CHAPTER 5

EFFECT OF GAMMA RADIATION ON THE DECOMPOSITION OF HYDRATED FERROUS (II) AND BARIUM (II) OXALATES

The effect of gamma ray dose on the thermal decomposition of hydrated ferrous (II) and barium (II) oxalates is studied. The literature survey reveals that there are very few reports on the thermal study of pre-irradiated oxalates [1-3]. The non-isothermal studies of these oxalates were done by using TGA technique at various gamma ray doses. From non-isothermal data kinetic parameters are evaluated. The analysis of this kinetic data leads to the rarely observable phenomenon of ‘kinetic compensation effect’. These investigations are presented in detail in this chapter under the following headings,

5.1 Irradiation of samples
5.2 Non-isothermal study of gamma irradiated salts
  5.2.1 Non-isothermal TGA of hydrated ferrous (II) oxalate
  5.2.2 Non-isothermal TGA of hydrated barium (II) oxalate
  5.2.3 The nature of transients in gamma irradiated salts
    5.2.3.1 DSC study
    5.2.3.2 IR study
    5.2.3.3 Magnetic susceptibility study
    5.2.3.4 X-Ray diffraction of unirradiated and irradiated ferrous (II) and barium (II) oxalates
5.3 Kinetic parameters from non-isothermal study
5.4 Isothermal study of hydrated ferrous (II) and barium (II) oxalates and evaluation of kinetic parameters
5.5 Kinetic Compensation effect
  5.5.1 Compensation phenomenon in heterogeneous reactions
  5.5.2 Compensation effect in the present study

5.1 Irradiation of samples

Irradiation of samples was done by using $^{60}$Co $\gamma$-rays having dose rate 3.95 Gy/min which is available at Department of chemistry, University of Pune, Pune. The dose rate was measured with the help of Fricke dosimeter based on conversion of ferrous to ferric ions and was found to be $1.995 \times 10^3$ Gy per hour. The dose absorbed by the
samples was calculated by considering the difference in electron densities of the Fricke dosimeter and that of the salt. During the course of the experimental work, the dose rate of the source was checked from time to time. The oxalates were exposed to various doses (chapter 2, section 2.3) and then subjected to thermal analysis using TGA technique.

5.2 Non-isothermal study of gamma irradiated salts

The salts exposed to various doses of gamma radiation were then subjected to non-isothermal TGA study. The effect of irradiation on each salt is discussed as under.

5.2.1 Non-isothermal TGA of hydrated ferrous (II) oxalate

The results of non-isothermal TGA of unirradiated ferrous (II) oxalate are presented in chapter 3, section 3.1.1, which shows two mass loss steps; first the water loss and second the decomposition of the ferrous (II) oxalate. The weight loss data corresponding to first step of decomposition at seven different doses were recorded in Table 5.1. Fig 5.1 presents the thermograms of decomposition of ferrous (II) oxalate for seven typical doses in order to keep the clarity in the figure.

The effects of gamma radiations result in generation of defects, electronic excitation or ionization and bond rupture resulting in free radicals [4]. Due to generation of defects and dislocations, additional nucleation centers are created in the lattice which fractures the crystal, forming new potential centres and the reaction thereafter follows decomposition rather than displacement, consequently enhancing the reaction rate and decreasing the energy of activation [5]. Any physical or chemical change induced by radiation in substance is directly proportional to the dose and independent of dose rate and the nature of radiation. The effect of gamma irradiation on water generates $H^+$, $OH^-$, $H_2O^-$, $H_2O^+$, $H_+, H^-$, $OH^+$, $H_2$, $H_2O^+$, $HO_2^+$ and $H_2O_2$ while ferrous (II) oxalate, $Fe^{2+}$ converts to $Fe^{3+}$. The radiolysis of Fricke dosimeter solution ($10^{-3}$ M ferrous sulphate in 0.4 M sulphuric acid in presence of dissolved air) [4] shows some reactions with different fragments produced in water like,

\[
\begin{align*}
Fe^{2+} + OH^- & \rightarrow Fe^{3+} + OH^- \\
Fe^{2+} + H_2O_2 & \rightarrow Fe^{3+} + OH^+ + OH^- \\
Fe^{2+} + HO_2^+ & \rightarrow Fe^{3+} + HO_2^- \\
HO_2^- + H^+ & \rightarrow H_2O_2
\end{align*}
\]
Fig 5.1: Non-isothermal TGA of γ-irradiated ferrous (II) oxalate
Table 5.1: Data from non-isothermal TGA of pre-irradiated hydrated ferrous (II) oxalate in air

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Dose, $x 10^2$ Gy</th>
<th>Step</th>
<th>Temp. range (°C)</th>
<th>Onset of decompo. (°C)</th>
<th>% Wt. loss</th>
<th>Probable compn. or group lost</th>
<th>Residue</th>
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<td>0.00</td>
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<td>160-200</td>
<td>160</td>
<td>20.03</td>
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<td>FeC$_2$O$_4$</td>
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<td>220</td>
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<td>$3CO, CO_2$</td>
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</tr>
<tr>
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<td>1</td>
<td>140-260</td>
<td>140</td>
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<td>$2H_2O, 2CO_2$</td>
<td>$3/2Fe_3O_4, 3/2 Fe_3C, 1/2C$</td>
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<tr>
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<td>8.</td>
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<td>140</td>
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<td>$2H_2O, 2CO_2$</td>
<td>$3/2Fe_3O_4, 3/2 Fe_3C, 1/2C$</td>
</tr>
</tbody>
</table>

*The values in the parenthesis represent the calculated weight loss based on the probable decomposition reaction.
The above reaction supports the present work where these reactions are possible and due to that the irradiated ferrous (II) oxalate shows single step of decomposition in the temperature range of 140 to 260 °C while non-irradiated sample shows dehydration and decomposition in two steps in the temperature range 160 to 200 °C and 220 to 300 °C respectively. The decomposition due to gamma irradiation shows formation of CO, CO₂, CO₂⁻, C₂O₄²⁻, C₂O₄⁻, [OCOCO₂]²⁻, CO₃²⁻, O²⁻, CO²⁻, free C and (COOH)₂ which reacts with Fe²⁺ and proceeds decomposition faster.

