CHAPTER 4
RESULTS AND DISCUSSION

4.1. THERMAL EXPANSION

4.1.1. THERMAL EXPANSION OF KAOLINITE, MIXED LAYER KAOLINITE-ILLITE AND INTERCALATED KAOLINITE COMPLEXES WITH ALKALI-ACETATES

4.1.1.(a) KAOLINITE : INTERPLANNER SPACINGS AT DIFFERENT TEMPERATURES :

Interplanner spacings corresponding to 002 reflection ($2\theta = 25^\circ$) were used for the measurements of the coefficient of thermal expansion from 77K to 850K at about 25$^\circ$ intervals. The variation of $d_{002}$ with temperature for kaolinite (pure) is displayed in Fig. 21. It is seen that the expansion is uniform to about 680K, above which it slows down. No diffraction lines were observed above 850K. The samples heated above 850K and then quenched or annealing to room temperature also did not show any diffraction lines.

4.1.1.(b) KAOLINITE IN MIXED LAYER KAOLINITE-ILLITE :
SPACINGS AT DIFFERENT TEMPERATURES :

The values of the $d_{002}$ spacings of kaolinite in mixed layer kaolinite-illite at different
Fig. 21. Variation of $d_{200}$ with temperature in kaolinite specimen, (numerical data are given in Appendix TABLE 4, 5 and 9).
temperatures at about $25^\circ$ intervals were obtained and the results are shown in Fig.21. It is obvious that the thermal expansion of pure kaolinite and mixed layer kaolinite are identical in nature, with a little variation of the $d_{001}$ values.

4.1.1.(c) INTERCALATED POTASSIUM ACETATE-KAOLINITE COMPLEX : SPACINGS AT DIFFERENT TEMPERATURES :

The X-ray diffraction records were made from 77K to 820K. In the range 77K - 320K, the superlattice lines were present along with the basal reflections of kaolinite. (The line at $14.1^\circ$ is not a superlattice line in the crystallographic sense. Actually, this line is due to the expansion of the lattice as a result of complex formation. But this term is used only because of the nonavailability of other suitable term).

Above this range of temperature, superlattice lines disappeared. The observed spacings of the superlattice line are displayed in the Fig.22.

The interplanner spacings for kaolinite lines were also obtained at about $25^\circ$ intervals and the results shown in Fig.21C. The figure shows that the expansion of kaolinite in the complex is also more or less uniform. After the disappearance of SL lines,
Fig. 22. Variation of superlattice line with temperature in the nitride complex (numerical data are given in Table 7B).
potassium acetate lines appeared. No new lines except those of the acetate lines were observed.

4.1.1. (d) INTERCALATED CAESIUM ACETATE-KAOLINITE COMPLEX:

On intercalation with the acetate, a superlattice line with spacing 14.01 Å and another line with spacing 3.53 Å appeared (the latter is thought to be the 4th order of the first). There was practically no lines of kaolinite or of the acetate in the complex at room temperature or at any higher temperature (Fig. 23). Only a hump appeared in the position of d_{001} line of Kaolinite (7.1 Å). On heating or drying, the SL lines disappeared and two new lines at 17.18 Å appeared. These two lines persisted to about 475 K and disappeared above it. If the sample were cooled to room temperature and allowed to stay overnight, the SL lines reappeared and on heating or drying the same sequence of events took place.

The spacings of the first SL line were measured from 77 K to 320 K. The results are shown in Fig. 24.

4.1.1. (e) CO-EFFICIENTS OF THERMAL EXPANSION (CTE):

The CTE of kaolinite along [001] in pure, mixed layer, and intercalated complex of kaolinite were calculated from the observed values of d_{001} and the results
Fig. 23. X-ray diffraction Patterns of Caesium Acetate, and intercalated Cs-Acetate-kaolinite complex. Data given in Appendix Table 6.
are shown in Figs. 25. (A), (B) and (C).

It is seen that the CTE's of kaolinite in pure state increase slowly to about 450K and then gradually begin to decrease. Kaolinite in the mixed layer shows the similar behaviour. Some of the CTE values of kaolinite are shown in the Table II.

The CTE's of the superlattice line of potassium acetate-kaolinite complex as well as of caesium acetate-kaolinite complex are almost constant with a slight tendency to rise (Figs. 28 and 29).

TABLE II

Average co-efficients of thermal expansion

(\(\times 10^6\) C Deg\(^{-1}\))

<table>
<thead>
<tr>
<th>Kaolinite</th>
<th>Temperature range in °K</th>
<th>(\times 10^6)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure</td>
<td>80 - 450</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>450 - 760</td>
<td>16</td>
</tr>
<tr>
<td>Mixed layer</td>
<td>60 - 425</td>
<td>19</td>
</tr>
<tr>
<td></td>
<td>425 - 750</td>
<td>16</td>
</tr>
<tr>
<td>K-acetate</td>
<td>80 - 350</td>
<td>17</td>
</tr>
<tr>
<td>complex</td>
<td>350 - 600</td>
<td>13</td>
</tr>
</tbody>
</table>
Fig. 25. The thermal expansion of kaolinite along [001] (~perstratified with feldspar and muscovite (~tab, (numerical data are given in Ap...
4.1.2. THERMAL EXPANSION OF ILLITE IN PURE AND IN MIXED LAYER KAOLINITE-ILLITE:

The values of the interplanner spacings \(d_{001}\) measured from 006 reflection \((2\theta = 27^\circ)\) were used to determine the thermal expansion of illite from 77K to about 1300K.

4.1.2.(a) ILLITE (in pure state):

The \(d_{006}\) spacings are plotted against temperature at about 25° intervals and the result is shown in Fig.26.(A). It is seen that the lattice expands uniformly from 80K to about 1000K with a slight anomaly at about 500K. The expansion is rather rapid above 1000K.

4.1.2.(b) ILLITE IN MIXED LAYER KAOLINITE-ILLITE:

The values of the spacings \(d_{006}\) of illite in the complex are graphically represented in Fig.26.(B), which shows that the nature of expansion is nearly same as that of pure illite.

The CTE's of these samples as calculated from the observed expansion of \(d_{001}\) are shown in Figs.27.(A) and (B) respectively. The Figs. show that the temperature variations of the CTE's are also nearly same, both showing two anomalies at about 350K and 1050K.
Fig. 26. Variation of $d_{001}$ with temperature in Illite sample. (Numerical data are given in Appendix 1; see Table 8 and 9.)
4.1.3. ACTIVATION ENERGIES OF KAOLINITE AND ILLITE:

In order to see if Mott and Gurney's relation for thermal expansion is applicable in the present case, $\log_e(\Delta xT^2)$ is plotted against $\frac{1}{T}$ (Figs. 30, 31 and 32). It is seen that the graphs are linear in the temperature ranges 150 - 325K (pure kaolinite), 175 - 325K (mixed layer kaolinite) and 125 - 300K (complex).

