CHAPTER 3

EXPERIMENTAL

3.1. X-RAY DIFFRACTION METHOD

3.1.1. INTRODUCTION

Dilatometric and interferometric methods have long been used for the study of thermal expansion of solids in bulk. In addition to these microscopic methods, the X-ray diffraction technique, both in high and low temperature regions, had also been developed with the advent of X-ray crystallography. The method is based on the lattice parameter measurement of the crystalline solids at different temperatures and calculation of changes in the lattice parameter values, from which the coefficient of thermal expansion can be obtained. This method is superior to the macroscopic methods, because it is very accurate, non-destructive and the quantity of sample required is small and also phase and structural changes of the solid can be detected and followed from temperature to temperature. The disadvantage of this method is that it is applicable only in case of crystalline solids and solid-solutions. Gases, liquids and amorphous solids cannot be studied with this method.
3.1.2. WORKING PRINCIPLE OF THE DIFFRACTOMETER UNIT AND ITS ALIGNMENT

Philips Diffractometer Unit consisting of X-ray generator PW 1010, Wide range goniometer PW 1050 and electronic circuit panel and chart recorder PW 1051 was used to obtain diffractograms. The diffractometer operates on the parafocussing principle. The parafocussing geometry is illustrated in the Fig. 3. The goniometer is driven by a synchronous motor or it may be operated manually. The position of the counter arm giving the 2θ values can be read to 0.01° from the degree indicator dial. Proper alignment of the wide range goniometer was done by usual procedure.

The scale factor and multiplier selector in the recorder were set at 16 and 1.0 respectively, so as to keep the maximum detection within the scale when the X-ray generator worked at 36 Kv and 18 mA. The plate voltage of the Geiger tube was 1650 volts and the chart speed was kept at 300 mm/hour.

3.1.3. HIGH TEMPERATURE TECHNIQUE

3.1.3.(a) HIGH TEMPERATURE X-RAY DIFFRACTOMETER ATTACHMENT AND ITS ARRANGEMENT FOR WORKING:

The High Temperature X-ray Diffractometer
Fig. 3. Schematic Diagram of the High Temperature Experimental Arrangement.

Fig. 3. Diagram showing the Principle of Paraforessing.

Fig. 4. Schematic Diagram of the High Temperature Experimental Arrangement.

1. Metallic Blocks
2. Insulating Base
3. Elevation Align.
4. Azimuth Alignment.
5. Water-Power Connection

S-Specimen stage cum heater
1-Metallic Blocks
2-Insulating Base
3-Elevation Align.
4-Azimuth Alignment.
Attachment (model X86-N3), supplied by Material Research Corporation, New York, was used for high temperature work. With this attachment, temperature of the specimen could be varied from room temperature to 1500K. Vacuum down to $10^{-3}$ torr was readily obtained with the beryllium window and the temperature could be controlled with the proportional Temperature Controller (model X-8600-500-2). A schematic diagram of the experimental arrangement is given in Fig. 4. The specimen assembly was housed in a compact environmental chamber consisting of a polished aluminium shell with a cover. This was water cooled and evacuated with a double stage high vacuum rotary pump. The curved beryllium window was only 0.01 inch thick, and as such the absorptions of the incident and the diffracted X-ray beams were very small. The window provided a full diffraction angle of 2θ from $0^\circ$ to $160^\circ$.

After alignment of the goniometer, the Philips specimen stage mounting shaft was removed and the high temperature mounting shaft was fitted into the diffractometer sleeve. To the bottom of the specimen stage made of platinum and 40% rhodium, was welded a thermocouple of Pt/Pt-13% Rh. The external thermocouple extensions, waterpower assembly lines and the auxiliary heater were fitted properly to the Proportional Temperature Controller. The alignment of the specimen stage was made
with the precision alignment jig. A suspension of fine silicon powder in alcohol was made. Two drops of this suspension were placed on the specimen stage. The diffractograms obtained from this sample was used for checking the adjustment of the goniometer. A cross checking was also made by taking the diffraction records of pure platinum foils. A schematic diagram for water circulation and heating current supply is shown in Fig. 7.

3.1.3.(b) THERMO-COUPLE CALIBRATION AND MEASUREMENT OF TEMPERATURE OF THE SPECIMEN:

The e.m.f. developed in the thermo-couple was shown automatically in the temperature indicating dial of the Controller in both °C and °F. Practically, there was no difference in temperature between the specimen and the thermo-couple, as the latter was welded to the bottom of the specimen stage. The calibration of the thermo-couple and hence the temperature indicating dial was made in terms of lattice parameter values of pure platinum at different temperatures. The results were checked also by using the lattice constants of pure aluminium foil.