Thermal stability of these radicals in the crystal matrix and the end products resulting from interaction of these radicals with the host lattice will pronouncedly affect the nature of the thermograms obtained at various doses. The decomposition end products are also different in unirradiated and irradiated ferrous (II) oxalate. The extent of formation of stable products appears to be increasing with absorbed dose thereby leading to decrease in final weight loss. The decomposition reactions of unirradiated and irradiated ferrous (II) oxalate are shown in following reactions. Unirradiated ferrous (II) oxalate as,

1) 160 °C-200 °C

FeC₂O₄.2H₂O → FeC₂O₄ + 2H₂O

[Observed Wt. loss = 20.03%, (20.01%)]

2) 220 °C-300 °C

FeC₂O₄ → Fe₂O₃ + 3CO↑ + CO₂↑

[Observed Wt. loss = 45.19%, (45.18%)]

Irradiated ferrous (II) oxalate as,

1) 140 °C-260 °C

FeC₂O₄.2H₂O → 3/2Fe₃O₄ + 3/2Fe₃C + 2H₂O + 2CO₂ + 2CO + 1/2C

[Observed Wt. loss = 54.62%, (54.77%)]

Another important results observed in the present work is in regards to the final weight loss observed in the samples of ferrous (II) oxalate exposed to varying gamma radiation doses. The reduction in the weight loss to the extent of approximately 10.0% at all doses of irradiation suggests that the final products contain combination of oxide and carbides as major constituent. These stable products are probably formed by the interaction of radicals with the oxalate ions or among themselves during heating. These
Fig 5.2: Variation of activation energy and onset of decomposition temperature with dose in non-isothermal TGA of γ-irradiated ferrous (II) oxalate.
Fig 5.3: Kinetic plots for non-isothermal TGA of (a) ferrous (II) oxalate and (b) barium (II) oxalate
results obtained by non-isothermal decomposition by TGA technique are well supported by XRD of end products and IR of non-irradiated and irradiated (18.62 and 45.00 x 10^2 Gy) samples shown in Fig 5.12 and 5.8. The decrease in the onset temperature in the irradiated salt can be quantitatively explained in terms of defects induced by gamma radiations. The energy absorbed from gamma radiation is stored in the crystal in the form of crystal defects and this energy is made available at the time of dehydration process thereby leading to decrease in onset temperature of decomposition. The variation of onset of decomposition temperature and activation energy with dose is presented in Fig 5.2 and the kinetic data are given in the Table 5.2. The f (α) versus 1 / T plots is presented in Fig 5.3.

There is an initial decrease in activation energy at lower doses and the reverse phenomenon occurs at higher one, this may be attributed to encapsulation resulted due to residual carbon [5].

5.2.2 Non-isothermal TGA of hydrated barium (II) oxalate

The critical examination of the Fig 5.4 reveals that the unirradiated barium (II) oxalate decomposes by three distinct stages corresponding to dehydration, decomposition to carbonate and oxide. The data are recorded in Table 5.4. The mechanism of this decomposition has already been discussed in chapter 3 (section 3.1.2).

The influence of dose absorbed on the TGA characteristics is clearly seen from Fig 5.4. The onset temperature of dehydration as well as decomposition is found to decrease in agreement with earlier results obtained by ferrous (II) oxalate system (section 5.2.1). The variation of onset of decomposition temperature and activation energy with absorbed dose is presented in Fig 5.5 and the data are tabulated in Table 5.3. The overall decomposition is described by three stages similar to that for unirradiated salt, but the characteristic of decomposition are distinctly different. The first step of dehydration in non-irradiated and irradiated samples takes place in the temperature range of 150 °C to 210 °C and 140 °C to 160 °C the effect of irradiation on dehydration is explained in previous subsection 5.2.1. The second step of decomposition corresponds to conversion of barium oxalate to barium carbonate. The non-irradiated barium (II) oxalate shows 100 % conversion to carbonate and not to barium oxide while 100% carbonate and 50% barium oxide formation observed in the doses of 0.98, 4.79, 9.59 and 19.18 x 10^2 Gy.
Fig 5.4: Non-isothermal TGA of γ-irradiated barium (II) oxalate
The 100% carbonate and 82% barium oxide formation is observed in the doses of 25.00, 38.00 and 45.00 x 10² Gy. For all irradiation doses of barium (II) oxalate shows increase in weight loss for every decomposition step, this is due to the irradiation facilitates the decomposition, the effect being higher at higher doses [6]. In the present case ionization will lead to decomposition. Due to irradiation, there will be atoms and ions in the interstitial positions, whereas the fragments bearing the same charge as the parent ion will be in the lattice position. These damaged species constitute decomposition nuclei themselves (irradiation nuclei). Due to increased amount of point defects and additional nucleation centers, sufficient strain is created in the lattice, which ultimately fractures the crystal, thus generating new reactive centers, facilitating the decomposition process [6].

S. Bose, K. Sahu and D. Bhatta studied the effect of γ-irradiation on thermal decomposition of barium (II) oxalate [5]. They observe that the discharge of energy into the lattice irregularities producing local hot spots, where the energy available is of the order of 10 eV but this would produce decomposition rather than displacement of molecular ions.

The decomposition reactions of unirradiated barium (II) oxalate is as follows,

1) 150 °C-210 °C

\[ \text{BaC}_2\text{O}_4\cdot0.62\text{H}_2\text{O} (s) \rightarrow \text{BaC}_2\text{O}_4 (s) + 0.62 \text{H}_2\text{O} (g) \]  
[Observed Wt. loss = 4.57%, (4.57%)]

2) 430 °C- 510 °C

\[ \text{BaC}_2\text{O}_4 (s) \rightarrow \text{BaCO}_3 (s) + \text{CO} (g) \]  
[Observed Wt. loss = 12.50%, (12.42%)]

3) 730 °C-800 °C

\[ \text{BaCO}_3 (s) \rightarrow \text{BaO} (s) + \text{BaCO}_3 (s) + \text{CO}_2 (g) \text{ (partial decomposition)} \]  
[Observed Wt. loss = 4.00%, (3.00%)]

Irradiated barium (II) oxalate as,

1) 120 °C-160 °C

\[ \text{BaC}_2\text{O}_4\cdot0.62\text{H}_2\text{O} (s) \rightarrow \text{BaC}_2\text{O}_4 (s) + 0.62\text{H}_2\text{O} (g) \]  
[Observed Wt. loss = 4.57%, (5.00%)]

2) 400 °C-450 °C

\[ \text{BaC}_2\text{O}_4 (s) \rightarrow 2/10\text{BaCO}_3 (s) + 4/5\text{BaO} (s) + \text{CO} (g) + 1/2 \text{CO}_2 (g) \]
Fig 5.5: Variation of activation energy and onset of decomposition temperature with dose in non-isothermal TGA of γ-irradiated barium (II) oxalate
3) 600 °C-650 °C

\[ \frac{2}{10}\text{BaCO}_3 (s) + \frac{4}{5}\text{BaO} (s) \rightarrow \frac{1}{10}\text{BaO} (s) + \frac{1}{10}\text{BaCO}_3 (s) + \frac{1}{10}\text{CO}_2 (g) \]

[Observed Wt. loss = 8.51%, (8.57%)]

These results obtained by non-isothermal decomposition by TGA technique are well supported by XRD of end products and IR of non-irradiated and irradiated (19.18 and 45.00 x 10^2 Gy) samples shown in Fig 5.13 and 5.9. The barium oxalate follows the general trend of decrease in activation energy up on irradiation. The variation of onset of decomposition temperature and activation energy with dose is presented in Fig 5.4 and the kinetic data are given in the Table 5.3. The \( f(\alpha) \) versus \( 1 / T \) plots is presented in Fig 5.3.

