Chapter VI
EXPERIMENTAL
VI-1. Preparation of base glasses:

Batch Materials: Base glasses were prepared from A.R. quality sodium dihydrogen phosphate, trisodium phosphate and ammonium phosphate.

A.R. quality sodium dihydrogen phosphate (NaH$_2$PO$_4$·4H$_2$O) was used for making sodium metaphosphate glass (Na/P = 1). This is formed by complete dehydration and subsequent fusion of the mass.

$$\text{NaH}_2\text{PO}_4 \rightarrow \text{H}_2\text{O} + \frac{1}{2} (\text{Na}_2\text{O}·\text{P}_2\text{O}_5)$$

For glasses containing more Na$_2$O than metaphosphate glass, i.e. with Na/P ratios more than 1, mixtures of calculated amounts of sodium dihydrogen phosphate and trisodium phosphate (Na$_3$P$_4$O$_{12}$·12H$_2$O) were used. For glasses with Na/P ratio less than 1, mixtures of calculated amounts of sodium dihydrogen phosphate and ammonium phosphate ($\text{(NH}_4\text{)}_2\text{HPO}_4$) were used; the latter decomposes into ammonia, water and P$_2$O$_5$.

Melting: The batch materials were taken in a platinum basin and heated on an electric heater. When most of the bound water was driven out the mass became hard. The basin was then placed in an electric muffle furnace and heated for sufficient time to give clear glass. The temperature was kept around 900°C during this melting.

The melt was then chilled by pouring into a clean aluminium cup placed over cold water. The glass was broken to smaller pieces.
and preserved in stoppered glass bottles placed in desiccators to avoid absorption of moisture.

The compositions of the glasses were verified by estimating their \( \text{P}_2\text{O}_5 \) contents.

Determination of loss due to volatilization: As \( \text{P}_2\text{O}_5 \) is volatile, it was feared that some \( \text{P}_2\text{O}_5 \) would volatilise away during equilibrating and thereby the composition of the glass would change. So, loss due to volatilisation was determined at different temperatures for glasses of different Na/P ratios. \( \text{P}_2\text{O}_5 \) in the glasses was determined after heating by the magnesia mixture method and compositions of the glasses were corrected, where necessary.

Estimation of \( \text{P}_2\text{O}_5 \) in glass: A weighed quantity of glass was dissolved by gentle boiling in about 3N HCl. All the \( \text{P}_2\text{O}_5 \) is converted into orthophosphate by this treatment. The acid solution was neutralised with ammonia, again acidified with a few drops of HCl and was then precipitated by magnesia mixture. The precipitate of magnesium hydrogen orthophosphate was ignited to magnesium pyrophosphate, \( \text{Mg}_2\text{P}_2\text{O}_7 \) and weighed. Percentage of \( \text{P}_2\text{O}_5 \) in the glass was calculated from the weight of the ignited precipitate and the weight of the glass taken.

VI-2. Incorporation of Minor (Redox) Constituents into Base glasses: Iron was introduced as pure (99.9%) \( \text{Fe}_2\text{O}_3 \) prepared by igniting precipitated ferric hydroxide. Requisite amount of \( \text{Fe}_2\text{O}_3 \) was mixed thoroughly with the base glass ground to powder in a 'diamond' mortar.
and freed of any iron contamination by a powerful magnet. The mixture was melted in a muffle furnace at about 900°C, stirring from time to time until a clear homogeneous melt was obtained. This molten glass was then chilled by pouring into a clean aluminium cup placed over cold water. It was then ground to powder and preserved in stoppered glass bottles in desiccators.

Iron was also introduced as ferrous oxalate, FeC₂O₄·2H₂O into one glass of metaphosphate composition. Ferrous oxalate was prepared by precipitating it from Mohr salt (NH₄)₂SO₄·FeSO₄·6H₂O solution by oxalic acid. The precipitate was filtered, washed, dried and used in glass.