Diffractograms for the platinum foil were recorded for temperatures 25°, 200°, 400°, 800° and 1000°C, as shown in the indicating dial of the Controller. Lattice constants were determined accurately by the graphical extrapolation method. Lattice parameter values
Fig. 5. Lattice Parameter Vs Temperature for Platinum.
(numerical data given in Appendix, table 1. (A).)
\( \times \times \times \) Given values, \( \bullet \bullet \bullet \) Observed values.

Fig. 6. Plot of Lattice Parameter Vs Temperature for Aluminium.
(numerical data given in Appendix, table 1. (B) and (C).)
\( \times \times \times \) Observed values, \( \bullet \bullet \bullet \) Given values.
of platinum were taken from Edwards et al.\textsuperscript{45} and these data were used to draw a graph of lattice constants vs temperature (Fig. 5). From this graph, temperatures were determined corresponding to observed lattice constants. Comparison of these temperatures with those recorded by the Controller, showed that the Controller indicated slightly higher values with an average 4.5\textdegree{}C than the actual temperature of the specimen. The lower range upto 530\textdegree{}C was checked by using pure aluminium foil as a standard and taking lattice constant data of Wilson\textsuperscript{46}. From the results as shown in Fig. 6, it is evident that the dial showed slightly higher values with an average 4.0\textdegree{}C than the actual temperature of the specimen. In the present work therefore, a correction of -4.0\textdegree{}C was to be made. But in view of the inefficiency of the temperature Controller, uncertainty of about ±5\textdegree{}C (maximum) had to be tolerated. So this correction was practically absurd. It was found that the automatic temperature Controller did not function efficiently. Manual control was found to be more efficient, the variation being only very slight. The accuracy of the dial reading of ±5\textdegree{}C was thus easily obtained.

3.1.3.(c) SPECIMEN MOUNTING, RECORDING AND MEASUREMENTS:

The sample was ground to pass through 200 mesh (2/\kappa) sieve and a suspension was made with distilled water.
Three drops of the suspension were deposited carefully on the mounting surface of the specimen stage so that a smooth and flat coating was spread over the surface and then the sample was allowed to dry for 24 hours.

At any steady temperature, the pattern was recorded automatically by the electronic recorder on a chart. Scale factor, multiplier selector and scanning speed were set to suitable values as mentioned in section 3.1.2. Scanning of the thermograms was made from 20 = 3° to 45° to get all the intense peaks.

Diffraction records were taken by the continuous temperature increase method (CTE) i.e. the sample was heated at a particular temperature for about 3 hours before taking a record and then raised to a higher temperature (of about 25°C) without allowing it to cool to room temperature for the next record and so on.

The line positions in the diffractograms in terms of 2θ were measured with a film measuring instrument with uncertainty of ±0.001 cm. Each line was measured independently three times and the mean was taken for the calculation of dhkl from the relation,

\[ a = 2dhkl \sin \theta \]

The 'd' values were then plotted against temperature and a graph was carefully drawn. From this graph,
d values at intervals of about 20°C were noted and calculated. Further, the co-efficient of thermal expansion $\alpha$ was determined from the relation,

$$\frac{(d_{hkl})_{T_2} - (d_{hkl})_{T_1}}{(d_{hkl})_{T_1} (T_2 - T_1)}$$

3.1.3.(d) SOURCES OF ERROR AND THEIR ELIMINATION:

Parrish and Wilson\textsuperscript{47} and others have reviewed the major sources of error in counter diffractometry and recommended appropriate methods to eliminate and minimise them. But in the present investigation many of the sources of errors did not arise due to the following reasons:

The instrument alignments and 2 : 1 setting and zero angle calibration were done very carefully. Use of small time constant and scanning speed reduced the errors of recording to a minimum. The likely source of error was the specimen displacement. The Bragg angles at which the reflections were obtained, were considerably lower than those desirable for accurate measurement. Nevertheless, in the thermal expansion measurement as in the present case only relative displacements of lines were involved. The reproducibility of measurements in the film measuring instrument was quite satisfactory, an average of
Fig. 7. Schematic diagram showing water circulation through specimen chamber and blocks.
(plastic tubes are in positions for high temp. work and one end open for Liq. N\textsubscript{2} work.)

Fig. 8. Schematic diagram of low temperature arrangement.
5 readings having an uncertainty of \( \pm 0.001 \) cm. Now, 1° Bragg angle was equal to 1.012 cm. of the chart. So the above uncertainty corresponded to an uncertainty of about 0.00099° Bragg angle. This was equivalent to an uncertainty of about \( \pm 0.0015 \) in the measurement of spacing of about 3.58 Å. The absolute accuracy was not known, as the highest angle of measurement was only 20 = 25°.

3.1.4. LOW TEMPERATURE TECHNIQUE

3.1.4.(a) OUT-LINE OF THE EXPERIMENTAL ARRANGEMENT:

There was an extra provision for low temperature work in the High Temperature Attachment described in section 3.1.3.(a). Here instead of circulating water, other coolants could be used to lower the temperature of the specimen. In the present investigation, Liquid Nitrogen was used as coolant.