5.2.3 The nature of transients in gamma irradiated salts

The results obtained from TGA study of \( \gamma \)-irradiated samples differ widely from those for the unirradiated ones. In order to support these observations further investigations have been carried out using independent techniques like DSC, IR and magnetic susceptibility measurements. The data obtained from these techniques are discussed below.

5.2.3.1 DSC study

It is well-known [3, 6-8] that the radiation induced defects are susceptible to recombination upon isothermal annealing. Further, short lived species undergo easy recombination compared to long live ones. This aspect could be investigated with the help of DSC technique. Defect recombination is an exothermic process, hence if the DSC peak is initially exothermic, irradiation will add to it and the area under the peak would increases. Alternatively, if DSC peak is endothermic, the area under the peak would be reduced upon irradiation. Former kind of observation is evident from the DSC of hydrated ferrous (II) oxalate (Fig 5.6). In the unirradiated and irradiated ferrous (II) oxalate dehydration reaction is strongly endothermic with onset temperature lowered to 140 °C and 160 °C. In the unirradiated and irradiated ferrous (II) oxalate decomposition reaction is strongly exothermic in the temperature lowered to 295 °C and 250 °C respectively. The quantitative estimation of energy per mole of ferrous (II) oxalate has
Fig 5.6: DSC of ferrous (II) oxalate a) irradiated b) unirradiated
been carried out and the resulting values for unirradiated and irradiated salts are noted to be 170 and 250 kJ/mole respectively.

The DSC curve of unirradiated and irradiated barium (II) oxalate is shown in Fig 5.7. The onset of dehydration temperature in unirradiated and irradiated barium (II) oxalate observed is 145 °C and 110 °C respectively. Thermal decomposition of unirradiated and irradiated barium (II) oxalate to barium carbonate begins at 420 °C and 400 °C respectively. The decomposition of barium carbonate to oxide is not completed to 1000 °C. The quantitative estimation of energy per mole of barium (II) oxalate has been carried out and the resulting values for unirradiated and irradiated salts are noted to be 38 and 27 KJ/mole respectively.

The calculated values of energies liberated per mole are found to be decreased for irradiated salt than unirradiated salt. The difference in these energies indicates that the large amount of energy is stored in the lattice in the form of imperfections which is released upon annealing. Due to this net energy required for decomposition process is lowered. One can conclude from these observations that the radiation born nuclei/defects make the parent lattice unstable which in turn becomes more susceptible to undergo easy and faster decomposition of the lattice. This could be the only reason for variation in the kinetic parameter of unirradiated and irradiated samples. In actual practice it is rather difficult to predict the exact nature of defects produced or the rearrangement occurring during the irradiation. In order to support the DSC data, IR and magnetic susceptibility studies were also carried out for both the sample.

5.2.3.2 IR study

As mentioned above, though the identification of the species is very difficult upon irradiation, the species existing in the oxalate lattice of the pre-irradiated sample would most probably be C₂O₄²⁻ and CO₂⁻ radicals. While in the IR spectra of unirradiated ferrous (II) oxalate (Fig 5.8) 820 cm⁻¹ peak disappears in irradiated sample, indicates formation of oxide. The small peak at 1625 cm⁻¹ has been observed indicates small amount of carbon is remained in irradiated sample while peak at 3547, 1317, 822 and 490 cm⁻¹ has been found to disappear in the spectra of irradiated sample, indicates formation of oxide.
Fig 5.7: DSC of barium (II) oxalate a) irradiated b) unirradiated
Fig 5.8: IR spectra of a) unirradiated and b) irradiated ferrous (II) oxalate
Table 5.2: Kinetic data derived from non-isothermal TGA studies of hydrated ferrous (II) oxalate

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Dose, $x 10^2$ Gy</th>
<th>Onset of decomp (°C)</th>
<th>Coats-Redfern</th>
<th>Freeman-Carroll</th>
<th>Horowitz-Metzer</th>
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<td>Ea</td>
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Table 5.3: Kinetic data derived from non-isothermal TGA studies of hydrated barium (II) oxalate

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<th>Sr. No.</th>
<th>Dose, $x 10^2$ Gy</th>
<th>Onset of decomp (°C)</th>
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<th>Freeman-Carroll</th>
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<td>20.23</td>
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Table 5.4: Data from non-isothermal TGA of pre-irradiated hydrated barium (II) oxalate in air