Chromium was introduced as A.R. potassium dichromate. Calculated amount of the salt was mixed with the glass and the mixture was then melted.

Manganese was used in the form of a solution of KMnO₄ of known strength. A solution prepared from laboratory reagent quality KMnO₄ (minimum assay 99%) was filtered through glass wool and then standardised against sodium oxalate solution. The solution together with the ground glass in a platinum crucible was carefully dried and fused over a gas burner. The crucible was then placed in the electric muffle furnace, stirred from time to time until it became clear and homogeneous. The melt was chilled and then ground and preserved for equilibrium studies.

Cerium was introduced as A.R. Ce(SO₄)₂. Copper, uranium,
molybdenum, vanadium and titanium were introduced as A.R. Copper nitrate $\text{Cu(NO}_3\text{)}_2 \cdot 2\text{H}_2\text{O}$, A.R. uranyl acetate $\text{UO}_2 (\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, A.R. ammonium molybdate $\text{(NH}_4\text{)}_6 \text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, sodium meta-vanadate (Na$\text{VO}_3$) and pure titania (TiO$_2$) respectively.

Requisite amount of the compound of the colouring constituent was thoroughly mixed with glass and was then melted in a muffle at about 900°C. The time required to form a clear homogeneous melt was about 2 hours. These glasses were ground and preserved in stoppered bottles kept in desiccators for use in experiments for the equilibrium studies.

When the minor constituents were introduced as their sodium and potassium salts (e.g. sodium vanadate, potassium dichromate and potassium permanganate), the proportion of alkali in the glass increased. But in view of the very small amounts of these salts in the glass, this increase was not taken into consideration.

VI-3. Method of studying the equilibria:

The equilibrium studies were performed by maintaining about 2 gms. of glass at a particular temperature in a tube furnace with air as the ambient atmosphere. Heating was continued for increasing periods of time till the ratio $M^{x+} / M^{y+}$ became constant indicating that an equilibrium was attained between the different states of oxidation, $M^{x+}$ and $M^{y+}$ of an element $M$. The powdered glass containing the redox oxide (as described in the previous section) was taken in a boat and was then placed at the centre of the tube furnace. The boats were on the average 60 mm. in length (excluding handle) and
10 mm in both width and height.

The furnace used had platinum wound heating element and was provided with an energy regulator along with a temperature indicating unit. The maximum operating temperature of the furnace was 1500°C. The tube was 30 cms. in length and 3.6 cms. in internal diameter. A zone of about 6 cms. where temperature remained uniform could be obtained at the centre of the furnace. The mouth of the tube could be closed with a movable refractory door, the interior of the tube could then be viewed through a glass window. The other end of the tube was closed.

The temperature of the furnace could be accurately controlled within ±10°C. The pyrometer was calibrated by comparing the melting temperatures of pure salts and metals (e.g. K₂Cr₂O₇, NaCl, Na₂CO₃, Ag metal).

The boat containing the glass was carefully pushed with the help of an iron rod to the centre of the furnace just below the tip of the thermocouple. The furnace was maintained at a steady temperature (±10°C) at which the equilibrium was to be attained. After a definite time interval, the boat was pulled out of the furnace by a platinum wire fastened at one end of the boat and then again weighed. The glass was then analysed for the relative proportions of the element in different states of oxidation between which equilibrium was to be established. The equilibrium was taken to be

*The results are given on the basis of the weight of glass after heating. When the loss was considerable, the composition of the glass was calculated by assuming the loss to be entirely due to P₂O₅ (see Results & Discussion).*
established when the ratio, $\frac{M^{x+}}{2M}$ became constant i.e. when further heating did not change the ratio.

To be sure that equilibrium was actually attained within the time determined by the method described and a metastable condition was not taken for equilibrium, iron was introduced in a glass of definite composition in the ferric state ($\text{Fe}_3\text{O}_4$) as well as in the ferrous state (ferrous oxalate), total iron being the same in both. These two glasses were maintained for increasing periods of time at a particular temperature. So long the equilibrium was not attained the ratio of $(\text{Fe}^{2+})/(\text{Fe}^{3+})$ and as such, $\text{Fe}^{2+}/\text{total iron}$ would be different.