A copper cold-stage coated with gold was fitted in place of the high temperature specimen stage provided with a copper-constantan thermocouple. The experimental arrangement is shown in Fig.8. A heating arrangement was made to regulate the rate of evaporation of the liquid nitrogen so that the temperature of the specimen could be regulated thereby.
The specimen temperature up to 155K could be attained with this arrangement. The liquid nitrogen temperature was obtained by directly pouring in liquid nitrogen into the specimen chamber on to the specimen stage.

3.1.4.(b). THERMO-COUPLE CALIBRATION AND MEASUREMENT OF TEMPERATURE:

The copper-constantan thermo-couple was calibrated by measuring the e.m.f. given by it at the melting points of ice (0°C), pure carbon tetrachloride (-23°C), absolute alcohol (-114°C) and directly keeping the thermo-couple junction at the liquid nitrogen (-196°C). The standard e.m.f. $E_t$ values for the thermo-couple at fixed temperatures were taken from International tables and a graph was drawn (Fig.9a). The deviation curve ($\Delta E$ vs $E_C$) was drawn (Fig.9b). This graph was later on used for determination of specimen temperatures.

At different temperatures the thermo-e.m.f. generated in the thermo-couple was read from the direct reading potentiometer with an uncertainty of ±5 microvolts (±1°C). When steady state was attained, the records of the diffractograms were taken.
Fig. 9(A) E.m.f. Vs. temperature for Copper-Constantan thermo-couple.

Fig. 9(B), Calibration for Copper-Constantan thermo-couple.
(numerical data given in Appendix, table 2.)
As a check in the measurement of low temperature, the lattice constants of pure aluminium foil at different temperatures were determined and compared with the data given by Figgins et al. It was found that the uncertainty in the measurement of temperature of the specimen was only \( \pm 2^\circ C \) (Fig. 6).
3.2. PREPARATION OF SAMPLES

3.2.1. INTRODUCTION:

The raw clay minerals collected from different localities of Assam and Meghalaya were used for the preparation of the pure clays. The detailed identification of these minerals was reported elsewhere\textsuperscript{49,50}.

3.2.2. CLAY SEPARATION FROM RAW SAMPLES:

Mackenzie's method\textsuperscript{51} for clay separation from raw samples was used. The raw samples were ground and about 100g of the sample was shaken with distilled water in a beaker to which about 40 drops of conc. NH\textsubscript{4}OH was added. After 16 hours, the suspension was syphoned out without disturbing the residues and was centrifuged. The residues were again shaken with distilled water and the above procedure was repeated thrice to get the adequate amount of the sample. The centrifuged slurry was dried in evaporating dishes and then ground to pass through a 200 mesh sieve.

3.2.3. PURITY OF THE SAMPLES:

The purity of the samples used in the present study was determined by the methods of chemical analyses described by Kum\textsuperscript{r} and Sinha\textsuperscript{52}. The results are
given in Table I.

**TABLE I**

**Chemical analyses of the Clays**

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>FeO</th>
<th>TiO₂</th>
<th>CaO</th>
<th>MgO</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>Ign loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>49.60</td>
<td>35.98</td>
<td>0.82</td>
<td>0.08</td>
<td>1.13</td>
<td>0.34</td>
<td>trace</td>
<td>0.09</td>
<td>0.18</td>
<td>11.82</td>
</tr>
<tr>
<td>B</td>
<td>51.88</td>
<td>26.73</td>
<td>0.88</td>
<td>0.96</td>
<td>1.11</td>
<td>0.52</td>
<td>2.58</td>
<td>0.31</td>
<td>7.35</td>
<td>7.78</td>
</tr>
<tr>
<td>C</td>
<td>50.48</td>
<td>30.76</td>
<td>0.99</td>
<td>0.68</td>
<td>0.92</td>
<td>0.70</td>
<td>1.23</td>
<td>0.29</td>
<td>5.91</td>
<td>8.22</td>
</tr>
</tbody>
</table>

A = Kaolinite, B = Illite
C = Interstratified kaolinite-illite

The proportion of alumina (Al₂O₃) and the amount of loss on ignition of the sample A agreed well with the ideal values for kaolinite, based on the chemical formula Al₂O₃·2SiO₂·2H₂O. The compositions of the sample B agreed almost with the ideal values for illite given elsewhere. The presence of K₂O in the sample C indicated the presence of micaceous clay together with kaolinite. To describe the nature of the micaceous clay, i.e. whether this was mica, muscovite or illite, X-ray powder photographs of the heat treated samples were taken. The study of these
photographs, as also the proportion of $K_2O$, indicated that the micaceous character was due to the presence of illite. The relative abundance of these two minerals in the sample C obtained from the measurements of the peak heights of the basal reflections was (Fig. 10C):

$$\text{Kaolinite} : \text{illite} = 11 : 14$$

3.3. PREPARATIONS OF INTERSALATED CLAY COMPLEXES WITH ALKALI-ACETATES AND THE STUDY OF THE CONCENTRATION EFFECT ON THE COMPLEX FORMATION

