The Reaction Between Calcium Oxide and Nitrogen Dioxide in the Presence of Oxygen: a Variable Solid Property Grain Model.

Kenneth Charles Reibert

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The Louisiana State University and Agricultural and Mechanical Col. Ph.D. 1982

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THE REACTION BETWEEN CALCIUM OXIDE 
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PRESENCE OF OXYGEN: A VARIABLE 
SOLID PROPERTY GRAIN MODEL

A Dissertation
Submitted to the Graduate Faculty of the 
Louisiana State University and 
Agricultural and Mechanical College 
in partial fulfillment of the 
requirements for the degree of 
Doctor of Philosophy

in
The Department of Chemical Engineering

by
Kenneth Charles Reibert 
B.S., Louisiana State University, 1974 
M.S., Louisiana State University, 1976 
May, 1982
Dedicated to my father
Kenneth Howard Reibert
whose total commitment to my
education enabled me to complete
this work.
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# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>CHAPTER</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>I. INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>The NOx Air Pollution Problem</td>
<td>1</td>
</tr>
<tr>
<td>Current Stationary Source Control Techniques</td>
<td>4</td>
</tr>
<tr>
<td>Reactions of NOx with CaO</td>
<td>11</td>
</tr>
<tr>
<td>Objectives of Research</td>
<td>16</td>
</tr>
<tr>
<td>Literature Cited</td>
<td>18</td>
</tr>
<tr>
<td>II. THERMODYNAMIC STUDY</td>
<td>21</td>
</tr>
<tr>
<td>Free Energy Minimization</td>
<td>23</td>
</tr>
<tr>
<td>Procedure for Thermodynamic Study</td>
<td>26</td>
</tr>
<tr>
<td>Gaseous Species Considered</td>
<td>27</td>
</tr>
<tr>
<td>Condensed Species Considered</td>
<td>28</td>
</tr>
<tr>
<td>Results of Thermodynamic Study</td>
<td>29</td>
</tr>
<tr>
<td>Alkali Metal Oxides</td>
<td>31</td>
</tr>
<tr>
<td>Alkaline Metal Oxides</td>
<td>36</td>
</tr>
<tr>
<td>Summary of Results of the Thermodynamic Study</td>
<td>47</td>
</tr>
<tr>
<td>Literature Cited</td>
<td>51</td>
</tr>
<tr>
<td>III. APPLICABLE NON-CATALYTIC GAS-SOLID REACTION MODELS</td>
<td>55</td>
</tr>
<tr>
<td>Non-Catalytic Gas-Solid Reactions</td>
<td>55</td>
</tr>
<tr>
<td>Conventional Models</td>
<td>57</td>
</tr>
<tr>
<td>Unreacted Core Model</td>
<td>60</td>
</tr>
<tr>
<td>Grain Model</td>
<td>64</td>
</tr>
<tr>
<td>Effect of Solid Properties</td>
<td>70</td>
</tr>
<tr>
<td>Variable Solid Property Models</td>
<td>73</td>
</tr>
<tr>
<td>CHAPTER</td>
<td>PAGE</td>
</tr>
<tr>
<td>----------</td>
<td>------</td>
</tr>
<tr>
<td>Model of Howard, Williams, and Ghazal.</td>
<td>73</td>
</tr>
<tr>
<td>Model of Gidaspow - Pore Closure Model</td>
<td>76</td>
</tr>
<tr>
<td>Model of Hartman and Coughlin</td>
<td>83</td>
</tr>
<tr>
<td>Model of Georgakis, Chang, and Szekely</td>
<td>86</td>
</tr>
<tr>
<td>Model of Ramachandran and Smith - Single-Pore Model</td>
<td>89</td>
</tr>
<tr>
<td>Reaction/Sintering Model of Ramachandran and Smith</td>
<td>98</td>
</tr>
<tr>
<td>Model of Ranade and Harrison</td>
<td>103</td>
</tr>
<tr>
<td>Literature Cited</td>
<td>112</td>
</tr>
</tbody>
</table>

**IV. EXPERIMENTAL APPARATUS AND PROCEDURE**

<table>
<thead>
<tr>
<th>SUB-TOPIC</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermodynamic Equilibrium of Reactant Gas Mixture</td>
<td>116</td>
</tr>
<tr>
<td>Major Experimental Apparatus - The TGA</td>
<td>119</td>
</tr>
<tr>
<td>Materials</td>
<td>124</td>
</tr>
<tr>
<td>Procedure</td>
<td>127</td>
</tr>
<tr>
<td>Auxiliary Equipment</td>
<td>131</td>
</tr>
<tr>
<td>Experimental Difficulties</td>
<td>133</td>
</tr>
<tr>
<td>Literature Cited</td>
<td>137</td>
</tr>
</tbody>
</table>

**V. EXPERIMENTAL RESULTS**

<table>
<thead>
<tr>
<th>SUB-TOPIC</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experimental Results for CaO Pellets</td>
<td>141</td>
</tr>
<tr>
<td>Reaction Reproducibility</td>
<td>146</td>
</tr>
<tr>
<td>Effect of Temperature</td>
<td>149</td>
</tr>
<tr>
<td>Effect of Reactant Gas Concentration</td>
<td>160</td>
</tr>
<tr>
<td>Effect of Oxygen Concentration</td>
<td>164</td>
</tr>
<tr>
<td>Effect of Total Gas Flowrate</td>
<td>168</td>
</tr>
<tr>
<td>CHAPTER</td>
<td>PAGE</td>
</tr>
<tr>
<td>---------</td>
<td>------</td>
</tr>
<tr>
<td>Effect of Pellet Properties</td>
<td>168</td>
</tr>
<tr>
<td>Reaction Parameter Analysis</td>
<td>175</td>
</tr>
<tr>
<td>Post Reaction Analyses</td>
<td>188</td>
</tr>
<tr>
<td>CaO Powder Data</td>
<td>192</td>
</tr>
<tr>
<td>Literature Cited</td>
<td>203</td>
</tr>
<tr>
<td>VI. COMPARISON OF EXPERIMENTAL DATA WITH A VARIABLE PROPERTY GRAIN MODEL</td>
<td>204</td>
</tr>
<tr>
<td>The Model</td>
<td>204</td>
</tr>
<tr>
<td>Dimensionless Model Equations</td>
<td>205</td>
</tr>
<tr>
<td>Evaluation of Model Parameters</td>
<td>207</td>
</tr>
<tr>
<td>Numerical Solution Procedure</td>
<td>212</td>
</tr>
<tr>
<td>Model Results Using the Constant Property Grain Model</td>
<td>214</td>
</tr>
<tr>
<td>Predictions of the Variable Property Grain Model</td>
<td>219</td>
</tr>
<tr>
<td>VPGM Predictions at 150°C</td>
<td>220</td>
</tr>
<tr>
<td>VPGM Predictions at 250°C</td>
<td>227</td>
</tr>
<tr>
<td>Alternate Approaches to Matching the VPGM to Experimental Data at 150°C and 250°C</td>
<td>238</td>
</tr>
<tr>
<td>VPGM Predictions at 350°C</td>
<td>246</td>
</tr>
<tr>
<td>VPGM Predictions at 450°C</td>
<td>260</td>
</tr>
<tr>
<td>VPGM Results at 550°C</td>
<td>267</td>
</tr>
<tr>
<td>Improvement in VPGM Predictions at 350°C, 450°C, and 550°C</td>
<td>274</td>
</tr>
<tr>
<td>Quantitative Relative Resistance Analysis</td>
<td>281</td>
</tr>
<tr>
<td>The Temperature Dependence of $D'_r$</td>
<td>288</td>
</tr>
<tr>
<td>Summary</td>
<td>293</td>
</tr>
<tr>
<td>Literature Cited</td>
<td>299</td>
</tr>
<tr>
<td>CHAPTER</td>
<td>PAGE</td>
</tr>
<tr>
<td>---------</td>
<td>------</td>
</tr>
<tr>
<td>VII. OVERALL CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK</td>
<td>301</td>
</tr>
<tr>
<td>APPENDICES</td>
<td>313</td>
</tr>
<tr>
<td>A CaO Pellet Reaction Data</td>
<td>314</td>
</tr>
<tr>
<td>B CaO Powder Reaction Data</td>
<td>336</td>
</tr>
<tr>
<td>C Computer Programs - VPGM, VPGMC, CPGM.</td>
<td>349</td>
</tr>
<tr>
<td>VITA</td>
<td>398</td>
</tr>
<tr>
<td>TABLE</td>
<td>Description</td>
</tr>
<tr>
<td>---------</td>
<td>-----------------------------------------------------------------------------</td>
</tr>
<tr>
<td>II-1</td>
<td>Denitrification Potential of Alkali Metal Oxides</td>
</tr>
<tr>
<td>II-2</td>
<td>Melting Points of Alkaline Earth Metal Compounds</td>
</tr>
<tr>
<td>II-3</td>
<td>Denitrification Potential of Alkaline Earth Metal Oxides</td>
</tr>
<tr>
<td>IV-1</td>
<td>Thermogravimetric Analyzer Specifications</td>
</tr>
<tr>
<td>IV-2</td>
<td>Typical Contaminants of Matheson Gases</td>
</tr>
<tr>
<td>IV-3</td>
<td>Maximum Limits of Impurities in Mallinekrodt CaO Powder</td>
</tr>
<tr>
<td>IV-4</td>
<td>Surface Area Results</td>
</tr>
<tr>
<td>V-1</td>
<td>Reaction Rate Data for the Reaction Between CaO Particles and NO₂ and O₂</td>
</tr>
<tr>
<td>V-2</td>
<td>Comparison of Typical Die-Off Fractional Conversions with Those of Run 251</td>
</tr>
<tr>
<td>V-3</td>
<td>Thermodynamic Data Used in $\Delta F^\circ(T)$ Equation</td>
</tr>
<tr>
<td>V-4</td>
<td>Initial Rate Data (Analysis Based on Spherical Pellet Geometry)</td>
</tr>
<tr>
<td>V-5</td>
<td>Experimental Data for CaO Powder (200-100 mesh) Reacting with NO₂ and O₂</td>
</tr>
<tr>
<td>V-6</td>
<td>Comparison of Maximum Fractional Conversion for Powder and Pellet Forms of CaO</td>
</tr>
<tr>
<td>VI-1</td>
<td>Best Values for $D'$ at 150°C</td>
</tr>
<tr>
<td>VI-2</td>
<td>Best Values for $D'$ at 250°C</td>
</tr>
<tr>
<td>VI-3</td>
<td>Best Values for $D'$ at 350°C</td>
</tr>
<tr>
<td>VI-4</td>
<td>Best Values for $D'$ at 450°C</td>
</tr>
<tr>
<td>VI-5</td>
<td>Best Values for $D'$ at 550°C</td>
</tr>
<tr>
<td>VI-6</td>
<td>Best Values for $D'$ at 350°C, 450°C, and 550°C for VPGMC</td>
</tr>
</tbody>
</table>
## LIST OF FIGURES

<table>
<thead>
<tr>
<th>FIGURE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>II-1</td>
<td>Location of Alkali and Alkaline Earth Metals in the Periodic Table</td>
</tr>
<tr>
<td>II-2</td>
<td>Case A - Denitrification Potential of Alkaline Earth Metal Oxides</td>
</tr>
<tr>
<td></td>
<td>Case B - Denitrification Potential of Alkaline Earth Metal Oxides</td>
</tr>
<tr>
<td>II-3</td>
<td>Case A - Thermodynamically Stable Solids</td>
</tr>
<tr>
<td></td>
<td>Case B - Thermodynamically Stable Solids</td>
</tr>
<tr>
<td>III-1</td>
<td>Schematic Diagram of Unreacted-Core Model</td>
</tr>
<tr>
<td>III-2</td>
<td>Diagram of Grain Model</td>
</tr>
<tr>
<td>III-3</td>
<td>Diagram of Howard's et al. Grain Model</td>
</tr>
<tr>
<td>III-4</td>
<td>Model of Gidaspow for (a) $E&lt;1$ and (b) $E&gt;1$</td>
</tr>
<tr>
<td>III-5</td>
<td>Single-Pore Model</td>
</tr>
<tr>
<td>III-6</td>
<td>Changes in Pore Radius for Single-Pore Model</td>
</tr>
<tr>
<td>III-7</td>
<td>Ramachandran and Smith's Model for Case in which Grains Increase in Size with Reaction (No Sintering)</td>
</tr>
<tr>
<td>III-8</td>
<td>Modified Grain Model of Ranade and Harrison</td>
</tr>
<tr>
<td>IV-1</td>
<td>Equilibrium Concentration of NO$_2$ as a Function of Temperature</td>
</tr>
<tr>
<td>IV-2</td>
<td>TGA Reactor System</td>
</tr>
<tr>
<td>IV-3</td>
<td>Typical Thermobalance Response Curve</td>
</tr>
<tr>
<td>V-1</td>
<td>Typical TGA Response Curve</td>
</tr>
<tr>
<td>V-2</td>
<td>A Test of Reaction Reproducibility</td>
</tr>
<tr>
<td>V-3</td>
<td>A Test of Reaction Reproducibility</td>
</tr>
<tr>
<td>V-4</td>
<td>The Effect of Temperature on Time-Conversion Behavior of the Reaction Between CaO Particles and NO$_2$ and O$_2$</td>
</tr>
</tbody>
</table>
FIGURE

V-5 The Response of the Fractional Conversion of CaO in the Die-Off Regime to an Increase in the Concentration of NO₂ . . . 154

V-6 The Response of the Conversion of CaO in the Die-Off Regime to Successive Increases in Temperature . . . . . . . . 155

V-7 The Effect of NO₂ Concentration on the Fractional Conversion of CaO Particles at 350°C . . . . . . . . . . . . . . . . 161

V-8 The Effect of NO₂ Concentration on the Fractional Conversion of CaO Particles at 450°C . . . . . . . . . . . . . . 163

V-9 The Effect of NO₂ Concentration on the Fractional Conversion of CaO Particles at 250°C . . . . . . . . . . . . . . 165

V-10 The Effect of O₂ on the Conversion of CaO at 450°C . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 166

V-11 The Effect of O₂ on the Conversion of CaO at 550°C . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 167

V-12 Flowrate Effects on the Fractional Conversion on CaO Particles at 450°C . . . . . . . . . . . . . . . . . . . . . . . . . 169

V-13 The Effect of Pellet Size on the Fractional Conversion of CaO Particles (T = 450°C, 1.0 mole % NO₂) . . . . . . . . . . 172

V-14 The Effect of Pellet Size on the Fractional Conversion of CaO Particles (T = 250°C, 1.0 mole % NO₂) . . . . . . . . . . 173

V-15 The Effect of Pellet Size on the Fractional Conversion of CaO Particles (T = 450°C, 1.8 mole % NO₂) . . . . . . . . . . 174

V-16 Reaction Order with Respect to NO₂ Concentration . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 185

V-17 Arrhenius Plot of κₜ (Spherical Pellet Geometry) . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 187

V-18 Microscopic Photograph of Pellet Used in Run 211 (T=450°C, 1.8 mole % NO₂) . . . . . 190

V-19 Microscopic Photograph of Pellet Used in Run 232 (T=550°C, 1.8 mole % NO₂) . . . 191
The Conversion of CaO Powder as a Function of Temperature ........................................ 198

The Conversion of CaO Powder for a NO₂/O₂/CaO Reaction as a Function of Time and Solid Sample Size ........................................ 201

Comparison of Experimental Data to Constant Property Grain Model Predictions (No Grain Diffusion Resistance) T=150°C, T=350°C ........................................ 215

Comparison of Experimental Data to Constant Property Grain Model, Effect of Grain Diffusion Resistance, T=350°C ........................................ 217

Comparison of Experimental Data to Constant Property Grain Model, Effect of Grain Diffusion Resistance, T=150°C ........................................ 218

Comparison of Experimental Data with VPGM Predictions, Effect of Grain Diffusion Resistance, T=150°C (Run 241) ........................................ 221

Comparison of Experimental Data with VPGM Predictions, Effect of Grain Diffusion Resistance, T=150°C (Run 249) ........................................ 222

Local Fractional Conversion Profiles at an Overall Conversion of 0.08 - Effect of Grain Diffusion Resistance, T=150°C ........................................ 224

Local Porosity Profiles at Various Overall Conversions Predicted by the VPGM - Negligible Grain Diffusion Resistance ........................................ 226

Comparison of Experimental Data with Predictions of the VPGM - Use of Average Grain Diffusion Coefficient, T=150°C ........................................ 229

Comparison of Experimental Data with VPGM and CFGM Predictions, Using Average Value of D', T=250°C ........................................ 231

Comparison of Experimental Data with Predictions of the VPGM, T=250°C ........................................ 234

Comparison of Experimental Data with VPGM Predictions - Use of Average Grain Diffusion Coefficient, T=250°C ........................................ 235
<table>
<thead>
<tr>
<th>FIGURE</th>
<th>Description</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>VI-12</td>
<td>Comparison of Experimental Data to VPGM Predictions, T=250°C.</td>
<td>236</td>
</tr>
<tr>
<td>VI-13</td>
<td>Local Fractional Conversion Profiles at an Overall Conversion of .08 - Effect of Grain Diffusion Resistance, T=250°C.</td>
<td>237</td>
</tr>
<tr>
<td>VI-14</td>
<td>Comparison of Experimental Data with Predictions of the VPGM - Use of $k'_g$ to Match Data, T=150°C.</td>
<td>239</td>
</tr>
<tr>
<td>VI-15</td>
<td>Comparison of Experimental Data with Predictions of the VPGM - Use of $k'_g$ to Match Data, T=250°C.</td>
<td>240</td>
</tr>
<tr>
<td>VI-16</td>
<td>Comparison of Experimental Data with Predictions of the VPGM - Use of $k'_g$ to Match Data, T=350°C.</td>
<td>242</td>
</tr>
<tr>
<td>VI-17</td>
<td>Comparison of Experimental Data with Predictions of the VPGM - Effect of $k'_g$, T=150°C.</td>
<td>244</td>
</tr>
<tr>
<td>VI-18</td>
<td>Comparison of Experimental Data with Predictions of the VPGM - Effect of $k'_g$, T=250°C.</td>
<td>245</td>
</tr>
<tr>
<td>VI-19</td>
<td>Comparison of Experimental Data with Predictions of the VPGM and CPGM (T=350°C) Run 189.</td>
<td>247</td>
</tr>
<tr>
<td>VI-20</td>
<td>Comparison of Experimental Data with Predictions of the VPGM and CPGM (T=350°C) Run 190.</td>
<td>248</td>
</tr>
<tr>
<td>VI-21</td>
<td>Local Fractional Conversion Profiles at Various Overall Conversion Levels as Predicted by the VPGM (T=350°C).</td>
<td>250</td>
</tr>
<tr>
<td>VI-22</td>
<td>Local Porosity Profiles at Various Overall Conversions as Predicted by the VPGM (T=350°C).</td>
<td>252</td>
</tr>
<tr>
<td>VI-23</td>
<td>Dimensionless NO$_2$ Concentration at Various Overall Conversion Levels as Predicted by the VPGM (T=350°C).</td>
<td>253</td>
</tr>
<tr>
<td>VI-24</td>
<td>Comparison of Experimental Data with Predictions of the VPGM - Use of Average Grain Diffusion Coefficient (T=350°C) (Run 231).</td>
<td>257</td>
</tr>
<tr>
<td>FIGURE</td>
<td>PAGE</td>
<td></td>
</tr>
<tr>
<td>---------</td>
<td>------</td>
<td></td>
</tr>
<tr>
<td>VI-25</td>
<td>258</td>
<td></td>
</tr>
<tr>
<td>Comparison of Experimental Data with Predictions of the VPGM - Use of Average Grain Diffusion Coefficient (T=350°C) (Run 204)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>VI-26</td>
<td>259</td>
<td></td>
</tr>
<tr>
<td>Comparison of Experimental Data with Predictions of the VPGM - Effect of $k_s'$ T=350°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>VI-27</td>
<td>261</td>
<td></td>
</tr>
<tr>
<td>Comparison of Experimental Data with Predictions of the VPGM and CPGM, T=450°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>VI-28</td>
<td>262</td>
<td></td>
</tr>
<tr>
<td>Comparison of Experimental Data with Predictions of the VPGM - Effect of Grain Diffusion Coefficient, T=450°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>VI-29</td>
<td>264</td>
<td></td>
</tr>
<tr>
<td>Local Porosity Profiles at Various Overall Conversions as Predicted by the VPGM, T=450°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>VI-30</td>
<td>265</td>
<td></td>
</tr>
<tr>
<td>Dimensionless NO2 Concentration at Various Overall Conversions as Predicted by the VPG, T=450°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>VI-31</td>
<td>266</td>
<td></td>
</tr>
<tr>
<td>Dimensionless Grain Radius Profile at Various Overall Conversions as Predicted by the VPGM, T=450°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>VI-32</td>
<td>269</td>
<td></td>
</tr>
<tr>
<td>Comparison of Experimental Data with Predictions of the VPGM - Use of Average Grain Diffusion Coefficient, T=450°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>VI-33</td>
<td>270</td>
<td></td>
</tr>
<tr>
<td>Comparison of Experimental Data with Predictions of the VPGM and CPGM, T=550°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>VI-34</td>
<td>272</td>
<td></td>
</tr>
<tr>
<td>Comparison of Experimental Data with Predictions of VPGM - Effect of Grain Diffusion Resistance, T=550°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>VI-35</td>
<td>276</td>
<td></td>
</tr>
<tr>
<td>Comparison of Experimental Data with Predictions of the VPGM and VPGMC, T=350°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>VI-36</td>
<td>277</td>
<td></td>
</tr>
<tr>
<td>Comparison of Experimental Data with Predictions of the VPGM and VPGMC, T=450°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>VI-37</td>
<td>278</td>
<td></td>
</tr>
<tr>
<td>Comparison of Experimental Data with Predictions of the VPGM and VPGMC, T=550°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>VI-38</td>
<td>284</td>
<td></td>
</tr>
<tr>
<td>Quantitative Relative Resistance Analysis Using VPGMC, T=250°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>VI-39</td>
<td>286</td>
<td></td>
</tr>
<tr>
<td>Quantitative Relative Resistance Analysis Using VPGMC, T=450°C</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
FIGURE PAGE

