>3</td>
<td>0.20</td>
<td>1.79</td>
</tr>
<tr>
<td>4</td>
<td>0.30</td>
<td>1.80</td>
</tr>
<tr>
<td>5</td>
<td>0.40</td>
<td>1.79</td>
</tr>
<tr>
<td>6</td>
<td>0.60</td>
<td>1.82</td>
</tr>
</tbody>
</table>

The pH values of the reaction mixtures are tabulated in the next table.

TABLE 51
pH Values

<table>
<thead>
<tr>
<th>No.</th>
<th>Glycolic acid 0.30 N</th>
<th>Chromic acid 0.010 N</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Concentration of potassium sulphate (N)</td>
<td>pH</td>
</tr>
<tr>
<td>1</td>
<td>0.00</td>
<td>2.10</td>
</tr>
<tr>
<td>2</td>
<td>0.10</td>
<td>2.25</td>
</tr>
<tr>
<td>3</td>
<td>0.20</td>
<td>2.45</td>
</tr>
<tr>
<td>4</td>
<td>0.30</td>
<td>2.55</td>
</tr>
<tr>
<td>5</td>
<td>0.40</td>
<td>2.60</td>
</tr>
<tr>
<td>6</td>
<td>0.60</td>
<td>2.65</td>
</tr>
</tbody>
</table>

The effect of potassium sulphate was also studied by taking the second concentration of glycolic acid and keeping the concentrations of other substances as before.
The rate constants obtained with the second concentration of glycolic acid are recorded in table 52.

### TABLE 52

<table>
<thead>
<tr>
<th>No.</th>
<th>Concentration of potassium sulphate (N)</th>
<th>( k_1 ) (min.(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>25°C</td>
</tr>
<tr>
<td>1</td>
<td>0.20</td>
<td>0.004315</td>
</tr>
<tr>
<td>2</td>
<td>0.10</td>
<td>0.003485</td>
</tr>
<tr>
<td>3</td>
<td>0.20</td>
<td>0.003123</td>
</tr>
<tr>
<td>4</td>
<td>0.30</td>
<td>0.002913</td>
</tr>
<tr>
<td>5</td>
<td>0.40</td>
<td>0.002856</td>
</tr>
<tr>
<td>6</td>
<td>0.60</td>
<td>0.002674</td>
</tr>
</tbody>
</table>

**Summary of Results:**

Kinetic data of reaction mixtures show that the order of reaction with respect to chromic acid remains one in presence of potassium sulphate. However, similar to the effect of sodium sulphate, the rate of reaction is also retarded continuously by the increasing concentrations of potassium sulphate (table 49). The nature of the curve for decrease in rate constant by increasing concentration of potassium sulphate (Fig.7) is exponential, similar to that of sodium sulphate (Fig.6).
Of the three sulphates, the effect of lithium sulphate is different than that of sodium and potassium. Unlike sodium and potassium sulphates, lithium sulphate (as is evident from tables 41 and 44 and Fig. 5), retards the reaction up to a lithium sulphate concentration of 0.40 M and further increase in concentration increases the reaction rate, whereas sodium and potassium sulphates show only retarding effect on the reaction. The rate of reaction at 25°C (with 0.30 N glycic acid) is decreased from 0.002702 to 0.002186 min$^{-1}$ by 0.40 M lithium sulphate, while for the same concentration of sodium sulphate (0.40 M) the rate is decreased from 0.002702 to 0.001908 min$^{-1}$ and for potassium sulphate the rate constant is brought down to 0.001730 min$^{-1}$. Thus for the same range of concentration (upto 0.40 M) in which all three sulphates produce retarding effect, the effect due to potassium sulphate is maximum and that due to lithium sulphate is the least of the three.

A study of the tables 42, 46 and 50 show that the value of temperature coefficients are not affected by the presence of the three sulphates.

The values of pH are seen to increase slightly by the presence of these sulphates. This increase is slightly more in case of potassium sulphate than in case of sodium sulphate. Effect of lithium sulphate in increasing the pH of the reaction mixtures is less than the other two sulphates (tables 43, 47 and 51).
II - E

EFFECT OF LITHIUM SULPHATE IN PRESENCE OF SULPHURIC ACID

To investigate the effect of lithium sulphate in presence of sulphuric acid, a number of reaction mixtures were prepared with the concentration of sulphuric acid, kept constant at 0.32 N, while the concentration of lithium sulphate was varied from 0.00 to 1.60 N. Glycolic acid and chromic acid concentrations were as usual 0.30 N and 0.010 N respectively.

The rate constants for all the reaction mixtures are given in next table.

<table>
<thead>
<tr>
<th>No.</th>
<th>Concentration of lithium sulphate (N)</th>
<th>Glycolic acid 0.30 N</th>
<th>Chromic acid 0.010 N</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>25°C</td>
<td>35°C</td>
</tr>
<tr>
<td>1</td>
<td>0.00</td>
<td>0.01950</td>
<td>0.02824</td>
</tr>
<tr>
<td>2</td>
<td>0.08</td>
<td>0.01603</td>
<td>0.02252</td>
</tr>
<tr>
<td>3</td>
<td>0.20</td>
<td>0.01130</td>
<td>0.01632</td>
</tr>
<tr>
<td>4</td>
<td>0.40</td>
<td>0.008570</td>
<td>0.01198</td>
</tr>
<tr>
<td>5</td>
<td>0.60</td>
<td>0.006971</td>
<td>0.009788</td>
</tr>
<tr>
<td>6</td>
<td>1.00</td>
<td>0.004841</td>
<td>0.006822</td>
</tr>
<tr>
<td>7</td>
<td>1.60</td>
<td>0.004543</td>
<td>0.006672</td>
</tr>
</tbody>
</table>

Fig. 8 shows the variation of the rate constants with the concentration of lithium sulphate, in presence of sulphuric acid.
FIG. 8 EFFECT OF LITHIUM SULPHATE & SULPHURIC ACID ON THE RATE OF REACTION BETWEEN GLYCOLIC ACID & CHROMIC ACID AT 25°C

GLYCOLIC ACID 0.300 N
CHROMIC ACID 0.010 N
SULPHURIC ACID 0.320 N

mls of LITHIUM SULPHATE IN 100 mls of reaction mixture
### TABLE 54

**Temperature coefficients**

Glycolic acid 0.30 N  
Chromic acid 0.010 N  
Sulphuric acid 0.32 N

<table>
<thead>
<tr>
<th>No.</th>
<th>Concentration of lithium sulphate (N)</th>
<th>$k_{35}/k_{25}$</th>
<th>$k_{45}/k_{35}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.00</td>
<td>1.48</td>
<td>1.53</td>
</tr>
<tr>
<td>2</td>
<td>0.08</td>
<td>1.41</td>
<td>1.53</td>
</tr>
<tr>
<td>3</td>
<td>0.20</td>
<td>1.44</td>
<td>1.52</td>
</tr>
<tr>
<td>4</td>
<td>0.40</td>
<td>1.40</td>
<td>1.51</td>
</tr>
<tr>
<td>5</td>
<td>0.60</td>
<td>1.40</td>
<td>1.41</td>
</tr>
<tr>
<td>6</td>
<td>1.00</td>
<td>1.41</td>
<td>1.40</td>
</tr>
<tr>
<td>7</td>
<td>1.60</td>
<td>1.40</td>
<td>1.40</td>
</tr>
</tbody>
</table>

The pH values of all the reaction mixtures are given in table 55.

### TABLE 55

**pH Values**

Glycolic acid 0.30 N  
Chromic acid 0.010 N  
Sulphuric acid 0.32 N

<table>
<thead>
<tr>
<th>No.</th>
<th>Concentration of lithium sulphate (N)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.00</td>
<td>1.10</td>
</tr>
<tr>
<td>2</td>
<td>0.08</td>
<td>1.15</td>
</tr>
<tr>
<td>3</td>
<td>0.20</td>
<td>1.25</td>
</tr>
<tr>
<td>4</td>
<td>0.40</td>
<td>1.30</td>
</tr>
<tr>
<td>5</td>
<td>0.60</td>
<td>1.35</td>
</tr>
<tr>
<td>6</td>
<td>1.00</td>
<td>1.40</td>
</tr>
<tr>
<td>7</td>
<td>1.60</td>
<td>1.45</td>
</tr>
</tbody>
</table>
The effect of lithium sulphate in presence of sulphuric acid was also investigated by taking the second concentration of glycolic acid (0.40 N) and keeping the concentrations of all other substances same as before.

**TABLE 56**

**Rate Constants**

<table>
<thead>
<tr>
<th>No.</th>
<th>Concentration of lithium sulphate (N)</th>
<th>k₁ (min⁻¹) 25°C</th>
<th>k₁ (min⁻¹) 35°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.00</td>
<td>0.02085</td>
<td>0.03256</td>
</tr>
<tr>
<td>2</td>
<td>0.08</td>
<td>0.01740</td>
<td>0.02600</td>
</tr>
<tr>
<td>3</td>
<td>0.20</td>
<td>0.01356</td>
<td>0.01953</td>
</tr>
<tr>
<td>4</td>
<td>0.40</td>
<td>0.009461</td>
<td>0.01480</td>
</tr>
<tr>
<td>5</td>
<td>0.60</td>
<td>0.008533</td>
<td>0.01206</td>
</tr>
<tr>
<td>6</td>
<td>1.00</td>
<td>0.006610</td>
<td>0.008576</td>
</tr>
<tr>
<td>7</td>
<td>1.60</td>
<td>0.005842</td>
<td>0.008874</td>
</tr>
</tbody>
</table>

**Summary of Results:**

The order of reaction remains one with respect to chromic acid in presence of lithium sulphate and sulphuric acid together.