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<th>Sr. No.</th>
<th>Dose, x $10^6$ Gy</th>
<th>Step</th>
<th>Temp. range (°C)</th>
<th>Onset of decompo. (°C)</th>
<th>% Wt. loss</th>
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<td>400</td>
<td>17.43 (17.51)</td>
<td>CO, 1/2CO$_2$</td>
<td>1/2BaCO$_3$, 1/2BaO</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>3</td>
<td>540-720</td>
<td>540</td>
<td>10.5 (10.32)</td>
<td>3/10CO$_2$</td>
<td>3/10 BaCO$_3$, 3/10 BaO</td>
</tr>
<tr>
<td>4.</td>
<td>9.59</td>
<td>1</td>
<td>120-160</td>
<td>120</td>
<td>5.00 (4.57)</td>
<td>0.62H$_2$O</td>
<td>BaC$_2$O$_4$</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>2</td>
<td>400-470</td>
<td>400</td>
<td>17.43 (17.51)</td>
<td>CO, 1/2CO$_2$</td>
<td>1/2BaCO$_3$, 1/2BaO</td>
</tr>
<tr>
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<td></td>
<td>3</td>
<td>520-720</td>
<td>520</td>
<td>10.5 (10.32)</td>
<td>3/10CO$_2$</td>
<td>3/10 BaCO$_3$, 3/10 BaO</td>
</tr>
<tr>
<td>5.</td>
<td>19.18</td>
<td>1</td>
<td>120-160</td>
<td>120</td>
<td>5.00 (4.57)</td>
<td>0.62H$_2$O</td>
<td>BaC$_2$O$_4$</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>2</td>
<td>400-460</td>
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</tr>
<tr>
<td>3</td>
<td></td>
<td>3</td>
<td>520-720</td>
<td>520</td>
<td>10.5 (10.32)</td>
<td>3/10CO$_2$</td>
<td>3/10 BaCO$_3$, 3/10 BaO</td>
</tr>
<tr>
<td>6.</td>
<td>25.00</td>
<td>1</td>
<td>120-160</td>
<td>120</td>
<td>5.00 (4.57)</td>
<td>0.62H$_2$O</td>
<td>BaC$_2$O$_4$</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>2</td>
<td>400-450</td>
<td>400</td>
<td>20.00 (21.03)</td>
<td>CO, 2/10CO$_2$</td>
<td>2/10BaCO$_3$, 4/5BaO</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>3</td>
<td>500-720</td>
<td>500</td>
<td>8.51 (8.93)</td>
<td>1/10CO$_2$</td>
<td>1/10 BaCO$_3$, 1/10 BaO</td>
</tr>
<tr>
<td>7.</td>
<td>38.00</td>
<td>1</td>
<td>120-160</td>
<td>120</td>
<td>5.50 (4.57)</td>
<td>0.62H$_2$O</td>
<td>BaC$_2$O$_4$</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>2</td>
<td>400-440</td>
<td>400</td>
<td>20.00 (21.03)</td>
<td>CO, 2/10CO$_2$</td>
<td>2/10BaCO$_3$, 4/5BaO</td>
</tr>
<tr>
<td>3</td>
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<td>3</td>
<td>440-720</td>
<td>440</td>
<td>8.51 (8.93)</td>
<td>1/10CO$_2$</td>
<td>1/10 BaCO$_3$, 1/10 BaO</td>
</tr>
<tr>
<td>8.</td>
<td>45.00</td>
<td>1</td>
<td>120-160</td>
<td>120</td>
<td>5.65 (4.57)</td>
<td>0.62H$_2$O</td>
<td>BaC$_2$O$_4$</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>2</td>
<td>400-440</td>
<td>400</td>
<td>20.00 (21.03)</td>
<td>CO, 2/10CO$_2$</td>
<td>2/10BaCO$_3$, 4/5BaO</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>3</td>
<td>440-720</td>
<td>440</td>
<td>8.51 (8.93)</td>
<td>1/10CO$_2$</td>
<td>1/10 BaCO$_3$, 1/10 BaO</td>
</tr>
</tbody>
</table>
A careful comparison of the IR spectra of both, unirradiated and pre-irradiated samples of ferrous (II) oxalate and barium (II) oxalate shows 2-3 fold increase in the intensity despite the shift in the peak position (Fig.5.8 and 5.9). The characteristic absorption frequencies for the oxalate group [3] are 1650 cm⁻¹ for asymmetric C=O stretch and approximately 1350 cm⁻¹ for C-O symmetric stretch and at about 820, 780, 535 cm⁻¹ due to the deformation of O-C-O group. All are evident in the spectra of unirradiated as well as pre-irradiated samples of barium (II) oxalate (Fig 5.9) [9]. However, one of the peak at 3547 cm⁻¹ has been found to disappear in the spectra of irradiated barium (II) oxalate, indicates effect of irradiation on H₂O molecules present in the oxalate. The IR peak in unirradiated barium (II) oxalate at 1601, 1327, 772 and 536 cm⁻¹ indicates stretching of CO, C-C, O(OCO) and Ba-O respectively. The peaks of unirradiated barium (II) oxalate shifts to 1749, 1334, 693 and 422 cm⁻¹ in irradiated sample due to the effect of γ-radiations. Such observations were attributed to the formation of CO₂⁻ radicals.

5.2.3.3 Magnetic susceptibility study

It has been seen from DSC and IR studies that irradiation creates defects in the lattice which in turn increases the number of decomposition prone nuclei. The radiation induced defects mostly include free and/or trapped electrons, ions and radicals which could be detected by a magnetic susceptibility study.

The formation of the above mentioned radiation induced defects/fragments usually change the magnetic behaviour of the parent compound. Recently, it has been reported that diamagnetic barium (II) oxalate becomes paramagnetic upon irradiation.

To confirm the above observation, the irradiated samples of barium (II) oxalate and ferrous (II) oxalate were subjected to magnetic study using Faraday balance. The study of all dose of both irradiated oxalate revealed that the ratio of ∆W/M increases slowly in barium (II) oxalate up to 25.00 x10² Gy, beyond which it remains nearly constant. The ferrous (II) oxalate shows that the ratio of ∆W/M increases suddenly up to 25.6 x10² Gy, beyond which it remains nearly constant. The increase in ∆W/M is an indication that diamagnetic barium (II) oxalate is becoming paramagnetic upon
Fig 5.9: IR spectra of a) unirradiated and b) irradiated barium (II) oxalate
Fig 5.10: Plots of irradiated dose versus $\Delta W / M$ of ferrous (II) oxalate
Fig 5.11: Plots of irradiated dose versus $\Delta W / M$ of barium (II) oxalate
irradiation. The plot of ΔW/M versus dose for ferrous (II) oxalate and barium (II) oxalate are shown in Fig 5.10 and Fig 5.11 illustrates these features.

5.2.3.4 X-Ray diffraction of unirradiated and irradiated ferrous (II) oxalate and barium (II) oxalate

The end products obtained from non-isothermal TGA of unirradiated and irradiated ferrous (II) oxalate and barium (II) oxalate were taken for XRD study. The unirradiated and irradiated ferrous (II) oxalate of dose 18.62 x 10^2 Gy and 45.00 x 10^2 Gy are shown in Fig 5.12. Their XRD patterns were recorded in 2Θ range of 20°-80°. Fig 5.12 (a) showed that there is formation of Fe_2O_3 while Fig 5.12 (b) showed that there is formation of Fe_3O_4, Fe_3C and free C (Fig 5.12. b). The intensity of Fe_3O_4 peak increase up on increase in dose.

The unirradiated and irradiated barium (II) oxalate of dose 19.18 x 10^2 Gy and 45.00 x 10^2 Gy are shown in Fig 5.13. Their XRD patterns were recorded in 2Θ range of 20°-80°. All XRD pattern showed formation of BaCO_3 and BaO, but unirradiated sample shows high intensity peak of BaCO_3 which decreases and BaO peak increases up on increase in dose.