VI-40  Arrhenius Plot. Grain Diffusion Coefficient, $D'_s$ (VPGM) ............. 289

VI-41  Arrhenius Plot. Grain Diffusion Coefficient, $D'_s$ (VPGMC) ............. 291

VI-42  Comparison of Experimental Data with the Predictions of VPGMC at 150°, 350°, 450°C, and 550°C. ..................... 294

VI-43  Comparison of Experimental Data with Predictions of VPGMC. Effect of NO$_2$ Concentration, $T=350^\circ$C. ............. 296

VI-44  Comparison of Experimental Data with Predictions of VPGMC. Effect of NO$_2$ Concentration. Use of Average Value for $D'_s$, $T=450^\circ$C .......... 297
ABSTRACT

The effect of variable solid properties on the kinetics of the reaction of spherical calcium oxide pellets with nitrogen dioxide (in the presence of excess oxygen) was studied. Experimental kinetic data was collected on a thermogravimetric analyzer, which measured weight change in a single pellet during reaction as a function of time. Reactions were carried out at temperatures of 150° to 550°C for gas streams containing 0.5 to 1.8 mole percent nitrogen dioxide and 8.7 mole percent oxygen. No reaction occurred at 600°C. At 150° and 250°C the conversion was found to proceed at a slow but steady rate with overall fractional conversions less than 0.15 after one hour of reaction time. At higher temperatures (350°, 450°, and 550°C) severe reaction die-off was observed with die-off fractional conversion increasing with temperature.

A variable property grain model (VPGM) which allowed for radial solid property variations due to reaction was used to analyze the experimental data. Four resistances were considered in the model: external mass transfer, pore diffusion, grain diffusion, and intrinsic chemical reaction. Parameters characterizing mass transfer, pore diffusion and chemical reaction were developed from literature correlations and independent measurements so that only a single parameter, the grain diffusion coefficient, had to be determined by numerical analysis.
The experimental time-conversion data was compared to the predictions of both the constant property grain model (CPGM) and the VPGM. At 150° and 250°C, the CPGM and VPGM were approximately equal in matching experimental data. However, at 350° and above, the VPGM was vastly superior since the CPGM cannot predict reaction "die-off". The predictions of VPGM were further improved by modifying the expression for the particle effective diffusivity employed in the model.
A) The NO$_x$ Air Pollution Problem

Nitrogen oxide air pollutants (NO$_x$) formed during the combustion of fossil fuels are a major concern in the United States. It is estimated that NO$_x$ emissions may rise from $22 \times 10^6$ tons per year in 1977 to $28 \times 10^6$ tons per year in 1990 [1].

Whenever high temperature processes are carried out in the presence of air, nitric oxide (NO) is formed by the combination of elemental nitrogen and oxygen.

\[ \text{N}_2 + \text{O}_2 \rightarrow 2\text{NO} \]  \hspace{1cm} (I-1)

This reaction is believed to proceed via the following mechanism. At high temperatures the usually stable O$_2$ molecule dissociates to the reactive O atom, which in turn reacts with a N$_2$ molecule to form NO and a reactive N atom. The N atom is free to react with an O$_2$ molecule to form NO and another reactive O atom, etc. Above 2000°K the equilibrium composition is rapidly achieved. The decomposition reaction is very slow below 2000°K. Below 1800°K the nitric oxide concentration becomes "frozen" at the high temperature equilibrium values [2,3,4].

For several years it was assumed that nitric oxide formed from combustion processes came solely from thermal fixation of atmospheric nitrogen and oxygen. However, experimental studies have shown that fuel bond nitrogen is
also converted to NO during coal and fuel oil combustion [3]. The importance of fuel bound nitrogen varies with the type of flame used during combustion, oxygen availability, and with the nitrogen content of the fuel [3,4].

Since the residence time in most stationary source combustion processes is short, very little of the nitric oxide formed is oxidized to nitrogen dioxide. Thus, the term NO\textsubscript{x} emissions refers to combined NO and NO\textsubscript{2}, even though ninety percent of the NO\textsubscript{x} in combustion gases is in the form of nitric oxide [3,4]. Oxidation of the unreactive nitric oxide to the highly reactive, smog-forming nitrogen dioxide occurs slowly in the atmosphere [4,5].

Typically, concentrations of NO\textsubscript{x} in flue gases vary from 50 to 1500 ppm depending on the fuel used, burner arrangement and excess oxygen level [4]. Although concentrations of NO\textsubscript{x} are low, significant amounts are released due to the large volumes of flue gases emitted. For example, a 750 MW gas-fired power plant emits five tons of NO\textsubscript{x} per hour in a volume of 70 x 10\textsuperscript{6} standard cubic feet per hour of flue gas [3].

As with all air pollutants, concern over NO\textsubscript{x} emissions is related to human health and property damage. The following adverse health effects have been directly attributed to NO\textsubscript{x} [1]:

1. New data has linked even low level NO\textsubscript{x} concentration to respiratory infection.

2. NO\textsubscript{x} causes eye and nose irritation.

NO\textsubscript{x} affects human health indirectly since [1]
(1) NO\textsubscript{2} has been shown to participate in processes which are depleting the ozone layer, and

(2) NO\textsubscript{x} plays a vital role in the photo-chemical reactions forming smog.

NO\textsubscript{x} emissions have caused property damage as a result of high nitrate rains which lead to nitric acid corrosion [6]. Therefore, stringent regulations limiting NO\textsubscript{x} emissions are being imposed by the EPA (Environmental Protection Agency) [7,8].

Sources of NO\textsubscript{x} may be divided into two broad classifications:

1) Mobile - autos, buses, trains, planes, etc.
2) Stationary - chemical plants, refineries, utility power plants, etc.

More than 55% of all nitrogen oxides emissions in this country come from stationary sources, and 93% of all stationary source NO\textsubscript{x} emissions come from burning fossil fuels for steam, electricity, or space heating [2,7].

Past research on control of NO\textsubscript{x} has concentrated upon mobile source emissions. However, two current trends may result in stationary source emissions becoming of greater importance. The first results from the current EPA policy which recommends relaxing and/or postponing NO\textsubscript{x} limitations from mobile sources in an effort to increase mileage efficiency. This may mean additional reduction in allowable NO\textsubscript{x} emissions from stationary sources if ambient air quality standards are to be maintained. The second concerns the
likely increase in the nitrogen content of the fuel used in large stationary sources. To avert a critical energy shortage, natural gas containing low nitrogen is being phased out of such applications and is being replaced by relatively high nitrogen fuel oil and coal [2]. Also, such new fuels as shale oil have still higher nitrogen content. It is known that high nitrogen fuels produce greater NO\textsubscript{x} emissions because of the higher reactivity of the fuel bound nitrogen [3]. The need for an effective NO\textsubscript{x} control technique is clear.

B) Current Stationary Source Control Techniques

Control techniques fall into one of three classifications: (1) fuel type, (2) combustion modification, and (3) flue gas treatment.

Fuel type affects NO\textsubscript{x} formation in several ways. The type of fuel, along with the fuel-to-air ratio, determines flame temperature and the rate of radiative heat transfer; both increase in the order gas-oil-coal. Thus, NO\textsubscript{x} formation tends to increase in the order gas-oil-coal [9]. Nitrogen content of the fuel is important because part of this nitrogen is converted to NO, which is subsequently oxidized to NO\textsubscript{2} upon release to the atmosphere. The role of fuel nitrogen is dominant at low temperatures and small at high temperatures. This technique of controlling NO\textsubscript{x} emissions will see limited use in the future since fuel oil and coal are being pressed into service to avert a critical natural gas shortage.
Combustion modification reduces NO\textsubscript{x} emissions via the following techniques:

(a) Flue gas recirculation - recirculation of flue gas to the combustion zone lowers both the peak flame temperature and the oxygen concentration, thus reducing NO\textsubscript{x} formation [2,9].

(b) Low excess air firing - effectively reduces NO\textsubscript{x} emissions provided problems involving unburned fuel, smoke, and CO emissions can be overcome [2,9].

(c) Burner modification - tangential firing has been shown to decrease NO\textsubscript{x} emissions by allowing the flames to radiate widely to the surrounding cooling surfaces thus decreasing the overall flame temperature, and reducing NO\textsubscript{x} emissions. Other changes in burner configurations, spacings and number of burners have been studied to reduce flame temperature [9].

(d) Staged combustion - two-stage combustion has been shown to be effective in reducing NO\textsubscript{x} formation. All fuel is fired in the first stage along with substoichiometric quantities of primary air. NO\textsubscript{x} formation is limited by the unavailability of oxygen. Complete fuel burn-out is achieved by introducing secondary air in the second stage. This reduces the flame temperature and NO\textsubscript{x} formation in this stage [2,9].

The above design and combustion modifications reduce atmospheric nitrogen fixation but are relatively ineffective in controlling NO\textsubscript{x} from fuel-bound nitrogen. Thus, organic nitrogen compounds in the fuel may put a lower limit on the NO\textsubscript{x} production from coal and fuel oil [7,10,11,12]. Ando et al. [10] report that when an oil with 0.2% nitrogen content is burned, the amount of NO\textsubscript{x} generated from the fuel is about equal to that from atmospheric fixation. Also, commercial attempts have shown that combustion modifications can only reduce NO\textsubscript{x} by about 60% [13].
Flue gas treatment will likely be required if higher levels of control become necessary. Flue gas treatment falls into two categories - wet and dry processes. Wet scrubbing processes show promise of removing both NO\textsubscript{x} and SO\textsubscript{x}. Among these are the limestone and the Chiyoda Company processes \cite{14,15}. The Chiyoda process scrubs with dilute H\textsubscript{2}SO\textsubscript{4} containing an iron catalyst. The acid sorbs SO\textsubscript{2} and the catalyst reduces NO\textsubscript{x}. Injection of ozone, chlorine dioxide, hydrogen peroxide, or potassium permanganates to convert NO to the more readily soluble NO\textsubscript{2} has also been studied \cite{2,13,14,15}. Generally, wet processes cannot compete with dry processes for NO\textsubscript{x} abatement alone \cite{15}. The two major problems are high pumping costs and the environmental impact related to disposal of liquid and solid wastes.

Among the dry processes, catalytic decomposition has received much attention because the thermodynamics are favorable. Unfortunately the kinetics are too slow for known catalysts, reportedly due to an unusually small pre-exponential term in the reaction rate constant \cite{2,9,15}.

Selective and non-selective catalytic reduction methods have shown potential. Of the two, selective catalytic reduction (SCR) has received more attention with twenty-three such processes having been reviewed in a recent EPA report \cite{15}. Most SCR processes being considered in this country originated in Japan where strict emissions standards have existed for some time. SCR using NH\textsubscript{3} as the reductant
and catalysts such as Pt, CaO, V₂O₅ or Fe₂O₃ supported on Al₂O₃, TiO₂, or Cr₂O₃ have been used commercially in Japan since 1973 [2,10].

Ammonia selectively reacts with NO and NO₂ at 300° to 450°C according to the following reactions in the presence of the proper catalyst [2,13,15]:

\[ 4\text{NH}_3 + 4\text{NO} + \text{O}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O} \quad (I-2) \]
\[ 4\text{NH}_3 + 2\text{NO}_2 + \text{O}_2 \rightarrow 3\text{N}_2 + 6\text{H}_2\text{O} \quad (I-3) \]

Claims of over 90% NOₓ reduction have been made using NH₃:NOₓ ratios of about 0.8 to 1.4:1 with less than 10 ppm NH₃ present in the treated flue gas.

SCR catalysts are either metal or carbon based. The metal catalysts are grouped into noble and non-noble metal catalysts, but the noble metal catalysts are generally considered impractical due to high cost and severe SOₓ poisoning [13,15,16]. Non-noble metal catalysts are less efficient and require higher temperatures, but they are less expensive and more resistant to SOₓ poisoning [9,15,17,18,19].

Carbon based SCR catalysts have the unique capability of removing both NOₓ and SOₓ. Carbon has been shown to remove SO₂ and activated carbons have been developed with special structures or metallic additions (copper or vanadium which permit the NOₓ-NH₃ reduction reaction to occur [13,15].

Most of the work thus far with nonselective catalytic reduction processes has been oriented towards control of
nitric acid plant tail gases. Power plant application requires CH₄, CO, or H₂ as the reducing agent using noble metal catalysts such as Pt, Pd, or Rh [9]. Since the process is nonselective, sufficient reductant must be added for the reduction of O₂, SOₓ, and NOₓ. A typical reaction using CO as the reductant is as follows [15]:

\[
\text{NO} + 3\text{CO} + \text{excess O}_2 \rightarrow 3\text{CO}_2 + \frac{1}{2}\text{N}_2
\]  

(I-4)

Two major problems associated with this control technique are that high temperatures (~1000°F) are required and some catalysts promote the production of toxic H₂S and COS [15, 20].

Selective noncatalytic reduction is advantageous because it requires no catalyst and very little capital investment. Exxon has patented such a process called Thermal Denox in which a reductant (NH₃) is combined with the NOₓ in the flue gas at the appropriate temperature to produce the following reaction [15,21,22,23]:

\[
4\text{NH}_3 + 4\text{NO} + \text{O}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O}
\]  

(I-2)

At the temperature of interest, NH₃ and O₂ will not react to form NO. The optimum temperature if only NH₃ is injected is 1000°C (1850°F); however, the optimum temperature can be lowered to 730°C (1350°F) if H₂ is injected along with the NH₃. The disadvantages to this process are fourfold [15,22,23]:

(1) Only 60-70% NOₓ removal can be achieved.

(2) Relatively large amounts of reductant (NH₃) are needed (NH₃/NOₓ mole ratio > 3:1).
(3) Operates effectively over only a narrow temperature range; thus, emissions of NH\textsubscript{3} and NO during boiler load variations are likely.

(4) Safety aspects of using explosive H\textsubscript{2} in a power plant have not yet been fully considered.

Two problems associated with the use of NH\textsubscript{3} which are applicable to both SCR and selective noncatalytic reduction processes have not yet been discussed. The first deals with the formation of NH\textsubscript{4}HSO\textsubscript{4}. Whenever NH\textsubscript{3} and SO\textsubscript{x} are present in the flue gas the following reaction can occur [2,15]:

\[
\text{NH}_3(g) + \text{SO}_3(g) + \text{H}_2\text{O}(g) \rightarrow \text{NH}_4\text{HSO}_4(l)
\]  

NH\textsubscript{4}HSO\textsubscript{4} is corrosive and interferes with heat transfer. Also, at lower temperatures it may solidify and require washing with water or steam blowing to remove it from the processing equipment [15]. The second problem concerns the cost and availability of NH\textsubscript{3}. A 30 to 50\% increase in NH\textsubscript{3} production in the U.S. will be necessary to achieve a 100 ppm NO\textsubscript{x} emission limit in coal-fired boilers alone in 1985 [15]. Japan would require an additional 400,000 tons of NH\textsubscript{3} per year to attain ambient NO\textsubscript{x} standards using SCR processes. This is roughly one-half the total annual consumption of nitrogen fertilizers in Japan. Thus, this technique would appear to have social ramifications since world food production is currently limited by a shortage of fixed nitrogen fertilizer [15].

A unique method of removing both NO\textsubscript{x} and SO\textsubscript{x} involves treating the flue gas with electron beam radiation. A powdery substance comprised of S, N, O, and H of unknown
composition is formed. The major disadvantages at present are high capital investment cost and waste product handling [13,15].

Molecular sieves for NO\textsubscript{x} removal have been widely used in treating nitric acid plant tail gases. However, molecular sieves are inappropriate for stack gas cleanup due to temperature limitations and interference from H\textsubscript{2}O and SO\textsubscript{x}.

NO\textsubscript{x} removal via reaction with a solid has also been investigated. In 1971, Leung and Gidaspow [24] reported the use of iron oxide deposited on or coprecipitated with alumina to remove NO\textsubscript{x} in flue gases (200-350°C), with the sorbent being regenerated in air at about 450°C. Both ferric oxide and reduced iron oxide were used. Ferric oxide was shown to remove NO\textsubscript{x} in the presence of oxygen. Unfortunately, water vapor interfered with the reaction. Water vapor did not interfere with sorption of NO on the reduced oxide.

Onischak and Gidaspow [25] investigated the reaction of NO with ferrous sulfate salt containing lithium chloride on a silica gel support. Nitric oxide reacts according to the reaction

\[
\text{FeSO}_4 + \text{NO} + 5\text{H}_2\text{O} \rightarrow \text{Fe(H}_2\text{O)}_5\text{SO}_4 \cdot \text{NO}
\]  

The presence of highly hygroscopic lithium chloride was justified because water vapor was required for NO sorption to occur. Conversion of ferrous sulfate ranged from 2 to 4%. Their results were favorable at low temperatures (below 140°C), but they report no measurable rate above 140°C. The necessity of water vapor and low temperatures renders this
process useful only to cooled combustion exhaust gas cleanup.