Ferrous and total iron were estimated separately in each glass. Ferric iron was calculated by subtracting the ferrous iron content from the total iron.

Total concentrations of chromium, manganese, cerium and copper were estimated in parent glasses i.e. in the glasses prepared for equilibrium studies. To determine whether equilibrium was attained, concentrations of $\text{Cr}^{6+}$, $\text{Mn}^{3+}$, $\text{Ce}^{4+}$, and $\text{Cu}^{+}$ were estimated after each experiment. For calculating the ratio $\frac{M^{x+}}{\Sigma M}$, the total concentrations of chromium, manganese, cerium and copper, as determined for the parent glasses were taken for $\Sigma M$, due to allowance being given for the loss due to volatilisation during equilibrating.

Concentrations of uranium, molybdenum, vanadium and titanium were estimated in their $\text{U}^{4+}$, $\text{Mo}^{5+}$, $\text{V}^{5+}$ and $\text{Ti}^{3+}$ states after each.
experiment and for the calculation of the ratio, $M^+ / \Sigma M$, the total concentrations of these elements calculated from the batch compositions, were used, due allowance being given for the loss of glass during the preparation of the present glasses as well as during equilibration.

VI-4. Estimation of the Minor constituents in their different valency states:

Estimation of iron in ferrous and ferric states: About 50 ml. of 3-4N HCl was taken in a 250 ml. Erlenmeyer flask having a ground neck fitting to a standard ground glass stopper provided with a stop cock (Fig. 6), and was heated to boiling. Boiling was continued for a few minutes to drive out the air in the flask. The boat containing the glass in which ferrous iron was to be estimated was then carefully dropped into the boiling acid. After the glass had dissolved, heating was discontinued and the glass stopper with stop-cock was

* Preliminary experiments showed that in the presence of metaphosphate glass dissolved in cold water ferrous iron in Mohr salt (ferrous ammonium sulphate) solution could not be titrated with $K_2Cr_2O_7$ solution. It was found that even after addition of $K_2Cr_2O_7$ the solution did not give any blood red colouration with ammonium thiocyanate indicating that no free Fe$^{3+}$ ion was formed. It was, however, found that, when the metaphosphate glass was dissolved in boiling HCl, its presence did not create any difficulty in the titration.

This was most probably due to the decomposition of metaphosphate during boiling in acid.

In all estimations of the redox oxides in different glasses, solutions were always made by boiling in dil. HCl although all glasses in the Na$_2$O - P$_2$O$_5$ system could be dissolved in water or acid in the cold.
Fig. 6. Conical flask fitted with a standard joint and stopcock.
fitted at the mouth. The solution was cooled under tap water keeping
the stop-cock closed to avoid contact with air during cooling.
Vacuum was then released by opening the stop-cock and the stopper was
removed. The solution was diluted with boiled out distilled water to
about 2N HCl strength, 1 ml. of phosphoric acid was added and the
solution titrated with 0.01 N potassium dichromate solution using
Ba-diphenylamine sulphonate indicator. The end point was sharp and
the titre value gave a measure of the amount of iron in the ferrous
state in the glass.

Before estimating ferrous iron by this method, ferrous sulphate
solution of known titre value was similarly treated and it was found
that there was no change in the titre value indicating that under the
above conditions no ferrous iron was converted into ferric iron due
to oxidation.

After titrating the ferrous iron the flask with the contents
was gently heated when the blue colour of the indicator disappeared.
Conc. HCl was then added to make the strength above 4N. The hot yellow
solution was subjected to reduction by dropwise addition of SnCl2
solution. The solution was then cooled and excess of mercuric chloride solution added. The solution was then titrated with standard
potassium dichromate solution (0.1N or 0.01N) using Ba-diphenylamine sulphonate indicator.