Similar graphs for illite, in both pure and mixed states, are given in Figs. 33 and 34 respectively. These graphs show linearity in certain ranges of temperatures. It may thus be assumed that Mott and Gurney's relation is perhaps applicable in the present case also.

From the slopes of the linear portions of the curves, the activation energies of all the samples are evaluated and the results shown in the Table III.

<table>
<thead>
<tr>
<th>Sl. no.</th>
<th>Sample</th>
<th>Temperature range (°K)</th>
<th>Activation Energy (Kcal.mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Kaolinite</td>
<td>150 - 350</td>
<td>1.15</td>
</tr>
<tr>
<td>2.</td>
<td>Kaolinite in mixed layer</td>
<td>175 - 350</td>
<td>0.92</td>
</tr>
<tr>
<td>3.</td>
<td>Kaolinite in the complex</td>
<td>125 - 300</td>
<td>0.69</td>
</tr>
<tr>
<td>4.</td>
<td>Illite in pure</td>
<td>80 - 180</td>
<td>0.60</td>
</tr>
<tr>
<td>5.</td>
<td>Illite in mixed layer</td>
<td>870 - 1025</td>
<td>27.72</td>
</tr>
</tbody>
</table>
Fig. 27. The Co-efficients of thermal expansion of Illite along (001) plane, (numerical data are given in Appendix Table 8 and 9).

(A) Pure, and (B) In mixed layer kaolinite-illite.
Fig. 28. The co-efficients of thermal expansion of the SL superlattice line of CH₃COOCa-Kaolinite complex. Numerical data are given in Appendix TABLE 7A.

Fig. 29. The co-efficients of thermal expansion of the SL superlattice line of CH₃COOCa-Kaolinite Complex. Numerical data are given in Appendix TABLE 7B.
Fig. 31: Plot \( \log_e (\Delta a_r^2) \) vs \( \frac{1}{t} \) for kaolinite interstratified with illite. Numerical data are given in Appendix TABLE 10B.

Numerical data are given in Appendix TABLE 10A.
Fig. 32. Plot of $\log_e(\Delta a, T^2)$ vs. kaolinite in the CH$_3$COOK-kaolinite complex (numerical data are given in Appendix TABLE 9C).

Fig. 33. Plot of $\log_e(\Delta a, T^2)$ vs. $\frac{1}{T}$ for kaolinite pure.
(numerical data are given in appendix TABLE 9C.)
4.1.4. DISCUSSION:

The results of the thermal expansion experiments show that, on heating, OH- groups from the structures of various clays and their complexes are gradually removed. Consequently, a distinct phase change is brought about around 350K. The removal of the structural water causes the intensity of the basal reflections to decrease. It has been found that this process does not affect the room temperature values of the spacings. Detailed results are given elsewhere. In case of kaolinite, disappearance of diffraction patterns above 850K indicates the complete destruction of kaolinite structure. In case of illite, a complete new phase appears above about 1050K.

It is seen from Figs.21.(A) and (B) that the thermal expansion of kaolinite, both in pure and mixed layer state, are almost the same. This indicates that kaolinite and illite maintain their individual characteristics in the mixed layer state more or less like a mixture.

On intercalation with potassium acetate, the $d_{001}$ values of kaolinite decrease in the low temperature region whereas $d_{h00}$ values of the acetate increase, the decrease in case of the former being nearly equal to the increase in case of the latter (Figs.21 and 35). In case
Fig. 34. Plot of $\log_{10}(\Delta a^r)$ vs. $1/T\times 10^4$ for illite in mixed-layer kaolinite-illite. (Numerical data are given in Appendix I. Table 10.3).
Fig. 35. Variation of $d_{100}$ with Temperature in Potassium Acetate.
(numerical data are given in Appendix Table 5.)

A - Potassium Acetate (pure),
B - Potassium Acetate after complex formation with Kaolin.
of intersalated caesium acetate complex, the mechanism of superlattice formation at room temperature is perhaps the same as that in potassium acetate complex. The presence of a wide hump in the diffractogram (Fig. 10) at about 7.1 Å indicates that the crystallinity of this plane is significantly tampered. At higher temperatures, appearance of new lines at about 17.18 Å and 3.45 Å with disappearance of superlattice lines, indicates the formation of some new anhydrous structure, which however may not be radically different from the hydrated one.

In case of kaolinite, activation energy (about 1 Kcal.mol⁻¹) is perhaps connected with the removal of adsorbed water. In the thermal expansion experiment, this results in a broad peak at the temperature around 350K. In case of illite, in addition to a broad maximum in the same temperature range, a sharp peak at about 1050K is also observed. The mechanism for the origin of the low temperature broad peak is considered to be the same as that of kaolinite. The sharp peak in the high temperature region is related to the phase change of illite to a spinel form. This phase change is evident in the D.T.A. thermograms as well, and has also been suggested by many investigators.¹³,¹⁴,¹⁶
4.2. DIELECTRIC PROPERTIES

4.2.1. DIELECTRIC PROPERTIES NORMAL TO THE PREFERRED ORIENTATION OF THE SPECIMENS

4.2.1.(a) CAPACITANCE AND CONDUCTANCE OF KAOLINITE:

Three runs of measurements on capacitance \( C_p \) at 1 KHz, in the temperature range 295K to 1030K at about 20° intervals were recorded. The first run was made on heating. The sample was then cooled to room temperature and then the second run was made on heating and cooling to complete the thermal cycle. The third run was made for another sample, sedimented under the same conditions. This was preheated to about 1223K for 6 hours 9 months ago and kept in an open petridish protecting it from dust.

The results are shown in Fig.36. The Fig. shows that capacitance decreases at first to about 500k and then remains almost constant showing slight increase up to about 800K, above which it increases rapidly. Reproducible results have been obtained for all runs only at higher temperature above 600K.

Capacitance \( C_p \) and conductance \( G_p \) measurements from room temperature to about 1033K at about 20° intervals at frequencies 50 Hz, 500 Hz, 1 KHz, 5 KHz, 10 KHz and 20 KHz were made and their results at...
Fig. 36. Variation of Capacitance with temperature at 1 KHz with kaolinite as dielectric material. (Numerical data are given in Appendix Table II(A)).
50 Hz, 1 KHz, 10 KHz and 20 KHz are shown in Fig.37. The variation of $C_p$ and $G_p$ with frequency for four higher temperatures are displayed in Fig.38. taking $C_p$ vs log(frequency) and $G_p$ vs log(frequency), since measurements at higher temperatures were more accurate.