The rate constant decreases continuously with increasing concentration of lithium sulphate at a constant sulphuric acid concentration. This decrease is of exponential nature (Fig.8).

Temperature coefficients are not much affected by the presence of lithium sulphate in presence of sulphuric acid.

The pH values of the reaction mixtures slightly increase with increasing concentration of lithium sulphate.
EFFECT OF SODIUM SULPHATE IN PRESENCE OF SULPHURIC ACID

In order to study the effect of sodium sulphate in presence of sulphuric acid, the concentration of the later was maintained at 0.32 N. Concentration of sodium sulphate was varied from 0.00 to 0.60 N by adding appropriate quantities of 1.00 N sodium sulphate solution to the different reaction mixtures. Concentrations of glycolic acid and chromic acid were 0.30 N and 0.010 N respectively.

The rates of reaction for all the reaction mixtures at 25, 35 and 45° C are recorded in Table 57.

**TABLE 57**  
Rate Constants

<table>
<thead>
<tr>
<th>Glycolic acid 0.30 N</th>
<th>Chromic acid 0.010 N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulphuric acid 0.32 N</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>No.</th>
<th>Concentration of sodium sulphate (N)</th>
<th>k₁ (min⁻¹)</th>
<th>25°</th>
<th>35°</th>
<th>45°</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0.00</td>
<td>0.01980</td>
<td>0.02824</td>
<td>0.04313</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>0.10</td>
<td>0.01419</td>
<td>0.02113</td>
<td>0.03063</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0.20</td>
<td>0.01140</td>
<td>0.01537</td>
<td>0.02239</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>0.30</td>
<td>0.008849</td>
<td>0.01238</td>
<td>0.01722</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>0.40</td>
<td>0.007142</td>
<td>0.01019</td>
<td>0.01484</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>0.60</td>
<td>0.005882</td>
<td>0.008061</td>
<td>0.01183</td>
<td></td>
</tr>
</tbody>
</table>

The variation of rate constant with the concentration of sodium sulphate at 25° C is shown in Fig. 9.
FIG. 9 EFFECT OF SODIUM SULPHATE ON SULPHURIC ACID ON THE RATE OF REACTION BETWEEN GLYCOLIC ACID AND CHROMIC ACID AT 25°C

GLYCOLIC 0.300N ACID
CHROMIC ACID 0.010N
SULPHURIC ACID 0.320N

Kx10^4

ML. S. OF IN SODIUM SULPHATE IN 100 ML. OF REACTION MIXTURE
### Table 58
**Temperature Coefficients**

<table>
<thead>
<tr>
<th>No.</th>
<th>Concentration of sodium sulphate (N)</th>
<th>k₃₅/k₂₅</th>
<th>k₄₅/k₃₅</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.00</td>
<td>1.48</td>
<td>1.53</td>
</tr>
<tr>
<td>2</td>
<td>0.10</td>
<td>1.49</td>
<td>1.45</td>
</tr>
<tr>
<td>3</td>
<td>0.20</td>
<td>1.53</td>
<td>1.45</td>
</tr>
<tr>
<td>4</td>
<td>0.30</td>
<td>1.40</td>
<td>1.39</td>
</tr>
<tr>
<td>5</td>
<td>0.40</td>
<td>1.43</td>
<td>1.43</td>
</tr>
<tr>
<td>6</td>
<td>0.60</td>
<td>1.45</td>
<td>1.40</td>
</tr>
</tbody>
</table>

The values of pH for the above reaction mixtures are given in table 59.

### Table 59
**pH values**

<table>
<thead>
<tr>
<th>No.</th>
<th>Concentration of sodium sulphate (N)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.00</td>
<td>1.10</td>
</tr>
<tr>
<td>2</td>
<td>0.10</td>
<td>1.20</td>
</tr>
<tr>
<td>3</td>
<td>0.20</td>
<td>1.25</td>
</tr>
<tr>
<td>4</td>
<td>0.30</td>
<td>1.30</td>
</tr>
<tr>
<td>5</td>
<td>0.40</td>
<td>1.35</td>
</tr>
<tr>
<td>6</td>
<td>0.60</td>
<td>1.40</td>
</tr>
</tbody>
</table>

The effect of sodium sulphate in presence of sulphuric acid was also investigated with the second concentration of glycolic acid (0.40 N).
The values of the rate constants for all reaction mixtures are recorded in the next table.

**TABLE 60**  
Rate Constants

Glycolic acid 0.40 N  
Chromic acid 0.010 N  
Sulphuric acid 0.32 N

<table>
<thead>
<tr>
<th>No.</th>
<th>Concentration of sodium sulphate (N)</th>
<th>( k_1 ) (min. (^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>25°C</td>
</tr>
<tr>
<td>1</td>
<td>0.00</td>
<td>0.02085</td>
</tr>
<tr>
<td>2</td>
<td>0.10</td>
<td>0.01887</td>
</tr>
<tr>
<td>3</td>
<td>0.20</td>
<td>0.01257</td>
</tr>
<tr>
<td>4</td>
<td>0.30</td>
<td>0.01036</td>
</tr>
<tr>
<td>5</td>
<td>0.40</td>
<td>0.008804</td>
</tr>
<tr>
<td>6</td>
<td>0.60</td>
<td>0.0076864</td>
</tr>
</tbody>
</table>

**Summary of Results:**

The reaction remains first order with respect to chromic acid and is not altered by the presence of sodium sulphate and sulphuric acid together.

A perusal of Table 57 shows that the rate constant decreases with increase in the concentration of sodium sulphate. Fig. 9 shows the decrease in the rate constant with increasing sodium sulphate concentration is
exponential in nature. Effect of sodium sulphate is same at the three temperatures as is evident from tables 57 and 60.

The values of the temperature coefficients are not affected by the presence of sodium sulphate and sulphuric acid together.

pH values of the reaction mixtures are slightly increased by increasing concentrations of sodium sulphate (table 59).
II - M

EFFECT OF POTASSIUM SULPHATE IN PRESENCE OF SULPHURIC ACID

In order to study how potassium sulphate affects the reaction in presence of sulphuric acid, the concentration of potassium sulphate was varied by adding appropriate amounts of 1.00 N potassium sulphate solution, while that of glycic, chromic and sulphuric acids were kept constant at 0.30 N, 0.010 N and 0.32 N respectively. Kinetics of these reaction mixtures were followed at 25, 35 and 45°C.

The rate constants for all the reaction mixtures are recorded in the following table.

<table>
<thead>
<tr>
<th>TABLE 61</th>
<th>Rate Constants</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glycolic acid 0.30 N</td>
<td>Chromic acid 0.010 N</td>
</tr>
<tr>
<td>Sulphuric acid 0.32 N</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>No.</th>
<th>Concentration of potassium sulphate (N)</th>
<th>k₁ (min⁻¹)</th>
<th>25°C</th>
<th>35°C</th>
<th>45°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.00</td>
<td>0.01950</td>
<td>0.02824</td>
<td>0.04313</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>0.10</td>
<td>0.01371</td>
<td>0.02018</td>
<td>0.02922</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0.20</td>
<td>0.01057</td>
<td>0.01510</td>
<td>0.02144</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>0.30</td>
<td>0.007923</td>
<td>0.01115</td>
<td>0.01644</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>0.40</td>
<td>0.006618</td>
<td>0.008692</td>
<td>0.01279</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>0.60</td>
<td>0.004744</td>
<td>0.006955</td>
<td>0.009576</td>
<td></td>
</tr>
</tbody>
</table>

The variation of rate constant with concentration of potassium sulphate in presence of sulphuric acid at 25°C is plotted in Fig. 10.
FIG. 10 EFFECT OF POTASSIUM SULPHATE & SULPHURIC ACID ON THE RATE OF REACTION BETWEEN GLYCOLIC ACID & CHROMIC ACID AT 25°C

GLYCOLIC ACID 0.300 N
CHROMIC ACID 0.010 N
SULPHURIC ACID 0.320 N

MLS OF IN POTASSIUM SULPHATE IN 100 MLS OF REACTION MIXTURE
The values of temperature coefficients and pH for the different reaction mixtures at 25°C are recorded in tables 62 and 63 respectively.

**TABLE 62**

Temperature Coefficients

<table>
<thead>
<tr>
<th>No.</th>
<th>Concentration of potassium sulphate (N)</th>
<th>k_{35}/k_{25}</th>
<th>k_{45}/k_{35}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.00</td>
<td>1.48</td>
<td>1.53</td>
</tr>
<tr>
<td>2</td>
<td>0.10</td>
<td>1.46</td>
<td>1.46</td>
</tr>
<tr>
<td>3</td>
<td>0.20</td>
<td>1.46</td>
<td>1.42</td>
</tr>
<tr>
<td>4</td>
<td>0.30</td>
<td>1.40</td>
<td>1.47</td>
</tr>
<tr>
<td>5</td>
<td>0.40</td>
<td>1.40</td>
<td>1.47</td>
</tr>
<tr>
<td>6</td>
<td>0.60</td>
<td>1.46</td>
<td>1.38</td>
</tr>
</tbody>
</table>

**TABLE 63**

pH Values

<table>
<thead>
<tr>
<th>No.</th>
<th>Concentration of potassium sulphate (N)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.00</td>
<td>1.10</td>
</tr>
<tr>
<td>2</td>
<td>0.10</td>
<td>1.20</td>
</tr>
<tr>
<td>3</td>
<td>0.20</td>
<td>1.25</td>
</tr>
<tr>
<td>4</td>
<td>0.30</td>
<td>1.35</td>
</tr>
<tr>
<td>5</td>
<td>0.40</td>
<td>1.40</td>
</tr>
<tr>
<td>6</td>
<td>0.60</td>
<td>1.50</td>
</tr>
</tbody>
</table>
The effect of potassium sulphate was also studied with second concentration of glycolic acid. Concentrations of all other substances were kept as before.