This second titration gives the total amount of iron in the
glass and hence the amount of iron remaining in the ferric state in
the glass was obtained by subtracting the amount of ferrous iron from the total iron.

Estimation of manganese, chromium and cerium in the manganic (Mn\(^{3+}\)), chromic (Cr\(^{6+}\)), and ceric (Ce\(^{4+}\)) states:

About 50 ml. of 2N HCl solution was heated to boiling in an Erlenmeyer flask of the type shown in Fig. 6. 10 ml. of 0.1N Mohr salt solution was added to it. The platinum boat containing the glass of known weight was then cautiously dropped into the solution. Then the procedure followed was exactly the same as done in the case of estimation of ferrous iron in glass.

A blank titration was carried out side by side, taking same amounts of HCl and Mohr salt solution but without the glass. If the volume of potassium dichromate consumed in this blank titration is \(v\) ml. and if \(v'\) ml. is the volume of dichromate solution required to titrate the solution containing the dissolved glass, then \((v-v')\) gives a measure of the amount of the respective ions in glass.

Estimation of cuprous copper and titanous titanium and molybdenum(v):

In these cases the process followed was just the reverse of the process followed in the estimation of manganic (Mn\(^{3+}\)), chromic (Cr\(^{6+}\)) and ceric (Ce\(^{4+}\)) ions. Cu\(^{+}\), Ti\(^{3+}\) and Mo\(^{5+}\) ions were allowed to

N.B. During dissolution of cerium containing glasses in HCl (or H\(_2\)SO\(_4\)) a white precipitate appeared which, however, disappeared almost fully when the solution was cooled. Most probably it is due to cerous sulphate (Ce\(_2\)(SO\(_4\))\(_3\)) which has an inverse relationship with temperature, being 20% soluble at 0\(^0\)C but less than 1% at 100\(^0\)C.
react in solution with \( \text{Fe}^{2+} \) ion added as ferric alum solution and the ferrous iron formed was titrated with potassium dichromate solution of known strength (0.01 N).

50 ml. of about 2N \( \text{H}_2\text{SO}_4 \) solution was taken in an Erlenmeyer flask of the type shown in Fig. 6, and 10 ml. of approximately 0.2N ferric alum solution was added. The mixture was heated to boiling and the platinum boat containing glass of known weight in which the cuprous copper or titanous titanium was to be estimated, was put into it.* After complete dissolution the flask was stoppered and the stop cock was closed. The flask was then cooled, vacuum released and the ferrous iron formed was titrated with standard (0.01 N) \( \text{K}_2\text{Cr}_2\text{O}_7 \) solution.

A blank titration was also carried out side by side performing all the operations but without any glass. The volume of potassium dichromate solution required in this blank titration which was usually was within 0.1 ml. was deducted from the volume of dichromate required in the corresponding titrations with glass.

Estimation of Uranous Uranium:

The glass contained in the boat was dissolved by boiling in about 2N \( \text{H}_2\text{SO}_4 \) out of contact with air, as in the previous cases and \( \text{U}^{4+} \) was titrated directly in the solution at 50°C with 0.01N ceric ammonium sulphate solution using N-phenyl-anthranilic acid.

*It may be noted here that when sodium metaphosphate glass (with or without any minor constituent) was added to ferric alum solution - a heavy white precipitate appeared which subsequently dissolved during boiling. This is most probably due to the formation of complex metaphosphates or polyphosphates of ferric iron. Subsequent dissolution of the precipitate is probably due to further decomposition of the complexes.*
Estimation of pentavalent vanadium ($V^{5+}$) in the vanadium glasses:

Vanadates are reduced in strongly acid solution by iodides in an atmosphere of CO$_2$ to the quadrivalent condition.

$$2\text{VO}_4^{3-} + 2\text{I}^- + 12\text{H}^+ = 2\text{VO}^{2+} + \text{I}_2 + 6\text{H}_2\text{O} \quad \text{(1)}$$

The liberated iodine and the excess of iodide can be determined by titration with standard KIO$_3$ solution.