4.2.1.(b) CAPACITANCE AND CONDUCTANCE OF ILLITE:

The results of measurements $C_p$ in the temperature range 295K to 1030K at 1 KHz for three runs are shown in Fig.39. The runs were made as stated in the section 4.2.1.(a).

The Fig. shows that capacitance remains more or less constant up to about 500K after which it begins to increase slowly to about 800K, and then there is a rapid increase of it above this temperature.

Measurements of $C_p$ and $G_p$ were made from room temperature to 1033K at about 20° intervals at frequencies 50 Hz, 500 Hz, 1 KHz, 5 KHz, 10 KHz and 20 KHz. The results at 50 Hz, 1 KHz, 10 KHz and 20 KHz are displayed in Fig.40.

The Fig. shows that at higher temperatures, $C_p$ increases rapidly, the rate of increase being more for lower frequencies, whereas $G_p$ shows the reverse behaviour. The variations of $C_p$ and $G_p$ with log(freq.) are shown in Fig.41, for temperatures 987, 1001, 1015 and 1030K. The tendency of the capacitance to decrease
Fig 37. Variation of Capacitance and Conductance with temperature at different frequencies with kaolinite as dielectric material, (numerical data are given in Appendix Table 12.(A).).
and the conductance to increase with the increase of frequency is similar to that observed in kaolinite.

4.2.1.(c) \( C_p \) AND \( G_p \) OF MIXED LAYER KAOLINITE-ILLITE:

Measurements of \( C_p \) and \( G_p \) from room temperature to 1033K were made at 50 Hz, 1 KHz, 10 KHz and 20 KHz. The results are displayed in the Fig.42. It is seen that the capacitance decreases gradually up to about 500K showing predominant kaolinite characteristic and the tendency to rise slowly to about 800K is characteristic of illite. The rapid rise of \( C_p \) and \( G_p \) at higher temperatures is a common feature of both kaolinite and illite.

4.2.1.(d) \( C_p \) AND \( G_p \) OF INTERSALATED POTASSIUM ACETATE-KAOLINITE COMPLEX:

Measurements of \( C_p \) and \( G_p \) of this sample were made from 255K to 500K at frequencies 50 Hz, 500 Hz, 1 KHz, 5 KHz, 10 KHz and 20 KHz and the results are shown in Fig.43. Higher temperatures were arbitrarily chosen because, at low temperatures changes were small. It is seen that \( C_p \) increases slowly up to about 450K and above this both \( C_p \) and \( G_p \) increase rapidly. The variations of \( C_p \) and \( G_p \) with frequency at 456K, 468K, 483K and 498K are displayed in Fig.44.

At a particular temperature as frequency increases, the capacitance decreases and the
Fig. 38. Variation of $C_p$ and $\beta_p$ with frequency with kaolinite as dielectric material, (numerical data are shown in Appendix Table 12. (A)).
Fig. 59. Variation of $C_p$ with temperature at 1 KHz with illite as dielectric material. (numerical data are given in appendix Table 11.)
conductance increases.

4.2.1.(e) \( C_p \) AND \( G_p \) OF INTERSALATED CAESIUM ACETATE-KAOLINITE COMPLEX:

The \( C_p \) and \( G_p \) values for this sample were also measured for the same temperature and frequency ranges as for the other complex. The results are displayed in Fig.45. The variation of \( C_p \) and \( G_p \) with frequency at a particular temperature is shown in Fig.46. The variation of the values with frequency and temperature are similar to that of the intersalated potassium acetate-kaolinite complex.

4.2.1.(f) \( C_p \) OF KAOLINITE HEATED IN LITHIUM VAPOUR:

Measurements of capacitance at about \( 10^0 \) intervals at 1 KHz from room temperature to about 500K were made for the kaolinite samples: (A) unheated, (B) heated to 425K and cooled to room temperature and (C) heated in the lithium vapour. The results are shown in Fig.68.

There is no significant variation of the capacitance values for the above samples excepting in the low temperature region. The slight differences upto about 360K are probably due to the absorbed water.
Fig. 40. Variation of $C_p$ and $G_p$ with temperature at different frequencies with illite as dielectric material. (Numerical data are given in Appendix Table 12.)
Variation of $C_p$ and $G_p$ with frequency in illite. Numerical data are given in Appendix Table 8. B.
Figure 4c. Variation of $C_p$ and $G_p$ with temperature at different frequencies with the mixed layer kaolinite-illite as dielectric material, (numerical data are given in Appendix Table 12.(C).).
4.2.1.(g) Cₚ AND Gₚ OF KAOLINITE HEATED IN SODIUM VAPOUR:

Three runs of measurements of Cₚ of the doped sample were made at 1 KHz at about 10° intervals from room temperature to about 520K. The first run was on heating. The second run was made on both heating and cooling to complete the thermal cycle. The sample was cooled and kept overnight at room temperature and then the third run was made. The results are shown in Fig.47.

The variation of Cₚ with temperature for all the runs are similar. The capacitance increases rapidly from about 400K.

Cₚ and Gₚ measurements of the sample were made at about 10° intervals at 50 Hz, 500 Hz, 1 KHz, 5 KHz, 10 KHz and 20 KHz respectively. Gₚ values could be detected only above 400K. The results are shown in Fig.48. The variations of Cₚ and Gₚ with frequency for 461K, 477K, 494K and 503K are shown in Fig.49. The variation of Cₚ is rather small at lower temperatures, but the values rise rapidly above 400K.

4.2.2. RELATIVE PERMITTIVITY ε' AND LOSS FACTOR ε'':

The relative permittivity ε' and loss factor ε" were obtained over a range of temperatures using the values of Cₚ and Gₚ observed only in the process of
Fig. 43. Variation of $C_p$ and $G_p$ with temperature at different frequencies with $\text{CH}_3\text{COOK}$-kaolinite complex. (Numerical data are given in Appendix Table 12.(D).).
Fig. 44. Variation of $C_p$ and $G_p$ with frequency in $\text{Cl}_3\text{COOK}$-kaolinite complex. (Numerical data are given in Appendix Table 12. (D).)
Figure 48. Variation of $g_p$ with temperature at different frequencies for the $XOC$-kaolinite complex, (numerical values are given in Appendix Table 12.3).
heating the samples (kaolinite, illite, potassium acetate-kaolinite complex, caesium acetate-kaolinite complex and sodium doped kaolinite). The equations used for the calculations were:

$$C_0 \varepsilon' = C_p$$

and

$$C_0 \varepsilon'' = \frac{G_p}{\omega}$$

Where $C_0$ is the capacity of the cell with no dielectric in between the electrodes and $\omega = 2\pi f$, $f$ is the frequency in Hz.