5.3 Kinetic parameters from non-isothermal study

The non-isothermal TGA study, as mentioned earlier, is helpful in evaluating the kinetic parameters of the decomposition reactions. The kinetic parameters for pre-irradiated ferrous (II) oxalate and barium (II) oxalate are calculated by using Coats-Redfern [10], Freeman-Carroll [11-12] and Horowitz-Metzger [13-14] equations. The data for ferrous (II) oxalate and barium (II) oxalate are presented in Tables 5.2 and 5.4 respectively. The analysis of data for both oxalates shows that the activation energy (Ea) increases at lower doses, it decreases again.

5.4 Isothermal study of hydrated ferrous (II) and barium (II) oxalates and evaluation of kinetic parameters

From the non-isothermal curves of both oxalates the isothermal temperatures were selected. The isothermal decomposition of ferrous (II) oxalate was investigated at temperatures 200 °C, 210 °C, 220 °C and 230 °C while temperatures of 350 °C, 400 °C, 450 °C, 500 °C and 550 °C were chosen for decomposition of barium (II) oxalate. The α
Fig 5.12: XRD pattern of a) irradiated and b) non-irradiated ferrous (II) oxalate at 300 °C (1. Fe₂O₃, 2. Fe₃O₄, 3. Fe₃C and 4. C)
Fig 5.13: XRD pattern of a) irradiated and b) non-irradiated barium (II) oxalate at 1000 °C (1. BaO₂, 2. BaO)
versus time plots for ferrous (II) oxalate and barium (II) oxalate are presented in Fig 5.14 and 5.15 respectively for typical doses of irradiation.

The kinetic parameters like activation energy, rate constants, for ferrous (II) and barium (II) oxalates were obtained by using Coats-Redfem [10] equation and data are presented in Tables 5.5 and 5.6 respectively. The activation energy for decomposition of irradiated ferrous (II) oxalate is found to be increasing at low doses of irradiation, then decreases slowly and constant at higher doses. The activation energy for decomposition of irradiated ferrous (II) oxalate are higher than unirradiated sample, this may be attributed to cage effect. At higher doses the damaged entities encapsulated the host nuclei and act as barrier for further decomposition to proceed [15]. The same observation was found for rate constants and irradiated barium (II) oxalate.

Up on irradiation thermal decomposition of ferrous (II) oxalate is found to take place by two dimensional diffusion (D₂ α) growth mechanism followed by three dimensional diffusion (D₄ α) controlled mechanism. In case of irradiated barium (II) oxalate thermal decomposition takes place by three dimensional diffusion (D₃ α) controlled mechanism followed by two dimensional phase boundary (R₂ α) [16] mechanism.

The exhaustive kinetic data that have been evolved from the isothermal and non-isothermal decomposition study of irradiated samples of ferrous (II) oxalate and barium (II) oxalates leads to the occurrence of kinetic compensation effect. It is a happy coincidence that both the systems exhibit such a rarely observable effect. The occurrence of kinetic compensation effect has been thoroughly discussed in the following section.

5.5 Kinetic compensation effect

The chemical reaction is feasible only if a free energy change for the reaction is favourable and is given by the wellknown thermodynamic relationship,

\[ \Delta G^o = \Delta H^o - T \Delta S^o \]

Where, \( \Delta G^o \) is the free energy change, \( \Delta H^o \) is the enthalpy change, \( \Delta S^o \) is the entropy change and \( T \) is the absolute temperature (°K). In the reaction kinetics, these terms gain the meaning of “activation” hence the relation can be written in the form.

\[ \Delta G^* = \Delta H^* - T \Delta S^* \]
Fig 5.14: Isothermal TGA plots of $\gamma$-irradiated ferrous (II) oxalate
Fig 5.15: Isothermal TGA plots of γ-irradiated barium (II) oxalate
Activation enthalpy ($\Delta H^*$) is an activation energy ($E_a$) in the real kinetic sense. It is known [16] that free energies are simpler functions than activation energies which are sensitive to external factors such as those brought about by solvent, pressure and as demonstrated in the present work to irradiation as well. For such systems, it has been found that $\Delta H^*$ and $T\Delta S^*$ show a linear relationship with approximately unit slope. There is a well-known historical example of the alkaline hydrolysis of ethyl benzoate in alcohol water mixtures [16]. Such a linear relationship could exist if there is a general tendency of a reaction for heats ($\Delta H$) and entropies ($\Delta S$) to compensate each other so that the changes in free energy ($\Delta G$) are negligibly smaller.

The plots of $\Delta H^*$ versus $T\Delta S^*$ are expected to be linear with a unit slope [17] from which isokinetic temperature for the reaction could be obtained. It is obvious that below this compensating point chemical reaction is primarily governed by $\Delta H^*$ while above this point $\Delta S^*$ is the controlling factor.

**5.5.1 Compensation phenomenon in heterogeneous reactions**

The compensation effect may simply arise not from any kinetic properties of a system but as an experimental artifact.

The Arrhenius equation is,

$$k = A \cdot e^{\frac{E_a}{RT}}$$

where $A$ is the pre-exponential factor.

The energy of activation of a chosen reaction is determined by measuring rate constants at various temperatures by using Arrhenius equation. The wide applicability of Arrhenius equation in the heterogeneous kinetics is mainly due to two reasons;

1. The relationship is well established in homogeneous kinetics and
2. The form of the equation assures that constants in the equation can be calculated.

The correlation of Arrhenius parameters with various experimental variables involves consideration of the "kinetic compensation effect". Procedural variables have considerable influence on the kinetic parameters of thermal decomposition reactions. Variations of these parameters are not independent of each other and certain general correlation exists between them. The kinetic compensation effect was first observed in
catalytic dehydrogenation of ethanol using copper catalyst [18] of different activities. It has been found that an increase in the activation energy $E_a$, of the reaction does not lead to the expected decrease in the rate constant, due to a simultaneous increase in the pre-exponential factor $A$, in the Arrhenius equation compensating the change in activation energy. Thus the compensation effect is a compensating change in the activation energy corresponding to a change in the pre-exponential function. This effect has been observed to operate in various systems, not only in heterogeneous catalysis but also in thermal decomposition reactions and is described by the relationship,

$$\ln A = a \cdot E_a + b$$

which is the rearrangement of the Arrhenius equation.

Comparison of equations (1) and (2) show that $a = 1 / RT$ [19] and $b = \ln k$.