3.3.1. PREPARATION OF THE COMPLEXES:

In trying to make complexes of the clay minerals with alkali-acetates, Wada's method was followed. Potassium acetate ($99\%$ purity), sodium acetate ($99\%$ purity) and lithium acetate (L.R.) supplied by B.D.H. and caesium acetate (suprapur) supplied by E.M.D. (Germany) were used. Kaolinite and sufficient amount of potassium acetate were mixed thoroughly and ground gently till the mass become moist. This was done inside an air conditioned room as the acetate is very deliquescent. After 48 hours of reaction, it was washed with distilled water, centrifuged and evaporated to dryness in atmosphere. Similar procedure was adopted to get complexes with other
FIG 10  X-RAY DIFFRACTION OF CLAYS AND INTERSALATED COMPLEXES

(A) KAOLINITE

(B) ILLITE

(C) MIXED KAO-ILLITE

(D) INTERSALATED CH₃COOK-KAO.COMPLEX

(E) INT. CH₃COOK-KAO.COMPLEX (DRY)

(F) INTERSALATED CH₃COOC₂-KAO.COMPLEX

(G) INT. CH₃COOC₂-KAO.COMPLEX (H₂O)
acetates of sodium, lithium and caesium.

3.3.2. THE STUDY OF THE CONCENTRATION EFFECT:

To study the concentration effect of the intersalts on intersalation, different amounts of the alkali acetates were mixed with clay minerals. The proportions of the clay minerals and the alkali acetates were 1:0.2, 1:0.5, 1:0.75, 1:1.0, 1:1.5, 1:2.0, 1:2.5, 1:3.0, 1:3.5 and 1:4.0 by weight.

Lithium and sodium acetates did not respond to form intersalated complexes with kaolinite, whereas acetates of potassium and caesium did so. In addition to first superlattice line at 14.07\(\AA\), another new line at 3.52\(\AA\) (the fourth order reflection of the superlattice) was observed in intersalated potassium acetate-kaolinite complex as shown in Fig.10(D). With the increase in proportion of the interlayer potassium acetate in the same amount of kaolinite, the relative intensity of the line for d_{001}(kaolinite) decreased and that of the superlattice line increased as shown in Fig.11.

On heating the complex, the superlattice line disappeared even at 60°C accompanied by the reappearance of the original potassium acetate lines. The two superlattice lines could be made to disappear even when
Fig. 11. Variation of Peak Height with Concentration of K-Acetate in CH$_3$CCOK-kaolinite Complex (numerical data given in Appendix Table 3(A)).

- - - d$_{001}$(kaolinite), x x x d$_{001}^s$ (supperlattice)

Fig. 12. Variation of Peak Height with Concentration of C$_8$-Acetate in Intersalated CH$_3$CCCO$_8$-kaolinite Complex (numerical data given in Appendix Table 3(B)).

- - - d$_{001}$ (kaolinite), x x x d$_{001}^s$ (supperlattice).
the sample atmosphere was made quite dry with CaCl₂ or when the sample was kept in vacuum for a long time. What remained was a wide hump in the position of the first superlattice line. These results are evident in the diffractogram (Fig.10E).

The intersalation of caesium acetate into sheets of kaolinite caused the lattice expansion to 14.01\(\text{Å}\). A wide hump was observed at the position of the basal reflection of kaolinite (Fig.10F). On heating to 50°C, superlattice lines 14.01\(\text{Å}\) and 3.53\(\text{Å}\) were shifted to 17.18\(\text{Å}\) and 3.46\(\text{Å}\) respectively. Even if the sample atmosphere was made quite dry or it was kept in vacuum, the same phenomenon was observed (Fig.10G). With increase of interlayer caesium acetate, the relative intensity of the superlattice lines increased, while that of kaolinite decreased. The results are shown in Fig.12.

Refering to Figs.11 and 12, it is evident that intersalation phenomena in both acetates are same, but the process of reactions are not same. Figs.10(E) and 10(G) show that water plays an important role for the formation of intersalated complexes. The complexes get their saturation states when kaolinite and potassium acetate and kaolinite and caesium acetate are in the ratios 1 : 2 and 1 : 2.5 respectively (Figs.11 and 12).

Wada \(^8\) and others \(^29\) claimed to have observed
that the super-lattice line 14.01 Å of potassium acetate kaolinite complex shifted to 11.62 Å on dehydration at 110°C. But in the present investigation no such effect was observed even on many trials.