Figs. 51, 52, 53, 54 and 50 represent the variation of $\varepsilon'$ and $\varepsilon''$ with log(frequency) at four temperatures for kaolinite, illite, potassium acetate-kaolinite complex, caesium acetate-kaolinite complex and sodium-doped kaolinite respectively. These Figs. show that at a particular temperature, as the frequency increases, the relative permittivity $\varepsilon'$ and loss factor $\varepsilon''$ decrease correspondingly.

To study the interfacial polarization effects, another sets of graphs $\log_{10} \varepsilon''$ against $\log_{10}$ (frequency) were drawn for all samples and the results are shown in Figs. 55, 56, 57, 58 and 59.

The variation of $\varepsilon'$ and $\varepsilon''$ for pure kaolinite, intersalated kaolinite complexes with the acetates of potassium and caesium and of sodium doped-kaolinite
Fig. 46. Variation of $C_p$ and $G_p$ with frequency in CH$_3$CCOC$_8$-kaolinite complex, (numerical data are given in Appendix Table 12.(E).)
Fig. 47. Variation of Capacitance with temperature at 1 KHz in doped complex of kaolinite with sodium metal. Numerical data are given in Table 14.

- ● ● ● First run on heating,
- ▲ Second run on heating
- ● ● ● Second run on cooling
- ● ● ● Third run on heating of complex after annealing.
are shown in the Table IV.

**TABLE IV**

Relative permittivity $\varepsilon'$ and loss factor $\varepsilon''$ for the samples at different frequencies and temperatures

<table>
<thead>
<tr>
<th>Freq. °K</th>
<th>Temp. °K</th>
<th>kaolinite</th>
<th>$\varepsilon'$</th>
<th>$\varepsilon''$</th>
<th>$\varepsilon'$</th>
<th>$\varepsilon''$</th>
<th>$\varepsilon'$</th>
<th>$\varepsilon''$</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 KHz</td>
<td>450</td>
<td>3.17</td>
<td>5.33</td>
<td>0.8</td>
<td>4.68</td>
<td>10.4</td>
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<td>0.2</td>
</tr>
<tr>
<td></td>
<td>460</td>
<td>3.16</td>
<td>5.66</td>
<td>4.3</td>
<td>5.35</td>
<td>18.5</td>
<td>2.86</td>
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<td></td>
<td>470</td>
<td>3.17</td>
<td>5.79</td>
<td>6.9</td>
<td>6.04</td>
<td>33.0</td>
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</tr>
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<td>10 KHz</td>
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<td>3.28</td>
<td>6.00</td>
<td>0.9</td>
<td>5.76</td>
<td>13.4</td>
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<td>-</td>
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<td></td>
<td>460</td>
<td>3.27</td>
<td>6.85</td>
<td>5.0</td>
<td>6.89</td>
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<td>470</td>
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<td>7.34</td>
<td>8.4</td>
<td>8.86</td>
<td>39.5</td>
<td>3.50</td>
<td>0.6</td>
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<td>1 KHz</td>
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<td>3.49</td>
<td>8.28</td>
<td>13.4</td>
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<td>470</td>
<td>3.54</td>
<td>10.53</td>
<td>53.2</td>
<td>14.14</td>
<td>176.0</td>
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<td>4.8</td>
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<td>50 Hz</td>
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<td>10.05</td>
<td>30.7</td>
<td>12.32</td>
<td>340.0</td>
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<td>45.4</td>
<td>14.58</td>
<td>649.0</td>
<td>4.73</td>
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<td></td>
<td>470</td>
<td>3.68</td>
<td>13.21</td>
<td>237.2</td>
<td>16.92</td>
<td>1160.0</td>
<td>5.21</td>
<td>74.3</td>
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</table>
\[\text{Figure 4.48: Variation of } C_p \text{ and } G_p \text{ with temperature at different frequencies in doped complex of kaolinite with sadal metal, (numerical data are given in Appendix Table 16)}\]
Fig. 49. Variation of $C_p$ and $G_p$ with frequency in sodium doped kaolinite complex, (numerical data are given in Appendix Table 15).

Fig. 50. Variation of $\varepsilon'$ vs $\varepsilon''$ with frequency in sodium doped kaolinite complex, (numerical data are given in Appendix Table 16).
4.2.3. THE ACTIVATION ENERGY FROM LOSS FACTOR:

For all the samples, \( \log_e \varepsilon' \) were plotted against \( \frac{1}{T} \) at two frequencies and the results are shown in Figs. 61, 62, 63, 64 and 60 respectively. The graphs are practically straight lines and at different frequencies the straight lines are almost parallel, suggesting that some activation process with constant activation energy is involved. From the slopes of the curves, the activation energies of the samples were calculated and are shown in the Table V.

**TABLE V**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Freq. in KHz</th>
<th>Temperature range in °K</th>
<th>W in Kcal.mol(^{-1})</th>
<th>W average</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kaolinite</td>
<td>20</td>
<td>970 - 1030</td>
<td>36.6</td>
<td>37.0</td>
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<td>1</td>
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<td>37.5</td>
<td></td>
</tr>
<tr>
<td>Illite</td>
<td>20</td>
<td>960 - 1030</td>
<td>46.0</td>
<td>45.6</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>970 - 1030</td>
<td>45.3</td>
<td></td>
</tr>
<tr>
<td>CH(_3)COOK-kaolinite comp.</td>
<td>20</td>
<td>468 - 498</td>
<td>26.6</td>
<td>26.6</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>468 - 498</td>
<td>26.7</td>
<td></td>
</tr>
<tr>
<td>CH(_3)COCs-kaolinite comp.</td>
<td>20</td>
<td>430 - 475</td>
<td>25.8</td>
<td>25.4</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>430 - 475</td>
<td>25.1</td>
<td></td>
</tr>
<tr>
<td>Na-doped kaolinite</td>
<td>10</td>
<td>460 - 503</td>
<td>7.5</td>
<td>8.1</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>460 - 503</td>
<td>8.8</td>
<td></td>
</tr>
</tbody>
</table>
Fig. 51. Variation of $\varepsilon'$ and $\varepsilon''$ with frequency in musolinite (numerical data are given in Appendix Table 13(A)).
Fig. 82. Variation of $\epsilon'$ and $\epsilon''$ with frequency in illite.