The rate constants for all reaction mixtures are tabulated in table 64.

<p>| TABLE 64 |
| Rate Constants |
| Glycolic acid 0.40 N | Chromic acid 0.010 N | Sulphuric acid 0.32 N |</p>
<table>
<thead>
<tr>
<th>No.</th>
<th>Concentration of potassium sulphate (N)</th>
<th>$k_1$ (min.$^{-1}$)</th>
<th>25°C</th>
<th>35°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.00</td>
<td>0.02085</td>
<td>0.03256</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>0.10</td>
<td>0.01462</td>
<td>0.02194</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0.20</td>
<td>0.01186</td>
<td>0.01765</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>0.30</td>
<td>0.009642</td>
<td>0.01361</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>0.40</td>
<td>0.007832</td>
<td>0.01170</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>0.60</td>
<td>0.005978</td>
<td>0.008478</td>
<td></td>
</tr>
</tbody>
</table>

Summary of Results:

Similar to the effects of lithium sulphate and sodium sulphate in presence of sulphuric acid, the reaction remains first order with respect to chromic acid in presence of potassium sulphate and sulphuric acid together.

However, the reaction rate is retarded by potassium sulphate in presence of sulphuric acid. This is evident from tables 61 and 64.
The decrease in rate constants due to sulphates of lithium, sodium and potassium in presence of sulphuric acid is quite comparable. In presence of 0.32 N sulphuric acid and with 0.30 N glycolic acid and 0.010 N chromic acid, 0.60 N lithium sulphate at 25°C retards the reaction from 0.01950 to 0.006971 min.\(^{-1}\) (table 53), while 0.6 N sodium sulphate under the same conditions retards the reaction to 0.005882 min.\(^{-1}\) (table 57). The corresponding value of rate constant for potassium sulphate under similar conditions is 0.004744 min.\(^{-1}\) (table 61). Thus the retarding effect due to potassium sulphate is maximum than that due to sodium sulphate, while effect of lithium sulphate is the least of the three.

A study of tables 54, 58 and 62 show that the values of temperature coefficients are not much affected by the presence of the three sulphates in presence of sulphuric acid.

The pH values of the reaction mixtures are slightly increased by the presence of the three sulphates and sulphuric acid (tables 55, 59 and 63).
EFFECT OF LITHIUM CHLORIDE IN PRESENCE OF HYDROCHLORIC ACID

The solution of lithium chloride was standardised against a standard solution of silver nitrate using dichlorofluorescein as an indicator. In order to study the effect of lithium chloride in presence of hydrochloric acid, a number of reaction mixtures were taken, in which the concentration of glycolic acid, chromic acid and hydrochloric acid were kept at 0.30 N, 0.010 N and 0.32 N respectively. The concentration of lithium chloride was varied from 0.00 to 1.00 N.

In table below the rate constants of all reaction mixtures are tabulated.

<table>
<thead>
<tr>
<th>No.</th>
<th>Concentration of lithium chloride (N)</th>
<th>Glycolic acid 0.30 N</th>
<th>Chromic acid 0.010 N</th>
<th>Hydrochloric acid 0.32 N</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.00</td>
<td>0.02499</td>
<td>0.04048</td>
<td>0.06072</td>
</tr>
<tr>
<td>2</td>
<td>0.10</td>
<td>0.02174</td>
<td>0.03388</td>
<td>0.04597</td>
</tr>
<tr>
<td>3</td>
<td>0.20</td>
<td>0.01888</td>
<td>0.02985</td>
<td>0.03786</td>
</tr>
<tr>
<td>4</td>
<td>0.40</td>
<td>0.01443</td>
<td>0.02142</td>
<td>0.02844</td>
</tr>
<tr>
<td>5</td>
<td>0.60</td>
<td>0.01184</td>
<td>0.01712</td>
<td>0.02274</td>
</tr>
<tr>
<td>6</td>
<td>1.00</td>
<td>0.007379</td>
<td>0.01121</td>
<td>0.01455</td>
</tr>
</tbody>
</table>
FIG. 11 EFFECT OF LITHIUM CHLORIDE & HYDROCHLORIC ACID ON THE RATE OF REACTION BETWEEN GLYCOLIC ACID & CHROMIC ACID AT 25°C

GLYCOLIC ACID 0.300N
CHROMIC ACID 0.010N
HYDROCHLORIC ACID 0.320N

Mls of 2N Lithium chloride in 100 mls of Reaction mixture
Fig. 11 shows the variation of rate constant with the concentration of lithium chloride in presence of hydrochloric acid at 25°C.

**TABLE 66**

<table>
<thead>
<tr>
<th></th>
<th>Glycolic acid 0.30 N</th>
<th>Chromic acid 0.010 N</th>
<th>Hydrochloric acid 0.32 N</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Concentration of lithium chloride (N)</td>
<td>$k_{35}/k_{25}$</td>
<td>$k_{45}/k_{35}$</td>
</tr>
<tr>
<td>No.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0.00</td>
<td>1.61</td>
<td>1.80</td>
</tr>
<tr>
<td>2</td>
<td>0.10</td>
<td>1.55</td>
<td>1.36</td>
</tr>
<tr>
<td>3</td>
<td>0.20</td>
<td>1.53</td>
<td>1.32</td>
</tr>
<tr>
<td>4</td>
<td>0.40</td>
<td>1.48</td>
<td>1.34</td>
</tr>
<tr>
<td>5</td>
<td>0.60</td>
<td>1.45</td>
<td>1.34</td>
</tr>
<tr>
<td>6</td>
<td>1.00</td>
<td>1.52</td>
<td>1.31</td>
</tr>
</tbody>
</table>

The pH values of the reaction mixtures at 25°C are recorded in table 67.

**TABLE 67**

<table>
<thead>
<tr>
<th></th>
<th>Glycolic acid 0.30 N</th>
<th>Chromic acid 0.010 N</th>
<th>Hydrochloric acid 0.32 N</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Concentration of lithium chloride (N)</td>
<td>pH</td>
<td></td>
</tr>
<tr>
<td>No.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0.00</td>
<td>0.90</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>0.10</td>
<td>0.85</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0.20</td>
<td>0.85</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>0.40</td>
<td>0.80</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>0.60</td>
<td>0.75</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>1.00</td>
<td>0.75</td>
<td></td>
</tr>
</tbody>
</table>
The effect of lithium chloride in presence of hydrochloric acid was also studied at 25 and 35°C by taking 0.40 N glycolic acid. Concentrations of all other substances were kept same as before.

The rate constants for all the reaction mixtures are recorded in table 68.

**TABLE 68**

*Rate Constants*

<table>
<thead>
<tr>
<th>Glycolic acid 0.4 N</th>
<th>Chromic acid 0.010 N</th>
<th>Hydrochloric acid 0.32 N</th>
</tr>
</thead>
<tbody>
<tr>
<td>No.</td>
<td>Concentration of lithium chloride (N)</td>
<td>$k_1$ (min.$^{-1}$) @ 25°C</td>
</tr>
<tr>
<td>-----</td>
<td>----------------------------------------</td>
<td>----------------</td>
</tr>
<tr>
<td>1</td>
<td>0.00</td>
<td>0.02552</td>
</tr>
<tr>
<td>2</td>
<td>0.10</td>
<td>0.02241</td>
</tr>
<tr>
<td>3</td>
<td>0.20</td>
<td>0.01922</td>
</tr>
<tr>
<td>4</td>
<td>0.40</td>
<td>0.01466</td>
</tr>
<tr>
<td>5</td>
<td>0.60</td>
<td>0.01184</td>
</tr>
<tr>
<td>6</td>
<td>1.00</td>
<td>0.008160</td>
</tr>
</tbody>
</table>

**Summary of Results:**

The order of reaction with respect to chromic acid remains unaltered by the presence of lithium chloride.
and hydrochloric acid together. However, the rate of reaction between glycolic acid and chromic acid in presence of hydrochloric acid, is decreased continuously by the increasing concentrations. of lithium chloride (tables 65 and 68). A glance at fig. 11 shows that this decrease in rate constant with concentration of lithium chloride is of exponential nature. Effect of lithium chloride at 35 and 45°C is similar to that at 25°C (tables 65 and 68).

The temperature coefficients are not appreciably affected by increasing concentrations of lithium chloride (table 66).

The values of pH of reaction mixtures are very slightly, decreased by the increasing lithium chloride concentration (table 67).
EFFECT OF SODIUM CHLORIDE IN PRESENCE OF HYDROCHLORIC ACID

In order to study the effect of sodium chloride in presence of hydrochloric acid, various reaction mixtures were taken, in which the concentration of glycolic, chromic and hydrochloric acids were 0.30, 0.010 and 0.32 N respectively. Concentration of sodium chloride was varied from 0.00 to 1.00 N. Kinetic data for these reaction mixtures was measured at 25, 35 and 45°C.

The rate constants of the various reaction mixtures at the three temperatures are recorded in table 69.