Arastoopour, Hariri, and Gidaspow [26] studied the reaction of nitric oxide with various coprecipitated transition metal oxides (Co$_3$O$_4$, Fe$_3$O$_4$ and MnO$_2$). An iron oxide-cobalt oxide-sodium oxide sorbent on an alumina support was developed. This mixed-oxide sorbent had a capacity of the order of 10 grams of NO$_x$ per 100 grams of sorbent. The reactions assumed to be occurring were

\[
\begin{align*}
\text{Co}_3\text{O}_4 + 6\text{NO} + 4\text{O}_2 & \rightarrow 3\text{Co(NO}_3)_2 \\
\text{Fe}_3\text{O}_4 + 6\text{NO} + 4\text{O}_2 & \rightarrow 3\text{Fe(NO}_3)_2 \\
\text{Na}_2\text{O} + 2\text{NO} + 3/2\text{O}_2 & \rightarrow 2\text{NaNO}_3
\end{align*}
\]

The capacity of this sorbent was reported to be invariant in the temperature range of 200° to 350°C and with nitric oxide concentrations of 400 to 800 ppm. It was also said to be thermally regenerable.

C) Reactions of NO$_x$ with CaO

Another proposed dry flue gas treatment method is the reaction between alkaline earth metal oxides (CaO, SrO, BaO) and NO$_x$ to form the solid nitrate and/or nitrite. The NO$_x$ can then be disposed of as a solid or released in concentrated form when the solid reactant is thermally regenerated.

The reaction between NO$_x$ (NO and/or NO$_2$) and CaO has been known for many years. In 1933, Pauling [27] reported a process for making alkaline earth nitrates from alkaline earth oxides. Rate data was not reported, but the process was qualitatively described. The gases from burning NH$_3$
were partly absorbed in water and partly in dry alkaline earth oxides (e.g., CaO) to form the alkaline earth nitrate \( \text{(Ca(NO}_3\text{)}_2\text{)} \). The nitric acid formed in the first absorption step was added to the dry alkaline earth compounds to convert the remaining dry oxide to nitrate.

In 1934, Kipper [28] patented a totally dry method of producing alkaline earth nitrates from alkaline earth oxides. Rate data were not given. Finely divided oxides of alkaline earth metals, such as calcium oxide (CaO), were heated to 1200°C. The heated oxide was then sealed in a reaction chamber whose interior surface was lined with insulating asbestos saturated with platinum black. A mixture of oxygen and nitrogen gases (1:4 mixture) was immediately admitted at a pressure of 2000 psi. The contents were allowed to cool within the sealed reaction chamber for several hours and analysis of the contents showed approximately one-third of the oxide had been converted to the nitrate \( \text{(Ca(NO}_3\text{)}_2\text{)} \). The chemical reaction was expressed symbolically as follows:

\[
\text{CaO} + \text{N}_2 + \frac{5}{2} \text{O}_2 \rightarrow \text{Ca(NO}_3\text{)}_2
\]  

(K-10)

Kipper stated that the role of the platinum black was an "undetermined factor" but the process occurs rapidly in its presence. Today it is known that platinum catalyzes the gas phase reaction [15]

\[
\text{N}_2 + \text{O}_2 \rightarrow 2\text{NO}
\]  

(K-11)

Therefore, Kipper's process is more accurately described by the following reactions.
In 1953, Addison and Lewis [29] carried out a detailed investigation of the reactions of calcium oxide, zinc oxide, and sodium peroxide with nitrogen dioxide and nitric oxide. Kinetics were not studied but maximum conversions were reported. For the case of calcium they reported that the maximum conversion of CaO to Ca(NO$_3$)$_2$ at 260°C was 54.3% after 4.25 hours. The corresponding conversion to nitrite during this experimental run was 0.6%. Addison and Lewis blamed the incomplete conversion of oxide on the "cohesive nature of the calcium nitrate formed as a coating round each oxide particle...sufficiently cohesive to decrease (and even inhibit) the reaction."

In 1965, Atroshchenko et al. [30] studied the reaction of 10\% NO$_2$ (diluted by N$_2$) with CaO pellets packed in a chamber. The reaction chamber contained 220 pellets with a total weight of 12 to 14 grams. The pellets occupied a volume of 30 cc. Nitrogen dioxide was circulated at a rate of 0.19 gmoles NO$_2$ per hour. From 50° to 250°C calcium nitrate and some calcium nitrite were formed. Conversion data and product distribution were not given. At temperatures greater than 250°C, the nitrate was converted to nitrate, presumably due to oxidation by NO$_2$

$$\text{Ca(NO}_2\text{)}_2 + \text{NO}_2 + \text{Ca(NO}_3\text{)}_2 \rightarrow \frac{1}{2}\text{N}_2$$

The optimum nitrogen dioxide removal rate occurred between 250° and 300°C. At higher temperatures the removal rate
decreased. The nitrogen dioxide removal rates at 50, 150 and 250°C were 0.5, 1.75, and 2.95 g moles NO$_2$/m$^2$ hour, respectively. The optimum diameter of the CaO pellets was found to be in the range 0.3 to 0.5 mm.

With the exception of a paper by James and Hughes [31], very little work has been published on the kinetics of the reaction of NO$_x$ with calcium oxide in the presence of oxygen. James and Hughes used a differential reactor to measure the kinetics of NO sorption on five samples of calcined limestone and dolomite. Their experiments were carried out in the presence of oxygen and nitrogen. The investigation included temperatures from 250° to 420°C; NO concentrations were varied from 500 to 10,000 ppm. The reactions of importance to their study were

\[
2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2 \quad (I-14)
\]

\[
\text{CaO} + 2\text{NO}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{Ca(NO}_3)_2 \quad (I-15)
\]

Flow conditions were chosen such that external mass transfer resistance was negligible so that true chemical kinetics were measured.

Their results for the five samples of limestone and dolomite in powdered form showed that the sorption rates of the five samples were different. This difference was attributed to the difference in the physical properties of the five samples. Surface areas and pore volumes of the samples were determined by the BET method (nitrogen absorption at 77°K) and mercury porosimetry, respectively. All samples were fully calcined at 980°C for 120 minutes. Comparison of
the sorption rate and surface area of each sample pointed out that a high surface area gave a high rate of sorption. The authors stated that this observation was in agreement with the generally accepted conclusion that "the most important consideration for efficient sorption is a high area calcine."

First order behavior with respect to nitric oxide was exhibited throughout the concentration range of 500 to 10,000 ppm NO. Arrhenius constants were obtained over a temperature range of 250° to 420°C. Their rate constant for a reaction first order with respect to gas and zero order with respect to solid is

\[ k = 1.565 \times 10^4 \exp \left[ -\frac{(22,600 \pm 150)}{RT} \right] \text{m/sec} \]

(1-16)

The high value of the activation energy reaffirms that the reaction was occurring free from external mass transfer resistance. However, they noted that the nitrate formed had "a pronounced retarding effect" on the reaction rate and incomplete conversions of the CaO resulted.

The authors attempted to quantify this retarding effect on an empirical basis. They assumed that their sorption rate data were collected under differential conditions where the nitric oxide concentration did not change appreciably in flowing through the shallow bed and for a given temperature the rate constant, \( k \), was assumed constant. Thus, during the reaction the only quantity changing was the conversion of oxide to nitrate. A log-log plot of sorption rate versus
nitrate loading (conversion) showed a definite correlation. For experiments performed using nitric oxide concentrations of 5000, 3000, and 1000 ppm, the corresponding slopes on the log-log plot were -1.52, -1.58, and -1.72, respectively. Therefore, the retarding effect of the nitrate was considered approximately inversely proportional to the three-halves (3/2) power of the nitrate loading (conversion).

D) Objectives of Research

The reaction of major interest to this research is

\[ \text{CaO} + 2\text{NO}_2 + \frac{1}{2}\text{O}_2 + \text{Ca(NO}_3)_2 \quad (I-15) \]

The reaction is to be studied over a temperature range of 100° to 550°C (200 to 1000°F). Concentration of nitrogen dioxide will be varied from 0.5 to 2.5 mole percent, and oxygen will be present at a concentration of 10 mole percent. Nitrogen is to be used as the diluent.

The specific objectives are

(1) Establish the thermodynamic feasibility limits for the reaction

\[ \text{CaO} + 2\text{NO}_2 + \frac{1}{2}\text{O}_2 + \text{Ca(NO}_3)_2 \quad (I-15) \]

and identify other thermodynamically feasible solid reactants among the alkali and alkaline earth metal oxides.

(2) Obtain basic kinetic data for the reaction of calcium oxide with NO₂ in the presence of oxygen.

(3) Analyze the kinetic data with a gas-solid reaction model which includes the effects of external mass transfer, particle diffusion,
and surface reaction. The model will also account for varying structural properties of the solid which occur as the reaction proceeds.
Literature Cited


CHAPTER II
THERMODYNAMIC STUDY

The primary purpose of this chapter is to identify solid reactants among the alkali and alkaline earth metal oxides which are thermodynamically feasible for reaction with gaseous $NO_x$ and $O_2$ to form solid nitrates and/or nitrites. Two typical reactions are shown here with $Me_2O$ representing an alkali metal oxide and $MeO$ an alkaline earth metal oxide.

\begin{align*}
Me_2O + 2NO_2 + \frac{1}{2}O_2 &\rightarrow 2MeNO_3 \quad (II-1) \\
MeO + 2NO_2 + \frac{1}{2}O_2 &\rightarrow Me(NO_3)_2 \quad (II-2)
\end{align*}

The alkali and alkaline earth elements are shown in periodic table form in Figure II-1. The reactivity of the alkali and alkaline earth metal oxides with $NO_x$ has long been known. The works of Pauling [1], Kipper [2], Atroshchenko et al. [3], and James and Hughes [4] involving the reaction of $NO_x$ with CaO were discussed in the previous chapter. Numerous other reports of reaction of $NO_x$ with alkali or alkaline earth metal oxides may be found in the literature.

A systematic thermodynamic screening was performed to determine which alkali and alkaline earth metal oxides have denitrification potential over the temperature range of interest ($160^\circ$-$560^\circ$C). The principles of free energy minimization were employed to carry out the thermodynamic study.
Figure II-1. Location of Alkali and Alkaline Earth Metals in the Periodic Table
A) Free Energy Minimization

At equilibrium, there is a unique composition of a reaction mixture at which the free energy of the system is a minimum. Thus, once the components of an equilibrium mixture are defined and their free energy functions are known, an optimization technique may be applied to find that composition possessing the minimum free energy at a fixed temperature and pressure. It is not necessary that the species composition of the reactant mixture be known. Instead only knowledge of the elemental composition of the reaction mixture and of the possible species present at equilibrium is required. With this information the predicted equilibrium composition will be accurate within the limits of the accuracy of the thermodynamic data and the numerical procedure.

The computational procedure used in this study was developed by del Valle, April, and Pike [5]. Their computer program, CHEMEQ, calculated equilibrium among ideal gases and pure condensed species. del Valle et al. [5] used CHEMEQ to study reactions occurring on space vehicle heat shields upon re-entry. Stinnett, Harrison, and Pike [6] applied CHEMEQ to the study of coal gasification with emphasis on sulfur species distribution. Westmoreland and Harrison [7] used CHEMEQ for the evaluation of candidate solids for high temperature desulfurization of low-BTU gas.

Detailed derivations of the free energy minimization equations are available in the excellent text by van Zeggeren
and Storey [8]. A brief discussion of the equations and assumptions employed by CHEMEQ will be presented here.

The total free energy of a system composed of \( n \) gaseous species (assumed ideal) and \((q-n)\) pure condensed species (assumed to have an activity coefficient of one) is

\[
F(\bar{x}) = \sum_{i=1}^{n} x_i \left[ \left( \frac{F^\circ_T}{RT} \right)_i + \ln P + \ln \frac{x_i}{\bar{x}} \right] + \sum_{i=n+1}^{q} x_i \left( \frac{F^\circ_T}{RT} \right)_i
\]

(II-3)

where

- \( x_i \) = number of gram-moles of species \( i \)
- \( \bar{x} \) = total gram-moles of gaseous species, \( \bar{x} = \sum_{i=1}^{n} x_i \)
- \( \frac{F^\circ_T}{RT} \) = dimensionless free-energy of the pure components
- \( R \) = universal gas constant (1.987 cal/grmole\(^\circ\)K)
- \( T \) = absolute temperature (\(^\circ\)K)
- \( P \) = total pressure (atm)

In equation (II-3) the \( \frac{F^\circ_T}{RT} \) terms represent the free energy function for the pure components while the logarithmic terms represent the free energy of mixing for ideal gases. It should be noted that \( F(\bar{x}) \) in equation (II-3) is actually \( F(T,P,\bar{x})/RT \). However, for a given temperature and pressure \( F(T,P,\bar{x})/RT \) becomes \( F(\bar{x})/RT \). Also, minimization of \( F(\bar{x})/RT \) gives the same solution set of \( x_i \)'s as would be obtained from the minimization of \( F(\bar{x}) \). Thus, for ease of notation equation (II-3) is represented as \( F(\bar{x}) \).
The problem is to find the proper distribution of gas and solid species, \( x_i \)'s, at fixed temperature and pressure, such that \( F(\bar{x}) \) in equation (II-3) is minimized. This minimization must also satisfy the following material balance constraint since the number of gram-atoms of each element in the system is fixed by the initial elemental composition:

\[
b_j = \sum_{i=1}^{n} a_{ij} x_i + \sum_{i=n+1}^{q} a_{ij} x_i
\]

\[j=1,2,\ldots,m\] (II-4)

where

- \( b_j \) = number of gram-atoms of each element
- \( m \) = total number of elements
- \( a_{ij} \) = number of gram-atoms of the \( j \)th element in the \( i \)th species

CHEMEQ employs Newton's optimization method and satisfies constraints using Lagrange multipliers. The mathematical procedure used requires no prior knowledge of the chemistry of the system, nor does it require accurate first guesses - although accurate guesses reduce computing time.

Three pieces of information are required as program input:

1. The standard free energy function, \( F_T^\circ \), for each of the \( n \) gaseous species and \((q-n)\) condensed species present in the mixture.

2. An initial estimate of the equilibrium composition of the gases and condensed species satisfying the constraint imposed by equation (II-4).

3. The temperature and pressure of interest.

\( F_T^\circ \) data are usually available in tabular form; however, for use in a computer program an equation representing \( F_T^\circ \)
is preferable. As input to this program the tabulated data were fitted to a polynomial of the form suggested by McBride et al. [9]:

\[
\frac{F_T}{RT} = A_1 (1 - \ln T) - \frac{A_2 T}{2} - \frac{A_3 T^2}{6} - \frac{A_4 T^3}{12} - \frac{A_5 T^4}{20} - \frac{A_6}{T} - A_7
\]  

(II-5)

Thus, the coefficients \(A_1\) through \(A_7\) are the actual input data to CHEMEQ for \(F_T\). A computer program (THERMFIT) to calculate the constants \(A_1\) through \(A_7\) was developed by Esch, Siripong, and Pike [10]. Westmoreland [11] modified THERMFIT to broaden the types of permissible input data to include types normally available for solids, liquids, and gases of metallic compounds. Principal data sources used by Westmoreland [11] in the modified THERMFIT were the JANAF Tables [12], U.S. Bureau of Mines Bulletin 584 by Kelley [13], the Tracor data base [14], and the U.S. National Bureau of Standards Technical Note 270 Series [15-19]. For the present research, these data sources were supplemented by additional data from a Radian Corporation report [20] titled "A Theoretical Study of NOx Absorption Using Aqueous Alkaline and Dry Sorbents."

B) Procedure for Thermodynamic Study

The denitrification potential of the solid alkali and alkaline earth metal oxides was analyzed by observing the thermodynamic behavior of these oxides in the presence of gaseous \(\text{NO}_x\) and \(\text{O}_2\) at concentrations typical of stack gases.
The overall temperature range of interest was chosen to be 160° to 560°C; the total pressure was fixed at one atmosphere. The temperature range and pressure chosen include those typical of stack gas conditions.

**Gaseous Species Considered**

Nitrogen dioxide (NO\(_2\)), nitric oxide (NO), oxygen (O\(_2\)), and an inert (H\(_2\)) were the only gas phase species allowed. Carbon dioxide (CO\(_2\)), carbon monoxide (CO), water (H\(_2\)O), and sulfur dioxide (SO\(_2\)) are also typical stack gas components but were not included here because the purpose of the thermodynamic study was to ascertain only the denitrification potential of the alkali and alkaline earth metal oxides.

Elemental nitrogen (N\(_2\)), although a major constituent in typical stack gases, was not permitted in this equilibrium analysis. N\(_2\) and O\(_2\) are thermodynamically favored with respect to NO and NO\(_2\) at the conditions of this study. That is, equilibrium calculations predict total decomposition of NO and NO\(_2\) when O\(_2\) and N\(_2\) are permitted. Such decomposition reactions will not occur, however, to any appreciable extent at the study temperatures because of kinetic limitations. Thus, the thermodynamic predictions in the absence of nitrogen, thereby preventing NO and NO\(_2\) decomposition, were deemed more representative of reality. Elemental hydrogen (H\(_2\)), which was chosen to replace N\(_2\), served as an inert since no other hydrogen compounds were permitted.
The conclusions of Stern [21] and preliminary CHEMEO runs were used to justify the exclusion of nitrogen oxide gas species other than NO and NO₂. N₂O₅ is unstable with respect to either N₂O₄ or N₂O₃ above 25°C. Also the equilibrium of

\[ \text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2 \]

and

\[ \text{N}_2\text{O}_3 \rightleftharpoons \text{NO}_2 + \text{NO} \]

both shift markedly to the right above 125°C. Thus, these three "dinitrogen" oxides were not included in the thermodynamic studies.

Condensed Species Considered

Seven of the alkali and alkaline earth metal oxides (Li₂O, Na₂O, K₂O, MgO, CaO, SrO, and BaO) were subjected to thermodynamic analysis. The oxides of beryllium, rubidium, cesium, francium, and radium were not considered because of their radioactivity, toxicity and limited availability. The only condensed species allowed in each system were the solid metal oxide, the solid metal nitrate, and the solid metal nitrite. For certain runs the metal nitrate was artificially removed from the reaction mixture to determine the stability of the metal nitrate with respect to the metal oxide.

The initial molar composition (gas and solid) used in this study is given below.
### Gas Species

<table>
<thead>
<tr>
<th>Species</th>
<th>Moles</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>96.63</td>
</tr>
<tr>
<td>O₂</td>
<td>3.30</td>
</tr>
<tr>
<td>NO</td>
<td>0.063</td>
</tr>
<tr>
<td>NO₂</td>
<td>0.007</td>
</tr>
</tbody>
</table>

### Solid Species

**Alkali Metals (Me=Li, Na, K)**

<table>
<thead>
<tr>
<th>Species</th>
<th>Moles</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me₂O</td>
<td>1.0</td>
</tr>
<tr>
<td>MeNO₃</td>
<td>10⁻⁹</td>
</tr>
<tr>
<td>MeNO₂</td>
<td>10⁻⁹</td>
</tr>
</tbody>
</table>

**Alkaline Earth Metals (Me=Ca, Sr, Ba)**

<table>
<thead>
<tr>
<th>Species</th>
<th>Moles</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeO</td>
<td>1.0</td>
</tr>
<tr>
<td>Me(NO₃)₂</td>
<td>10⁻⁹</td>
</tr>
<tr>
<td>Me(NO₂)₂</td>
<td>10⁻⁹</td>
</tr>
</tbody>
</table>

The concentration of O₂ and NOₓ is typical of stack gas conditions [23]. The metal oxide (Me₂O or MeO) is always present in large excess. The small but finite initial values for the nitrates and nitrites (10⁻⁹ mole) are necessary to allow formation of these compounds within CHEMEQ.