3.4. DOPING OF KAOLINITE WITH ALKALI METALS

3.4.1. INTRODUCTION:

Injection of impurity salt or metal (doping) to a crystal can be made by heating the crystal to a high temperature in the vapour of the impurity. Van Doorn have pointed out that the method of additive coloration can be applied to all substances which have a low vapour pressure at their triple points. Concepts and experimental methods derived from the study of the color centers in the alkali halides could also be applied successfully to learn about the electronic processes and defects in other materials. Following these views, the doping of sodium and lithium metals into the kaolinite crystal were attempted.

3.4.2. EXPERIMENTAL ARRANGEMENT:

The apparatus consisted of a stainless steel tube 24 cms in length, 2 cms in diameter and open at one end. The tube could be connected to a pump for evacuation (Fig.13).
Fig. 13. Experimental arrangement for Doping.
For X-ray diffractometer study, an oriented aggregate in the form of a fine coating of clay mineral was made on a Tantalum base (Fig. 13a). The base was then suspended inside the tube from the brass rod of the plug by means of a platinum wire. For dielectric measurement, an oriented aggregate of a fine clay coating was made on the copper electrode, made specially for this purpose (Fig. 13b). The electrode was hung inside the tube from the rod by means of a platinum wire. The height of the suspended systems could be adjusted so as to keep the sample at different temperatures. A high vacuum pump ($10^{-3}$ torr) with a cold trap and a stop-cork was used for evacuation.

The lower end of the steel tube was introduced into a cylindrical furnace made for the purpose, upto about two-third of its length, and the upper end was kept cool by water circulation through a spiral copper tubing in contact with the steel tube. A variac was used to regulate the heating voltage which could maintain the temperature at about $\pm 2^\circ$C. The temperature of the furnace at any depth was recorded by a calibrated Pyrometer.

A small amount of sodium metal (B.D.H., m.pt. $97.5^\circ$C and b.pt. $880^\circ$C) was put into the bottom of the steel tube. The plug with the specimen was fitted to the open end. After evacuation, the lower end of the tube
was placed inside the furnace at about 750°C. The specimen temperature was adjusted to about 250°C. After heating to about 3 hours, the specimen was cooled in the same vacuum tube and was stored in a dessicator for future experiment. The doped specimen was found to be pale yellowish and hard, indicating that doping had been achieved. For doping with lithium metal, similar procedure was tried. For lithium (E.M.D., Germany, m.pt. 186°C and b.pt. 1336°C), the furnace and the specimen temperatures were set at 900°C and 300°C respectively. However, no perceptible change either in color or in hardness was observed indicating there might not be any doping in this case.
3.5. MEASUREMENTS OF DIELECTRIC PROPERTIES

3.5.1. INTRODUCTION:

In the present study of dielectric properties of the clay minerals and other complexes, the frequency range chosen was 50 - 20,000 Hz. The study of the dielectric properties of the clay minerals and their complexes in this frequency range and at the temperature range 0°C - 800°C, revealed informations which could be profitably used to understand the thermal behaviours of the samples.

3.5.2. THE UNIVERSAL BRIDGE:

The Universal Bridge used was a direct reading type (Marconi TF 2700), which measured directly capacitance \( C_p \) from 0.5 PF to 1100 \( \mu \)F with maximum accuracy \( \pm 2\% \) and resistance \( R \) from 10 mohm to 11 Mohm with accuracy \( \pm 2\% \) in a parallel combination. A Wheatstone Bridge circuit was used in the Bridge for resistance measurement, while capacity was measured by comparision with a standard capacitor in \( R - C \) ratio arm (Figs. 14A and 14B). The frequency of the internal generator was fixed at 1 KHz. For other frequencies from 20 Hz to 20,000 Hz, an external Oscillator was used. The external source with an isolating transformer in series was connected to the Bridge via a jacket plug. Insertion of the jacket plug into
Fig. 14(A). Basic Capacitance Bridge.

Fig. 14(B). Basic Resistance Bridge.

Fig. 14(C). Experimental arrangement of the bridge with external source.
the a.c. socket of the Bridge, switched off the internal oscillator.

The detector consisted of an emitter follower, an amplifier and a diode rectifier. The same detector could be used for both internal and external sources.

To minimise the effect of external connections, short and low capacity cables were used to connect dielectric cell to the Bridge and shieldings of the cables were grounded. Care was taken to ensure that the positions of the cables remained unchanged throughout the whole work. The experimental arrangement is shown in Fig.14(C).

The working of the Universal Bridge was checked with standard capacitors and resistors. The maximum accuracy for the measurements of capacitance and resistance were +0.2 PF and +1 ohm respectively.

3.5.3. DIELECTRIC CELLS:

The dielectric cells for different temperature ranges had to be designed, because the thermostates available were of different nature.