The vanadium containing sodium metaphosphate glasses used for equilibrium studies, were dissolved in about 2N HCl out of contact with air as described before. The cold solution was transferred into a 250 ml. glass-stoppered reagent bottle and rapid current of CO$_2$ was passed into the bottle (but not through the solution) for 2-3 minutes. Sufficient HCl was added to make the strength about 8N. A known volume of excess KI solution was introduced. After mixing the contents of the bottles, the mixture was allowed to stand for 2-3 minutes and 5 ml. of CCl$_4$ was added. This was followed by rapid titration with standard KIO$_3$ (0.01M) solution with vigorous shaking until no more iodine colour could be detected in the CCl$_4$ layer.

A portion of the added iodide reacts with the vanadate according to equation (1) and corresponding amount of iodine is liberated. The iodate oxidises the remaining iodide first to iodine.

$$\text{IO}_3^- + 6\text{H}^+ + 5\text{I}^- = 3\text{I}_2 + 3\text{H}_2\text{O} \quad \text{(2)}$$
This liberated iodine along with the iodine liberated by vanadate is further oxidised to iodine-monochloride.

\[ \text{IO}_3^- + 2\text{I}_2 + 6\text{H}^+ = 5\text{I}^+ + 3\text{H}_2\text{O} \] (3)

The volume of KI solution which was added to the glass solution before titration was separately titrated with the standard KIO\textsubscript{3} solution (0.01M). To the KI solution sufficient HCl was added to make the solution about 8N with acid, 5 ml. of CCl\textsubscript{4} was added and the solution was titrated with KIO\textsubscript{3} solution with vigorous shaking till no more iodine colour could be detected in the CCl\textsubscript{4} layer.

Therefore, if \( V \) ml. of KIO\textsubscript{3} would have required for a definite volume of KI solution and if \( v \) ml. is the volume of KIO\textsubscript{3} that is required for titration of the glass solution in which the same volume of KI had been added then, \( v \) will be less than \( V \) in amount proportional to the amount of VO\textsubscript{4}\textsuperscript{3-}. Hence the amount of vanadium in the V\textsuperscript{5+} state could be calculated.

\[ 1 \text{ ml. of } 0.01 \text{ M KIO}_3 = 0.000204 \text{ g. v (as VO}_4^{3-}) \]

VI-5. Estimation of total concentrations of chromium, manganese, cerium and copper in the parent glasses:

Total chromium: Chromic salts are oxidised to dichromates by boiling with excess of a persulphate solution in the presence of a little silver nitrate (catalyst). The excess of persulphate remaining after the oxidation is complete, is destroyed by boiling the solution for a short time. The dichromate content of the resultant solution is
determined by the addition of excess of a standard ferrous solution and titration of excess of the latter with standard potassium dichromate.

$$2\text{Cr}^{3+} + 3\text{S}_2\text{O}_8^{2-} + 7\text{H}_2\text{O} \rightarrow 2\text{Cr}_2\text{O}_7^{2-} + 6\text{HSO}_4^- + 8\text{H}^+$$

$$2\text{S}_2\text{O}_8^{2-} + 2\text{H}_2\text{O} \rightarrow 4\text{H}_2\text{SO}_4^-$$

About 1.0 g of the glass containing chromium was accurately weighed dissolved by boiling in 50 ml. water in a 250 ml. Erlenmeyer flask. The solution was cooled, and 0.5 ml. of 0.1 N AgNO₃ was added followed by the addition of about 0.2 g of ammonium persulphate. The solution was gently boiled for about 30 minutes and then after cooling 5 ml. of 1:1 H₂SO₄ was added and 10 ml. of 0.1 N Mohr salt solution was introduced. The excess of ferrous iron in Mohr salt was titrated with 0.1N potassium dichromate.