<table>
<thead>
<tr>
<th>No.</th>
<th>Concentration of sodium chloride (N)</th>
<th>k₁ (min⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>25°C</td>
</tr>
<tr>
<td>1</td>
<td>0.00</td>
<td>0.02492</td>
</tr>
<tr>
<td>2</td>
<td>0.10</td>
<td>0.02153</td>
</tr>
<tr>
<td>3</td>
<td>0.20</td>
<td>0.01830</td>
</tr>
<tr>
<td>4</td>
<td>0.40</td>
<td>0.01387</td>
</tr>
<tr>
<td>5</td>
<td>0.60</td>
<td>0.01081</td>
</tr>
<tr>
<td>6</td>
<td>1.00</td>
<td>0.006995</td>
</tr>
</tbody>
</table>

Fig. 12 shows the variation of rate constant with the concentration of sodium chloride in presence of hydrochloric acid at 25°C.
FIG. 12 EFFECT OF SODIUM CHLORIDE & HYDROCHLORIC ACID ON THE RATE OF REACTION BETWEEN GLYCOLIC ACID & CHROMIC ACID AT 25°C

GLYCOLIC ACID 0.300N
CHROMIC ACID 0.010N
HYDROCHLORIC ACID 0.320N

Mls of 2N SODIUM CHLORIDE IN 100 mls OF REACTION MIXTURE
The values of temperature coefficients for the above reaction mixtures are tabulated in the next table.

**TABLE 70**

**Temperature Coefficients**

<table>
<thead>
<tr>
<th></th>
<th>Glycolic acid 0.30 N</th>
<th>Chromic acid 0.010 N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrochloric acid 0.32 N</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>No.</th>
<th>Concentration of sodium chloride (N)</th>
<th>$k_{35}/k_{25}$</th>
<th>$k_{45}/k_{35}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.00</td>
<td>1.61</td>
<td>1.50</td>
</tr>
<tr>
<td>2</td>
<td>0.10</td>
<td>1.47</td>
<td>1.34</td>
</tr>
<tr>
<td>3</td>
<td>0.20</td>
<td>1.45</td>
<td>1.30</td>
</tr>
<tr>
<td>4</td>
<td>0.40</td>
<td>1.46</td>
<td>1.31</td>
</tr>
<tr>
<td>5</td>
<td>0.60</td>
<td>1.40</td>
<td>1.34</td>
</tr>
<tr>
<td>6</td>
<td>1.00</td>
<td>1.49</td>
<td>1.30</td>
</tr>
</tbody>
</table>

The values of pH for the above reaction mixtures at 25°C are given in table 71.

**TABLE 71**

**pH values**

<table>
<thead>
<tr>
<th></th>
<th>Glycolic acid 0.30 N</th>
<th>Chromic acid 0.010 N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrochloric acid 0.32 N</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>No.</th>
<th>Concentration of sodium chloride (N)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.00</td>
<td>0.90</td>
</tr>
<tr>
<td>2</td>
<td>0.10</td>
<td>0.90</td>
</tr>
<tr>
<td>3</td>
<td>0.20</td>
<td>0.85</td>
</tr>
<tr>
<td>4</td>
<td>0.40</td>
<td>0.80</td>
</tr>
<tr>
<td>5</td>
<td>0.60</td>
<td>0.80</td>
</tr>
<tr>
<td>6</td>
<td>1.00</td>
<td>0.75</td>
</tr>
</tbody>
</table>
The effect of sodium chloride in presence of hydrochloric acid was also studied with second concentration of glycolic acid (0.40 N). Concentration of chromic acid was kept constant at 0.010 N, while the concentration of sodium chloride was varied from 0.00 to 1.00 N as before and kinetic measurements were made at 25 and 35°C.

The values of all the reaction mixtures are summarized in Table 72.

<table>
<thead>
<tr>
<th>TABLE 72</th>
<th>Rate constants</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glycolic acid 0.40 N</td>
<td>Chromic acid 0.010 N</td>
</tr>
<tr>
<td>Hydrochloric acid 0.32 N</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>No.</th>
<th>Concentration of sodium chloride (N)</th>
<th>k₁ (min⁻¹) 25°C</th>
<th>k₁ (min⁻¹) 35°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.00</td>
<td>0.02552</td>
<td>0.04121</td>
</tr>
<tr>
<td>2</td>
<td>0.10</td>
<td>0.02193</td>
<td>0.03321</td>
</tr>
<tr>
<td>3</td>
<td>0.20</td>
<td>0.01898</td>
<td>0.02978</td>
</tr>
<tr>
<td>4</td>
<td>0.40</td>
<td>0.01433</td>
<td>0.00293</td>
</tr>
<tr>
<td>5</td>
<td>0.60</td>
<td>0.01142</td>
<td>0.01765</td>
</tr>
<tr>
<td>6</td>
<td>1.00</td>
<td>0.007870</td>
<td>0.01194</td>
</tr>
</tbody>
</table>

Summary of Results:

As in case of lithium chloride, the order of reaction with respect to chromic acid remains one in presence
of sodium chloride and hydrochloric acid together.

With increase in the concentration of sodium chloride a continuous decrease in the value of rate constant is observed (table 69).

The values of temperature coefficients are slightly decreased by the presence of sodium chloride in the reaction mixtures (table 70). Effect of sodium chloride is same at 35 and 45°C as is on 25°C (table 69).

The pH values of the reaction mixtures are very slightly decreased by increasing amounts of sodium chloride in the reaction mixtures (table 71).
II - P

EFFECT OF POTASSIUM CHLORIDE IN PRESENCE OF HYDROCHLORIC ACID

In order to investigate how potassium chloride affects the rate of reaction in presence of hydrochloric acid the same concentrations of the acids as were used in case of lithium and sodium chlorides, were taken in each reaction mixture. Potassium chloride concentrations were also similar to that were kept in case of sodium chloride. Kinetic measurements were made at 25, 35 and 45°C.

Rate constants obtained for all the reaction mixtures are recorded in table 73.

**TABLE 73**

**Rate constants**

<table>
<thead>
<tr>
<th>Glycolic acid 0.30 N</th>
<th>Chromic acid 0.010 N</th>
<th>Hydrochloric acid 0.32 N</th>
</tr>
</thead>
<tbody>
<tr>
<td>No.</td>
<td>Concentration of potassium chloride (N)</td>
<td>k_1 (min.⁻¹) 25°C</td>
</tr>
<tr>
<td>-----</td>
<td>-------------------------------------</td>
<td>----------------</td>
</tr>
<tr>
<td>1</td>
<td>0.00</td>
<td>0.02492</td>
</tr>
<tr>
<td>2</td>
<td>0.10</td>
<td>0.02094</td>
</tr>
<tr>
<td>3</td>
<td>0.20</td>
<td>0.01778</td>
</tr>
<tr>
<td>4</td>
<td>0.40</td>
<td>0.01302</td>
</tr>
<tr>
<td>5</td>
<td>0.60</td>
<td>0.009840</td>
</tr>
<tr>
<td>6</td>
<td>1.00</td>
<td>0.005986</td>
</tr>
</tbody>
</table>

Fig. 13 shows the variation of rate constant with increasing concentrations of potassium chloride, in presence
FIG. 13 EFFECT OF POTASSIUM CHLORIDE & HYDROCHLORIC ACID ON THE RATE OF REACTION BETWEEN GLYCOLIC ACID AND CHROMIC ACID AT 25°C

GLYCOLIC ACID 0.300N
CHROMIC ACID 0.010N
HYDROCHLORIC 0.320 N ACID

$K_1 \times 10^4$

mLs of 2 N Potassium chloride in 100 mLs of reaction mixture
of a constant hydrochloric acid concentration at 25°C.

The values of the temperature coefficients and
the pH of reaction mixtures are recorded in tables 74 and
75, respectively.

**TABLE 74**

Temperature coefficients

<table>
<thead>
<tr>
<th>Glycolic acid 0.30 N</th>
<th>Chromic acid 0.010 N</th>
<th>Hydrochloric acid 0.32 N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration of potassium chloride (N)</td>
<td>k₄5/k₂₅</td>
<td>k₄5/k₃₅</td>
</tr>
<tr>
<td>1</td>
<td>0.00</td>
<td>1.61</td>
</tr>
<tr>
<td>2</td>
<td>0.10</td>
<td>1.37</td>
</tr>
<tr>
<td>3</td>
<td>0.20</td>
<td>1.38</td>
</tr>
<tr>
<td>4</td>
<td>0.40</td>
<td>1.44</td>
</tr>
<tr>
<td>5</td>
<td>0.60</td>
<td>1.44</td>
</tr>
<tr>
<td>6</td>
<td>1.00</td>
<td>1.36</td>
</tr>
</tbody>
</table>

**TABLE 75**

pH Values

<table>
<thead>
<tr>
<th>Glycolic acid 0.30 N</th>
<th>Chromic acid 0.010 N</th>
<th>Hydrochloric acid 0.32 N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration of potassium chloride (N)</td>
<td>pH</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0.00</td>
<td>0.90</td>
</tr>
<tr>
<td>2</td>
<td>0.10</td>
<td>0.85</td>
</tr>
<tr>
<td>3</td>
<td>0.20</td>
<td>0.85</td>
</tr>
<tr>
<td>4</td>
<td>0.40</td>
<td>0.85</td>
</tr>
<tr>
<td>5</td>
<td>0.60</td>
<td>0.80</td>
</tr>
<tr>
<td>6</td>
<td>1.00</td>
<td>0.75</td>
</tr>
</tbody>
</table>
The effect of potassium chloride in presence of hydrochloric acid was also investigated with 0.40 N glycolic acid. Concentrations of other chemicals were kept as before. The rate constants for all the above reaction mixtures are tabulated in next table.