3.5.3.(a) DIELECTRIC CELLS FOR 250 to 573K(sample orientation - parallel to [001] ):

For dielectric measurements in the temperature range 253 - 573K, the dielectric cell as shown in Fig.15(I)
Fig. 15. Dielectric Cells: (I) Cell for dielectric study in temp. range -20° to 300°C, (II) Cell for study along the plane perpendicular to (001) plane, (III) Electrode for temp. range 20°-780°C, and (IV) Process of sedimentation of the specimen.
was used. This was a parallel plate arrangement. The circular electrodes were made of copper which were silvered by electrolysis. One electrode was welded to a thick tungsten rod which was sealed through a temperature resistant glass tube. The other electrode was fitted to a brass tube, which had a hole H for evacuation. The distance between the electrodes could be adjusted at will with the cone and socket arrangement as shown in the Fig. 15(I).

The temperature of the specimen could be measured by a Pt - Pt 13% Rh thermocouple inserted through a hole in the cone. (For the complexes, the room temperature capacitance was about 60 to 80 PF).

3.5.3.(b) DIELECTRIC CELL FOR 253 to 573K (sample orientation - perpendicular to [001]):

For qualitative study of dielectric properties along the direction perpendicular to [001], another dielectric cell as shown in Fig. 15(II) was used. Temperature resistant glass slides were silvered chemically leaving a narrow gap (~0.05cm) at the middle for deposition of the samples. The silvered strips were used as the fixed parallel plate electrodes. The electrodes with the sample could be inserted into a glass cone and socket arrangement similar to the cell no.(I). Heating and evacuation were done with the same experimental set up as in (I).
(The capacitance was about 5 to 9 PF for room temperature including contribution from the glass substrate)

3.5.3.(c). DIELECTRIC CELL FOR TEMPERATURE RANGE 293 to 1053K (sample orientation parallel to [001]).

Another cell with the parallel plate arrangement was used for dielectric measurements in the temperature range 293 - 1053K. The electrodes C₁ and C₂ (Fig.15(III)) consisted of two copper discs to which two platinum wires were welded. The furnace enclosing the electrodes consisted of two hemispherical cups of platinum on which heating elements made of platinum wires were mounted by means of alumina cement. These platinum cups were meant for keeping the temperature uniform over the cell. These cups had circular holes at the bottoms, and a Pt - Pt 13 % Rh thermocouple was fixed through the hole at the lower cup. An insulating hollow cylinder M, made of high temperature cement was mounted vertically on the thermo-couple sheath at the lower part of the furnace. A nichrom wire spring N, was fitted on the upper part of M, such that it could spring up and down smoothly. The design was made in such a way that the electrode C₂ seated on the spring occupied the central position of the furnace. The function of the spring was to keep the lower electrode C₂ firmly in contact with
the upper electrode $C_1$ when the latter was placed on it. The whole furnace was enclosed in a metallic casing consisting of two halves. The lower electrode $C_2$ was grounded via the lower half of the casing and the terminal of the upper electrode $C_1$ was led out through the upper half and kept insulated from it by means of a pyrex glass tube. The gap between the two electrodes could be varied by sliding the glass tube $T$ manually. Both electrodes were silvered by electrolysis. (The capacitance of the cell with the clays was about 140 to 190 PF at room temperature).

3.5.4. HIGH TEMPERATURE ARRANGEMENTS

3.5.4.(a) ARRANGEMENT FOR TEMPERATURE RANGE 253 to 573K:

Ultra-Thermostat, Type NBE (Germany), was used for this temperature range (Fig. 16). It consisted of a copper reservoir of 12 litre capacity, a heater $H$, a contact thermometer $T_1$, a check thermometer $T_2$ and a stirrer $S$. To avoid the excessive loss of heat by thermal radiation, the reservoir was placed in an another reservoir, the space between them being filled with an insulating material.

A superheated steam cylinder oil having an adequately high flash point was used as a bath fluid for
Fig. 16. The oil bath for temperature control in dielectric work (description in the text)

Fig. 17. Experimental arrangement for electric measurements in the temperature range -20°C to 780°C.
temperature control up to 573K. For low temperature up to 253K, a freezing mixture of NaCl and ice in the ratio 33 : 100 was used.

3.5.4.(b) ARRANGEMENT FOR TEMPERATURE RANGE

293 - 1053K:

The furnace described in the section 3.5.3.(c) was used to the highest temperature of measurements in this investigation. A schematic diagram of the experimental arrangement is given in Fig. 17. The furnace was evacuated by a rotary pump (10^-3 torr). To keep the furnace surface cool, an arrangement for circulation of tap water was made. The furnace voltage was stabilised, and the furnace temperature was increased in steps with an auto transformer. The thermo-couple position was kept fixed very near to the specimen.