The equation (2) could be rewritten as, $\ln A = \ln k + E_a / RT$ (3)

For compensation effect to appear, the $k$ (i.e $\ln k$) should be nearly constant even if the temperature $T$ changes. This necessitates the variation in $A$ (i.e $\ln A$) as well as in $E_a$. If temperature $T$ and rate constant $k$ are considered constant [i.e $T$ and $f(\frac{da}{dt})$] then $\ln A$ and $E_a$ obey a linear relationship. Thus, the Arrhenius equation produces straight lines for both $\ln k$ versus $1/T$ and $\ln A$ versus $E_a$.

According to Gorbachev [20], the criterion for the occurrence of genuine kinetic compensation effect is the appearance of “common point” called as the “isokinetic point” in the plot of $\ln k$ against $1 / T$ for a series of similar type of transformations. For inspecting this criterion, the Arrhenius equation was used in the following forms.

$$K = \exp \left( \frac{E_a}{RT_c} \right) \cdot \exp \left( -\frac{E_a}{RT} \right)$$

Where, $T_c$ is the critical temperature or reversal temperature or isokinetic temperature [21] at which $\ln k$ equal to zero. If no such point is existing, then the observed linear relationship between $\ln A$ and $E_a$ may be fictitious. For the true compensation effect the factor $A$ in the Arrhenius equation is given by,

$$\ln A = \frac{E_a}{RT_c}$$
Table 5.5: Kinetic data obtained from isothermal TGA studies of hydrated ferrous (II) oxalate

<table>
<thead>
<tr>
<th>Sr No.</th>
<th>Dose, $x 10^2$ Gy</th>
<th>Temperature (°C)</th>
<th>$\ln A$</th>
<th>$E_a$ (KJ/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>230</td>
<td>220</td>
<td>210</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$k$</td>
<td>$\ln k$</td>
<td>$k$</td>
</tr>
<tr>
<td>1.</td>
<td>1.86</td>
<td>5.80 $x 10^{-3}$</td>
<td>-7.45</td>
<td>6.05 $x 10^{-4}$</td>
</tr>
<tr>
<td>2.</td>
<td>4.65</td>
<td>6.25 $x 10^{-3}$</td>
<td>-5.07</td>
<td>6.51 $x 10^{-3}$</td>
</tr>
<tr>
<td>3.</td>
<td>9.31</td>
<td>6.19 $x 10^{-3}$</td>
<td>-5.08</td>
<td>6.44 $x 10^{-3}$</td>
</tr>
<tr>
<td>4.</td>
<td>18.62</td>
<td>5.74 $x 10^{-3}$</td>
<td>-5.16</td>
<td>5.99 $x 10^{-3}$</td>
</tr>
<tr>
<td>5.</td>
<td>25.6</td>
<td>3.79 $x 10^{-3}$</td>
<td>-5.57</td>
<td>3.94 $x 10^{-3}$</td>
</tr>
<tr>
<td>6.</td>
<td>37.24</td>
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<td>-5.72</td>
<td>3.38 $x 10^{-3}$</td>
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<tr>
<td>7.</td>
<td>45.00</td>
<td>3.26 $x 10^{-4}$</td>
<td>-5.72</td>
<td>3.38 $x 10^{-3}$</td>
</tr>
</tbody>
</table>

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Table 5.6: Kinetic data obtained from isothermal TGA studies of hydrated barium (II) oxalate

<table>
<thead>
<tr>
<th>Sr No.</th>
<th>Dose, $x 10^6$ Gy</th>
<th>Temperature (°C)</th>
<th>lnA</th>
<th>Ea (KJ/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>550</td>
<td>500</td>
<td>450</td>
</tr>
<tr>
<td></td>
<td>k</td>
<td>lnk</td>
<td>k</td>
<td>lnk</td>
</tr>
<tr>
<td>1.</td>
<td>0.98</td>
<td>1.34 x10^{-5}</td>
<td>-11.2</td>
<td>1.52 x10^{-5}</td>
</tr>
<tr>
<td>2.</td>
<td>4.79</td>
<td>1.45 x10^{-5}</td>
<td>-11.1</td>
<td>1.65 x10^{-5}</td>
</tr>
<tr>
<td>3.</td>
<td>9.59</td>
<td>9.70 x10^{-6}</td>
<td>-11.5</td>
<td>1.10 x10^{-5}</td>
</tr>
<tr>
<td>4.</td>
<td>19.18</td>
<td>1.20 x10^{-5}</td>
<td>-11.3</td>
<td>1.36 x10^{-5}</td>
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<tr>
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<td>9.50 x10^{-6}</td>
<td>-11.5</td>
<td>1.08 x10^{-5}</td>
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<tr>
<td>6.</td>
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<td>9.40 x10^{-6}</td>
<td>-11.5</td>
<td>1.06 x10^{-5}</td>
</tr>
<tr>
<td>7.</td>
<td>45.00</td>
<td>8.70 x10^{-6}</td>
<td>-11.6</td>
<td>9.90 x10^{-6}</td>
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</table>
Therefore, for a series of chemical reactions, with similar value of $T_c$ at which $\ln k$ equal to zero, the compensation effect will be automatically satisfied, i.e. the relationship between $\ln A$ and $E_a$ will be linear. This effect appears in number of chemical reactions like dehydration of Mg-EDTA chelate, rare earth succinates and maleates. The occurrence of compensation effect has been reported in numerous systems [22-31].

More recently the occurrence of compensation effect, which is known as ‘isokinetic effect’ or ‘$\Theta$’ rule has been critically discussed by Agarwal [32]. According to him the use of Arrhenius equation, successfully used for homogeneous gas phase reaction kinetics, has no meaning for solid state reaction kinetics. This is because there is no definition for a ‘mole of solid’ so that both $A$ and $E_a$ have little significance. Therefore, for solid state reactions ‘$A$’ should be called pre-exponential factor instead of frequency factor, and ‘$E_a$’ as the apparent activation energy rather than the amount of energy in excess of the average energy level which reactants should have for the reaction to proceed.

The linear relation between $\ln A$ and $E_a$ is expressed as [33],

$$\ln A = \ln k_{iso} + \frac{E_a}{RT_{iso}}$$

where, $k_{iso}$ is the isokinetic rate constant and $T_{iso}$ is the absolute isokinetic temperature [34].

Although in the thermogravimetric literature pre-exponential factor data derived from TG curves are very scarce, the occurrence of compensation effect seems to relatively common. A systematic and parallel decrease of both $\log A$ and $E_a$ values with increasing heating rate have been reported [35]. On the other hand, the decomposition temperature interval is known to be increased and shifted towards higher temperature with increasing heating rate [36-40].