**TABLE 76**

<table>
<thead>
<tr>
<th>Rate constants</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glycolic acid 0.40 N</td>
</tr>
<tr>
<td>Hydrochloric acid 0.32 N</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>No.</th>
<th>Concentration of potassium chloride (N)</th>
<th>k₁ (min⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>25°C</td>
</tr>
<tr>
<td>1</td>
<td>0.00</td>
<td>0.02552</td>
</tr>
<tr>
<td>2</td>
<td>0.10</td>
<td>0.02188</td>
</tr>
<tr>
<td>3</td>
<td>0.20</td>
<td>0.01862</td>
</tr>
<tr>
<td>4</td>
<td>0.40</td>
<td>0.01313</td>
</tr>
<tr>
<td>5</td>
<td>0.60</td>
<td>0.01082</td>
</tr>
<tr>
<td>6</td>
<td>1.00</td>
<td>0.006645</td>
</tr>
</tbody>
</table>

**Summary of Results:**

From the kinetic data it was observed that like lithium and sodium chlorides, potassium chloride also, does not alter the order of reaction with respect to chromic acid, which remains one.

Similar to the effects of lithium and sodium chlorides, the rate constant is also decreased continuously by the presence of potassium chloride and hydrochloric acid.
together (tables 73 and 76) and the decrease with concentrations of potassium chloride is of exponential nature as shown by Fig. 13.

In case of lithium chloride (table 65), the rate constant at 25°C is decreased from 0.02492 min⁻¹ to 0.007379 min⁻¹ for increase in concentration of lithium chloride from 0.00 to 1.00 M. For the same increase in concentration of sodium chloride (table 69), the rate constant is decreased to 0.006995 min⁻¹, while the corresponding value in case of potassium chloride is 0.005986 min⁻¹. Thus for the same increase in concentration of the chlorides, the decrease in rate constant is more in case of potassium chloride than in case of sodium chloride, while the decrease is minimum of the three in case of lithium chloride. From Fig. 11, 12 and 13, it is evident that the variation of rate constant with the concentration of the three chlorides is of same nature.

From the study of tables 66, 70 and 74, it is clear that lithium chloride does not appreciably affect the temperature coefficients, while sodium chloride slightly decreases it. The decrease in value of temperature coefficients is more in case of potassium chloride than that with sodium chloride.

The values of pH of the reaction mixtures are slightly decreased by the three chlorides (tables 67, 71 & 75).
EFFECT OF MANGANESE SULPHATE

The effect of manganese sulphate on the rate of reaction between glycolic acid and chromic acid in aqueous medium was studied at 25, 35 and 45°C. Concentrations of glycolic acid and chromic acid were kept at 0.30 N and 0.010 N respectively. It has been observed that the rate of reaction is first decreased with increasing concentrations of manganese sulphate and then increased at higher concentrations. Hence the concentrations of manganese sulphate is selected as to bring out its effect clearly.

The rate constants for the different reaction mixtures containing varying amounts of MnSO₄.4H₂O at 25, 35 and 45°C are recorded in table 7.7.

### TABLE 7.7

<table>
<thead>
<tr>
<th>Glycolic acid 0.30 N</th>
<th>Chromic acid 0.010 N</th>
<th>Rate constants</th>
<th>25°C</th>
<th>35°C</th>
<th>45°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>No.</td>
<td>Concentration of MnSO₄.4H₂O (gm. in 100 ml)</td>
<td>k₁ (min⁻¹)</td>
<td>25°C</td>
<td>35°C</td>
<td>45°C</td>
</tr>
<tr>
<td>---</td>
<td>----------------</td>
<td>-------</td>
<td>------</td>
<td>------</td>
<td>------</td>
</tr>
<tr>
<td>1</td>
<td>0.00</td>
<td>0.002702</td>
<td>0.004718</td>
<td>0.008520</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>0.02</td>
<td>0.002557</td>
<td>0.004595</td>
<td>0.008053</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0.08</td>
<td>0.002460</td>
<td>0.004376</td>
<td>0.007738</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>0.20</td>
<td>0.002282</td>
<td>0.004038</td>
<td>0.007083</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>1.00</td>
<td>0.002045</td>
<td>0.003684</td>
<td>0.006463</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>2.00</td>
<td>0.002241</td>
<td>0.003939</td>
<td>0.007087</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>3.00</td>
<td>0.002492</td>
<td>0.004334</td>
<td>0.007716</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>5.00</td>
<td>0.002722</td>
<td>0.004779</td>
<td>0.008750</td>
<td></td>
</tr>
</tbody>
</table>
FIG. 14 - EFFECT OF MANGANESE SULPHATE ON THE RATE OF REACTION BETWEEN GLYCOLIC ACID & CHROMIC ACID
AT 25°C

GLYCOLIC ACID 0.300 N
CHROMIC ACID 0.010 N

K1 x 10^4

GM. OF MnSO₄·4H₂O IN 100mL OF REACTION MIXTURE
Fig. 14 shows the variation of rate constant with increasing amounts of manganese sulphate.

The values of temperature coefficients for all the above reaction mixtures are tabulated in Table 78.

| TABLE 78 |
| Temperature Coefficients |

<table>
<thead>
<tr>
<th>Glycolic acid 0.30 N</th>
<th>Chromic acid 0.010 N</th>
</tr>
</thead>
<tbody>
<tr>
<td>No.</td>
<td>Concentration of MnSO₄·4H₂O (gm. in 100 ml)</td>
</tr>
<tr>
<td>----------------------</td>
<td>-----------------------------------------------</td>
</tr>
<tr>
<td>1</td>
<td>0.00</td>
</tr>
<tr>
<td>2</td>
<td>0.02</td>
</tr>
<tr>
<td>3</td>
<td>0.08</td>
</tr>
<tr>
<td>4</td>
<td>0.20</td>
</tr>
<tr>
<td>5</td>
<td>1.00</td>
</tr>
<tr>
<td>6</td>
<td>2.00</td>
</tr>
<tr>
<td>7</td>
<td>3.00</td>
</tr>
<tr>
<td>8</td>
<td>5.00</td>
</tr>
</tbody>
</table>

The pH values of all the reaction mixtures at 25°C are given in Table 79.

| TABLE 79 |
| pH Values |

<table>
<thead>
<tr>
<th>Glycolic acid 0.30 N</th>
<th>Chromic acid 0.010 N</th>
</tr>
</thead>
<tbody>
<tr>
<td>No.</td>
<td>Concentration of MnSO₄·4H₂O (gm. in 100 ml)</td>
</tr>
<tr>
<td>----------------------</td>
<td>-----------------------------------------------</td>
</tr>
<tr>
<td>1</td>
<td>0.00</td>
</tr>
<tr>
<td>2</td>
<td>0.02</td>
</tr>
<tr>
<td>3</td>
<td>0.08</td>
</tr>
<tr>
<td>4</td>
<td>0.20</td>
</tr>
<tr>
<td>5</td>
<td>1.00</td>
</tr>
<tr>
<td>6</td>
<td>2.00</td>
</tr>
<tr>
<td>7</td>
<td>3.00</td>
</tr>
<tr>
<td>8</td>
<td>5.00</td>
</tr>
</tbody>
</table>
The effect of manganese sulphate was also studied by taking the second concentration of glycolic acid. The rate constants of all the reaction mixtures are recorded in Table 30.

<table>
<thead>
<tr>
<th>Glycolic acid 0.40 N</th>
<th>Chromic acid 0.010 N</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Rate Constants</strong></td>
<td></td>
</tr>
<tr>
<td>No.</td>
<td>Concentration of ( \text{MnSO}_4 \cdot \text{4H}_2\text{O} ) (gm. in 100 ml)</td>
</tr>
<tr>
<td>1</td>
<td>0.00</td>
</tr>
<tr>
<td>2</td>
<td>0.02</td>
</tr>
<tr>
<td>3</td>
<td>0.08</td>
</tr>
<tr>
<td>4</td>
<td>0.20</td>
</tr>
<tr>
<td>5</td>
<td>1.00</td>
</tr>
<tr>
<td>6</td>
<td>2.00</td>
</tr>
<tr>
<td>7</td>
<td>3.00</td>
</tr>
<tr>
<td>8</td>
<td>5.00</td>
</tr>
</tbody>
</table>

**Summary of Results:**

The order of reaction with respect to chromic acid is not altered by the presence of manganese sulphate.

The rate constant is first decreased and then increased by the increasing amounts of manganese sulphate in the reaction mixtures (Tables 77 and 80). This is similar to the effect of lithium sulphate.

The values of temperature coefficients and pH are not much affected by the presence of manganese sulphate (Tables 78 and 79).
II - R

EFFECT OF MANGANESE SULPHATE IN PRESENCE OF SULPHURIC ACID

The kinetics of the reaction between glycolic acid and chromic acid in aqueous medium was also followed in presence of manganese sulphate and sulphuric acid together. A number of reaction mixtures were prepared with 0.30 N glycolic acid, 0.010 N chromic acid and 0.32 N sulphuric acid and with varying amounts of manganese sulphate. Concentration of \( \text{MnSO}_4 \cdot 4\text{H}_2\text{O} \) was varied from 0.00 to 5.00 gm. in 100 ml of the reaction mixture.