3.5.5. TEMPERATURE MEASUREMENTS:

The contact point in the contact thermometer was set at a particular temperature by rotating the magnet placed at the top of the thermometer. The temperature of the oil was controlled by automatic make and break of the heater circuit. The controlled temperature was checked by the check thermometer kept nearer to the cell. The specimen temperature was rechecked by measuring the
e.m.f. generated in the thermocouple with a potentiometer, which was kept very near to the specimen. The error in the measurement of temperature was less than $\pm 1.5^\circ C$.

The Pt - Pt $13\%$ Rh thermocouple used in the present study, up to 1053K was already calibrated. The current in the furnace could be controlled within $\pm 5$ microvolts of thermocouple readings. This introduced an uncertainty in the temperature measurement of about $\pm 1^\circ C$.

3.5.6. SPECIMEN MOUNTING AND MEASUREMENTS OF CAPACITANCE AND CONDUCTANCE:

Cell No.(I)

The upper electrode of cell I was clamped vertically as shown in Fig.15(IV). A few drops of the sample suspension in water were placed on the disc to get a fine and smooth coating of the sample ($\sim 0.01$ to $0.02$ cm). It was then allowed to dry in air. The electrode with the sample on it was brought into the cell until it was firmly pressed against the surface of the lower electrode; taking adequate care not to remove any sample. Springs were fitted (as shown) to make the contact more firm. The cell thus charged with the sample was immersed into the oil bath up to the neck of the cell.
Cell No.(II)

The sample were sedimented on the gap of the silvered glass plates. After drying in air, the slides were connected to the leads of the bridge with clips. (as shown), and fitted inside the cell. The cell thus charged with the sample was immersed into the oil bath upto its neck.

Cell No.(III)

The upper electrode of the third cell was also coated with a fine sediment of the sample. The glass extension of the electrode was inserted through the hole of the upper half of the furnace casing. This was then fitted to the lower half, and the glass tube was carefully pressed down until it came in contact with the lower electrode. The electrode was pressed gently and sealed with the casing by plasticine. The surface of the air dried samples were smooth and the spring arrangements pressed the electrodes to eliminate any gap between the electrode and the specimen. The cells were evacuated to expel any air that might be entrapped in between the electrodes.

The capacitance was directly read from the meter of the Impedence Bridge. From the observed values of the resistances, the values for conductance were also calculated.
The reproducibilities of measurements in capacitance and resistance at a particular temperature were quite satisfactory. An average of four readings of capacitance had a maximum deviation of ±0.2 PF from the mean and that for resistance was ±5.0 ohms in the range $10^4$ to $10^7$ ohms which could be neglected.
3.6. STUDY OF THERMODYNAMICAL PROPERTIES BY DIFFERENTIAL THERMAL ANALYSIS

3.6.1. INTRODUCTION:

It would be extremely valuable to supplement the study of the thermal behaviour of the present investigation with the differential thermal analysis data of clay minerals and their complexes with alkali-acetates. The small differences in the physical behaviour of hydroxyl groups at different sites in the crystal, may cause large differences in the peak area or the peak temperature of an endothermic transition in the D.T.A. thermograms. Hence D.T.A. technique may be used as a sensitive calorimetric method for quantitative analysis.

3.6.2. EXPERIMENTAL ARRANGEMENT:

A Leeds and Northrup D.T.A. apparatus (Type G) used in the investigation, consisted of a furnace, a sample holder, three thermo-couples, a ceramic block for holding the above accessories and temperature measuring and control arrangements (Fig. 18). Thermo-couple A was inserted into the experimental sample, and B into the reference sample α - alumina, the latter showing no thermal anomaly in the temperature range (to 1000°C) used. Any temperature difference between the
Fig. 18. Schematic diagram of Differential Thermal Analysis System. 
A-Thermocouple to the Sample
B-Thermocouple to the Inert material
C-Thermocouple
D-The Ceramic Block

Rate of Change
Sample Temperature Signal

Cell Assembly
Amplifier
Range Control
Recorder

TEMPERATURE PROGRAMMER CONTROLLER
inert material and the experimental sample arising from possible thermal abnormality of the latter, produced a resultant net voltage which was recorded as a function of temperature in the Speedomax recorder. The sample and the reference material were placed close together in the ceramic block D, whose temperature could be changed uniformly by means of Temperature-Programmer-Controller, and the difference in temperature between the sample and the inert material was recorded on a chart in the Micromax. A third thermo-couple C measured the temperature of the block.

Certain precautions had to be taken to obtain reliable results:

(a) The rate of heating had to be kept constant, which was done by the temperature controller in the apparatus.

(b) The rate of heating had to be maintained at an optimum value as determined by trial runs.

(c) The sample had to be packed tightly in the cavity of the sample holder.