(numerical data are given in Appendix Table 13(B)).
Fig. 53. Variation of $\varepsilon'$ and $\varepsilon''$ with frequency in CH$_3$OK-kaolinite complex, (numerical data are given in Appendix Table 13. (C).)
Fig. 54. Variation of $\varepsilon'$ and $\varepsilon''$ with frequency in CH$_3$COOC$_8$-kaolinite complex. (Numerical data are given in Appendix Table 13(D).)
MEASUREMENTS ON THE ANISOTROPIC BEHAVIOUR:

The measurements of $C_p$ and $G_p$ values along to the preferred orientation for kaolinite and the intersalated complexes of kaolinite with the acetates of potassium and caesium at 1 KHz and at different temperatures (room temperature to 500K) were made and the results are shown in Figs. 65, 66, and 67. From the graphs it appears that the observed $C_p$ and $G_p$ values with the specimens are the resultant of two capacitors (one with glass as dielectric and the other with the test material as dielectric) in parallel. So, $C_p$ and $G_p$ for the test materials are obtained from these graphs. The results are shown in the Table VI. It may be noted that the $G_p$ values rise rapidly above 440K, probably due to increased mobility of the alkali metal ions.

TABLE VI

$C_p$ and $G_p$ of the specimens along the preferred orientation at 1 KHz.

<table>
<thead>
<tr>
<th>Temp. (°K)</th>
<th>Kaolinite</th>
<th>CH$_3$COOK-kao.comp</th>
<th>CH$_3$COOCs-kao.comp</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$C_p$ (PF)</td>
<td>$G_p$ (mho) x10$^{-7}$</td>
<td>$C_p$ (PF)</td>
</tr>
<tr>
<td>300</td>
<td>1.8</td>
<td>2.6</td>
<td>1.7</td>
</tr>
<tr>
<td>320</td>
<td>1.6</td>
<td>2.6</td>
<td>1.6</td>
</tr>
<tr>
<td>340</td>
<td>1.4</td>
<td>2.5</td>
<td>1.4</td>
</tr>
</tbody>
</table>
Fig. 55. Plot of $\log_{10} \epsilon''$ vs $\log_{10}$ (frequency) for kaolinite. (Numerical data are given in Appendix Table 13A).

Fig. 56. Plot of $\log_{10} \epsilon''$ vs $\log_{10}$ (frequency) for illite. (Numerical data are given in Appendix Table 13B).
Fig. 57. Plot of $\log_{10} \epsilon'$ vs $\log_{10}$ (frequency) for $\text{M}_3\text{COOK}$-kaolinite complex (data are given in Appendix 13C).

Fig. 58. Plot of $\log_{10} \epsilon''$ vs $\log_{10}$ (frequency) for $\text{M}_2\text{COOCo}$-kaolinite complex (numerical data are given in Table 13D).
Referring to Fig. 36, it may be seen that kaolinite shows some degree of rehydration when left to itself for a long period, although freshly cooled samples fail to do so. The decrease in capacitance from room temperature to about 450K may be attributed mainly to the loss of surface water. The tendency for rising capacity from about 500K for both kaolinite and illite may be due...
Fig. 60. Plot of $\log_{10} \epsilon$ vs $\log_{10}$(frequency) for Na-doped kaolinite complex. (Numerical data are given in Appendix TABLE 16).
Fig. 61. Plot of $\log e''$ vs $\frac{1}{T}$ for kaolinite specimen.
(numerical data are given in Appendix TABLE 13a)

Fig. 62. Plot of $\log e''$ vs $\frac{1}{T}$ for illite specimen.
(numerical data are given in Appendix TABLE 13a).
Fig. 64. Plot of $\log_2 \epsilon$ vs $\frac{1}{T}$ for CH$_3$COOC$k$-kaolinite complex. Numerical data are given in Appendix 3D.
Fig. 66. Variation of $C_p$ and $g_p$ with temperature at 1 kHz in the CH$_3$COOK-kaolinite complex along the direction $\perp$ to the (001) plane. (Numerical data are given in Ap. 17(B)).
Fig. 67. Variation of $C_p$ and $G_P$ with temperature at
in CH$_3$COOC$_2$-kaolinite complex. Numerical data are given in Appendix Table 10.

Fig. 68. Variation of $C_p$ with temperature at:

(I) Unheated kaolinite, (II) Kaolinite quenched from
150°C and (III) Kaolinite with lithium metal.
Numerical data are given in Appendix Table 10.
to removal of hydroxyls in the form of water, from the
structures. Very rapid increase in $C_p$ and $G_p$ at higher
temperatures for kaolinite may be due to formation of
a new phase - metakaolinite with lattice defects.
Similarly, the rapid rise in case of illite also may be
attributed to the formation of a new phase - spinel with
lattice defects.

Both relative permittivity $\varepsilon'$ and loss
factor $\varepsilon''$ for all specimens show an increase with the
decrease of frequency (Figs. 51, 52, 53, 54 and 50). The
graphs of $\log_{10} \varepsilon''$ vs $\log_{10}$ (frequency) are straight lines
increasing with decrease of frequency (Figs. 55, 56, 57,
58 and 59). From these graphs, it is evident that the
polarization increases with decreasing frequency,
indicating thereby some mechanism with larger relaxation
time. The relative permittivity $\varepsilon'$ is found to behave as
if it is approaching a Debye relaxation region. On the
otherhand, the loss factor $\varepsilon''$ does not show the increase
needed for the formation of a relaxation absorption peak.
Such behaviour of $\varepsilon'$ and $\varepsilon''$ probably cannot be due to a
Debye relaxation effect. The effect therefore, can pro-
bably be explained on the basis of interfacial polariza-
tion of heterogeneous dielectrics. The interfacial
polarization arising out of any source can not be disting-
ished from orientational polarization by measuring $\varepsilon'$,
because its variation with frequency is the same as that for the case of Debye relaxation. But with measurement of $\varepsilon''$, it should be possible to distinguish the two types of polarization. For interfacial polarization, as frequency $\omega \to 0$, the loss represented by $\varepsilon'' \to \infty$, whereas in case of Debye relaxation, $\varepsilon'' \to 0$ as $\omega \to 0$. The graphs of $\log_{10} \varepsilon''$ vs $\log_{10}$ (frequency) in the present case show similar behaviours as found by Hatibarua and Parry\textsuperscript{60} in the alkali-acetates and Hamon\textsuperscript{61} using copper phthalocyanine and liquid n-primary alcohols dispersed in paraffin wax. In view of this, the interfacial polarization may be considered as a source of polarization in the present samples. Interfaces may be between the pure samples and the gases or vapours evolved out of the structures. Or, these may be caused by dislocations, and lattice defects inside the samples.
4.3. DIFFERENTIAL THERMAL ANALYSIS

4.3.1. RESULTS:

4.3.1.(a) THERMOGRAMS OF KAOLINITE, ILLITE AND MIXED LAYER KAOLINITE-ILLITE:

The thermograms of the samples kaolinite (A), illite (B) and mixed layer kaolinite-illite (C) are shown in Figs.69.(A), 69.(E) and 71.(C) for normal rate of heating. The temperatures of the phase transformations with their thermodynamical natures are given in the Table VII.

