CHAPTER VI
CALCULATIONS
The reaction of hypochlorite solution with starch has been followed by estimating the unconsumed oxidant. The results would, thus, give the change in the oxidant concentration with time. Though, the initial oxidant concentration was always known, it was found necessary to obtain effective initial oxidant concentration (Co) in each experiment by plotting a curve of 'log C' versus 't', where 'C' is concentration of the unconsumed oxidant at time 't' (mins). This plot gave a straight line and the extrapolation of the curve to zero time yielded effective initial oxidant concentration. This is illustrated in Fig. 37, for one of the reactions studied.

DETERMINATION OF RATE CONSTANTS

Method of Integration

(a) First order rate constant

The rate expression for a single component system is -

\[ - \frac{dC}{dt} = k'C^n \]

where 'dt' is the change in time and 'dc' is the change in concentration of the reactant with respect to 'dt'. "k'" is the specific rate constant of the reaction.

'C' is the concentration of the reactant, and 'n' is the order of the reaction.
Fig. 37: A Plot of log C versus Time at 37°, 10.0 pH
Equation (1) can be rewritten as -

\[- \frac{dC}{C^n} = k'dt \]  \(... \)  \(... \)  \( (2) \)

On integration between the limits \( C = C_0 \) at \( t = 0 \) and \( C \) at \( t = t \).

\[ \therefore \quad \int_{C_0}^{C} \frac{dC}{C^n} = k' \int_0^t dt \]  \(... \)  \(... \)  \( (3) \)

For \( n = 1 \) i.e., first order, the result is

\[ \ln \frac{C_0}{C} = k't \]  \(... \)  \(... \)  \( (4) \)

or \[ \frac{1}{t} \times \ln \frac{C_0}{C} = k' \]  \(... \)  \(... \)  \( (5) \)

Hence, the first order rate constant \( k' \) can be determined using formula (5), for every experimental point. If the values of \( k' \) remain reasonably constant without any drift or trend then the average value yields the first order rate constant. This is known as the 'tabular method'.

(b) Second order rate constant

Considering the change in the concentration of starch to be proportional to the change in oxidant concentration from time to time, the second order rate constant can also be calculated.

For \( n = 2 \) i.e. second order

\[ \frac{dx}{dt} = k' (a - x) (b - x) \]  \(... \)  \(... \)  \( (5) \)

i.e. \[ k' = \frac{1}{t} \frac{1}{b - a} \ln \frac{a (b - x)}{b (a - x)} \]  \(... \)  \(... \)  \( (7) \)
Here, 'a' = Initial oxidant concentration.
'b' = Initial oxidate concentration.
'x' = Consumption of oxidant after time 't'.
't' = Time at which oxidant consumption was measured.

The second order rate constants for every experimental point can be calculated. If these values are reasonably constant showing no specific trend or drift, the average rate constant can be estimated. As mentioned earlier, this method of calculations of rates for every experimental point is known as 'tabular method'.

A typical example of the calculation of first and second order rate constant is illustrated in Table LIV.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>First Order (k'_{I})</th>
<th>Second Order (k'_{II})</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5</td>
<td>0.0100</td>
<td>0.0153</td>
</tr>
<tr>
<td>5.0</td>
<td>0.0175</td>
<td>0.0283</td>
</tr>
<tr>
<td>7.5</td>
<td>0.0148</td>
<td>0.0244</td>
</tr>
<tr>
<td>10.0</td>
<td>0.0170</td>
<td>0.0275</td>
</tr>
<tr>
<td>15.0</td>
<td>0.0155</td>
<td>0.0275</td>
</tr>
<tr>
<td>20.0</td>
<td>0.0188</td>
<td>0.0313</td>
</tr>
<tr>
<td>25.0</td>
<td>0.0172</td>
<td>0.0288</td>
</tr>
<tr>
<td>30.0</td>
<td>0.0171</td>
<td>0.0288</td>
</tr>
<tr>
<td>40.0</td>
<td>0.0171</td>
<td>0.0292</td>
</tr>
<tr>
<td>50.0</td>
<td>0.0171</td>
<td>0.0293</td>
</tr>
<tr>
<td>60.0</td>
<td>0.0171</td>
<td>0.0295</td>
</tr>
<tr>
<td>80.0</td>
<td>0.0174</td>
<td>0.0307</td>
</tr>
<tr>
<td>100.0</td>
<td>0.0177</td>
<td>0.0316</td>
</tr>
<tr>
<td>120.0</td>
<td>0.0183</td>
<td>0.0330</td>
</tr>
</tbody>
</table>
Graphical Method

The graphical procedure can also be used to determine the rate of the reaction.

(a) First order rate constant

The integrated equation (5), predicts that a plot of \( \ln \frac{C_0}{C} \) versus \( t \) should give a straight line, the slope of which represents, the constant for the first order reaction. The unit for the first order rate constant is time\(^{-1}\) (i.e. \( \text{min}^{-1} \) or \( \text{sec}^{-1} \)).