### C) Results of Thermodynamic Study

Interpretation of thermodynamic equilibrium results should always be tempered with consideration of kinetic factors. Satisfying thermodynamic criteria is a necessary but not a sufficient condition for establishing denitrification potential. Kinetics often dictate the relationship between the equilibrium composition and the actual composition from a process, particularly at low temperatures.
For example, in the present study the metal nitrate was always favored over the metal nitrite. In an actual situation other factors (e.g., kinetics) may prevent nitrate formation, and the nitrite may be one of the solid species formed. Should the nitrite be formed, knowledge of its stability is important. Therefore, in the discussions which follow, the results for two cases will be presented:

Case A: Three solid species allowed in system (metal oxide, metal nitrate, metal nitrite)

Case B: Two solid species allowed in system (metal oxide, metal nitrite)

Another comment on the format of the results section should be made. In free energy minimization calculations, it does not matter from which direction a reaction is approached (i.e., reactants to products or products to reactants); the thermodynamically stable species will be identified. However, in experimental work the direction from which a reaction is approached is important because the kinetics of formation of a compound are not the same as the kinetics of decomposition. Thus, in the discussions to follow, the thermodynamic predictions will be compared to experimental results for the decomposition and formation of a given compound whenever such experimental results are available.
Alkali Metal Oxides

All three alkali metal oxides (Li$_2$O, Na$_2$O, K$_2$O) show 100% NO$_x$ removal capability over a portion of the range. The results are summarized in Table II-1. For all Cases A, the alkali metal nitrate is stable to its melting point. For all Cases B, the alkali metal nitrite is stable to its melting point. The study was stopped at the melting temperatures as we were not interested in the liquid phase and for the most part, thermodynamic data for the liquid species was not available. If this proposed NO$_x$ scheme should prove technically feasible, then it would be desirable if the metal oxide could be regenerated from the solid salt, as this would preserve the desirable solid properties (e.g., surface area, pore size, etc). It is readily seen that the melting points of the lithium and sodium salts are quite low and therefore may be least favorable for cleanup of hot stack gases.

Lithium Oxide (Li$_2$O).

Table II-1-(1), Case A shows that formation of LiNO$_3$ is favored over the nitrite and the oxide past the nitrate melting point of 253°C. Upon artificially removing LiNO$_3$ from the system (Case B), LiNO$_2$ would be favored over the oxide past the nitrite melting point of 220°C. NO$_x$ removal efficiency in both cases is 100%. Experimental verification of solid stability was sought. Bordyushkova, Protsenko, and Venerovskaya [24] experimentally found LiNO$_3$ to be the least stable of the alkali
TABLE II-1
Denitrification Potential of Alkali Metal Oxides
Basis: 1 mole Me$_2$O (Me = Li, Na, K)

<table>
<thead>
<tr>
<th>T(°C)</th>
<th>(1) Lithium Oxide (Li$_2$O)</th>
<th>(2) Sodium Oxide (Na$_2$O)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td><strong>Case A</strong></td>
<td><strong>Case B</strong></td>
</tr>
<tr>
<td></td>
<td>2NO$_x$ Removed</td>
<td>Solid Metal Species</td>
</tr>
<tr>
<td>160</td>
<td>100 Li$_2$O, LiNO$_3$</td>
<td>100 Li$_2$O, LiNO$_2$</td>
</tr>
<tr>
<td>185</td>
<td>100 Li$_2$O, LiNO$_3$</td>
<td>100 Li$_2$O, LiNO$_2$</td>
</tr>
<tr>
<td>210</td>
<td>100 Li$_2$O, LiNO$_3$</td>
<td>100 Li$_2$O, LiNO$_2$</td>
</tr>
<tr>
<td>235</td>
<td>100 Li$_2$O, LiNO$_3$</td>
<td>LiNO$_2$ melts at 200°C</td>
</tr>
<tr>
<td>260</td>
<td>LiNO$_3$ melts at 253°C</td>
<td>100 Na$_2$O, NaNO$_3$</td>
</tr>
<tr>
<td>285</td>
<td>100 Na$_2$O, NaNO$_3$</td>
<td>100 Na$_2$O, NaNO$_2$</td>
</tr>
<tr>
<td>310</td>
<td>NaNO$_3$ melts at 307°C</td>
<td></td>
</tr>
</tbody>
</table>

* Three solid species allowed in system (metal oxide, metal nitrate, metal nitrite)

** Two solid species allowed in system (metal oxide, metal nitrite)
<table>
<thead>
<tr>
<th>T(°C)</th>
<th>%KNO_3 Removed</th>
<th>Solid Metal Species</th>
<th>%KNO_3 Removed</th>
<th>Solid Metal Species</th>
</tr>
</thead>
<tbody>
<tr>
<td>160</td>
<td>100</td>
<td>K_2O, KNO_3</td>
<td>100</td>
<td>K_2O, KNO_2</td>
</tr>
<tr>
<td>185</td>
<td>100</td>
<td>K_2O, KNO_3</td>
<td>100</td>
<td>K_2O, KNO_2</td>
</tr>
<tr>
<td>210</td>
<td>100</td>
<td>K_2O, KNO_3</td>
<td>100</td>
<td>K_2O, KNO_2</td>
</tr>
<tr>
<td>235</td>
<td>100</td>
<td>K_2O, KNO_3</td>
<td>100</td>
<td>K_2O, KNO_2</td>
</tr>
<tr>
<td>260</td>
<td>100</td>
<td>K_2O, KNO_3</td>
<td>100</td>
<td>K_2O, KNO_2</td>
</tr>
<tr>
<td>285</td>
<td>100</td>
<td>K_2O, KNO_3</td>
<td>100</td>
<td>K_2O, KNO_2</td>
</tr>
<tr>
<td>310</td>
<td>100</td>
<td>K_2O, KNO_3</td>
<td>100</td>
<td>K_2O, KNO_2</td>
</tr>
<tr>
<td>335</td>
<td></td>
<td>KNO_3 melts at 334°C</td>
<td>100</td>
<td>K_2O, KNO_2</td>
</tr>
<tr>
<td>360</td>
<td></td>
<td></td>
<td>100</td>
<td>K_2O, KNO_2</td>
</tr>
<tr>
<td>385</td>
<td></td>
<td></td>
<td>100</td>
<td>K_2O, KNO_2</td>
</tr>
<tr>
<td>410</td>
<td></td>
<td></td>
<td>100</td>
<td>K_2O, KNO_2</td>
</tr>
<tr>
<td>435</td>
<td></td>
<td></td>
<td>100</td>
<td>K_2O, KNO_2</td>
</tr>
<tr>
<td>460</td>
<td></td>
<td></td>
<td>KNO_2 melts at 440°C</td>
<td></td>
</tr>
</tbody>
</table>
nitrates, decomposing just above its melting point according to

$$\text{LiNO}_3 \rightarrow \text{LiNO}_2 + \frac{1}{2}\text{O}_2$$  \hspace{1cm} (II-10)

giving a mixture of molten nitrate and nitrite.

Protsenko and Bordyushkova [25] reported that LiNO$_2$ melted at 220°C and was stable up to 300°C, decomposing rapidly at 350°C according to

$$2\text{LiNO}_2 \rightarrow \text{Li}_2\text{O} + \text{NO} + \text{NO}_2$$  \hspace{1cm} (II-11)

Stern [21], in a review of the high temperature behavior of inorganic nitrites and nitrates, supported the conclusions discussed here. Once formed the nitrates and nitrites of lithium are stable past the melting points of the respective salts.

No literature data on the reaction of Li$_2$O with NO$_x$ and O$_2$ to form the solid nitrate or nitrite could be found.

**Sodium Oxide (Na$_2$O).** As Table II-1-(2), Case A shows, formation of NaNO$_3$ is favored over the nitrite and the oxide past the nitrate melting point of 307°C. When NaNO$_3$ is artificially removed from the system (Case B), NaNO$_2$ would be favored over the oxide past the nitrite melting point of 281°C. NO$_x$ removal efficiency in both cases would be 100%. Experimental results were again consulted to verify solid stability.

Bordyushkova et al. [24] reported that NaNO$_3$ melted around 308°C without decomposition; the liquid nitrate was
stable in air at least to 500°C. Bond and Jacob [26] also found liquid NaNO₃ stable in air to around 500°C with appreciable decomposition near 584°C according to

\[
\text{NaNO}_3 \rightarrow \text{NaNO}_2 + \frac{1}{2}\text{O}_2
\]  

(II-12)

Freeman [27] stated that the stoichiometry of molten NaNO₂ decomposition in an inert atmosphere (argon) between 600° and 750°C was

\[
2\text{NaNO}_2 \rightarrow \text{Na}_2\text{O} + \text{N}_2 + \frac{3}{2}\text{O}_2
\]  

(II-13)

Evolution of N₂ was attributed to the formation of a superoxide (Na₂O₂) which later decomposed to Na₂O and O₂. Bond and Jacob [26] supported this view with experimental evidence and reported that reaction (II-13) also proceeds in air.

Published work on the reaction of Na₂O with NOₓ and O₂ to form solid nitrate and nitrite could not be found.

Potassium Oxide (K₂O). Table II-1-(3), Case A shows that KNO₃ is favored over the nitrate and the oxide past the nitrite melting point of 334°C. Upon artificially removing KNO₃ from the system (Case B), formation of KNO₂ would be favored over the oxide past the nitrite melting point of 440°C. NOₓ removal efficiency for either case is 100%.

Experimental evidence of Bordyushkova et al. [24] indicates that KNO₃ melts without decomposition to a liquid which is stable in air at least to 530°C. Freeman [28] found molten KNO₂ to decompose around 650°C in an oxygen
atmosphere. KNO₃ and KNO₂ were shown to decompose via the same mechanisms described for the comparable salts of sodium [24,28].

The search for data on the reaction of K₂O with NOₓ and O₂ to form the solid nitrate or nitrite proved fruitless.

**Alkaline Earth Metal Oxides**

With the exception of MgO, the alkaline earth metal oxides (CaO, SrO, BaO) show 100% NOₓ removal capability over a portion of the temperature range, (Figure II-2). The melting points of the alkaline earth compounds pertinent to this research are presented in Table II-2. Table II-3 presents the results of the thermodynamic denitrification study for the alkaline earth metal oxides. For Cases A, the alkaline earth metal nitrate is favored over the oxide and the nitrite. For Cases B, the alkaline earth metal nitrite (with the exception of Mg(NO₂)₂) is favored over the oxide. However, in contrast to the alkali salts, the nitrates and nitrites of the alkaline earth metals decompose to yield the oxide before melting (except Ba(NO₂)₂).

**Magnesium Oxide (MgO).** Magnesium oxide showed the poorest denitrification potential of the alkaline earth metal oxides studied. As shown in Table II-3-(1) Case A, Mg(NO₃)₂ is favored over the nitrite and partially favored over the oxide at 160°C; however, at 185°C complete nitrate decomposition is predicted. Mg(NO₂)₂ will not be formed within the
Figure II-2. Case A - Denitrification Potential of Alkaline Earth Metal Oxides

Basis: 1 mole Metal Oxide

Gas Composition:
- 96.63 moles H₂
- 3.30 moles O₂
- 0.063 mole NO
- 0.007 mole NO₂
Figure II-2. Case B - Denitrification Potential of Alkaline Earth Metal Oxides

Gas Composition:
96.63 moles H$_2$
3.30 moles O$_2$
0.063 mole NO
0.007 mole NO$_2$

Per Cent of NO$_x$ Removed by Solid

Temperature (°C)
TABLE II-2
Melting Points of Alkaline Earth Metal Compounds
(Melting Point °C)

<table>
<thead>
<tr>
<th>Metal</th>
<th>Oxide</th>
<th>Nitrate</th>
<th>Nitrite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>2802.</td>
<td>129.*</td>
<td>100.*</td>
</tr>
<tr>
<td>Ca</td>
<td>2603.</td>
<td>561.</td>
<td>392.</td>
</tr>
<tr>
<td>Sr</td>
<td>2460.</td>
<td>645.</td>
<td>403.</td>
</tr>
<tr>
<td>Ba</td>
<td>1923</td>
<td>595.</td>
<td>273.</td>
</tr>
</tbody>
</table>

* Values are for hydrates of these compounds. Melting point of anhydrous salt unavailable.
### TABLE II-3

**Denitrification Potential of Alkaline Earth Metal Oxides**

Basis: 1 mole MeO (Me = Mg, Ca, Sr, Ba)

<table>
<thead>
<tr>
<th>(1) Magnesium Oxide (MgO)</th>
<th>(2) Calcium Oxide (CaO)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Case A</strong></td>
<td><strong>Case B</strong></td>
</tr>
<tr>
<td>T(°C)</td>
<td>Removed</td>
</tr>
<tr>
<td>160</td>
<td>.482</td>
</tr>
<tr>
<td>185</td>
<td>0.00</td>
</tr>
<tr>
<td>210</td>
<td>0.00</td>
</tr>
<tr>
<td>235</td>
<td>0.00</td>
</tr>
<tr>
<td>260</td>
<td>0.00</td>
</tr>
<tr>
<td>285</td>
<td>0.00</td>
</tr>
<tr>
<td>310</td>
<td>0.00</td>
</tr>
<tr>
<td>335</td>
<td>0.00</td>
</tr>
<tr>
<td>360</td>
<td>0.00</td>
</tr>
<tr>
<td>385</td>
<td>0.00</td>
</tr>
<tr>
<td>410</td>
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<td>510</td>
<td>0.00</td>
</tr>
<tr>
<td>535</td>
<td>0.00</td>
</tr>
<tr>
<td>560</td>
<td>0.00</td>
</tr>
</tbody>
</table>

* Three solid species allowed in system (metal oxide, metal nitrate, metal nitrite)

** Two solid species allowed in system (metal oxide, metal nitrite)
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* Three solid species allowed in system (metal oxide, metal nitrate, metal nitrite)

** Two solid species allowed in system (metal oxide, metal nitrite)
temperature range of interest under any conditions. Maximum NO\textsubscript{x} removal efficiency was 48\%, which occurred at the lowest temperature of this study (160°C).

The lack of stability of Mg(NO\textsubscript{2})\textsubscript{2} was shown experimentally by Ray [29]. Under vacuum, he detected decomposition of the nitrite as low as 60°C; decomposition was rapid and complete by 120°C.

However, other experimental evidence does not agree with the predicted thermodynamics. Addison and Walker [30] obtained Mg(NO\textsubscript{3})\textsubscript{2} by heating Mg(NO\textsubscript{3})\textsubscript{2}·N\textsubscript{2}O\textsubscript{4} (prepared from a mixture of magnesium chloride, dinitrogen tetroxide, and ethyl acetate) to 150°C under vacuum; the anhydrous Mg(NO\textsubscript{3})\textsubscript{2} was stable to 300°C. Oza and Mirza [31] reported Mg(NO\textsubscript{3})\textsubscript{2} was stable to 350°C in vacuo. Above 350°C, the nitrate decomposition was represented by

$$\text{Mg(NO}_3\text{)}_2 \rightarrow \text{MgO} + \text{2NO}_2 + \frac{1}{2}\text{O}_2 \quad (\text{II-14})$$

Wendlandt [32] found Mg(NO\textsubscript{3})\textsubscript{2} to be stable in air to 310°C; above that temperature rapid decomposition to MgO was observed.

The lack of agreement between the thermodynamic equilibrium results of this study and the experimental evidence for Mg(NO\textsubscript{3})\textsubscript{2} stability may be explained in two ways. First, errors in thermodynamic data could cause erroneous predictions of decomposition temperatures. Secondly, the difference may arise from the dependence of the solid
stability on the nature of the gas phase. In the experimental findings cited above, the condition of the gas phase included a sealed vacuum and a slow stream of air. The reported decomposition temperatures were different. (The thermodynamic calculations would be best represented by a sealed vessel at constant pressure of one atmosphere in which the evolved gases are permitted to accumulate). Thirdly, thermodynamic equilibrium calculations do not take into account kinetic resistance to decomposition.

Data on the reaction of MgO with NO\(_x\) and O\(_2\) to form the solid nitrate and/or nitrite could not be found.

**Strontium Oxide (SrO).** Table II-3-(3), Case A shows that formation of Sr(NO\(_3\))\(_2\) is favored over the nitrite and the oxide up to 385°C. Decomposition is predicted to begin around 410°C and to be complete near 500°C. Therefore, NO\(_x\) removal efficiency should be 100% up to 410°C. When Sr(NO\(_3\))\(_2\) is artificially removed from the system (Case B), Sr(NO\(_2\))\(_2\) would be favored over the oxide up to 210°C. Nitrite decomposition would begin around 235°C and be complete near 350°C.

Wendlandt [32] observed that Sr(NO\(_3\))\(_2\) was stable up to 280°C in a slow stream of air. Above this temperature a rapid weight loss occurred, and then a constant weight was noted from 440° to 510°C. The composition of the solid in this region was unknown since its weight did not correspond
to either a nitrite or a basic nitrate. Above 510°C, further weight loss occurred to yield SrO at 645°C. Lazarini and Brcic [33] experimentally found Sr(NO$_3$)$_2$ stable to approximately 480°C under nitrogen flow. They did not detect the partial decomposition at 280°C observed by Wendlandt [32].

Published work on the reaction of SrO with NO$_x$ and O$_2$ to form the solid nitrite and/or nitrate could not be found.

Barium Oxide (BaO). As shown in Table II-3-(4), Case A, Ba(NO$_3$)$_2$ is favored over the nitrite and the oxide up to 435°C. NO$_x$ removal efficiency should be 100% to this temperature. Decomposition is predicted to begin between 435° and 460°C, but is only 55% complete at 560°C. Upon artificially removing Ba(NO$_3$)$_2$ from the system (Case B), formation of Ba(NO$_2$)$_2$ is favored to around 260°C. Thermodynamic predictions indicate that Ba(NO$_2$)$_2$ does not decompose prior to melting.

Protsenko and Bordyushkova [34] experimentally studied the decomposition of Ba(NO$_2$)$_2$. The primary decomposition reaction, which was irreversible was

$$\text{Ba(NO}_2\text{)}_2 \rightarrow \text{BaO} + \text{NO}_2 + \text{NO}. \quad (\text{II-15})$$

The reaction began as low as 250°C in argon. However, since at this temperature the nitrate is stable, the following reaction forming Ba(NO$_3$)$_2$ from Ba(NO$_2$)$_2$ occurred

$$\text{Ba(NO}_2\text{)}_2 + 2\text{NO}_2 \rightarrow \text{Ba(NO}_3\text{)}_2 + 2\text{NO}. \quad (\text{II-16})$$
Decomposition of Ba(NO$_3$)$_2$ was observed as low as 520°C by Oza, Jha, and Ezekiel [35]. The overall decomposition reaction was shown to be

$$\text{Ba(NO}_3\text{)}_2 + \text{BaO} + 2\text{NO}_2 + \frac{1}{2}\text{O}_2$$  \hspace{1cm} (II-17)

The same decomposition reaction, under vacuum, began at 450°C and was complete by 600°C, according to Patil et al. [36]. Addison and Coldrey [37] reported that Ba(NO$_3$)$_2$ was stable in air to just above its melting point of 595°C. The presence of O$_2$ in the air was believed to account for the stability of the salt past its melting point since O$_2$ was a decomposition product. Lazarini and Brcic [33] detected Ba(NO$_3$)$_2$ decomposition as low as 500°C under a flow of N$_2$, but showed that it was still slow at 550°C.

The search for experimental data on the reaction of BaO with NO$_x$ and O$_2$ to form solid nitrate and/or nitrite was carried out in vain.

**Calcium Oxide (CaO).** Table II-3-(2), Case A shows that formation of Ca(NO$_3$)$_2$ is favored over the nitrite and the oxide up to 260°C. NO$_x$ removal efficiency is 100% up to 260°C. Decomposition is predicted to begin around 285°C and be complete by 385°C. When Ca(NO$_3$)$_2$ is artificially removed from the system (Case B), Ca(NO$_2$)$_2$ should be present with the oxide up to 185°C.