Total manganese: Manganese salts are oxidised to permanganic acid by excess of sodium bismuthate in nitric acid.

$$2\text{Mn}^{2+} + 5\text{NaBiO}_3 + 14\text{H}^+ = 2\text{MnO}_4^- + 5\text{Bi}^{3+} + 5\text{Na}^+ + 7\text{H}_2\text{O}.$$  

The excess of bismuthate is removed by filtration and a measured excess of standard ferrous solution is added to reduce the permanganate to a manganous salt. The excess of ferrous iron is then determined by titration with standard potassium permanganate solution.

1.0 g of the glass containing manganese was dissolved by boiling in 50 ml. of 30% nitric acid in a beaker. The solution was
cooled and about 1.5 g. of A.R. sodium bismuthate was added in 2-3 portions, the solution being swirled after each addition of bismuthate.

The excess of bismuthate was removed by filtering the pink solution through a sintered glass filtering crucible and the filtrate along with the washings (washing of the precipitate was done with 3% nitric acid until the filtrate was free from any permanganate tint) was taken in a 500 ml. conical flask. 10 ml. of standard 0.04 N Mohr solution was introduced. The permanganate colour disappeared and the excess of ferrous iron was titrated by standard 0.05 N potassium permanganate solution following the standard procedure.

The ferrous ammonium solution was standardised by running a blank titration. Into an Erlenmeyer flask 50 ml. of 30% nitric acid was placed, a little of sodium bismuthate was added, and diluted with the same volume of 3% nitric acid as was required for washing the precipitate. An equal volume (10 ml.) of ferrous solution as was used in the determination, was added and the solution was titrated against the standard potassium permanganate solution. The difference between the titrations represents the permanganate equivalent of the permanganic acid formed in the determination.

Total cerium: Cerous salts are oxidised by boiling with excess of a persulphate solution in the presence of silver nitrate (catalyst). The excess of persulphate is decomposed by boiling the solution.
The cerium content of the solution can be determined by directly titrating the solution with a standard ferrous solution.

1.0 g of the glass was accurately weighed and dissolved by boiling in 50 ml. 2N H₂SO₄. The solution was cooled, and was treated with about 0.35 g. of ammonium persulphate and 0.5 ml. of 0.1 N silver nitrate solution, and then boiled for 15 minutes. The solution was cooled to room temperature and was directly titrated with standard 0.01 N ferrous ammonium sulphate solution, using N-phenyl anthranilic acid as indicator.

Total Copper: About 1.0 g. of accurately weighed powdered copper glass was dissolved in 50 ml. water by gentle heating. 10 ml. of saturated bromine water was added to the solution to oxidise any reduced copper that may be present in the glass, and the solution boiled until all the bromine was expelled. The solution was cooled and to the cold solution a few drops of dilute sodium carbonate solution was added. When a faint permanent precipitate was formed, this was recoved by adding a few drops of dilute acetic acid.

About 0.5 g of KI was then added to the solution and the liberated iodine was titrated with standard 0.01 N sodium thiosulphate using starch as indicator following the standard procedure.
VI-6. The Method of Calculation:

The method of calculating the final glass composition, the percentage of oxidised or reduced form of the colouring constituent etc. is exemplified below with the data obtained in a particular experiment.

While equilibrating the glass L₁, containing about 1% Fe₂O₃, the following data were obtained:

<table>
<thead>
<tr>
<th>Glass No.</th>
<th>Original composition (mol%)</th>
<th>Temp. (°C)</th>
<th>Time (hrs.)</th>
<th>Wt. of glass (g)</th>
<th>Ferric as iron (mg)</th>
<th>Total heating per g. of glass (mg per g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>L₁</td>
<td>Na₂O</td>
<td>P₂O₅</td>
<td>Taken heating after FeO₃ (mg)</td>
<td>Fe₂O₅</td>
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Composition after heating:

- The amount of P₂O₅ initially present in the glass
- \[ 1.7580 \times 0.8654 \text{ g} \]
- \[ = 1.5214 \text{ g} \]
- Taking the loss during heating to be entirely due to P₂O₅,
- P₂O₅ remaining after heating = \[ 0.9434 \text{ g} \equiv 0.006643 \text{ mol} \]
- Na₂O content of the glass before and after heating
- \[ (1.7580 - 1.5214) \text{ g} = 0.2366 \text{ g} \equiv 0.003816 \text{ mol} \]
- Hence, P₂O₅ after heating = \[ \frac{0.9434}{1.18} \times 100 \approx 79.95\% (wt) \]
- and \[ \frac{0.006643}{0.006643 + 0.003816} \times 100 \approx 63.51\% (mol) \]

*See Appendix-I (Table - I/A).*
Percent FeO:

Ferrous iron content of the glass after heating = 3.02 mg. FeO per g of glass
= 3.355 mg. Fe₂O₃ per g. of glass

Hence, \( \% \text{ FeO} = \frac{\text{ferrous iron as Fe₂O₃}}{\text{total iron as Fe₂O₃}} \times 100 \)

\( \frac{3.355}{14.72} \times 100 = 22.8 \)

\( \log \left( \frac{\text{Fe}^{2+}}{\text{Fe}^{3+}} \right) = \)

FeO = 3.02 mg. per g. of glass
Fe₂⁺ = 0.04196 mg. ion per g. of glass.

Ferric iron as Fe₂O₃ = total iron as Fe₂O₃ - ferrous iron as Fe₂O₃

\( = (14.72 - 3.355) = 11.365 \text{ mg. per g. of glass} \)

\( = 0.07104 \text{ millimole per g. of glass} \)

And Fe³⁺ = 0.14208 mg. ion per g. of glass.

Hence, concentration of Fe²⁺ in the equilibrated glass = \( \frac{0.04196}{1000} \times \frac{1000}{v} \) g ion/litre of glass,

where \( v = \text{sp. vol. (cc./g)} \)

and concentration of Fe³⁺ in the equilibrated glass = \( \frac{0.14208}{1000} \times \frac{1000}{v} \) g. ion/litre.

\( \log \left( \frac{\text{Fe}^{2+}}{\text{Fe}^{3+}} \right) = \log \left( \frac{0.04196}{0.14208} \right) = 1.47 = -0.53 \)
VI-7. Spectrophotometric Measurements

Preparation of glass-slab samples for spectrophotometric measurements:

For spectrophotometric measurements, slabs were prepared by pouring the molten glass into a rectangular mild steel die (26 mm x 9 mm x 5.0 mm) which was previously warmed to prevent any cracking due to sudden cooling. The slabs thus prepared were subsequently released from the die and were immediately put inside a furnace maintained at a temperature of about 200°C for annealing. The furnace was switched off and allowed to cool slowly to room temperature. The slabs were then immersed in dry benzene kept in small glass bottles which were kept in a desiccator. These glass slabs were used for spectrophotometric measurements. The thicknesses of the slabs were measured accurately with the help of a screw-gauge having a least count of 0.01 mm. It was around 5 mm in each case.

Measurement of Spectral Absorption:

For this purpose, a visible range spectrophotometer (Spectromom 360), in which spectral transmission in the range of 350 to 1000 nm wavelength could be measured, was used. The spectrophotometer was checked and adjusted before use with the help of a mercury discharge lamp (546 nm).

The glass slabs were dipped in benzene in the measurement cells to minimize scattering of light from the surfaces which were not perfectly smooth. Refractive index of benzene is 1.50 and is
very close to that of the glasses of which the slabs were made. In every case a blank glass of the same composition and comparable thickness but without any colouring ion was immersed in the reference cell, for which transmission was always adjusted at 100 percent. Optical densities for 5 mm. thickness were calculated (the actual measurements were made on slabs of thickness very close to 5 mm) and these were plotted against wavelength.