The values of the rate constants for all these reaction mixtures are recorded in table 81.

**TABLE 81**
Rate Constants

<table>
<thead>
<tr>
<th>No.</th>
<th>Concentration of ( \text{MnSO}_4 \cdot 4\text{H}_2\text{O} ) (gm. in 100 ml)</th>
<th>( k_1 ) (min.(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>25(^\circ)</td>
<td>35(^\circ)</td>
</tr>
<tr>
<td>1</td>
<td>0.000</td>
<td>0.01950</td>
</tr>
<tr>
<td>2</td>
<td>0.005</td>
<td>0.002981</td>
</tr>
<tr>
<td>3</td>
<td>0.020</td>
<td>0.002625</td>
</tr>
<tr>
<td>4</td>
<td>0.200</td>
<td>0.002581</td>
</tr>
<tr>
<td>5</td>
<td>1.000</td>
<td>0.002416</td>
</tr>
<tr>
<td>6</td>
<td>5.000</td>
<td>0.002074</td>
</tr>
</tbody>
</table>

The values of the temperature coefficients and pH of the above are recorded in tables 82 and 83 respectively.
### TABLE 62

Temperature Coefficients

<table>
<thead>
<tr>
<th>No</th>
<th>Glycolic acid 0.30 N</th>
<th>Chromic acid 0.010 N</th>
<th>Sulphuric acid 0.32 N</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Concentration of MnSO₄·4H₂O (gm. in 100 ml)</td>
<td>k₃₅/k₂₅</td>
<td>k₄₅/k₃₅</td>
</tr>
<tr>
<td>1</td>
<td>0.000</td>
<td>1.48</td>
<td>1.53</td>
</tr>
<tr>
<td>2</td>
<td>0.005</td>
<td>2.11</td>
<td>2.21</td>
</tr>
<tr>
<td>3</td>
<td>0.020</td>
<td>1.90</td>
<td>1.98</td>
</tr>
<tr>
<td>4</td>
<td>0.200</td>
<td>1.81</td>
<td>1.83</td>
</tr>
<tr>
<td>5</td>
<td>1.000</td>
<td>1.82</td>
<td>1.84</td>
</tr>
<tr>
<td>6</td>
<td>5.000</td>
<td>1.80</td>
<td>1.89</td>
</tr>
</tbody>
</table>

### TABLE 63

pH Values

<table>
<thead>
<tr>
<th>Glycolic acid 0.30 N</th>
<th>Chromic acid 0.010 N</th>
<th>Sulphuric acid 0.32 N</th>
</tr>
</thead>
<tbody>
<tr>
<td>No.</td>
<td>Concentration of MnSO₄·4H₂O (gm. in 100 ml)</td>
<td>pH</td>
</tr>
<tr>
<td>1</td>
<td>0.000</td>
<td>1.10</td>
</tr>
<tr>
<td>2</td>
<td>0.005</td>
<td>1.10</td>
</tr>
<tr>
<td>3</td>
<td>0.020</td>
<td>1.10</td>
</tr>
<tr>
<td>4</td>
<td>0.200</td>
<td>1.10</td>
</tr>
<tr>
<td>5</td>
<td>1.000</td>
<td>1.10</td>
</tr>
<tr>
<td>6</td>
<td>5.000</td>
<td>1.15</td>
</tr>
</tbody>
</table>
The effect of manganese sulphate in presence of sulphuric acid was also studied with 0.40 M glycolic acid. Concentration of chromic acid and sulphuric acid were kept at 0.010 and 0.32 N respectively, while that of manganese sulphate was varied from 0.00 to 5.00 gm. per 100 ml of reaction mixture.

Table 84 contains the values of the rate constants of the above reaction mixtures.

<table>
<thead>
<tr>
<th>No.</th>
<th>Concentration of MnSO₄·4H₂O (gm. in 100 ml)</th>
<th>k₁ (min⁻¹)</th>
<th>25°C</th>
<th>35°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.000</td>
<td>0.02085</td>
<td>0.03256</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>0.005</td>
<td>0.005689</td>
<td>0.01258</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0.020</td>
<td>0.004671</td>
<td>0.009369</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>0.200</td>
<td>0.004482</td>
<td>0.008602</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>1.000</td>
<td>0.004204</td>
<td>0.007568</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>5.000</td>
<td>0.003837</td>
<td>0.006904</td>
<td></td>
</tr>
</tbody>
</table>

Summary of Results:

From the kinetic data of various reaction mixtures the values of rate constants were found to be fairly constant showing that the order of reaction with respect to
chromic acid remains one in presence of manganese sulphate and sulphuric acid together.

A study of tables 81 and 84 shows a very large decrease in the rate constants by the presence of very small amounts of manganese sulphate. The rate of reaction at 25°C is decreased from 0.01950 min$^{-1}$ to 0.002981 min$^{-1}$ by the presence of 0.005 gm. of MnSO$_4$$\cdot$4H$_2$O in 100 ml of reaction mixture, when the concentration of glycolic, chromic and sulphuric acids were 0.30, 0.010 and 0.32 N respectively.

As is evident from tables 81 and 84, the decrease in the rate constant with concentration of manganese sulphate is of exponential nature.

Temperature coefficient is seen to increase by the presence of manganese sulphate (table 82), while the pH values of the reaction mixtures are not affected (table 83).
II - 3

EFFECT OF MANGANESE SULPHATE IN PRESENCE OF HYDROCHLORIC ACID

The effect of manganese sulphate in presence of hydrochloric acid was studied with glycolic acid and chromic acid concentrations 0.30 N and 0.010 N respectively. Concentration of hydrochloric acid used was 0.32 N, while that of manganese sulphate was varied from 0.00 to 5.00 gm. in 100 ml of reaction mixture.

The rate constants for various reaction mixtures at the three temperatures are recorded in table 85.

| TABLE 85 |
| Rate Constants |
| Glycolic acid 0.30 N | Chromic acid 0.010 N |
| Hydrochloric acid 0.32 N |

<table>
<thead>
<tr>
<th>No.</th>
<th>Concentration of MnSO₄·4H₂O (gm. in 100 ml)</th>
<th>k₁ (min⁻¹)</th>
<th>25°C</th>
<th>35°C</th>
<th>45°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.000</td>
<td>0.00406</td>
<td>0.004048</td>
<td>0.004072</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>0.005</td>
<td>0.004068</td>
<td>0.005916</td>
<td>0.006781</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0.020</td>
<td>0.002893</td>
<td>0.00616</td>
<td>0.01281</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>0.020</td>
<td>0.002292</td>
<td>0.004492</td>
<td>0.008134</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>1.000</td>
<td>0.002201</td>
<td>0.004402</td>
<td>0.007991</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>5.000</td>
<td>0.002120</td>
<td>0.004271</td>
<td>0.007816</td>
<td></td>
</tr>
</tbody>
</table>

The temperature coefficients and the values of pH of the different reaction mixtures at 25°C are tabulated in tables 86 and 87 respectively.
### Table 86
**Temperature Coefficients**

<table>
<thead>
<tr>
<th>No.</th>
<th>Concentration of MnSO₄·4H₂O (gm. in 100 ml)</th>
<th>k₄₅/k₂₅</th>
<th>k₄₅/k₅₅</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.000</td>
<td>1.61</td>
<td>1.50</td>
</tr>
<tr>
<td>2</td>
<td>0.005</td>
<td>2.40</td>
<td>2.33</td>
</tr>
<tr>
<td>3</td>
<td>0.020</td>
<td>2.16</td>
<td>2.22</td>
</tr>
<tr>
<td>4</td>
<td>0.200</td>
<td>1.96</td>
<td>1.81</td>
</tr>
<tr>
<td>5</td>
<td>1.000</td>
<td>2.00</td>
<td>1.81</td>
</tr>
<tr>
<td>6</td>
<td>5.000</td>
<td>1.91</td>
<td>1.85</td>
</tr>
</tbody>
</table>

### Table 87
**pH Values**

<table>
<thead>
<tr>
<th>No.</th>
<th>Concentration of MnSO₄·4H₂O (gm. in 100 ml)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.000</td>
<td>0.90</td>
</tr>
<tr>
<td>2</td>
<td>0.005</td>
<td>0.90</td>
</tr>
<tr>
<td>3</td>
<td>0.020</td>
<td>0.95</td>
</tr>
<tr>
<td>4</td>
<td>0.200</td>
<td>0.95</td>
</tr>
<tr>
<td>5</td>
<td>1.000</td>
<td>0.95</td>
</tr>
<tr>
<td>6</td>
<td>5.000</td>
<td>1.10</td>
</tr>
</tbody>
</table>

The effect of manganese sulphate was also investigated with the second concentration of glycolic acid (0.40 N). The concentrations of all other acids were kept as before.

The rate constants for all the reaction mixtures are given in Table 88.
TABLE 88
Rate Constants
Glycolic acid 0.40 N
Chromic acid 0.010 N
Hydrochloric acid 0.32 N

<table>
<thead>
<tr>
<th>No.</th>
<th>Concentration of MnSO₄·4H₂O (gm. in 100 ml)</th>
<th>k₁ (min⁻¹)</th>
<th>25°C</th>
<th>35°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.270</td>
<td>0.02552</td>
<td>0.04121</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>0.005</td>
<td>0.007006</td>
<td>0.01579</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0.020</td>
<td>0.003906</td>
<td>0.009251</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>0.200</td>
<td>0.003558</td>
<td>0.007068</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>1.000</td>
<td>0.003411</td>
<td>0.006651</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>5.000</td>
<td>0.003214</td>
<td>0.006215</td>
<td></td>
</tr>
</tbody>
</table>

Summary of Results:

The order of reaction with respect to chromic acid is not altered by the presence of manganese sulphate and hydrochloric acid together.