Wendlandt [32] reported that Ca(NO$_3$)$_2$ was stable from 220° to 425°C in air. (He started with the tetrahydrate of
Ca(NO₃)₂ and the last water of hydration was lost at 220°C. The nitrate began losing oxides of nitrogen above 425°C yielding CaO. Lazarini and Brcic [33] carried out similar decomposition experiments with Ca(NO₃)₂ under nitrogen flow; decomposition of Ca(NO₃)₂ began near 455°C. The reaction assumed to be occurring in both studies was

$$\text{Ca(NO}_3\text{)}_2 \rightarrow \text{CaO} + 2\text{NO}_2 + \frac{1}{2}\text{O}_2$$  \hfill (II-18)

Centnerszwer and Piekielny [38] studied the decomposition of Ca(NO₂)₂ in an inert atmosphere with decomposition noted above 270°C. They reported the following reactions:

$$\text{Ca(NO}_2\text{)}_2 \rightarrow \text{CaO} + \text{NO}_2 + \text{NO}$$  \hfill (II-19)

Since Ca(NO₃)₂ was stable at this temperature, the NO₂ reacted with the undecomposed Ca(NO₂)₂ to form nitrate according to

$$\text{Ca(NO}_2\text{)}_2 + 2\text{NO}_2 \rightarrow \text{Ca(NO}_3\text{)}_2 + 2\text{NO}.$$  \hfill (II-20)

James and Hughes [4] investigated the kinetics of the reactions of limestones and dolomites with NO and O₂ at one atmosphere pressure and from 250° to 420°C. The NO concentration was varied from 500 ppm to 10,000 ppm. Their thermodynamic calculations indicated that two reactions were of importance:

$$2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$$  \hfill (II-21)

$$\text{CaO} + 2\text{NO}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{Ca(NO}_3\text{)}_2$$  \hfill (II-22)

The conversion of CaO to Ca(NO₃)₂ varied from 22.4 to 39% depending on the type of stone used. The low final conversion of CaO to Ca(NO₃)₂ was attributed to an ever thickening
product layer of Ca(NO_3)_2 which inhibited the diffusion of NO and O_2 into the solid, and was not due to thermodynamic limitations.

D) Summary of Results of the Thermodynamic Study

With the exception of MgO, all of the metal oxides showed 100% NO_x removal capability over at least a portion of the temperature interval of interest (160° - 560°C). According to thermodynamics, nitrogen removal is 100% for the alkali metal oxides (Li_2O, Na_2O, K_2O) past the melting points of their nitrates (Case A) and nitrites (Case B).

With the exception of MgO, three temperature regions can be identified in the thermodynamic results for the alkaline earth metal oxides (CaO, SrO, BaO): (i) low temperature region - complete denitrification, (ii) intermediate temperature region - partial denitrification, (iii) high temperature region - no denitrification, only the metal oxide is stable.

Figure II-2, Case A shows nitrogen removal for MgO is never greater than 48% and this occurs at the lowest temperature of the study (160°C). Nitrogen removal exceeds 95% for CaO between 160° - 310°C, for SrO from 160° - 435°C, and for BaO from 160° to 510°C (Figure II-2, Case A). Case B of Figure II-2 shows Ca(NO_2)_2 formation could never result in 95% NO_x removal over the temperature range, Sr(NO_2)_2 formation could achieve better than 95% NO_x removal up to 235°C, and Ba(NO_2)_2 formation would remove greater than 95%
of the NO\textsubscript{x} past the nitrite melting point of 273°C. The solid stability results for all systems are summarized in Figure II-3.

If this proposed NO\textsubscript{x} control scheme should prove technically feasible, it would be desirable to regenerate the metal oxide from the solid salt, as this would better preserve the solid properties of the metal oxide (e.g., surface area, pore size, etc). The alkali metal oxides (Li\textsubscript{2}O, Na\textsubscript{2}O, K\textsubscript{2}O) do not meet this criterion, since the nitrates and nitrites of these metals melt prior to decomposition. By contrast, the nitrates and nitrites of calcium, strontium, and barium (except Ba(NO\textsubscript{2})\textsubscript{2}) do meet this criterion since decomposition of these salts occurs before melting.

Thus, CaO, SrO, and BaO are viewed as possible candidate solids. However, calcium oxide is cheaper and more readily available than the oxides of strontium and barium. In addition to the increased cost, strontium and barium possess lower nitrogen capacity per mass of oxide. To remove 28 lb of nitrogen would require 56 lb of CaO, 104 lb of SrO, or 153 lb of BaO. Thus, the choice of CaO as the metal oxide for the present research.
Figure II-3. Case A - Thermodynamically Stable Solids
Figure II-3. Case B - Thermodynamically Stable Solids
Literature Cited


CHAPTER III
APPLICABLE NON-CATALYTIC GAS-SOLID REACTION MODELS

The goal of this chapter is to review the literature of non-catalytic gas-solid reaction models with particular attention given to those models which incorporate varying solid structural properties. The chapter begins with an introduction to gas-solid reactions. A brief description of two conventional models follows along with a discussion of the importance of solid physical properties. Next, an extensive development of variable solid property models is presented.

A) Non-Catalytic Gas-Solid Reactions

Non-catalytic fluid-solid reactions refer to a class of reactions in which the solid reactant is converted to solid and/or fluid products. Interest in non-catalytic fluid-solid reactions has been growing for a number of years. This growth can be attributed to the increasing economic and environmental importance of this class of reactions. The broad range of processes depending on fluid-solid reactions include iron oxide reduction, roasting of sulfide ores, solid fuel combustion, gasification of coal, desulfurization of stack gases, and solid waste incineration. Fluid-solid non-catalytic reactions can be divided into two subgroups: (1) liquid-solid and (2) gas-solid. This chapter will address only the gas-solid subgroup.
The global (overall) rate of a gas-solid reaction is often conceived as proceeding through the following intermediate steps:

(1) Mass transfer of gaseous reactants from the bulk gas phase to the exterior surface of the solid particle.

(2) Diffusion of gaseous reactants into the solid particle through the pores of a solid reaction product or a partially reacted solid.

(3) Adsorption of gaseous reactant on the solid reactant surface.

(4) Chemical reaction between gas and solid reactants.

(5) Desorption of gaseous products from the solid surface.

(6) Diffusion of gaseous products out of the solid through the pores of a solid product or a partially reacted solid to the exterior surface of the solid particle.

(7) Mass transfer of gaseous product from the exterior surface of the solid particle to the bulk gas phase.

An important step which has only recently gained considerable attention is

(8) Alteration of structural properties of the solid (that is, size, surface area, pore size, porosity, etc) due to reaction and/or sintering.

All seven (or eight) steps are often not included in conventional gas-solid reaction models. Instead, steps such as 3, 4, and 5 are often combined and represented by a simple $n^{th}$ order rate expression. Also, if no gaseous products are produced then steps 5, 6, and 7 do not occur.
The alteration of solid structural properties has until recently been neglected and as such did not appear in the earlier gas-solid reaction models discussed in the next section.

Thus, the simplified concept of gas-solid reactions incorporates three major resistances - external mass transfer, internal diffusion and chemical reaction - that determine the global rate of reaction.

B) Conventional Models

The two non-catalytic gas-solid reaction models discussed here are the unreacted-core model \([1,2,3,4]\) and the grain model \([4,5]\). These two models were chosen for discussion because they are the basis for more sophisticated gas-solid reaction models to be presented in a subsequent section. Also, the unreacted-core model is of interest from a historical viewpoint and for its conceptually simple approach to gas-solid reaction modeling. Portions of the grain model make use of the unreacted-core solution.

The development for both will be based on a single, porous spherical pellet exposed to a flowing reactant gas stream. The reaction system is assumed isothermal. The chemical reaction considered is

\[
a_G G(\text{gas}) + a_S S(\text{solid}) \rightarrow a_P P(\text{solid}) + a_D D(\text{gas})
\]

(III-1)

where \(a_G\) and \(a_S\) are the stoichiometric coefficients, considered negative for the reactant gas \(G\) and solid \(S\),
respectively. \( a_D \) and \( a_P \) are the stoichiometric coefficients for the product gas D and solid P, respectively. The material balances for the gas and solid are obtained by applying the species continuity equations.

For gaseous reactant G the continuity equation is (neglecting the bulk flow term since it is assumed that gaseous reactant mole fraction is low)

\[
\frac{1}{r^2} \frac{\partial}{\partial r} \left( D_e \frac{\partial C_G}{\partial r} \right) + \frac{\partial}{\partial r} \left( \rho \frac{\partial C_G}{\partial r} \right) = \varepsilon \frac{\partial C_G}{\partial r} + \frac{\partial \rho}{\partial r} + \frac{\partial}{\partial r} \left( \rho u \right)
\]

(III-2)

where

\( r \) = radial position within the pellet (1)
\( D_e \) = effective diffusivity for gaseous reactant G (1/t)
\( C_G \) = molar concentration of gaseous reactant G (moles/1^3)
\( \dot{R}_G \) = rate of production of gaseous reactant G by chemical reaction per unit volume (moles/1^3 t)
\( \varepsilon \) = pellet porosity
\( t \) = time

The binary gas diffusivity usually found in the general species continuity equation [6] has been replaced by an effective diffusivity, \( D_e \), to account for the tortuous pore structure and the reduction in diffusion area due to the solid. \( D_e \) is comprised of both molecular and Knudsen diffusion coefficients. Any expression ranging from a multi-constant Langmuir-Hinshelwood to a simple first order may be used in equation (III-2) for the reaction term, \( \dot{R}_G \).

Simplification of equation (III-2) to facilitate solution is accomplished by elimination of the time
dependent term. A common assumption is that

\[ \frac{\partial C_G}{\partial t} = 0 \]  

(III-3)

This assumption is known as the pseudo-steady state approximation. It states mathematically that the quantity of reactant gas within the pores of the solid is small compared to the quantity required to completely react all of the solid. This approximation has been shown valid for cases in which the molar density ratio of solid and reactant gas is greater than 1000 \[1,7,8,9,10\]. In the present study the average value of this ratio is 6000.

When the pseudo-steady state approximation is used equation (III-2) becomes

\[ \frac{1}{r^2} \frac{d}{dr} \left( D_e r^2 \frac{dC_G}{dr} \right) + \vec{R}_G = 0 \]  

(III-4)

Note that equation (III-2) is changed from a partial differential equation to an ordinary differential equation when the time dependent term is dropped. This change makes solution of this equation less difficult.

The material balance equation for solid reactant S is

\[ \frac{dC_S}{dt} = \vec{R}_S \]  

(III-5)

where

\[ \vec{R}_S = \text{rate of production of solid reactant S by chemical reaction per unit volume. (moles/1^2 t)} \]

\[ C_S = \text{molar concentration of solid reactant S (moles/1^2)} \]

The relation between \( \vec{R}_G \) in equation (III-4) and \( \vec{R}_S \) in equation (III-5) is dictated by stoichiometry as follows
The above development is general and is the starting point for both of the models to be discussed – the unreacted-core and the grain model.

**Unreacted-Core Model.** The unreacted-core model is the simplest of the gas-solid reaction models. It assumes the reaction occurs at a sharp interface between the solid reactant and product. This interface is initially the outer surface of the solid, but as the reaction progresses, the interface moves into the interior leaving behind a completely reacted product layer. As the reaction interface moves inward toward the center of the particle, two concentric spheres are formed, the inner one composed of an unreacted core which shrinks with time. (Hence this model is also referred to as the shrinking-core model). This model can be applied to systems in which the solid is non-porous or for cases in which the internal diffusion rate is much slower than the intrinsic reaction rate. Examples of such systems are the oxidation of metals and the combustion of ashy coal [4].

Figure III-1 depicts the unreacted-core model for a case where external mass transfer, internal diffusion and intrinsic chemical reaction all contribute to the overall rate of reaction. Gibson [11] reviewed published work on the unreacted-core model for isothermal, non-isothermal, and

\[ \dot{\bar{R}}_g = \left( \frac{\alpha_G}{\alpha_s} \right) \dot{\bar{R}}_s \]  

(III-6)
Figure III-1. Schematic Diagram of Unreacted-Core Model
simultaneous reaction systems. Yagi and Kunii [12] are generally credited with the original development, while Cannon and Denbigh [13] were among the first to study non-isothermal gas-solid systems using this model. Wen and Wei [14,15] applied the unreacted core model to simultaneous reactions.

In the mathematical presentation of the unreacted-core model the following is assumed: (a) the reaction occurs under isothermal conditions; (b) the spherical shape and size of the pellet is retained throughout the reaction; (c) the pseudo-steady state approximation is valid; (d) the effective diffusivity is constant. The subscripts o,s, and c signify bulk conditions, conditions at the surface of the pellet, and conditions at the surface of the unreacted core, respectively.

With the previous assumptions the material balance for gaseous reactant $G$ in the product layer surrounding the unreacted core is equation (III-4) without the reaction term (the product layer is considered inert).

$$\frac{d}{dr} \left( r^2 \frac{dC_G}{dr} \right) = 0 \quad r_c < r < r_s \quad (III-7)$$

The boundary conditions for equation (III-7) are

$$D_e \left( \frac{dC_G}{dr} \right) = -R_G \quad \text{at} \quad r = r_c \quad (III-8)$$

and

$$D_e \left( \frac{dC_G}{dr} \right) = k_m \left( C_{G_o} - C_{G_s} \right) \quad \text{at} \quad r = r_s \quad (III-9)$$
where

\[ R_G = \text{rate of production of } G \text{ per unit surface area by chemical reaction (moles/l}^2 \text{ t)} \]

\[ k_m = \text{mass transfer coefficient for gaseous reactant } G \text{ from the bulk gas phase to the exterior surface of the solid (1/t)} \]

The following rate expression which is first order with respect to gas (independent of solid concentration) is used

\[ R_G = a_G k_s C_S O C_C \quad (\text{III-10}) \]

where

\[ k_s = \text{intrinsic reaction rate constant based on the surface area of the unreacted core (1/mole t)} \]

\[ C_{S O} = \text{initial bulk solid concentration, assumed constant (mole/l)} \]

The solution of equation (III-7) with boundary conditions (III-8) and (III-9) gives the gaseous reactant profile in the product layer and more importantly the value of \( C_G \) at the surface of the unreacted core \( (r=r_C) \)

\[ C = \frac{C_{G O}}{1 - \frac{a_G k_s C_{S O} r_C}{k_m} - \frac{a_G k_s C_{S O} r_C}{D_e} (1 - \frac{r_C}{r_s})} \]

(III-11)

To obtain the time dependence of the reaction system it is necessary to solve equation (III-5) which can be written

\[ \frac{dr_C}{dt} = a_P k_s C_C \quad (\text{III-12}) \]

The initial condition is

\[ r_C = r_s \quad \text{at } t=0 \quad (\text{III-13}) \]
When the value of $C_{Gc}$ from equation (III-11) is substituted into equation (III-12), integration yields the following time-conversion relationship for the unreacted-core model:

$$+ = \frac{a_G r_s C_S}{a_P C_{G_o}} \left[ \frac{x}{3k_m} + \frac{r_s}{D_e} [1+2 (1-x)- 3 (1-x)^{2/3} \right]$$

$$- \frac{1}{a_G k_s C_{G_o}} [1 - (1-x)^{1/3}] \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) 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Figure III-2. Diagram of Grain Model
solid surface, intergrain diffusion, intragrain diffusion, and finally chemical reaction on the spherical unreacted core associated with each grain. The grain model incorporates key structural parameters of the solid (that is, pellet porosity, grain size, etc) as well as the solid-state diffusivity. Also, the grain model can reduce to either the unreacted-core model or the volumetric model. Szekely and Evans [16] introduced the grain model in 1970. Since that time many applications of this versatile model have appeared in the literature [17,18].

In the mathematical development of the grain model and the following assumptions are made: (a) initial size and shape of the spherical pellet is retained throughout the reaction; (b) the reaction occurs under isothermal conditions; (c) the pseudo-steady state approximation holds; (d) the effective diffusivity, $D_e$, does not vary with radial position.

The intrinsic rate expression per unit surface area (remembering that the chemical reaction is occurring within the grains) is

$$ R_G = a_G k_S' C_S' C_G' $$

and the rate expression per unit volume is

$$ \dot{R}_G = \left( \frac{3r^2_s}{3} \right) (1 - \varepsilon) a_G k_S' C_S' C_G' $$

Primed quantities refer to grain properties and $(1 - \varepsilon)$ is the solid fraction per unit pellet volume. The gas phase
material balance, equation (III-4), for the grain model becomes

\[
\frac{D_e}{r^2} \frac{d}{dr} \left( r^2 \frac{dC_G}{dr} \right) + \left( \frac{3}{r_s^3} \right) \left( 1 - \varepsilon \right) \frac{a_G k' c' c' c'}{D_e} = 0
\]

Substituting equation (III-11) (without the mass transfer term) for \( C'_G \) and replacing \( C'_G \) with \( C'_s / (1 - \varepsilon) \), equation (III-17) is transformed to

\[
\frac{D_e}{r^2} \frac{d}{dr} \left( r^2 \frac{dC_G}{dr} \right) + \frac{3a_G r_s^2 k' c'_s c_s c_G}{r_s^3 [1 - \left( \frac{r_c}{r_s} \right)]} = 0
\]

In the above equation \( C_G \) is the gaseous reactant concentration within the pores of the pellet and it is assumed that this concentration is the same as the concentration at the surface of a grain (that is, \( C_G = C'_G \) ).

The boundary conditions for equation (III-18) are

\[
D_e \left( \frac{dC_G}{dr} \right) = k_m (C_G - C_G), \quad \text{at} \quad r = r_s \quad (III-19)
\]

and

\[
\left( \frac{dC_G}{dr} \right) = 0, \quad \text{at} \quad r = 0 \quad (III-20)
\]

The solid material balance, equation (III-5), for the grain model using the proper rate expression for \( \bar{R}_G \) (that is, equation (III-15) with \( a_G \) replaced by \( a_s \)) becomes

\[
\frac{dC_s}{dt} = \frac{3a_s r_c^2 k' c'_s c_s c_G}{r_s^3 [1 - \left( \frac{r_c}{r_s} \right)]} \quad (III-21)
\]
This can be rewritten in terms of the radius of the unreacted core of a grain to give
\[
\frac{dr_c'}{dt} = \frac{a_s k_s' C_G}{a_g k_g' C_s' r_c' \left[ 1 - \frac{D_e'}{D_e} \left( 1 - \frac{r_c'}{r_s} \right) \right]}
\tag{III-22}
\]
The initial condition for (III-22) is
\[
r_c' = r_s' \quad \text{at } t=0 \quad \tag{III-23}
\]
The local (X) and overall (\(\bar{X}\)) fractional conversions are determined by the position of the grain unreacted core radius (\(r_c'\))
\[
X = 1 - \left( \frac{r_c'}{r_s'} \right)^3 \quad \tag{III-24}
\]
\[
\bar{X} = \frac{3}{r_s^3} \int_0^{r_s} r^2 \left[ 1 - \left( \frac{r_c'}{r_s} \right)^3 \right] dr \quad \tag{III-25}
\]
Parameters common to the unreacted-core and the grain model which are readily measured or calculated are:

i) Pellet initial mass, \(W_0\) (mass)

ii) Pellet radius, \(r_s\) (1)

iii) Pellet porosity, \(\varepsilon = 1 - \frac{3W_0}{4\pi r_s^3 \rho_s'}\)

iv) Pellet effective diffusivity, \(D_e = D_e \varepsilon^2\) via the random pore model of Wakao and Smith [19]. (m^2/s).

v) Mass transfer coefficient, \(k_m\), from the modified Froessling method [20]
\[
\text{Sh} = \frac{2k_m r_s}{D_G} = K + 3Re^m Sc^n \quad \tag{III-26}
\]
where
\[
\rho_s' = \text{true crystalline density of solid reactant (mass/l}^3\text{)}
\]
\[ D_G = \text{proper combination of molecular (} D_m \text{) and Knudsen (} D_k \text{) diffusion coefficients (} t^2/\text{t}), \]
\[ \frac{1}{D_G} = \frac{1}{D_M} + \frac{1}{D_K} \]  
(III-27)

vi) Solid reactant concentration in pellet
\[ \left( \frac{\text{moles}}{\text{mol}} \right), \]
\[ C_{S_O} = (1 - \varepsilon) C'_{S_O} \]  
(III-28)

The intrinsic rate constant for both models \((k_s \text{ and } k'_s)\) must be measured experimentally.