(b) Second order rate constant

The equation (7), suggests that a plot of \( \frac{1}{b-a} \ln \frac{a(b-x)}{b(a-x)} \) versus \( t \) should give a straight line. The slope of the line then, represents the second order rate constant in mole x litre\(^{-1}\) x time\(^{-1}\). Figs. 38 and 39 illustrate an example of the graphical method for the selected experiments.

In many cases, the data fitted well into the first order and the second order curves, by the graphical procedure as well as tabular method. Excepting a few cases, all the results in this thesis are based on first order rate constants derived by the graphical method, because in the tabular method the initial oxidant concentration \( C_0 \) is very important, and therefore, the rates often show undue variation whereas the graphical method gives reasonably accurate "\( k' \)" values.
Fig. 38: A First Order Plot (In Co/C versus t) for the Gncatalyzed Reaction at Various pH levels and 37°. Oxidant Concentration is 112 m.moles/l
Fig. 39: A Second Order Plot for the Uncatalyzed Reaction at Various pH Levels and 37°.
Oxidant Concentration is 112 m.moles/1
Absolute Rate Constant (Equilibrium Constant)

The relationship between observed rate constant or specific rate constant \( k' \) and the constant \( k^* \) for the equilibrium between the activated complex and the reactants is given as follows:

\[
k' = \frac{kT}{h} k^*
\]

where
- \( k \) = Boltzman constant
- \( T \) = Temperature in absolute degree Kelvin
- \( h \) = Planck's constant
- \( k' \) = Specific rate constant
- \( k^* \) = Equilibrium constant

ENERGY OF ACTIVATION

The temperature dependence of the observed rate constant is given by the Arrhenius Law

\[
\frac{d \ln k'}{dT} = \frac{-\Delta E}{RT^2}
\]

which on integration gives

\[
\ln k' = -\frac{\Delta E}{RT} + \text{constant}
\]

or

\[
k' = A e^{-\Delta E/RT}
\]

Thus, a plot of \( \ln k' \) (or \( \ln k^* \)) versus the reciprocal of the absolute temperature, according to equation (10) should give a straight line. Its slope is \(-\Delta E/R\), from which the apparent or experimental energy of activation \( \Delta E' \) can be calculated. Fig. 40 shows one such plot.
Fig. 40: Arrhenius Plot
The apparent energy of activation is related to the actual energy of activation for the formation of activated complex from the reactants as follows:

\[ E_{\text{exp}} = RT + E^* \]  \hspace{1cm} (12)

**GIBBS FREE ENERGY**

Gibbs free energy change for the formation of the activated complex from the reactants is related to the equilibrium constant \( k^* \) as follows:

\[ \Delta G^* = -RT \ln k^* \]  \hspace{1cm} (13)

**ENTROPY OF ACTIVATION**

Relation between energy of activation, Gibbs free energy change and change in the entropy of activation is given as follows:

\[ \Delta G^* = \Delta E^* - T \Delta S^* \]  \hspace{1cm} (14)

or \( T \Delta S^* = \Delta E^* - \Delta G^* \)

or \[ \Delta S^* = \frac{\Delta E^* - \Delta G^*}{T} \]  \hspace{1cm} (15)

A decrease in entropy or -ve entropy of activation suggests lowering the rate of reaction because for the formation of the activated complex, the reactants lose certain degrees of freedom. Conversely, an increase in entropy or +ve entropy of activation suggests increase in the rate of reaction.
FREQUENCY FACTOR

As seen above, the temperature dependence of the observed rate constant is as follows:

\[ \ln k' = \frac{-E}{RT} + \text{constant} \quad \ldots \quad \ldots \quad (10) \]

or \[ k' = Ae^{-E/RT} \quad \ldots \quad \ldots \quad (11) \]

According to the theory of the absolute rates the observed rate of reaction is:

\[ k' = \frac{kT}{h} e^{\Delta S^*/R} e^{-E_{\text{exp}}/RT} \quad \ldots \quad \ldots \quad (16) \]

Therefore,

\[ A = \frac{kT}{h} e^{\Delta S^*/R} \quad \ldots \quad \ldots \quad (17) \]

Thus, the frequency factor is related to the entropy of activation, except that its dependence on temperature is governed by the term \( kT/h \).

The frequency factor, according to the theory of absolute reaction rate should be \( 10^{10} - 10^{11} \) sec\(^{-1} \) for the normal reaction, i.e., the reaction between a charged ion and a neutral molecule.

If the frequency factor is lower than this value then the reaction may be taking place between two charged particles of similar sign and if it is higher than the above value, the reaction may be presumed to take place between two oppositely charged ions.

Frequency factor, free energy of activation and entropy of activation have been calculated for each of the temperature studied. The variations between the values at different