A pronounced decrease in rate constant due to the presence of manganese sulphate in presence of hydrochloric acid is evident from tables 85 and 88. In presence of hydrochloric acid the change in rate constant with concentration of manganese sulphate is of exponential nature. This is also evident from a close study of the tables 85 and 88. Effect of manganese sulphate at 35 and 45°C is similar to that at 25°C.

The values of temperature coefficients are increased, slightly, by the presence of manganese sulphate (table 86). The pH values of the reaction mixtures are very slightly increased.
The effect of manganese sulphate in presence of o-phosphoric acid was also studied. The concentration of o-phosphoric acid used in each reaction mixture was 0.50 N, while the concentration of manganese sulphate was varied from 0.00 to 2.00 gm. MnSO₄·4H₂O in 100 ml of reaction mixture. Glycolic acid and chromic acid concentrations were as usual 0.30 and 0.010 N respectively.

The rate constants of various reaction mixtures at 25°C, 35°C and 45°C are recorded in table 89.

<table>
<thead>
<tr>
<th>Glycolic acid 0.30 N</th>
<th>Chromic acid 0.010 N</th>
<th>o-Phosphoric acid 0.50 N</th>
</tr>
</thead>
<tbody>
<tr>
<td>No.</td>
<td>Concentration of MnSO₄·4H₂O (gm. in 100 ml)</td>
<td>k₁ (min⁻¹)</td>
</tr>
<tr>
<td>1</td>
<td>0.000</td>
<td>0.003580</td>
</tr>
<tr>
<td>2</td>
<td>0.020</td>
<td>0.001382</td>
</tr>
<tr>
<td>3</td>
<td>0.200</td>
<td>0.001195</td>
</tr>
<tr>
<td>4</td>
<td>1.000</td>
<td>0.001768</td>
</tr>
<tr>
<td>5</td>
<td>2.000</td>
<td>0.002517</td>
</tr>
</tbody>
</table>

The values of temperature coefficients and pH for the above reaction mixtures are recorded in tables 90 and 91 respectively.
### TABLE 90
Temperature Coefficients

<table>
<thead>
<tr>
<th>No.</th>
<th>Concentration of MnSO₄·4H₂O (gm. in 100 ml)</th>
<th>k₃₅/k₂₅</th>
<th>k₄₅/k₃₅</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.000</td>
<td>1.63</td>
<td>1.62</td>
</tr>
<tr>
<td>2</td>
<td>0.020</td>
<td>2.43</td>
<td>2.11</td>
</tr>
<tr>
<td>3</td>
<td>0.200</td>
<td>2.20</td>
<td>2.13</td>
</tr>
<tr>
<td>4</td>
<td>1.000</td>
<td>2.12</td>
<td>2.09</td>
</tr>
<tr>
<td>5</td>
<td>2.000</td>
<td>2.12</td>
<td>2.20</td>
</tr>
</tbody>
</table>

### TABLE 91
pH Values

<table>
<thead>
<tr>
<th>No.</th>
<th>Concentration of MnSO₄·4H₂O (gm. in 100 ml)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.000</td>
<td>1.65</td>
</tr>
<tr>
<td>2</td>
<td>0.020</td>
<td>1.65</td>
</tr>
<tr>
<td>3</td>
<td>0.200</td>
<td>1.70</td>
</tr>
<tr>
<td>4</td>
<td>1.000</td>
<td>1.75</td>
</tr>
<tr>
<td>5</td>
<td>2.000</td>
<td>1.80</td>
</tr>
</tbody>
</table>

The effect of manganese sulphate in presence of o-phosphoric acid was also studied with the second concentration of glycolic acid (0.40 N). Concentration of other reactants were kept as in previous case.

The rate constants of all reaction mixtures are recorded in table 92.
Summary of Results:

The order of reaction with respect to chromic acid is not altered by the presence of manganese sulphate and o-phosphoric acid together. However, the rate constant is affected by manganese sulphate in presence of phosphoric acid. This is evident from tables 99 and 92. The rate of reaction is first decreased and then increased by increasing concentrations of manganese sulphate. Similar effect is observed at all the three temperatures.

The values of temperature coefficient are seen to be higher in presence of manganese sulphate than in absence of it (table 90).

The pH values of the reaction mixtures are slightly increased (table 91).
II - U

EFFECT OF MANGANESE SULPHATE IN PRESENCE OF ACETIC ACID

The kinetics of the glycolic acid-chromic acid system in aqueous medium was also followed in presence of manganese sulphate and acetic acid together. Concentration of acetic acid was kept at 1.00 N while that of MnSO₄·4H₂O was varied from 0.00 to 3.00 gm. in 100 ml of reaction mixture. Glycolic acid and chromic acid concentrations were kept at 0.30 N and 0.010 N, respectively.

The values of rate constants for all the above reaction mixtures are recorded in table 93.

| TABLE 93 |
| Rate Constants |

<table>
<thead>
<tr>
<th>Glycolic acid 0.30 N</th>
<th>Chromic acid 0.010 N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic acid 1.00 N</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>No.</th>
<th>Concentration of MnSO₄·4H₂O (gm. in 100 ml)</th>
<th>k₁ (min⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>25°C</td>
</tr>
<tr>
<td>1.</td>
<td>0.000</td>
<td>0.002978</td>
</tr>
<tr>
<td>2</td>
<td>0.200</td>
<td>0.002768</td>
</tr>
<tr>
<td>3</td>
<td>1.000</td>
<td>0.002382</td>
</tr>
<tr>
<td>4</td>
<td>2.000</td>
<td>0.002736</td>
</tr>
<tr>
<td>5</td>
<td>3.000</td>
<td>0.002959</td>
</tr>
</tbody>
</table>

The values of temperature coefficients and pH are recorded in tables 94 and 95 respectively.
### TABLE 94
Temperature Coefficients

<table>
<thead>
<tr>
<th>No.</th>
<th>Concentration of MnSO₄·4H₂O (gm. in 100 ml)</th>
<th>k₅₅/k₂₅</th>
<th>k₄₅/k₃₅</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.000</td>
<td>1.77</td>
<td>1.76</td>
</tr>
<tr>
<td>2</td>
<td>0.200</td>
<td>1.75</td>
<td>1.75</td>
</tr>
<tr>
<td>3</td>
<td>1.000</td>
<td>1.85</td>
<td>1.74</td>
</tr>
<tr>
<td>4</td>
<td>2.000</td>
<td>1.93</td>
<td>1.73</td>
</tr>
<tr>
<td>5</td>
<td>3.000</td>
<td>1.90</td>
<td>1.75</td>
</tr>
</tbody>
</table>

### TABLE 95
pH Values

<table>
<thead>
<tr>
<th>No.</th>
<th>Concentration of MnSO₄·4H₂O (gm. in 100 ml)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.000</td>
<td>2.00</td>
</tr>
<tr>
<td>2</td>
<td>0.200</td>
<td>2.05</td>
</tr>
<tr>
<td>3</td>
<td>1.000</td>
<td>2.10</td>
</tr>
<tr>
<td>4</td>
<td>2.000</td>
<td>2.15</td>
</tr>
<tr>
<td>5</td>
<td>3.000</td>
<td>2.15</td>
</tr>
</tbody>
</table>

The effect of manganese sulphate in presence of acetic acid was also followed with second concentration of glycolic acid (0.40 N) at 25 and 35°C. Concentrations of all other reactants were kept as before.
The rate constants for all above reaction mixtures are recorded in table below.

| TABLE 96 |
| Rate Constants |
| Glycolic acid 0.40 N | Chromic acid 0.010 N |
| Acetic acid 1.00 N |

<table>
<thead>
<tr>
<th>No.</th>
<th>Concentration of NaSO₄·4H₂O (gms. in 100 ml)</th>
<th>k¹ (min⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>25°C</td>
</tr>
<tr>
<td>1</td>
<td>0.000</td>
<td>0.004691</td>
</tr>
<tr>
<td>2</td>
<td>0.200</td>
<td>0.004547</td>
</tr>
<tr>
<td>3</td>
<td>1.000</td>
<td>0.008763</td>
</tr>
<tr>
<td>4</td>
<td>2.000</td>
<td>0.004813</td>
</tr>
<tr>
<td>5</td>
<td>3.000</td>
<td>0.004983</td>
</tr>
</tbody>
</table>

Summary of Results:

It is seen from the kinetic data of various reaction mixtures that the order of reaction with respect to chromic acid remains one. The value of rate constant, however, is seen to decrease first and then increase slightly with increasing concentrations of manganese sulphate in presence of a constant quantity of acetic acid (table 93 and 96). This is similar to the effect obtained in case of manganese sulphate in presence of o-phosphoric acid.

The values of temperature coefficients are seen to be increased a little by the presence of manganese sulphate (table 94).

The pH values of the reaction mixtures are slightly increased.
II - V

OXIDATION OF GLYCOLIC ACID BY CHROMIC ACID, POTASSIUM DICROMATE
AND POTASSIUM CHROMATE

In order to investigate the comparative oxidising powers of chromic acid, potassium dichromate and potassium chromate, equivalent concentrations of each oxidant was allowed to react with a fixed concentration of glycolic acid separately and their kinetics was studied at temperatures 25, 35 and 45°C. Following table gives the kinetic data of reactions between 0.30 N glycolic acid with 0.010 N of the each of the oxidising agents at 25°C.