The following parameters are required for the grain model only

vii) Solid reactant concentration in grain
\[ \left( \frac{\text{moles}}{\text{mol}} \right), \]
\[ C_{S'_O} = \frac{\rho'_s}{M_s} \]  
(III-29)

viii) Grain radius \((l), r'_s = \frac{3}{A_s \rho'_s} \)  
(III-30)

where

\[ M_s = \text{molecular weight of solid reactant} \]
\[ A_s = \text{average specific surface area of pellet} \]
\[ \left( \frac{1^2}{\text{mass}} \right) \]

Grain diffusion coefficients (that is, \(D'_s\)) are difficult to estimate \textit{a priori}, and are often determined by fitting experimental data.

In the models described above, the physical properties of the solid (that is, pellet porosity \((\varepsilon)\), effective diffusivity \((D'_s)\), grain radius \((r'_s)\)) were assumed constant. As will be pointed out in the next section that assumption is not necessarily a good one.
C) Effect of Solid Properties

When a solid reactant is converted to solid product during the course of a non-catalytic gas-solid reaction, the physical properties of the solid do not remain constant if the reactant and product solid properties are different.

Most noticeable is the change in the porosity of the solid particle if there are differences in the molar volumes, $V_p$ (of the product solid) and $V_R$ (of the reactant solid). The particle porosity will increase if $V_p < V_R$, while particle porosity will decrease if $V_p > V_R$ since the solid product will take up volume previously occupied by the pores. For the case $V_p > V_R$, the particle porosity can become so low that the reaction ceases at a conversion less than 100% due to extremely high pore diffusion resistance. This phenomenon is referred to as reaction "die-off" and it has been observed by many investigators for several gas-solid reaction systems.

One of the earliest reported observances of reaction "die-off" was in 1953 by Addison and Lewis [21] for the CaO-NO/NO$_2$ reaction system. At 260°C, they reported the maximum conversion of CaO to Ca(NO$_3$)$_2$ was 54.3% after 4.25 hours. Ca(NO$_2$)$_2$ was present in trace quantities in the reaction product mixture (that is, conversion to Ca(NO$_2$)$_2$ was only 0.6%). Addison and Lewis blamed the incomplete conversion on the "cohesive nature of the calcium nitrate formed as a coating round each oxide particle...sufficiently cohesive to decrease (and even inhibit) the reaction."
Perhaps the most widely known example of reaction "die-off" is the reaction of lime with SO\textsubscript{2} and O\textsubscript{2} which forms CaSO\textsubscript{4} \((V_p/V_R = 3.08)\). Potter \cite{22} reported for this system that the solid ceased reacting at a conversion of CaO equal to 45%. Borgwardt and Harvey \cite{23} and Hartman et al. \cite{24} both showed that the rate of calcined limestone sulfation became very small at conversions of about 50%.

Of particular interest to the current research is the study of James and Hughes \cite{25} on the reaction of NO and O\textsubscript{2} with CaO which forms Ca(NO\textsubscript{3})\textsubscript{2} \((V_p/V_R = 3.95)\). They report that "the nitrate formed has a pronounced retarding effect on the sorption rate."

Another factor which can cause structural changes in reactant solid properties is sintering. Sintering is the process by which a porous solid becomes more dense as a result of being held at an elevated temperature (but below its fusion temperature). Sintering reduces the surface area of a solid and limits access to the solid by the reactant gas. Thus, sintering can markedly reduce the overall rate of reaction.

Cracking is another structural property change which can alter the overall rate of reaction. When a reacting solid particle cracks or breaks it increases the overall rate for that solid particle because of increased diffusional access by the reactant gas to the solid through the crack. Thus, the phenomenon of cracking can lead to erroneous interpretations of kinetic data.
In the current research, "die-off" has been experimentally observed for the reaction

\[ \text{CaO} + 2\text{NO}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{Ca(NO}_3)_2. \]  

(I-17)

At 450°C, the typical conversion of CaO to Ca(NO₃)₂ was 29% after a reaction time of 30 minutes. An additional twenty minutes of reaction time only increased the conversion to 30.8%. This reaction is believed to be initially strongly influenced by external mass transfer at all temperatures. At low temperatures (150° and 250°C) after a product layer has formed diffusion through the product layer becomes very important (probably controlling). At higher temperatures (350°, 450°, and 550°C), the controlling resistance changes from external mass transfer to product layer diffusion to pore diffusion. Pore diffusion becomes important because of the thickening solid product layer due to the great difference in the molar volume of the reactant and product solids \((V_p/V_R = 3.95)\) which causes a decrease in pellet porosity.

Sintering of CaO is unimportant because reaction temperatures are so far below the melting point of CaO (2580°C). However, the solid product - \((\text{Ca(NO}_3)_2\) - melts at 561°C and sintering of the Ca(NO₃)₂ may be occurring. Very few of the particles reacted in this research have experienced the phenomenon of cracking. These particles will not be used for comparison with the model results.

In the next section gas-solid reaction models which account for variable solid properties will be reviewed. The phenomenon of cracking will not be included.
D) Variable Solid Property Models

Variable solid property models which account for structural changes due to chemical reaction alone are discussed first. These are followed by those models which include the effects of both chemical reaction and sintering.

The Model of Howard, Williams, and Ghazal [18]

In 1970, Howard et al. [18] proposed a variable solid property model to describe the reaction between calcined limestone and \( \text{SO}_2 \). Consider a spherical pellet consisting of an agglomeration of small, spherical calcium oxide grains which are assumed uniformly distributed. The void spaces between the grains form the pores of the pellet, therefore the grain surfaces make up the pore surfaces. (See Figure III-3). Thus, it is seen that the pellet structure is similar to the grain model. This model allows for external mass transfer, gas diffusion within the pores, chemical reaction on the outer surface of the grain, and solid diffusion within the grain. Solid diffusion within the grains requires that sulfur species (formed on the grain surface) diffuse rapidly into the grain or CaO species (within the grain) must diffuse to the grain surface. Thus, the difference between this model and the grain model lies in the manner in which the grains react.

Two versions of the model were considered.

Version 1: Values for grain size \( (r') \), pellet porosity \( (\epsilon) \), and specific surface area \( (A_g) \) are assumed constant.
Figure III-3. Diagram of Howard's et al. Grain Model
Version 2: $\varepsilon$, $A_r$, and $r'$ vary with conversion in accordance with the molar volume difference between CaO and CaSO$_4$. Also, for the second version, CaSO$_4$ is assumed uniformly distributed within the grain (that is, solid state diffusion within the grain is fast relative to chemical reaction rate at the grain surface).

The following assumptions are common to both versions:

1. Isothermal conditions exist,
2. Radial symmetry is assumed (that is, all grains at the same radial position behave identically),
3. The chemical reaction rate is considered first order with respect to SO$_2$ concentration,
4. The reaction rate decreases as conversion at the grain surface increases (that is, the rate per unit area of grain surface = $k(1-X_s) C_G$ where $X_s$ = local fractional conversion of CaO residing at grain surface and $C_G$ = molar concentration of SO$_2$).

Both versions of the model predict well the diffusion of gases within the pellet in the absence of chemical reaction (that is, the analytical solution to the diffusion equation with $k_s = 0$ compared well with the model results with $k_s = 0$). The process of comparing model predictions with experimental time-fractional conversion data involves finding that set of model parameters (effective diffusivity, reaction rate constant, solid state diffusivity, specific surface area, grain size, and pellet porosity) such that model predictions match data at all times.

The constant pore model (Version 1) was shown to fit the data better. The varying structural model (Version 2)
was considered less desirable because it required re-fitting base kinetic parameters for every new particle size and temperature. Howard et al. state that since the base value of each reaction parameter should be independent of temperature and pellet size, the first version of this model is more acceptable from a "physical and chemical point of view."

The Model of Gidaspow - Pore Closure Model [26]

Gidaspow modified the volumetric model to account for changes in solid porosity due to product formation. The solid is assumed porous and the overall dimensions of the solid pellet are assumed constant. An expansion factor \( E \) (which is a function of the molar volumes and stoichiometric coefficients of the product and reactant solids) accounts for expansion or contraction of the solid phase at the expense of pore volume as reaction occurs. This expansion or contraction of the solid phase alters the pellet porosity.

The following gas-solid reaction is assumed to occur:

\[
a_G \ G(g) + a_S \ S(s) + a_P \ P(s) + a_D \ D(g)\]

Gaseous \( G \) diffuses into the pellet through the pore structure and reacts with the solid \( S \). As the product layer develops, the pore volume will increase or decrease depending on whether the product solid occupies less or more volume than the reactant solid. Figure III-4 depicts this model in slab geometry for the case of contraction \((E<1)\) and expansion \((E>1)\). The changing pore volume is monitored in this model by accounting for the
Figure III-4. Model of Gidaspow for (a) $E<1$ and (b) $E>1$
change in the volume fraction of the pores (ε) as the solid reactant is consumed. For cases in which the expansion factor E is greater than unity pore closure can occur.

The following assumptions are made in the development of this model: (1) Overall dimensions of the porous, solid slab remain constant throughout the reaction, (2) Isothermal conditions exist, (3) Bulk diffusion is neglected, (4) Chemical reaction is first order with respect to gas reactant concentration and is irreversible, (5) External mass transfer resistance is negligible, (6) Effective diffusivity, $D_e$, is assumed independent of the spatial coordinate, X, (7) Slab geometry is assumed (the slab having thickness 2 L), (8) Pseudo-steady state approximation is valid.

The rate of consumption of gaseous reactant G per unit volume of solid $S$ is

$$ R_G = \left( \frac{a_G}{a_S} \right) k C_G \quad \text{(III-31)} $$

where

- $k$ = reaction rate constant ($\text{mole}^{-1} S/3 S^{-1} \text{sec}$)
- $C_G$ = molar concentration of gaseous reactant G ($\text{moles G}/\text{l}^3 \text{gas}$)
- $a_G, a_S$ = stoichiometric coefficients for gas G and solid S.

Equation (III-31) is used in the material balance equation for gas G within the pellet slab (on a per unit total pellet volume basis) as follows

$$ \left( \text{diffusion of G within the pellet} \right) = \left( \text{rate of consumption of G within the pellet by chemical reaction} \right) \; . $$
where

\[ D_e \frac{\partial}{\partial x} \left( \varepsilon \frac{\partial C_G}{\partial x} \right) = \varepsilon_S R_G = \varepsilon_S \left( \frac{a_G}{a_S} \right) k C_G \quad (\text{III-32}) \]

\[ D_e = \text{effective diffusivity of } G \text{ in pores of pellet} \left( \frac{\text{m}^2}{\text{s}} \right) \]

\[ X = \text{spatial coordinate in direction of pores (1)} \]

\[ \varepsilon = \text{volume fraction of pellet occupied by gas ie, the void fraction of the solid pellet,} \left( \frac{1^3 \text{gas}}{1^3 \text{total}} \right) \]

\[ \varepsilon_S = \text{volume fraction of solid } S, \left( \frac{1^3 S}{1^3 \text{total}} \right) \]

\( \varepsilon \) and \( \varepsilon_S \) are present in equation (III-32) to place the equation on a common basis of total pellet volume. On the left hand side, \( \varepsilon \) converts \( C_G \) from \( \text{moles } G \) to \( \frac{1^3 \text{gas}}{1^3 \text{total}} \). On the right hand side, \( \varepsilon_S \) converts \( R_G \) from \( \text{moles } G \) to \( \frac{1^3 \text{S-sec}}{1^3 \text{total-sec}} \).

The quantity "1\(^3\) total" refers to the total pellet volume (that is, solid plus void). The boundary conditions for equation (III-32) are

\[ C_G = C_{G_0} \quad \text{at } x=0 \text{ (surface of pellet)} \quad (\text{III-33}) \]

\[ \frac{\partial C_G}{\partial x} = 0 \quad \text{at } x=L \text{ (center of pellet)} \quad (\text{III-34}) \]

The time dependence of this reaction system is obtained from the solid material balance. The rate of consumption of solid reactant \( S \) per unit volume of \( S \) is

\[ R_S = kC_G \quad \text{(moles } S/1^3 \text{S-sec)} \quad (\text{III-35}) \]
which is used in the following material balance for solid S

\[ \frac{dC_S}{dt} = - R_S \varepsilon_S \left( \frac{\text{moles } S}{\text{m}^3 \text{ total}} \right) \]  

(III-36)

where

\[ C_S = \text{molar concentration of solid } S \text{ per unit pellet volume (moles } S/\text{m}^3 \text{ total)} \]

\[ \varepsilon_S \text{ is present in equation (III-36) to convert from } \frac{\text{moles } S}{\text{m}^3 \text{s-sec}} \]

to \[ \frac{\text{moles } S}{\text{m}^3 \text{total-sec}} \]. \( C_S \) can be written in terms of volume fraction of \( S \), \( \varepsilon_S \), by

\[ C_S = \frac{\rho_S \varepsilon_S}{M_S} \]  

(III-37)

where

\[ \rho_S = \text{void-free density of } S, \left( \frac{\text{mass } S}{\text{m}^3 \text{ s}} \right) \]

\[ M_S = \text{molecular weight of } S, \left( \frac{\text{mass } S}{\text{mole } S} \right) \]

Equation (III-36) becomes by use of (III-35) and (III-37)

\[ \frac{d\varepsilon_S}{dt} = - \left( \frac{M_S k C_G}{\rho_S} \right) dt \]  

(III-38)

Equation (III-38) may be integrated using the boundary condition

\[ \varepsilon_S = \varepsilon_{S_0} \text{ at } t = 0 \]  

(III-39)

to yield

\[ \varepsilon_S = \varepsilon_{S_0} e^{- \left[ \frac{M_S k}{\rho_S} \int_0^t C_G \, dt \right]} \]  

(III-40)

Equation (III-40) gives the time variation of the concentration of reactant solid \( S \) (in terms of \( \varepsilon_S \)) as a function of \( C_G \) (which varies as a function of position within the pellet as given by equation (III-32)).
For every mole of S consumed, \( \frac{a_P}{a_G} \) moles of solid product P are formed. If \( V_P \) and \( V_S \) are the void-free molar volumes of solid product and solid reactant respectively, then chemical reaction will cause the following change in solid phase volume at the site of the chemical reaction within the pellet (per mole of S reacted)

\[
E = \left( \frac{a_P}{a_G} \right) \frac{V_P}{V_S} \tag{III-41}
\]

The factor, \( E \), represents the expansion or contraction of the solid phase within the pellet due to chemical reaction. Product P appears at the expense of S; therefore, for a given change in \( \varepsilon_S (\Delta \varepsilon_S = \varepsilon_{S_0} - \varepsilon_S) \), the change in \( \varepsilon_P \), the volume fraction of solid product P, is given by

\[
\varepsilon_P = \varepsilon_{P_0} + E \Delta \varepsilon_S = \varepsilon_{P_0} + E(\varepsilon_{S_0} - \varepsilon_S) \tag{III-42}
\]

where

\[
\varepsilon_{S_0}, \varepsilon_{P_0} = \text{initial volume fractions for S and P, respectively.}
\]

Since the sum of the volume fractions (\( \varepsilon \), \( \varepsilon_S \) and \( \varepsilon_P \)) must always be one, and since it is assumed that the porous solid as a whole does not expand or contract, the void fraction of the solid, \( \varepsilon \), may be calculated by difference

\[
\varepsilon = 1 - \varepsilon_S - \varepsilon_P \tag{III-43}
\]

Substituting equation (III-42) for \( \varepsilon_P \) into (III-43) yields

\[
\varepsilon = 1 - \varepsilon_{P_0} - E \varepsilon_{S_0} + (E-1)\varepsilon_S. \tag{III-44}
\]

This model must be solved numerically since the gaseous concentration \( C_G \) couples equations (III-32) and (III-40).
Equation (III-32) is integrated for a spatial step $\Delta X$ to give a value of $C_G \Delta X$; this value of $C_G$ is used in equation (III-40) to move in time and to calculate $\varepsilon_S$ at $t = t + \Delta t$. Equation (III-44) is then solved for a new value of $\varepsilon$ at $X = X + \Delta X$ and $t = t + \Delta t$. This new value of $\varepsilon$ is returned to equation (III-32) and the numerical process is repeated until the desired level of conversion is reached.

The model can predict complete reaction or reaction "die-off" (due to pore closure) depending on the value of $E$ and $\varepsilon_{S_o}$. For values of $\varepsilon_{P_0} = 0$ and $E = 1.5$, the pores remain open and complete reaction is predicted if $\varepsilon_{S_o} \leq 0.50$. However, if $\varepsilon_{S_o} = 0.80$, the pores close after a conversion of only 6%. Both of the above examples were for a system with a large Thiele modulus, that is, with a large diffusional resistance.

The reactant gas profile within the pellet is also affected by the value of $\varepsilon_{S_o}$. For the case of $\varepsilon_{P_0} = 0$, $E = 1.5$, $\varepsilon_{S_o} = 0.50$, and a large Thiele modulus, the gaseous concentration profile within the slab becomes more uniform throughout the slab as reaction time increases because the pellet pores never close. For the case of $\varepsilon_{P_0} = 0$, $E = 1.5$, and $\varepsilon_{S_o} = 0.8$, and a large Thiele modulus, the gaseous reactant concentration profile within the slab becomes steeper as reaction time increases owing to decreased pellet porosity.
The Model of Hartman and Coughlin [27]

This is a modification of the grain model which takes into account the change in the porosity of a pellet caused by chemical reaction. In this model the grain size is constant. The authors developed this model to describe the reaction "die-off" observed by them [28] and others [22,23] for the limestone (CaO)-SO$_2$-O$_2$ reaction system.

A spherical, porous pellet of CaO made up of microscopic, non-porous spherical grains each of which reacts according to the unreacted-core model is considered. (See Figure III-2 for grain model). The rapid decrease in pellet porosity which occurs during sulfation is accounted for in terms of the molar volumes of CaO and CaSO$_4$ and the conversion of CaO.

The following assumptions are made in this model: (1) External mass transfer resistance is negligible; (2) Isothermal conditions exist; (3) Gas concentration of the surface of the grains is uniform; (4) The chemical reaction within each grain proceeds according to the unreacted-core mechanism and is first order with respect to reactant gas concentration. Also, the reaction occurs in the presence of excess O$_2$ and is considered irreversible, and (5) The pseudo-steady state approximation is valid.

The reaction occurring is represented by $a_G G(g) + a_S S(s) + a_P P(s) + a_D D(g)$. The rate of production of G per unit pellet volume is equation (III-16) for the grain model. Likewise, the gas and solid material balance equations for
the grain model (equations (III-18) and (III-22)) are applicable here. The grain model boundary conditions given by equations (III-20 and 23) apply. The boundary condition at the pellet surface is the same as equation (III-33). Local (\(X\)) and overall (\(\bar{X}\)) conversions are determined by equations (III-24 and 25), respectively.