There are several theories that have also been put forth for the prediction of such a linear compensation effect. However, the existence of this effect in heterogeneous reactions has been debated. Since the Arrhenius parameters are derived from the same kinetic data, the relation between the parameters $\ln A$ and $E_a$ becomes questionable. Anderson regards the parameters $A$, $E_a$ and order $n$ as mathematical parameters having empirical rather than theoretical significance [41]. Many scientists working in this field
do not have doubts about the reality of the effect and indeed none of the explanations reviewed by Galwey [27] are mutually exclusive and few provide convincing arguments in favor of one explanation in preference to all others. Later on, it has been argued that the Arrhenius equation being incomplete [42-43] and meaningless for heterogeneous reactions, little significance is attached A, Ea and n. Garn [44] whilst agreeing with many of these ideas, states that the Arrhenius equation is incomplete but often possible variables are excluded in the choice of reaction system. For example, if the series of reactions being studied; all occurring within the same temperature interval, then if either A or Ea varies, appropriate values of k are only possible if there is a measure of compensation [2, 45].

In order to overcome Garn’s argument that the compensation effect is due to deficiencies in the Arrhenius equation, Zsako [46] suggested that one can write the Arrhenius equation in the following form,
\[
\log k = \frac{-E_a}{2.3RT} + \log A
\]

or
\[
\log A = \frac{E_a}{2.3RT} + \log k
\]

Indicating that if the thermal decomposition occurs practically in the same temperature range, \( \log A \) will be a linear function of \( E_a \) obeying compensation law,
\[
\ln A = a \cdot E_a + b
\]

Zsako [46] accept certain points in Garn’s reappraisal of compensation behaviour but stresses that the existence of a linear relation between \( \log A \) and \( E_a \) is of more general characteristics. According to him the kinetic compensation effect is something real, given by the experiment, but it is formulated, in terms of Arrhenius equation, if one states that ‘activation energy’ and ‘pre-exponential factor’ vary in parallel, according to equation (2), or if one presumes the existence of a ‘characteristic temperature \( T_{iso} \)’ at which the rate constant has a characteristic value \( k_{iso} \) for all the processes correlated by the same compensation law (Fig 5.16).

Thus, while a physical interpretation for obedience to equation (2) cannot at present be provided, the relationship provides parameters which are useful in describing the reactivities of groups of related rate processes. Since Arrhenius equation does not require the existence of a characteristic temperature for more than two TG curves i.e. the
kinetic compensation effect is not due to the form of Arrhenius equation. In short the formation of kinetic compensation effect in terms of the Arrhenius equation is only formal and does not reveal the physical significance of the compensation parameters.

Gorbachev [20] suggested that when the existence of true compensation effect in non-isothermal kinetics is in doubt, then the isokinetic temperature will serve as a criterion. If the isokinetic point can be found in the graph of \( \ln k \) versus \( 1 / T \) then he argues that the kinetic compensation effect is real and has a physical significance (Fig 5.17).

The most important thing is that the compensation parameters characterize a whole family of TG curves. Therefore thermal decomposition processes can be better characterized by means of common kinetic parameters of decomposition temperature. Further, it could be attributed to the fact that the shape and position of TG curves and kinetic parameters derived can be very much influenced by procedural variables, but the compensation parameters are independent of them. Since the kinetic characteristics of surface processes may be applicable also to changes proceeding at a solid-solid interface (i.e. two surfaces). Some of the explanations [47] for compensation behaviour are:

1. There is characteristic temperature of onset of reaction,
2. The catalyst surface is energetically heterogeneous
3. There is more than a single active surface and
4. An inter-relationship exists between reaction entropy and enthalpy.

Agarwal [32] has illustrated some systems showing ‘true’ and ‘false’ compensation effects highlighting the importance of statistical analysis and use of simple Arrhenius plot (Fig 5.18). Exner [48-50] suggested that the appearance of real kinetic compensation effect is better understood by examining the plot of \( \ln k \) versus \( 1 / T \) rather than \( \ln A \) versus \( Ea \). Any speculation regarding the reaction mechanism must be made after establishing the occurrence of true compensation effect. Numerous occurrence of the reported compensation behaviour have utilized the plot of \( \ln A \) versus \( Ea \). Fig 5.16 is an illustration of compensation behaviour showing a linear relationship between \( \ln A \) and \( Ea \), theoretically calculated on the assumptions that the concentration of a participating surface intermediates varies with temperature.
Slope = $\frac{1}{RT_{iso}}$

Intercept = $\ln k_{iso}$

**Fig 5.16:** A plot generally accepted to test the existence of compensation effect

**Fig 5.17:** Arrhenius plot displaying obeyance of "True Compensation effect"
Fig. 5.18: Arrhenius plots;

'α' and 'c' false compensation effect

'β' no compensation effect
An alternative and more reliable method for detection of compensation behaviour involves the plotting of $\ln k$ versus $1/T$ (Fig 5.17). It can be seen from this figure that the occurrence of true compensation effect showing the existence of characteristic temperature, $T_{iso}$ at which all $k$ values are equal.

Further, it has been shown [29] that if the $T_{iso}$ is the average temperature range covered by measurement or if it is an unrealistically large value (Fig 5.18, a) the compensation behaviour could be simply an artifact due to experimental errors. If Arrhenius plot displays no such occurrence at a single point (Fig 5.18, a, b, c) the reacting system exhibits no compensation effect. If series of reactions display Fig 5.16 but fails to a single point occurrence (Fig 5.17) and instead shows trends as suggested in Fig 5.18. The system exhibits a ‘false’ compensation effect.

In order to establish a true compensation effect it has been suggested that the condition $\ln k_{iso}$ or $\log k_{iso}$ equal to zero should be satisfied within the experimental and computational errors. On the basis of the criterion established for compensation effect to occur, Agrawal have shown that, among the four different reactions [33] only one exhibited “true compensation”. Dollimore and Taylor [30] proposed the occurrence of true compensation effect in the rising temperature decomposition of pure carbonates. But actually a single point of occurrence is not observed in the plot of $\ln k$ versus $1/T$. But according to the criterion for a genuine kinetic compensation effect suggested earlier, an appearance of compensation effect in the series of carbonates decomposition suggested by Dollimore and Taylor [30] could be debated. Since the figure does not show an occurrence of a single ‘common point’, $T_{iso}$ or $k_{iso}$ have approximate values which have no significance in real compensation effect.