3.6.3. SPECIMEN PREPARATION, TEMPERATURE MEASUREMENT AND RECORDING:

About 500 mg of kaolinite (sample A) was mixed with the requisite amount of calcined alumina to
make the total weight 1.0 gm. Similarly, 550 mg each of illite (sample B) and interstratified kaolinite-illite (sample C) were diluted with requisite amount of calcined alumina to make the total weight 1.0 gm. These proportions were found to be best for reproducibilities of results.

These samples were ground to pass through 200 mesh sieve and were kept in a vacuum dessicator for two days over a saturated solution of $\text{Mg(NO}_3\text{)}_2\cdot6\text{H}_2\text{O}$ to control the relative humidity at about 56%. One gm of the inert material in one cavity and the same amount of the diluted test material in the other cavity of the sample holder, were packed under the same conditions. In case of the highly hygroscopic materials like caesium acetate and intersalated kaolinite complexes, extra precautions were taken to minimise absorption of moisture from the atmosphere. Moreover, these samples were heated to about 450K very rapidly and then allowed to cool to room temperature for immediate recording.

The hot junctions of the differential chromal-alumal thermo-couple were placed centrally in the cavities and well embedded in the materials packed inside them. The insulating refractory block, holding the sample holder and the thermo-couples, was placed properly in the furnace. The heating rate was adjusted at 10°C/min
generally, as at this rate, the control was quite sensitive showing sharp peaks. The temperatures were noted from the Micromax chart and also from the readings of a calibrated pyrometer (made by Cambridge Instruments Co. LTD.) with an uncertainty of ±1°C. To study the kinetic parameters of the dehydroxylation process of kaolinite both in pure and in mixed layer kaolinite-illite, the heating rate was adjusted between 3 to 15°C/min.

The records were made from 303 to 1273K for clay samples and intersalated complexes, and from 303 to 523K for caesium acetate.
3.7. TECHNIQUE FOR INFRARED ANALYSIS

3.7.1. INTRODUCTION:

Infrared spectroscopy is not only an efficient method for structural analysis, such as the study of hydrogen bonding, but also it provides considerable scope for adequate explanation of thermal reaction of samples particularly clay minerals and their complexes with other salts\textsuperscript{16,20,29}. The general principle of the apparatus is to provide records of the infrared transmittance of a sample as a function of the wave numbers or frequencies.

3.7.2. EXPERIMENTAL ARRANGEMENTS:

The infrared absorption spectrograms were recorded by a double beam infrared spectrometer (Perkin-Elmer Model 237 B) in the region 4000\textsuperscript{-1} to 700\textsuperscript{-1} cm\textsuperscript{-1} (frequency range about 1.9 x 10\textsuperscript{13} to 1.2 x 10\textsuperscript{14}Hz) using NaCl prism. The schematic diagram of the experimental arrangement is given in Fig.19.

The necessary precautions were taken as prescribed\textsuperscript{57} to obtain reproducible results.

3.7.3. SAMPLE PREPARATION AND RECORDING:

Perkin-Elmer Die (Fig.20) was used for preparation of the pellet. About 2.0 mg of a sample was
Fig. 19. A block diagram of the Infrared Spectrophotometer.

Fig. 20. A block diagram of the Die for Tablet preparation (Cutway View).
mixed throughly with about 400 mg KBr (E.M.), ground manually for about 15 minutes in an egate mortar. About 100 mg of the mixture was placed on the anvil and a pellet was prepared in the usual manner under the hydraulic pressure of about 17000 Psi in the Carver Hydraulic press (Model C).

To study the dehydration phenomenon of clay minerals, the samples were heated to requisite temperatures at the rate of 10°C/min. for two hours and quenched in a dessicator. The preparation of the pellets and their spectrograms were made soon after to prevent rehydration of the heated samples.

Instead of pellets, films were used for the study of Caesium acetate and its complex. The caesium acetate films were prepared by evaporating a solution of the acetate on the slit with a glass supporting plate, placed in an oven at about 100°C. Similar procedure was followed in the case of its complex as well.

The infrared spectra of the acetate and the intersalated Caesium acetate-kaolinite complex were recorded between the wave number region 4000⁻¹ to 2000⁻¹ cm⁻¹ in two steps: (a) immediately after the samples were removed from the oven under controlled humidity at 45% and (b) after the samples cooled to 24°C and rehydrated under humidity of 60% .
Two recording charts, one for wave number region 2500 to 4000\(^{-1}\) cm and the other for 700 to 2000\(^{-1}\) cm were used to record the infrared spectrograms. Slow scanning speed and normal slit were used.

The corrections were made for each recording chart with a polystyrene film (0.05 mm thick), which shows a very sharp absorption band at about 1601.4\(^{-1}\) cm. The absorption peak positions of the spectrograms were measured accurately with the help of the film measuring instrument having uncertainty of about ±0.001 cm.