The equations presented thus far are standard for the grain model. Hartman and Coughlin's modification is in the form of an additional expression which gives the porosity of the calcined pellet, \(\varepsilon(X)\), as a function of the molar volumes of the solids present and the local conversion (if complete calcination of the limestone has occurred) [28]

\[
\varepsilon(X) = 1 - (1 - \varepsilon_{LS}) \left\{ \rho_{LS} \frac{V}{M_{CC}} \left[ V_{CO} + X \left( V_{CS} - V_{CO} \right) \right] \right. \\
\left. - (1-Y) \rho_{CC} \right\} \tag{III-45}
\]

where

- \(\varepsilon_{LS}\) = porosity of natural limestone
- \(\rho_{LS}, \rho_{CC}\) = density of natural limestone and CaCO\(_3\), respectively. (mass/1\(^3\))
- \(M_{CC}\) = molecular weight of CaCO\(_3\) (mass/mole)
- \(y\) = weight fraction of CaCO\(_3\) in limestone
- \(V_{CO}, V_{CS}\) = molar volumes of void-free CaO and CaSO\(_4\), respectively (1\(^3\)/mole)
- \(X\) = local fractional conversion

The authors use equation (III-45) to evaluate current (in time and space) porosity of the pellet and adjust the effective diffusivity according to

\[
D_e = D \varepsilon(X) \tag{III-46}
\]
where $D$ is a Knudsen diffusion coefficient (referred to hereafter as a pore diffusion coefficient) which has been adjusted with a tortuosity factor of 1.5 suggested by Campbell et al. [29]. The value of $D$ was assumed constant by the authors. Therefore, as conversion increases the change in diffusion resistance is accounted for by a change in the effective diffusivity, $D_e$, via equations (III-45) and (III-46). The reduction of pellet porosity due to reaction (that is, sulfation) increases the resistance to diffusion of reactant gas into the pellet.

Individual values for $k'$, $D_e$, and $D_e'$, obtained from fitting the model to experimental data, were doubled to determine the effect each had on the progress of the CaO-$SO_2$-$O_2$ reaction. Doubling the rate constant, $k'$, altered the conversion-time profile only slightly. Doubling the pore diffusion coefficient, $D$, (thereby doubling $D_e$) increases both the final conversion and the conversion-time profile. A similar increase in the grain diffusivity, $D_e'$, increases the slope of the conversion-time curve but lowers the maximum conversion attained. This behavior results since with a high $D_e'$ the reaction proceeds faster initially, but the reaction is soon retarded by the dense product layer formed at the pellet surface.

The diffusion parameters also affect the predicted distribution of solid product (sulfate) within the pellet. For a given $D_e'$, increases in $D$ allow sulfate formation to occur in the center of the pellet. For a given $D$, increases in $D_e'$ move the sulfate distribution closer to the pellet.
surface. Again, the increased global reaction rate (owing to a higher $D'_e$) causes the pellet surface to react faster and the sulfate formed there soon retards further diffusion to the interior unreacted CaO. Reaction "die-off" was predicted by this model but for the case of small pellets the limiting conversions predicted were somewhat higher than those experimentally observed.

The Model of Georgakis, Chang, and Szekely [30]

This is also a modification of the grain model which takes into account the changes in the porosity of a pellet caused by chemical reaction. This model differs from Hartman and Coughlin [27] in that porosity changes are accounted for via the formation of a product layer on the grains which causes the grain size to vary as a result of differences in the stoichiometric coefficients and molar volumes of reactant and product solids. The authors make use of the data of others (23,28) for the reaction system limestone (CaO)-$\text{SO}_2-\text{O}_2$ to test their model's ability to predict reaction "die-off".

A spherical, porous pellet made up of microscopic, non-porous spherical grains each of which reacts according to the unreacted-core model is considered. (See Figure III-2 for grain model). The assumptions made by Hartman and Coughlin [27] are applicable for this model with the exception that while the number of grains is constant their size is not.
The reaction occurring is represented by \( a_G \text{ G}(g) + a_S \text{ S}(s) + a_P \text{ P}(s) + a_D \text{ D}(g) \). The rate of production of \text{ G} per unit pellet volume is equation (III-16) for the grain model.

The gas and solid phase material balance equations are

\[
\frac{1}{r^2} \frac{d}{dr} \left( r^2 D_e(r) \frac{dC_G}{dr} \right) = \frac{-3a_G r'_c^2 k'_c c_{S_0} c_G}{r'_s \left[ 1 - \left( \frac{D'_s}{D'_s} \right) r'_c \left( 1 - \frac{r'_c}{r'_s} \right) \right]}
\]

(III-47)

\[
\frac{dr'_c}{dt} = \frac{a_s k'_s c_G}{\left[ 1 - \left( \frac{D'_s}{D'_s} \right) r'_c \left( 1 - \frac{r'_c}{r'_s} \right) \right]}
\]

(III-48)

where

- \( r \) = radial coordinate within pellet (1)
- \( D_e(r) \) = effective diffusivity of gas reactant \text{ G} (\text{l}^2/\text{time}) = \text{D } \varepsilon / r
- \( \text{D} \) = diffusion coefficient in pore (\text{l}^2/\text{time})
- \( D'_s \) = diffusion coefficient thru product layer on grain (\text{l}^2/\text{time})
- \( \varepsilon \) = pellet porosity
- \( r \) = pellet tortuosity (assumed 1.0)

Equation (III-47) is seen to be similar to equation (III-18) for the constant property grain model with the exception that the grain radius \( r'_s \) is replaced by its initial value \( r'_s \) in the cubic term in the denominator, of (III-47).

The boundary conditions used by the authors for equations (III-47) and (III-48) are

\[
C_G = C_{G_0} \text{ at } r = r_s \text{ (pellet surface)} \quad (III-49)
\]

\[
\frac{dC_G}{dr} = 0 \text{ at } r = 0 \text{ (pellet center)} \quad (III-50)
\]
where

\[ C_G = \text{bulk concentration of reactant gas (mole/1}^3 \text{).} \]

Local \((X)\) and overall \((\bar{X})\) conversions are determined by equations (III-24 and 25), respectively.

Grain radius changes are calculated via the following equation

\[ r'_s = \gamma r'_c + (\gamma - 1) r'_c \]  

(III-52)

where

\[ \gamma = \left( \frac{a_p}{a_s} \right) \left( \frac{V_p}{V_s} \right) \left( \frac{1}{1 - \epsilon_p} \right) \]

(III-53)

and

\[ V_p, V_s = \text{void-free molar volumes of solid product} \]

\[ P \text{ and solid reactant, S, respectively} \]

\[ \epsilon_p = \text{porosity of product solid P}. \]

\( \gamma \) is an expansion factor which accounts for the growth or shrinkage in grain size depending on the relative magnitudes of \( V_p \) and \( V_s \). If \( V_p < V_s \), then the grains will decrease in size with reaction. If \( V_p > V_s \), then the grains will expand at the expense of pellet porosity (if the overall pellet radius remains constant). Depending on the value of the initial pellet porosity \( (\epsilon_o) \), values of \( \gamma > 1 \) may result in the pellet porosity \( (\epsilon) \) becoming very small. When this occurs resistance to diffusion of reactant gas into the pellet increases.

The authors compared their model results to the experimental data of Hartman and Coughlin [28] and Borgwardt et
al. [23]. This comparison was presented via time-conversion curves for three different particle sizes. Agreement with the data of Hartman and Coughlin was good for all three particle sizes. However, model predictions compared well with the data of Borgwardt et al. for only the largest and smallest particles. To match the data for the intermediate particle requires an 85% reduction in the value for the pore diffusivity (D) reported by Borgwardt et al.

Ramachandran and Smith - The Single-Pore Model [31]

The single-pore model provides a conceptually simple approach to analyzing gas-solid noncatalytic reactions. The time-conversion relationship for the system is predicted from the behavior of a single pore. The model accounts for (1) pore diffusion, (2) diffusion through a product layer forming on the pore walls, and (3) surface reaction. Changes in pore geometry are assumed to occur due to reaction. The important parameters are effective pore length (L), effective diffusivity in the product layer (De), and an expansion factor (γ), which is a function of the ratio of the molar volumes of the porous product to that of the reactant. If γ=1, the pore geometry remains constant; if γ<1, the pore structure opens as reaction proceeds; if γ>1, the pore structure closes as reaction proceeds. The advantage of this model lies in its requirement of few parameters, all of which are relatively easy to obtain from limited time-conversion data or from measured properties of the reacted and unreacted solid.
The reaction occurring is represented by
\[
\text{G}_G G(g) + a_S S(s) \rightarrow a_P P(s) + a_D D(g)
\]
and it is assumed the pellet (solid S) is made up of many parallel, cylindrical pores. Attention is fixed upon a single cylindrical pore of radius r and length L surrounded in a concentric fashion by a cylindrical solid with an overall radius \( \lambda \) (measured from pore axis). (See Figure III-5). Gaseous reactant G diffuses axially into the pore.

The following assumptions are made: (1) There is no radial variation of gas concentration in the pore; (2) Concentration of reactant gas G in the product layer varies radially but there is no axial diffusion of G in the product layer; (3) Isothermal conditions exist; (4) No external mass transfer resistance; (5) The pseudo-steady state approximation is valid; and (6) The chemical reaction is irreversible, first order with respect to gas G, and first order with respect to the interfacial surface area of solid S. The reaction is restricted to a sharp interface because solid reactant S is assumed non-porous. Thus, the original pellet contains only macropores.

Reaction occurs along the pore wall surface. The radius of the pore varies if the solid product has a different molar volume than the solid reactant. The changing pore radius is measured by \( \delta_1 \) and \( \delta_2 \), which describe the thickness of the product layer on either side of the initial position of the pore wall. \( \delta_1 \) is the distance between the original pore wall (at time = 0) and the current pore wall.
(at time = t). \( \delta_1 \) is positive between the original pore wall and the axis of the pore. \( \delta_2 \) is the distance between the original pore wall and the current reaction interface. (See Figure II-6).

Gaseous reactant within the pore must diffuse through the product layer to the reaction surface. The rate of reaction of gaseous reactant G within a differential cylindrical volume element of radial thickness \((r + \delta_2) - (r - \delta_1)\) and of length \(\Delta Z\) is (including the resistance from both surface reaction and product layer diffusion)

\[
R_G \left( \frac{\text{moles}}{\text{time}} \right) = 2\pi (\Delta Z) C_G \left[ \frac{1}{a_G k_s C_{S_0} (r + \delta_2)} \right]^{-1} \ln \left( \frac{r + \delta_2}{r - \delta_1} \right) + \frac{1}{D_e} \right]^{-1} \tag{III-54}
\]

where

\[k_s = \text{intrinsic reaction rate constant} \left( \frac{1}{\text{mole-t}} \right)\]

\[C_G = \text{concentration of gaseous reactant G} \left( \frac{\text{mole}}{1^3} \right)\]

\[C_{S_0} = \text{initial bulk solid concentration, assumed constant} \left( \frac{\text{mole}}{1^3} \right)\]

\[D_e = \text{effective diffusivity of gaseous reactant G through product layer} \left( \frac{1^2}{t} \right)\]

This reaction rate is used in the material balance for gaseous reactant G in the pore. The gas phase material balance is
Figure III-5. Single-Pore Model
Figure III-6. Changes in Pore Radius for Single-Pore Model
\[ D \left( r - \delta_1 \right)^2 \frac{d^2 c_G}{dz^2} - 2 \left( r - \delta_1 \right) D \left( \frac{dc_G}{dz} \right) \frac{d\delta_1}{dz} \]

\[ = 2 C_G \left[ -1 \frac{1}{a_G k C_{S_o} (r+\delta_2)} + \frac{\ln \left( \frac{r+\delta_2}{r-\delta_1} \right)}{D_e} \right]^{-1} \]

where

\[ D = \text{diffusivity of gas } G \text{ within the pore - includes bulk molecular diffusion and Knudsen diffusion } \left( \frac{12}{c} \right) \]

The second term on the left hand side of equation (III-55) accounts for the change in pore radius (as a result of chemical reaction) along the length of the pore.

The time dependence of the reaction system is determined by a solid material balance which keeps track of the variation of \( \delta_1 \) and \( \delta_2 \) with time. If the total thickness of the product layer \( \delta \left( \delta_1 + \delta_2 \right) \) changes by \( d\delta \) in time \( dt \), then the rate of product formation is given by

\[ 2\pi \frac{\rho_P}{M_P} \left( 1 - \varepsilon_P \right) \left( r + \delta_2 \right) \Delta Z \frac{d\delta}{dt} \left( \frac{\text{moles}}{\text{time}} \right) \text{ (III-56)} \]

where

\[ \rho_P = \text{void-free density of solid product } P \left( \frac{\text{mass}}{\text{l}^3} \right) \]

\[ M_P = \text{molecular weight of solid product } P \left( \frac{\text{mass}}{\text{mole}} \right) \]

\[ \varepsilon_P = \text{porosity of solid product } P \text{ (that is, porosity of the product layer)} \]

Since the rate of product layer formation is equal to \( \frac{a_P R_G}{a_G} \) by stoichiometry, the variation of \( \delta \) with time is
\[
\frac{d\delta}{dt} = \frac{d\delta_1}{dt} + \frac{d\delta_2}{dt} = \frac{a_p M_p}{\rho_p} \frac{C_G}{(r+\delta_2)} \left[ \frac{-1}{a_k k c_s c_s^0 (r+\delta_2)} + \ln \left( \frac{r+\delta_2}{r+\delta_1} \right) \right]_{-1} \tag{III-57}
\]

from
\[
\left( \frac{\rho_s}{M_s} \right) \left[ \pi ((r+\delta_2)^2 - r^2) \Delta Z \right] = \left( \frac{a_p}{a_s} \right) \left( \frac{\rho_p}{M_p} \right) \left[ \pi ((r+\delta_2)^2 - (r-\delta_1)^2) \Delta Z \right] \tag{III-58}
\]

In simplified form (III-58) is
\[
(r-\delta_1)^2 = (1-\gamma)(r+\delta_2)^2 + \gamma r^2 \tag{III-59}
\]
in which
\[
\gamma = \left( \frac{a_p}{a_s} \right) \left( \frac{V_p}{V_s} \right) \frac{1}{(1-\epsilon_p)} \tag{III-60}
\]

\(V_p, V_s\) = void-free molar volumes of P and S, respectively. (\(\frac{\text{m}^3}{\text{mole}}\))

Equation (III-59) may be differentiated for use in equation (II-57)
\[
(r-\delta_1) \frac{d\delta_1}{dt} = (\gamma-1)(r+\delta_2) \frac{d\delta_2}{dt} \tag{III-61}
\]

It is seen that the nature of the change in pore radius with time is dependent upon the value of the expansion factor, \(\gamma\).

As described earlier, if \(\gamma = 1\), \(\delta_1 = 0\); if \(\gamma < 1\), \(\delta_1\) is negative and the pore structure opens; if \(\gamma > 1\), \(\delta_1\) increases with time and the pore structure closes.

The boundary conditions for equations (III-55), (III-57), and (III-61) are
\[
C_G = C_G^0 \quad \text{at } Z = 0 \tag{III-62}
\]
\[ \frac{dC_G}{dz} = 0 \quad \text{at} \quad z = L \quad (III-63) \]

\[ \delta_1 = \delta_2 = 0 \quad \text{at} \quad t = 0 \quad (III-64) \]

where

\[ C_G = \text{concentration of reactant gas G in the bulk gas surrounding the pellet.} \]

The local conversion of solid reactant, \( X \), and average conversion for the entire pore, \( \bar{X} \), are functions of \( \delta_1 \) and \( \delta_2 \).

\[ X = 1 - \frac{\lambda^2 - (r+\delta_2)^2}{\lambda^2 - r^2} \quad (III-65) \]

\[ \bar{X} = \frac{1}{L} \int_0^L \left[ 1 - \frac{\lambda^2 - (r+\delta_2)^2}{\lambda^2 - r^2} \right] dz \quad (III-66) \]

Ramachandran and Smith applied this model to two reaction systems - one in which the pore structure opens and one in which the pores close. The data of Krasuk and Smith [31] on the reduction of NiO with CO \( (\gamma = 0.658) \) were used to examine the single-pore model predictions for a pore-opening reaction system. The measured and predicted pore size after reaction compared well. Also, the model predicted closely the experimentally reported time-conversion behavior.

Data for the reaction of CaO with SO\(_2\) and O\(_2\) \( (\gamma = 3.08) \) reported by Hartman and Coughlin [28] were chosen to test the model in a pore-closing situation. The model predictions follow closely the experimental data in the early stages of the reaction. In one particular case, the asymptotic conversion predicted by the single-pore model was 46% compared to the experimental maximum of 37%. The authors
feel that the disagreement between model and experimental asymptotic conversions may be the result of other structural changes such as sintering.

Chrostowski et al. [33] have presented a single-pore model similar to that of Ramachandran and Smith's discussed above. However, Chrostowski et al. allowed for variation of the pore diffusion coefficient with changing pore radius. Unfortunately, when they applied their model to the experimental data of Hartman and Coughlin [28], agreement was much less favorable than that of Ramanachandran and Smith's model [31] applied to the same data.

Ulrichson et al. [34] have also published a modification of the single-pore model. They extended the model of Chrostowski et al. [33] to include the effect of bulk flow and reversible reactions of the type depicted in equation (III-1). Both effects were shown to be significant in the chlorination of magnesia (MgO). When bulk flow and reversible effects were ignored, no realistic combination of remaining parameters could be found which would permit adequate prediction of experimental data.

Even when allowing for bulk flow and reversibility their "best fit" case required a 200% increase in the value of the rate constant determined from experimental data. This "best fit" still overpredicted the final conversion. For the experimental data presented reaction "die-off" occurred at a fractional conversion of 15% while the model predicted pore closure at 25% conversion. It is worthy to
note that neither Chrostowski et al. nor Ulrichson et al. accounted for external mass transfer resistance in their models.

The Reaction/Sintering Model of Ramachandran and Smith [35]

This model is based on the grain model concept modified to account for structural changes resulting from reaction and sintering. The authors consider isothermal and non-isothermal conditions. Only the isothermal case will be discussed here.

The reaction is represented by the following: $a_G G(g) + a_S S(s) + a_P P(s) + a_D D(g)$. The pellet is spherical and is made up of microscopic grains of high density, each of which reacts according to the unreacted-core model. The formation of a product layer on the grains can cause the grain size to vary as a result of differences in the stoichiometric coefficients and molar volumes of the reactant and product solids. This change in grain size affects the macroporosity which in turn affects the effective diffusivity. (See Figure III-7 for case in which grains grow with reaction). Sintering also reduces the effective diffusivity by removing pore interconnections.

The following assumptions are made: (1) Pellet radius remains unchanged throughout the reaction; (2) The grains maintain spherical shape throughout the reaction; (3) Sintering alters the diffusivity in macropores but not in the product layer associated with each grain; (4) Only the
Figure III-7. Ramachandran and Smith's Model for case in which grains increase in size with reaction (no sintering)
solid product layer sinters (the reactant solid is assumed not to sinter); (5) Reaction is first order with respect to gas reactant G and solid reactant S; (6) The pseudo-steady state assumption is valid; (7) Equimolar counter-diffusion is assumed.