In the present work, appearance of a compensation effect in the kinetic data obtained from both, rising temperature and isothermal decomposition of ferrous (II) oxalate and barium (II) oxalate for a series of doses is discussed below.

5.5.2 Compensation effect in the present study

The effect of $\gamma$-irradiation on the non-isothermal and isothermal decomposition of ferrous (II) oxalate and barium (II) oxalate has been discussed in sections Fig 5.2.1 and 5.2.2. Up on irradiation these salts generate radicals and electrons in the crystal lattice. Such species are highly susceptible for thermal annealing and are expected to cause some
Fig 5.19: Compensation plot (non-isothermal TGA) of γ-irradiated ferrous (II) oxalate
Fig 5.20: Compensation plot (non-isothermal TGA) of γ-irradiated barium (II) oxalate
changes in the kinetics of decomposition of the sample. It is thought of interesting to examine the occurrence of a compensation effect in these systems.

As mentioned earlier that the abeyance of a compensation law is based on following three conditions,

1. In A versus Ea plot should be linear with positive slope and intercept equal to ln k [32]
2. A single point of occurrence or isokinetic point in the plots of ln k versus 1 / T having isokinetic values for T and ln k [20]
3. The experimental data should lie on both the sides of the isokinetic point described in (2) [32]

In the present work all these three conditions are satisfied confirming the presence of a true kinetic compensation effect in both the systems. The plots of ln A versus Ea for ferrous (II) oxalate and barium (II) oxalate are shown in figures (Fig 5.19 and 5.20) and the corresponding data are tabulated in Tables 5.2 and 5.4. From which kiso are obtained for both ferrous (II) oxalate and barium (II) oxalate systems and these are found to be 1.34 x 10⁻³ min⁻¹ and 7.21 x 10⁻⁴ respectively from non-isothermal study. The plots of ln A versus Ea and ln k versus 1 / T (Fig 5.21, 5.22, 5.23 and 5.24) for ferrous (II) oxalate and barium (II) oxalates respectively from isothermal study indicates the occurrence of an isokinetic point. The data are presented in Tables 5.5. and 5.6. The values for the isokinetic parameters obtained from the plots are tabulated in Table 5.7. It is seen from the table the values of the kinetic parameters obtained from isothermal and non-isothermal methods generally do not match with each other.

However, a correlation among these parameters observed by using a chosen method could exist only when the system exhibits a true kinetic compensation effect. The values of the constants a and b for both the systems indicate the abeyance of a compensation law.

The compensation effect is an entropy effect which compensate for the change in Ea, so that the free energy of activation remains mostly unchanged. Therefore, it appears that irradiation is responsible for an entropy change that favors the occurrence of compensation effect.
Fig 5.21: Compensation plots (isothermal TGA) of γ-irradiated ferrous (II) oxalate

Fig 5.22: Compensation plots (isothermal TGA) of γ-irradiated ferrous (II) oxalate
Fig 5.23: Compensation plots (isothermal TGA) of γ-irradiated barium (II) oxalate

Fig 5.24: Compensation plots (isothermal TGA) of γ-irradiated barium (II) oxalate

Dose x $10^2$ Gy

- 4.79
- 9.59
- 19.18
- 25.00
- 45.00
Table 5.7: Isokinetic parameters of thermal decomposition studies of irradiated ferrous (II) and barium (II) oxalate

<table>
<thead>
<tr>
<th>Compound</th>
<th>parameters</th>
<th>From the plot of</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Non-isothermal</td>
<td>Isothermal TGA</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\ln A \text{ Vs } E_a$</td>
<td>$\ln A \text{ Vs } E_a$</td>
<td>$\ln k \text{ Vs } 1/T$</td>
<td></td>
</tr>
<tr>
<td>FeC$_2$O$_4$.2H$_2$O</td>
<td>a</td>
<td>0.05</td>
<td>0.08</td>
<td>0.03</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$T_{iso}$</td>
<td>189.72</td>
<td>187.67</td>
<td>197.63</td>
<td></td>
</tr>
<tr>
<td></td>
<td>b</td>
<td>-11.8</td>
<td>-12.0</td>
<td>-12.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$k_{iso}$</td>
<td>$1.34 \times 10^{-3}$</td>
<td>$1.34 \times 10^{-3}$</td>
<td>$5.74 \times 10^{-3}$</td>
<td></td>
</tr>
<tr>
<td>BaC$_2$O$_4$.0.6H$_2$O</td>
<td>a</td>
<td>0.536</td>
<td>0.666</td>
<td>0.555</td>
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<tr>
<td></td>
<td>$T_{iso}$</td>
<td>306.25</td>
<td>322.36</td>
<td>308.14</td>
<td></td>
</tr>
<tr>
<td></td>
<td>b</td>
<td>-13.0</td>
<td>-13.8</td>
<td>-13.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$k_{iso}$</td>
<td>$7.21 \times 10^{-4}$</td>
<td>$1.96 \times 10^{-4}$</td>
<td>$1.80 \times 10^{-4}$</td>
<td></td>
</tr>
</tbody>
</table>
The study of γ-radiation on thermal decomposition of ferrous (II) and barium (II) oxalates leads to the following findings and conclusions.

1. The decrease in the onset of decomposition temperature is observed in the pre-irradiation and sample.

2. There is an initial decrease in activation energy at lower doses and the reverse phenomenon occurs at higher one in ferrous (II) oxalate, this may be attributed to encapsulation resulted due to residual carbon [5]. Activation energy is found to decrease by increase in irradiation doses in barium (II) oxalate. In the pre-irradiated samples the total final weight loss in non-isothermal TGA is found to be less than that observed in unirradiated sample.

3. The unirradiated and irradiated ferrous (II) oxalate shows water loss step leading to a weight loss of 20.03% at 160 °C and 140 °C respectively. While the decomposition leading to a weight loss 45.19% and 34.77% at 300 °C and 260 °C respectively. The mass loss in irradiation is attributed to the escape of intermediated formed during irradiation.

4. The unirradiated and irradiated barium (II) oxalate shows water loss step leading to a weight loss of 4.54% at 150 °C and 120 °C respectively. While the decomposition leading to carbonate formation shows weight loss 12.50% and 20.00% at 430 °C and 400 °C respectively and the decomposition leading to oxide formation shows weight loss 4.00% and 8.5% at 730 °C and 440 °C respectively. The mass loss in irradiation is attributed to the escape of intermediated formed during irradiation.

5. One of the important results brought about from the studies of decomposition of irradiated salts is in regards to the occurrence of compensation effect which could be attributed to radiation damages produced in the matrix of oxalates.
References:

181, 1968, 1174.