<table>
<thead>
<tr>
<th>Concentration of glycolic acid</th>
<th>0.30 N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration of oxidant</td>
<td>0.010 N</td>
</tr>
<tr>
<td>Temperature</td>
<td>25°C</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>t</th>
<th>(a-x)</th>
<th>$k_1$ (min$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>17.05</td>
<td></td>
</tr>
<tr>
<td>90</td>
<td>14.00</td>
<td></td>
</tr>
<tr>
<td>135</td>
<td>12.65</td>
<td></td>
</tr>
<tr>
<td>180</td>
<td>10.80</td>
<td></td>
</tr>
<tr>
<td>225</td>
<td>9.25</td>
<td></td>
</tr>
<tr>
<td>270</td>
<td>8.15</td>
<td></td>
</tr>
<tr>
<td>315</td>
<td>7.05</td>
<td></td>
</tr>
</tbody>
</table>

Average 0.002702
<table>
<thead>
<tr>
<th>t</th>
<th>(a-x)</th>
<th>$k_1$ (min.$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxidant - Potassium Dichromate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>16.85</td>
<td>0.001786</td>
</tr>
<tr>
<td>90</td>
<td>14.35</td>
<td>0.001852</td>
</tr>
<tr>
<td>135</td>
<td>13.05</td>
<td>0.002051</td>
</tr>
<tr>
<td>180</td>
<td>11.65</td>
<td>0.002303</td>
</tr>
<tr>
<td>225</td>
<td>10.05</td>
<td>0.002471</td>
</tr>
<tr>
<td>270</td>
<td>8.65</td>
<td>0.002526</td>
</tr>
<tr>
<td>315</td>
<td>7.60</td>
<td></td>
</tr>
<tr>
<td>Average</td>
<td>0.002433</td>
<td></td>
</tr>
</tbody>
</table>

| Oxidant - Potassium Chromate |
| 0  | 17.20 | 0.001742            |
| 98 | 14.50 | 0.001876            |
| 135| 13.35 | 0.001977            |
| 180| 12.05 | 0.002088            |
| 225| 10.75 | 0.002257            |
| 272| 9.45  | 0.002312            |
| 315| 8.30  |                     |
| Average | 0.002219 |

The rate constants of the above reaction mixtures are given in next table.

<p>| TABLE 98 |
| Rate Constants |</p>
<table>
<thead>
<tr>
<th>Glycolic acid 0.30 N</th>
<th>Oxidant 0.010 N</th>
</tr>
</thead>
<tbody>
<tr>
<td>No. Oxidant $k_1$ (min.$^{-1}$)</td>
<td>25$^\circ$</td>
</tr>
<tr>
<td>1 Chromic acid 0.002702</td>
<td>0.004718</td>
</tr>
<tr>
<td>2. Potassium - Dichromate 0.002433</td>
<td>0.004355</td>
</tr>
<tr>
<td>3. Potassium - Chromate 0.002219</td>
<td>0.004232</td>
</tr>
</tbody>
</table>
The values of the temperature coefficients and pH at 25°C are recorded in table 99.

**TABLE 99**

**Temperature Coefficients and pH Values**

<table>
<thead>
<tr>
<th>No.</th>
<th>Oxidant</th>
<th>$k_{35}/k_{25}$</th>
<th>$k_{45}/k_{35}$</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Chromic acid</td>
<td>1.75</td>
<td>1.80</td>
<td>2.10</td>
</tr>
<tr>
<td>2</td>
<td>Potassium Dichromate</td>
<td>1.79</td>
<td>1.72</td>
<td>2.10</td>
</tr>
<tr>
<td>3</td>
<td>Potassium Chromate</td>
<td>1.35</td>
<td>1.74</td>
<td>2.10</td>
</tr>
</tbody>
</table>

Kinetic investigations similar to above were also with the second concentration (0.40 N) of glycolic acid.

The rate constants for all the reaction mixtures are given in table 100.

**TABLE 100**

Concentration of glycolic acid 0.40 N
Concentration of oxidant 0.010 N

<table>
<thead>
<tr>
<th>No.</th>
<th>Oxidant</th>
<th>$k_1$ (min.$^{-1}$)</th>
<th>25°C</th>
<th>35°C</th>
<th>45°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>Chromic acid</td>
<td>0.004315</td>
<td>0.007321</td>
<td>0.01340</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Potassium Dichromate</td>
<td>0.003850</td>
<td>0.007320</td>
<td>0.01285</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Potassium Chromate</td>
<td>0.003873</td>
<td>0.008320</td>
<td>0.01289</td>
<td></td>
</tr>
</tbody>
</table>

The kinetics of oxidation of glycolic acid was also studied by changing the concentration of the oxidants. Concentrations of glycolic acid taken were 0.30 and 0.40 N while that of oxidants was kept at 0.0050 N.
The kinetic data for three reaction mixtures at 25°C are recorded in table 101.

### TABLE 101

Concentration of glycolic acid 0.30 N
Concentration of oxidant 0.005 N
Temperature 25°C

<table>
<thead>
<tr>
<th>t</th>
<th>(a-x)</th>
<th>( k_1 ) (min.(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxidant - Chromic acid</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>12.90</td>
<td></td>
</tr>
<tr>
<td>45</td>
<td>11.75</td>
<td>0.002078</td>
</tr>
<tr>
<td>90</td>
<td>10.85</td>
<td>0.002180</td>
</tr>
<tr>
<td>135</td>
<td>9.55</td>
<td>0.002228</td>
</tr>
<tr>
<td>180</td>
<td>8.50</td>
<td>0.002313</td>
</tr>
<tr>
<td>225</td>
<td>7.65</td>
<td>0.002320</td>
</tr>
<tr>
<td>270</td>
<td>6.75</td>
<td>0.002400</td>
</tr>
<tr>
<td>315</td>
<td>6.00</td>
<td>0.002418</td>
</tr>
<tr>
<td></td>
<td>Average 0.002336</td>
<td></td>
</tr>
</tbody>
</table>

| Oxidant - Potassium Dichromate |
| 0   | 12.70 | 0.001726 |
| 45  | 11.75 | 0.002167 |
| 90  | 10.45 | 0.002181 |
| 135 | 9.50  | 0.002166 |
| 180 | 8.60  | 0.002195 |
| 225 | 7.75  | 0.002170 |
|     | Average 0.002170 |

| Oxidant - Potassium Chromate |
| 0   | 12.65 | 0.001643 |
| 45  | 11.75 | 0.001861 |
| 90  | 10.70 | 0.001929 |
| 135 | 9.75  | 0.001985 |
| 180 | 8.85  | 0.002209 |
| 225 | 8.05  | 0.001975 |
|     | Average 0.001975 |
The values of the rate constants are summarised in tables 102 and 103.

**TABLE 102**
Rate Constants

<table>
<thead>
<tr>
<th>No.</th>
<th>Oxidant</th>
<th>Glycolic acid 0.30 N</th>
<th>Oxidant 0.005 N</th>
<th>k1 (min.(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>25(^\circ)</td>
<td>35(^\circ)</td>
<td>45(^\circ)</td>
</tr>
<tr>
<td>1</td>
<td>Chromic acid</td>
<td>0.004236</td>
<td>0.004290</td>
<td>0.007491</td>
</tr>
<tr>
<td>2</td>
<td>Potassium Dichromate</td>
<td>0.002170</td>
<td>0.004155</td>
<td>0.007413</td>
</tr>
<tr>
<td>3</td>
<td>Potassium Chromate</td>
<td>0.001975</td>
<td>0.004032</td>
<td>0.007193</td>
</tr>
</tbody>
</table>

**TABLE 103**
Rate Constants

<table>
<thead>
<tr>
<th>No.</th>
<th>Oxidant</th>
<th>Glycolic acid 0.40 N</th>
<th>Oxidant 0.005 N</th>
<th>k1 (min.(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>25(^\circ)</td>
<td>35(^\circ)</td>
<td>45(^\circ)</td>
</tr>
<tr>
<td>1</td>
<td>Chromic acid</td>
<td>0.003772</td>
<td>0.007218</td>
<td>0.01255</td>
</tr>
<tr>
<td>2</td>
<td>Potassium Dichromate</td>
<td>0.003443</td>
<td>0.006613</td>
<td>0.01235</td>
</tr>
<tr>
<td>3</td>
<td>Potassium Chromate</td>
<td>0.003296</td>
<td>0.006415</td>
<td>0.01203</td>
</tr>
</tbody>
</table>

**Summary of Results:**

It is seen from the tables 97 and 101 that the order of reaction with respect to chromium(VI) remains one, irrespective of the oxidising agent used i.e. chromic acid, potassium dichromate and potassium chromate. It is clear from
the same table that the rate constant for the oxidation of glycolic acid with chromic acid at 25°C is $0.002703 \text{ min}^{-1}$, while the rate constant when potassium dichromate is used under similar conditions is $0.002433 \text{ min}^{-1}$. The corresponding value with potassium chromate is $0.002219 \text{ min}^{-1}$. This clearly indicates that the oxidising powers of the three oxidants are in the order chromic acid $\succ$ potassium dichromate $\succ$ potassium chromate. This is also true at higher temperatures. Data given in tables 98, 100, 102 and 103 support the above conclusion.

The values of temperature coefficients and pH are same with the three oxidants used (table 98).
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