TABLE VII

Transition temperatures of the samples (A),(B) and (C)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature range for transformation °K</th>
<th>Peak temperature Tm °K</th>
<th>Characteristic of transformation</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A) Kaolinite</td>
<td>645 - 939</td>
<td>850</td>
<td>endothermic</td>
</tr>
<tr>
<td></td>
<td>1225 - 1260</td>
<td>1249</td>
<td>exothermic</td>
</tr>
<tr>
<td>(B) Illite</td>
<td>375 - 463</td>
<td>427</td>
<td>endothermic</td>
</tr>
<tr>
<td></td>
<td>715 - 876</td>
<td>805</td>
<td>endothermic</td>
</tr>
<tr>
<td></td>
<td>1143 - 1190</td>
<td>1163</td>
<td>endothermic</td>
</tr>
<tr>
<td></td>
<td>1213 - 1258</td>
<td>1233</td>
<td>exothermic</td>
</tr>
<tr>
<td>(C) Mixed layer Kao.-illite</td>
<td>440 - 906</td>
<td>843</td>
<td>endothermic</td>
</tr>
<tr>
<td></td>
<td>1215 - 1265</td>
<td>1238</td>
<td>exothermic</td>
</tr>
</tbody>
</table>
Fig. 69. Traces of the Thermograms, rate of heating $10^\circ C/min$.

(A) Kaolinite, not heated.

(B) Kaolinite, heated to $600^\circ C$ for 1.5 hours, run after 40 hours.

(C) Kaolinite, heated to $600^\circ C$ for 1.5 hours, run after 9 months.

(D) Illite, not heated.

(E) Illite, heated to $800^\circ C$ for 1.5 hrs., run after 60 days.

(F) Illite, heated to $800^\circ C$ for 1.5 hrs., run after 9 months.
From the thermograms it is seen that the sample (A) exhibits an endothermic dip at 393K. The sample (C) shows two endothermic dips at about 403K and 1123K.

4.3.1.(b) DEHYDRATION AND REHYDRATION STUDIES OF THE CLAY MINERALS:

The observed behaviours of dehydration and rehydration of kaolinitite are given in Figs.69.(B) and (C). The preheated sample, heated at about 873K for 6 hours, shows only a dip instead of a sharp endothermic peak. However, the exothermic peak is not effected.

Behaviours of illite in this respect are shown in Figs.69. (F) and (G). The preheated illite sample heated to about 1073K, shows a small endothermic peak at a lower temperature. The higher temperature peaks are not changed. From the Fig.69.(G) it appears that regaining of lost structural water is rather very slow.

4.3.1.(c) ACTIVATION ENERGY OF KAOLINITE IN PURE AND IN MIXED LAYER KAOLINITE-ILLITE:

The thermograms at different heating rates for the sample (A) are given in Fig.70. With the increase of rate of heating \( \beta = \frac{dT}{dt} \), the peak temperature \( T_{\text{max}} \) changes from 809K to 863K for kaolinitite in pure state. The thermograms at different heating rates for the
Fig. 70. Traces of the Thermograms (A), (B), (C), (D), and (E) of Kaozinite (pure) at 3, 6, 9, 12 and 15°C/min respectively.
Fig. 71. Trace of the Thermograms (A), (B), (C), (D) and (E) of Kaolinite (interstratified with illite) at 5, 6, 9, 12 and 15°C/min respectively.
sample (C) are shown in Fig. 71. The peak temperature for this sample changes from 814K to 860K. The exothermic peak also changes correspondingly to the higher temperature side.

The graphs of $\log_e \left( \frac{E}{T_{\text{max}}} \right)$ against $\frac{T_{\text{max}}}{T_{\text{max}}}$ are shown in Figs. 72 and 73 for the samples (A) and (C) respectively. They are almost linear. This shows that the reaction is a first order one and it obeys the Arrhenius equation (see chapter 2.3.2.). From the slopes of these straight lines, the activation energies of kaolinite in pure as well as in mixed layer with illite are calculated and are found to be 37.6 Kcal.mol$^{-1}$ and 45.1 Kcal.mol$^{-1}$ respectively.

4.3.1.(d) THERMOGRAMS FOR INTERCALATED COMPLEXES OF KAOLINITE WITH ALKALI-ACETATES:

The thermograms of potassium acetate-kaolinite complex show three prominent endothermic peaks at about 425K, 574K and 825K and an exothermic peak at about 1233K (Fig. 75.(A).). There seems to be an endothermic dip near 329K.

The thermogram of caesium acetate-kaolinite complex is shown in Fig. 75.(B). It shows two endothermic peaks near 476K and 823K and an exothermic peak about 1233K.
Fig. 72. Plot of \( \log_e(\beta/T_m^2) \) vs \( 1/T_m \times 10^3 \) for mullite.

Fig. 73. Plot of \( \log_e(\beta/T_m^2) \) vs \( 1/T_m \times 10^3 \) for kaolinite (interstratified with Illite), (numerical data are given in Appendix Table 18.)
Fig. 74. Trace of the Thermogram of Caesium Acetate sample.

Fig. 75. Traces of the Thermograms of (A) CH₃COOK-kaolinite complex and (B) CH₃COOC₅-kaolinite complex.
For comparison, a thermogram for pure caesium acetate was also taken (Fig.74). It shows a very small endothermic peak at about 327K and a sharp endothermic peak at its melting point.

4.3.2. DISCUSSION:

From the thermograms of the dehydrated kaolinite sample (Fig.69.C), taken after 215 days of rehydration, it is evident that kaolinite absorbs a small amount of structural water. Illite sample also regains to some extent the surface as well as structural water after dehydration (Figs.69.F and G). But after certain amount of rehydration, further pickup of water is probably stopped. Inability of both the dehydrated samples to regain fully the original condition even after quite a long time, indicates that the original crystalline structures are permanently altered. These are in agreement with the observations made by Grim and Bradley.  

Some investigators concluded that this dehydroxylation reaction was diffusion controlled. But in the present investigation, the plots of $\log_\epsilon^{\beta/T_{max}}$ vs $1/r_{max}$ for the samples give linear curves indicating that the dehydroxylation reaction obeys the first order kinetics. The sifting of the peak with the increase of rate of heating indicates that the rate of reaction decreases with the increase of the rate of
The first two endothermic peaks in the intersalated potassium acetate-kaolinite complex are observed in the regions corresponding to the second phase-transition and the melting point of pure potassium acetate. This was observed by Hatibarua and Parry. Thus these two peaks in the complex indicate the persistence of properties of potassium acetate itself in the complex. The third endothermic peak is the dehydroxylation peak of kaolinite in the complex. Thus, at higher temperatures, both the acetate and kaolinite remains as mixture in the complex. The first sharp endothermic peak in the caesium acetate-kaolinite complex is due to the melting of the acetate present in the complex. The endothermic and exothermic transitions of kaolinite also exist in this complex, but these are less prominent. From the thermograms in Figs. 75.(A) and (B), it is evident that the temperatures of the dehydroxylation peaks are lowered. This may be due to the faster dehydroxylation of kaolinite at lower temperatures under the influence of interlayer alkali-acetates. The rate of nucleation of defects determines the rate of reaction. From the present investigation, it is evident that intersalation of sits creates defects and consequently increases the rate of reaction.
4.4.4. INFRARED ABSORPTION SPECTRA OF KAOLINITE, ILLITE AND INTERSALATED KAOLINITE COMPLEXES WITH ALKALI ACETATES

4.4.1. SPECTROGRAMS FOR KAOLINITE:

Four infrared spectrograms of heated and unheated kaolinite were taken. The first record was made at about 295K. The second and third were for samples quenched from 673K and 923K to room temperature and the fourth record for the preheated sample (heated to about 1173K 9 months ago). The first three records are shown in Figs. 76. (A), (B) and (C) respectively. The spectrogram for the unheated sample shows a triplet band with lines at 3696, 3661 and 3623 cm$^{-1}$ and also bands at 1638, 1100, 1034, 1001, 939 and 910 cm$^{-1}$.

The intensities of the triplet bands for the sample quenched from 673K are less compared to that for the unheated sample (Fig. 76. B) and the band at 1638 cm$^{-1}$ does not appear. For the sample quenched from 923K, only a broad band at about 1050 cm$^{-1}$ exists. There is no trace of the other bands (Fig. 76. C).

4.4.2. SPECTROGRAMS FOR ILLITE:

Four infrared spectrograms of heated and unheated illite were made. The first record for unheated
Fig. 76. Infrared Spectra of unheated and heated kaolinite and illite.

Kaolinite: (A) Unheated, (B) Heated to 400°C and (C) Heated to 650°C

Illite: (D) Unheated, (E) Heated to 450°C and (F) Heated to 800°C.
illite sample shows absorption bands at 3633, 1629, 1035, 940, 832 and 756 cm\(^{-1}\) (Fig. 76.D). The second one for the sample quenched from about 723K is shown in Fig. 76.E. It is seen that the intensities of bands at 3633 and 940 cm\(^{-1}\) are decreased and the band at 1629 cm\(^{-1}\) disappears. The third sample quenched from 1073K shows absorption bands at about 1060, 985 and 840 cm\(^{-1}\) (Fig. 76.F). The band at 3633 has completely disappeared. The fourth record of the preheated specimen (heated to about 1173K 9 months ago) shows a broad band at about 3700 cm\(^{-1}\) along with the bands observed in case of the sample quenched from 1073K.

The results of infrared records of heated and unheated samples of kaolinite and illite are given in the Table VIII.

**TABLE VIII**

Frequencies and assignment of infrared absorption bands of kaolinite and illite

**A) Kaolinite**

<table>
<thead>
<tr>
<th>Unheated cm(^{-1})</th>
<th>Quenched from 673K cm(^{-1})</th>
<th>Quenched from 923K cm(^{-1})</th>
<th>Preheated cm(^{-1})</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>(I) 3696</td>
<td>3697</td>
<td>-</td>
<td>-</td>
<td>OH- stretching</td>
</tr>
<tr>
<td>(II) 3661</td>
<td>3664</td>
<td>-</td>
<td>3650</td>
<td>vibration</td>
</tr>
<tr>
<td>(III) 3623</td>
<td>3625</td>
<td>-</td>
<td>-</td>
<td>(broad)</td>
</tr>
</tbody>
</table>
TABLE VIII (continued)

<table>
<thead>
<tr>
<th>Unheated</th>
<th>Quenched from 673K</th>
<th>Quenched from 923K</th>
<th>Preheated</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>cm⁻¹</td>
<td>cm⁻¹</td>
<td>cm⁻¹</td>
<td>cm⁻¹</td>
<td></td>
</tr>
<tr>
<td>1638</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>deformation</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>vibration of water (i)</td>
</tr>
<tr>
<td>1100</td>
<td>1100</td>
<td>-</td>
<td>-</td>
<td>stretching</td>
</tr>
<tr>
<td>1034</td>
<td>1035</td>
<td>-</td>
<td>1035</td>
<td>vibration of</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Si - O (iii)</td>
</tr>
<tr>
<td>1001</td>
<td>1003</td>
<td>-</td>
<td>-</td>
<td>H-O-Al⁢⁺ (iv)</td>
</tr>
<tr>
<td>939</td>
<td>939</td>
<td>-</td>
<td>-</td>
<td>Vibration (iv)</td>
</tr>
<tr>
<td>910</td>
<td>909</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

(B) Illite

<table>
<thead>
<tr>
<th>Unheated</th>
<th>Quenched from 723K</th>
<th>Quenched from 1073K</th>
<th>Preheated</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>cm⁻¹</td>
<td>cm⁻¹</td>
<td>cm⁻¹</td>
<td>cm⁻¹</td>
<td></td>
</tr>
<tr>
<td>3633</td>
<td>3640</td>
<td>-</td>
<td>3640</td>
<td>(i)</td>
</tr>
<tr>
<td>1629</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>(ii)</td>
</tr>
<tr>
<td>1035</td>
<td>1045</td>
<td>1060</td>
<td>1050</td>
<td>(iii)</td>
</tr>
<tr>
<td>940</td>
<td>930</td>
<td>970</td>
<td>950</td>
<td>(iv)</td>
</tr>
<tr>
<td>832</td>
<td>840</td>
<td>840</td>
<td>840</td>
<td></td>
</tr>
<tr>
<td>756</td>
<td>755</td>
<td>-</td>
<td>-</td>
<td>Si-O-Al⁢⁺ vibn.</td>
</tr>
</tbody>
</table>
Fig. 77. Infrared Spectra of
(A) Kaolinite at 21°C, (room temp.)
(B) CH$_3$COOK-kaolinite complex quenching from 70°C
(C) CH$_3$COOC$_2$ sample at room temp. quenching from 70°C
(D) CH$_3$COOC$_2$ sample at room temperature annealing from 70°C
(E) CH$_3$COOC$_2$-kaolinite complex at 21°C quenching from 70°C
(F) CH$_3$COOC$_2$-kaolinite complex at room temp. annealing from 70°C
4.4.3. INFRARED SPECTRA OF CAESIUM ACETATE-KAOLINITE COMPLEX AND THE ACETATE:

The infrared spectra of intersalated caesium acetate-kaolinite complex are shown in Fig. 77 (E) and (F). For comparison, records of pure Cs-acetate spectra of quenched and rehydrated samples are also shown in Figs. 77(C) and (D) respectively. The sample quenched from 343K shows a wide band in the 3400 cm⁻¹ region and two absorption bands at 2965 and 2935 cm⁻¹. The rehydrated sample shows a wide band with its maximum at about 3400 cm⁻¹. Other bands are not present. The intersalated caesium acetate-kaolinite complex quenched from 343K shows (Fig. 77E) triplet bands at 3694, 3660 and 3621 cm⁻¹ and other bands at 3608 and 2958 cm⁻¹. The rehydrated complex shows (Fig. 77F) bands at 3690, 3656, 3640 and 3600 cm⁻¹, a wide band at about 3440 cm⁻¹ and another small band at about 2975 cm⁻¹.

4.4.4. INTERSALATED POTASSIUM ACETATE KAOLINITE COMPLEX:

An infrared run was taken for this sample quenched from 343K to check the reliability of the present infrared work on the caesium acetate-kaolinite complex. This sample shows (Fig. 77B) the bands at 3693, 3660, 3624, 3600 and 2974 cm⁻¹. But the band at 2930 cm⁻¹
observed by Ledoux and White\(^{29}\) is not recognizable. A wide
and very weak band at about 3460 cm\(^{-1}\) is also present.

4.4.5. DISCUSSION:

The bands for OH- vibration frequencies
observed in the present measurements are compared with
those obtained by others in Table IX.

TABLE IX

Comparision of OH- vibration frequencies of kaolinite:

<table>
<thead>
<tr>
<th>Studied by</th>
<th>Bands(cm(^{-1}))</th>
<th>Vibrations attributed to</th>
</tr>
</thead>
<tbody>
<tr>
<td>Roy and Roy(^{65})</td>
<td>3705 (I)</td>
<td>Outer surface OH-groups</td>
</tr>
<tr>
<td></td>
<td>3665 (II)</td>
<td>Inner OH- groups</td>
</tr>
<tr>
<td></td>
<td>3450 (IV)</td>
<td>OH- groups at surfaces between the neutral layers</td>
</tr>
<tr>
<td>Van der Marel and Zwiers(^{66})</td>
<td>3698 (I)</td>
<td>Surface OH- groups</td>
</tr>
<tr>
<td></td>
<td>3660 (II)</td>
<td>Surface OH- groups of microcrystal bonded to external octahedral layer</td>
</tr>
<tr>
<td></td>
<td>3630 (III)</td>
<td>OH- groups of octahedral layer</td>
</tr>
<tr>
<td></td>
<td>3440 (IV)</td>
<td>OH- groups at the surface between the natural layer</td>
</tr>
</tbody>
</table>
TABLE IX (continued)

<table>
<thead>
<tr>
<th>Studied by</th>
<th>Bands(cm⁻¹)</th>
<th>Vibrations attributed to</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fripait and Toussaint</td>
<td>3710 (I)</td>
<td>OH-groups on upper</td>
</tr>
<tr>
<td></td>
<td>3680 (II)</td>
<td>octahedral layer</td>
</tr>
<tr>
<td></td>
<td>3620 (III)</td>
<td>OH-groups in the plane common to tetrahedral and octahedral layers</td>
</tr>
<tr>
<td>Present Investigator</td>
<td>3696 (I)</td>
<td>CH-groups at the</td>
</tr>
<tr>
<td></td>
<td>3664 (II)</td>
<td>octahedral surface</td>
</tr>
<tr>
<td></td>
<td>3623 (III)</td>
<td>CH-groups (inner hydroxyls) in the plane common to octahedral and tetrahedral layers.</td>
</tr>
</tbody>
</table>

Referring to Table IX, it will be seen that the triplet bands at 3696, 3664 and 3623 cm⁻¹ observed in case of kaolinite have been attributed to CH- stretching frequency. But in illite, only one band at about 3633 cm⁻¹ in the same range of frequency has been observed by the present investigator and also by others. This may be due to the different positions occupied by the CH-groups in the structure of kaolinite and illite. In the unit cell of illite, the OH-groups
remain as inner hydroxyls (Fig. 2) whereas in kaolinite, there are surface hydroxyls in addition to the inner ones (Fig. 1).

The observed bands at 1100, 1034 and 1011 cm⁻¹ in kaolinite and the band 1035 cm⁻¹ in illite are attributed to the vibrational frequency of Si-C, as found by others. The bands at 939 and 910 cm⁻¹ in kaolinite and 940 and 832 cm⁻¹ in illite, are attributed to H-O-Al⁺ vibrations.

From the results given in Table VIII and Figs. 76(C) and (E), it is seen that the peak heights of the triplet bands (I), (II), (III) near 3700 cm⁻¹ of kaolinite and the band at about 3633 cm⁻¹ of illite decrease as temperature is increased and disappear at higher temperature (Figs. 76 D and F), indicating that OH- groups have been removed from the structures. The spectrograms of the dehydrated samples show that these may be rehydrated to some extent after exposure to atmosphere for a long period.

The reasons for decrease of 3694 cm⁻¹ band of kaolinite after intercalation with Cs-acetate and the appearance of a new band at 3608 cm⁻¹ may be as follows:

The acetate ions which intercalate into the layers of kaolinite structure form hydrogen bonding with some of the surface hydroxyls. This perhaps accounts
for the appearance of the new band and the decrease in intensity of the original OH- band. From the study of K-acetate-kaolinite complex and also deuterated potassium acetate-kaolinite complex, Ledoux and White arrived at the same conclusion.

The bands observed at 2958 cm\(^{-1}\) for caesium acetate kaolinite complex in characteristic of the vibrations of the CH\(_3\) groups of the acetates. This is evident from the bands observed at 2965 and 2935 cm\(^{-1}\) in the pure caesium acetate (Fig. 76C).