The rate of reaction of gas reactant G per unit pellet volume is the same as that used in the gas-phase material balance for the standard grain model (equation (III-18)) with the exception that the grain radius \( r'_* \) is replaced by its initial value \( r'_* \) in the cubic term in the denominator:

\[
R_G = \frac{3r'_*^2 (a_G k'_S C_S C_G)}{r'_*^3 [1 - \frac{a_G k'_S C'_S C_G}{D_e} (1 - \frac{r'_*}{r'_S})]}
\]

(III-67)

The gas and solid phase material balance equations are:

\[
\frac{D_e(r)}{r^2} \frac{d}{dr} \left( r^2 \frac{dC_G}{dr} \right) + \frac{3a_G r'_*^2 k'_S C'_S C_G}{r'_*^3 [1 - \frac{a_G k'_S C'_S C_G}{D_e} (1 - \frac{r'_*}{r'_S})]}
\]

\[
= 0
\]

(III-68)

\[
\frac{dr'_C}{dt} = \frac{a_S k'_S C_G}{[1 - \frac{a_G k'_S C'_S C_G}{D_e} (1 - \frac{r'_*}{r'_S})]}
\]

(III-69)

where

\[ r = \text{radial coordinate within the pellet (1)} \]

\[ D_e(r) = \text{effective diffusivity of gas reactant G. Shown here as a function of pellet radial position. The term } (dD_e(r)/dr) \]

\[ (dC_G/dr) \text{ is not present in equation (III-68) because an order of magnitude analysis showed that it was negligible compared to the other terms in the equation (1^2/t).} \]
a_s = stoichiometric coefficient for solid reactant S.

The change in grain radius is given by

\[(r_s' - r_c') = \gamma (r_s^3 - r_c^3)\]  (III-70)

where

\[\gamma = \left( \frac{a_P}{-a_S} \right) \left( \frac{V_P}{V_S} \right) \left( \frac{1}{1-\varepsilon_P} \right)\]  (III-71)

and

\[V_P, V_S = \text{molar volumes of solid product P and solid reactant S, respectively (moles/1^3)}\]

\[\varepsilon_p = \text{porosity of product solid P.}\]

\[\gamma\] determines the change in the grain size due to reaction here in the same fashion as it did for Georgakis et al. [30] and also as it did for the pore size in the single-pore model and is mathematically identical.

The authors cite experimental evidence [36] that sintering causes a larger decrease in \(D_e\) that can be accounted for by porosity changes only. It is believed that sintering also removes some pore interconnections. The following relation was used to predict \(D_e\)

\[D_e = \frac{D}{g(\phi)} \{1 - (1-\varepsilon) \left( \frac{r_s'}{r_s^3} \right) \} (1 - \phi)^2\]  (III-72)

where

\[g(\phi) = \text{correlation of Kim and Smith [36] which gives the fractional increase in tortuosity due to removal of pore interconnections resulting from sintering.}\]

\[\phi = \text{Fraction of pores removed, assumed to vary with time according to an activated first order process}\]
\[
\frac{d\phi}{dt} = (1 - \phi) A_\phi \exp \left[ \frac{-E_s}{R_g(T - T_C)} \right] \quad (\text{III-73})
\]

in which \(E_s\) = the sintering activation energy, \(T_C\) = Tamman temperature, \(T\) = temperature, \(A_\phi\) = frequency factor for sintering.

\[D = \text{diffusion coefficient (combination of molecular and Knudsen diffusivities).}\]

Equation (III-72) gives the variation of \(D_e\) as a result of structural changes due to reaction and sintering.

The average conversion of solid reactant \(S\) is calculated by

\[X_s = 1 - \int_0^{r_s} \left( \frac{r_c'}{r_s} \right)^3 r^2 \, dr \quad (\text{III-74})\]

where \(r_s\) = pellet radius (1). The boundary and initial conditions for solution of this model are

\[D_e \left( \frac{dC_G}{dr} \right)_{r_s} = k_m \left( C_{G_0} - C_{G_s} \right) \text{ at } r = r_s \quad (\text{III-75})\]

\[\frac{dC_G}{dr} = 0 \quad \text{at } r = 0 \quad (\text{III-76})\]

\[r_c' = r_s' \text{ and } \phi = 0 \quad \text{at } t = 0 \quad (\text{III-77})\]

where

\[C_{G_0}, C_{G_s} = \text{concentration of gas reactant } G \text{ in bulk phase and at pellet surface, respectively (} \text{moles} \frac{1}{l^3} \text{)}\]

The solution of equations (III-68), (III-69), (III-70), (III-72), and (III-73) with the above boundary and initial conditions gives the time-conversion relationship for the pellet as a whole. The influence of \(\gamma\) is similar to that found in the single-pore model [31]. The time required for a given conversion is reduced as \(\gamma\) is reduced. High values
of $\gamma$ may lead to asymptotic conversions less than 100\% due to pore closure. The effect of sintering is to cause a decrease in both the rate of conversion and the maximum conversion attained. For a case in which sintering causes the tortuosity factor to increase by a factor of 2.5 and $\gamma = 0.5$, sintering dominates and asymptotic conversions less than 100\% occur.

The data of Calvelo and Smith [37] for the reaction $\text{UO}_2(3) + 4\text{HF}(g) \rightarrow \text{UF}_4(s) + 2\text{H}_2\text{O}(g)$ was used to test the model. $\gamma$ for this reaction is 1.7; the effects of sintering were assumed negligible since the reaction temperature was around 700\°K and UF$_4$ melts above 1230\°K. Thus, structural changes were basically the result of density changes. Agreement was good between the experimental time-conversion data and the model-predictions. Of particular interest was the fact that this model-predicted the asymptotic maximum conversion of 63\% observed experimentally for this reaction system.

The Model of Ranade and Harrison [38]

This model is based on the grain model with modifications to account for structural changes due to sintering and reaction. The key parameter is surface area which is presumed to change due to sintering and reaction, and is correlated with conversion ($X$) and time ($t$).

The chemical reaction is represented by $a_G \text{G}(g) + a_S \text{S}(s) \rightarrow a_P \text{P}(s) + a_D \text{D}(g)$. The solid reactant $S$ is assumed
spherical and is composed of microscopic spherical grains of high density each of which reacts according to the unreacted core mechanism. The model accounts for changes in grain size by allowing for changes in pellet specific surface area, $A_g(x,t)$, and grain density, $\rho'(X)$, both of which determine grain radius, $r'_s$, via

$$r'_s = \frac{3}{A_g(x,t)\rho'(X)}$$  \hspace{1cm} (III-78)

The process of sintering is conceived as causing adjacent grains to combine, thereby, increasing the size of the grains and reducing their number. The new (larger) grains retain their spherical shape and, for mathematical convenience, the unreacted cores from the smaller grains remain at the center of the larger grains. (See Figure III-8). Thus it is possible for the unreacted core for some grains to grow with time initially (due to formation of larger grains). However, this core growth will be reversed as the reaction proceeds and the unreacted solid grain core is consumed.

The following assumptions are made in the model development: (1) Pellet radius and spherical shape are maintained; (2) Isothermal conditions exist; (3) Intrinsic chemical reaction rate is first order with respect to gas concentration; and (4) Pseudo-steady state approximation is valid.

The reaction rate of gaseous reactant G per unit pellet volume is
Figure III-8. Modified Grain Model of Ranade and Harrison
\[ R_G = \frac{3r_c^2 \left( a_G k'_S C_S C_G \right)}{r' \left( 1 - \frac{a_G k'_S C_S C_G r'_{RC}}{D_e} (1 - \frac{r'}{r_0}) \right)} \]  

(III-79)

where

\[ r'_C, r'_S = \text{unreacted core radius for grain and the grain radius, respectively (1)} \]

\[ a_G = \text{stoichiometric coefficient for gaseous reactant G} \]

\[ C_{S_0} = \text{initial solid reactant concentration (moles)} \]

\[ C_G = \text{reactant gas concentration within the pellet (moles)} \]

\[ k_s = \text{intrinsic reaction rate constant (1/moles-t)} \]

\[ D'_e = \text{effective diffusivity of reactant gas G in the product layer of the grains (1^2/t)} \]

Equation (III-79) is used to formulate the following material balance equations from the grain model:

\[ \frac{D_e}{r^2} \frac{d}{dr} \left( r^2 \frac{dC_G}{dr} \right) + \frac{3a_G k'_S C_S C_G r'^2_{RC}}{r'_s \left( 1 - \frac{a_G k'_S C_S C_G r'_{RC}}{D_e} (1 - \frac{r'}{r_0}) \right)} = 0 \]  

(III-18)

\[ \frac{d}{dt} \frac{d}{dr} c_C = \frac{a_g k'_S C_G}{\left( 1 - \frac{a_G k'_S C_S C_G r'_{RC}}{D_e} (1 - \frac{r'}{r_0}) \right)} \]  

(III-22)

where

\[ r = \text{pellet radial coordinate (1)} \]

\[ a_s = \text{stoichiometric coefficient for solid reactant S} \]
t = time

\( C'_{S_0} \) = concentration of reactant solid within grain (theoretical molar density)

The boundary and initial conditions for equations (III-18) and (III-22) are

\[
\frac{dC_G}{dr} = k_m (C_{G_0} - C_G) \quad \text{at } r = r_s \quad \text{(III-19)}
\]

\[
\frac{dC_G}{dr} = 0 \quad \text{at } r = 0 \quad \text{(III-20)}
\]

\[
r'_C = r'_s \quad \text{at } t = 0 \quad \text{(III-23)}
\]

Local (X) and overall (\( \bar{X} \)) conversions are given by

\[
X = 1 - \left(\frac{r'_C}{r'_s}\right)^3 \quad \text{(III-24)}
\]

and

\[
\bar{X} = \frac{3}{r^3} \int_0^{r_s} r^2 \left[ 1 - \left(\frac{r'_C}{r'_s}\right)^3 \right] \, dr \quad \text{(III-25)}
\]

Structural changes are incorporated by the addition of variable specific surface area due to sintering and chemical reaction. Surface area is assumed to vary from sintering alone (that is, for a non-reacting solid) by

\[
\frac{A_i(t) - A_{e_i}}{A_{o_i} - A_{e_i}} = -k_j t \quad \text{(III-80)}
\]

where

\( A_{e_i}, A_{o_i} \) = equilibrium and initial specific surface area, respectively (i=reactant or product) \((1^2/\text{mass})\)

\( A_i(t) = \) surface area at time \( t \) \((1^2/\text{mass})\)

\( k_j \) = sintering rate constant \((\text{time}^{-1})\)

Specific surface area is allowed to vary with local fractional conversion \( X \) (for the case of no sintering) by
\[
\frac{A(X) - A_P}{A_R - A_P} = (1-X)^a
\]  

(III-81)

where

\[A(X) = \text{ specific surface area of solid at conversion } X (1^2/\text{mass})\]

\[A_R, A_P = \text{ specific surface area of solid reactant and product, respectively (1^2/\text{mass})}\]

\[a = \text{ empirical constant (obtained from experimental data)}\]

The combined effects of sintering and reaction on the specific surface area are determined from

\[
\frac{A_S(X,t) - A_P(t)}{A_R(t) - A_P(t)} = (1-X)^a
\]  

(III-82)

The time variation of \(A_R\) and \(A_P\) is obtained from equation (III-80). It is assumed that the rate of sintering is the same for reactant and product solids, therefore a single value for \(k_j\) is sufficient to describe sintering for this system.

The grain density is permitted to vary linearly with local fractional conversion via

\[
\rho'(X) = \rho_S + (\rho_P - \rho_S)X
\]  

(III-83)

where

\[\rho_S, \rho_P = \text{ true densities of solid reactant } S \text{ and solid product } P, \text{ respectively, ( moles/m}{\text{l}}^3 ),\]

Since \(X\) is a function of time and radial position in the pellet, both time and radial variation of \(\rho'\) are considered. The grain radius, \(r'_g\), varies with sintering and conversion because \(r'_g\) is a function of the changing specific surface area \(A_S(X,t))\) and the changing grain density \((\rho'(X))\) via equation (III-85)
The effective diffusivity, $D_e$, was assumed to vary with the pellet porosity, $\varepsilon(\bar{X})$, via

$$D_e = D_G (\varepsilon(\bar{X}))^2$$  \hspace{1cm} (III-84)

where

$$D_G = \text{proper combination of molecular and Knudsen diffusivities} \left( \frac{1}{\text{t}} \right)$$

The variation of pellet porosity with overall conversion is given by

$$\varepsilon(\bar{X}) = \varepsilon_S + (\varepsilon_P - \varepsilon_S)\bar{X}$$  \hspace{1cm} (III-85)

where

$$\varepsilon_S, \varepsilon_P = \text{porosity of unreacted pellet and completely reacted pellet, respectively.}$$

Thus, since $\bar{X}$ varies only with time, $D_e$ and $\varepsilon(\bar{X})$ vary only with time.

The authors state that the most significant property of their model is the prediction of reaction "die-off" without the necessity of zero porosity. The following example is for a fast reaction (that is, the system is initially controlled by pellet diffusion resistance). For a particular set of parameters, the standard grain model predicts 98% overall conversion after seven dimensionless time steps. The modified grain model, for a case in which sintering is slow, predicts an overall conversion of 80% for the same dimensionless time and 98% conversion is not predicted until approximately eleven dimensionless time steps. The decreased rate of conversion is caused by decreasing pellet porosity and increased grain diffusion resistance resulting
from reaction. However, for this case reaction "die-off" is not predicted (that is, conversion continued to rise slowly with time). When the sintering constant is raised, the model predicts a slower rate of reaction to an asymptotic overall conversion level of 70%. Thus, reaction "die-off" is predicted for the case of combined reaction and sintering because of the increased grain diffusion resistance.

Caillet [39] has also modified the grain model to allow for variable solid properties due to reaction and sintering. As in the model of Ranade et al. discussed above the key solid property monitored in the model is specific surface area of the solid. This model differs from that of Ranade by the manner in which the specific surface area varies with conversion and sintering. Caillet expressed specific surface area \( S \) as a function of time, temperature, and conversion via

\[
S = \frac{-a \frac{dM}{dt} \times S_p(t, T) \times + S_s(t, T) \times (1 - X)}{\frac{dM}{dt} \times X + (1 - X)}
\]

where \( S_p(t, T) \) and \( S_s(t, T) \) are the specific surface areas of the product and reactant solids, respectively. \( S_p(t, T) \) and \( S_s(t, T) \) are allowed to vary due to sintering with time \( t \) and temperature \( T \) via the power law expressions

\[
\frac{dS_p}{dt} = -B_p(T) \times S_p(t, T)^{b_p(T)} \quad (III-87)
\]

and

\[
\frac{dS_s}{dt} = -B_s(T) \times S_s(t, T)^{b_s(T)} \quad (III-88)
\]
in which the constants $B_s(T)$, $B_p(T)$, $b_s(T)$, and $b_p(T)$ must be determined at each temperature via fit to experimental sintering data.

This model was compared to data collected for the reaction

$$\text{MnO}(s) + \text{H}_2\text{S}(g) \rightarrow \text{MnS}(s) + \text{H}_2\text{O}(g)$$  

(III-89)

at temperatures 200° to 800°C. In all cases, except at 500°C, Caillet's model exhibited far better predictive capabilities than the constant property grain model. At 500°C the agreement with experimental data was approximately equal for the two models.
Literature Cited


The equipment and procedure used to collect experimental 
data for the reaction 

\[ \text{CaO(s)} + 2\text{NO}_2(g) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{Ca(NO}_3)_2(s) \] 

are described in this chapter. First, the thermodynamic 
equilibrium of the reactant gas mixture is analyzed. This 
is followed by a description of the experimental apparatus 
and materials used to collect the kinetic data for reaction 
(IV-1). Next the experimental procedure employed is out­
lined and the auxiliary equipment used is described. The 
chapter concludes with a brief discussion of the experi­
mental difficulties encountered.

A) Thermodynamic Equilibrium of Reactant Gas Mixture

The gas mixture fed to the experimental reactor con­
sisted of molecular nitrogen (N\text{\textsubscript{2}}), molecular oxygen (O\text{\textsubscript{2}}), 
and nitrogen dioxide (NO\text{\textsubscript{2}}). The purpose of this thermo­
dynamic analysis was to determine to what extent reactant 
gas decomposition could occur under simulated reactor 
conditions. Thermodynamically, it is known that N\text{\textsubscript{2}} and O\text{\textsubscript{2}} 
are favored with respect to NO\text{\textsubscript{2}}, however, kinetic limita­
tions render the decomposition of NO\text{\textsubscript{2}} to molecular N\text{\textsubscript{2}} and O\text{\textsubscript{2}} 
egligible at the temperatures of this study [1]. This 
decomposition reaction was not permitted in the thermodynamic 
analysis. Therefore, as in Chapter II, N\text{\textsubscript{2}} was replaced by
elemental hydrogen ($H_2$) in the thermodynamic calculations using the free-energy minimization computer program - CHEMEQ. The only gas phase equilibrium of interest to this research was that which existed between $NO_2$, $NO$, and $O_2$,

$$NO_2 \rightleftharpoons NO + \frac{1}{2}O_2 \quad (IV-2)$$

Thus, the only species allowed in the thermodynamic analysis were gaseous $NO_2$, $NO$, $O_2$, and an inert ($H_2$).

In all CHEMEQ runs, the initial concentration of $NO_2$ was 2 mole per cent. The pressure was fixed at one atmosphere and the temperature was varied from 150°C to 550°C. All experimental kinetic data was collected within this temperature range.

The results of the equilibrium calculations are presented in Figure IV-1. For a feed composition of 2% $NO_2$ - 98% Inert ($H_2$), curve A shows that decomposition of $NO_2$ (via equation (IV-2)) may begin around 100°C and be 50 per cent complete near 300°C; 75 per cent decomposition is possible by 375°C. With the addition of five moles of $O_2$ per mole of $NO_2$ (curve b) to the feed (Feed composition = 2% $NO_2$ - 10% $O_2$ - 88% Inert ($H_2$)), $NO_2$ decomposition cannot begin until approximately 175°C. At 300°C only 15 per cent of the $NO_2$ can decompose and 50 per cent decomposition is not possible until 400°C. Since most experimental data was collected within the temperature range 200°C to 450°C and with a $O_2/NO_2$ ratio between 4 and 5, $NO_2$ decomposition could be occurring in the reactor. However, it is unlikely that equilibrium is reached at low temperatures due to kinetic limitations.
Figure IV-1. Equilibrium Concentration of NO₂ as a Function of Temperature

Curve a - \( \frac{0 \text{ moles of O}_2}{\text{mole of NO}_2} \) in feed

Curve b - \( \frac{5 \text{ moles of O}_2}{\text{mole of NO}_2} \) in feed
Since gas analysis was not possible it was assumed that decomposition of NO₂ did not occur. It is understood that this assumption can lead to problems in data analysis. A discussion of such problems will be presented in a subsequent chapter.

B) Major Experimental Apparatus - The TGA

Kinetic studies were carried out using a modified Columbia Scientific Instruments (CSI) Model 1000 B Thermogravimetric Analysis Instrument (TGA). The TGA lends itself nicely to the study of gas-solid reactions since the conversion of the solid reactant (that is, CaO) to solid product (that is, Ca(NO₃)₂) results in a weight change (increase) which is directly proportional to the fractional conversion. The TGA provides a continuous monitor of sample weight as a function of time at various reaction conditions.

The TGA reactor system consisted of rotameters, a Cahn RG electrobalance, a water-cooled electric furnace, a CSI temperature programmer, and a Hewlett-Packard strip chart recorder. The calibrated Matheson rotameters were used to monitor and control gas flows. The electrobalance provided accurate weight measurements while the temperature programmer permitted a linearly increasing (or decreasing) temperature profile or isothermal operation. Temperature and mass were recorded on the Hewlett-Packard strip chart recorder. Table IV-1 presents the TGA reactor system specifications. A schematic diagram of the reactor system is
TABLE IV-I
THERMOGRAVIMETRIC ANALYZER SPECIFICATIONS

TGA: Columbia Scientific Industries Model 1000B, P500

Temperature
Programmer: Isothermal or 1°, 2.5°, 5°, 10°, 50° increase or decrease.

Thermocouple: Chromel-alumel, 316 stainless steel sheath with grounded junction.

Reactor: Quartz tube, 17 mm inside diameter, 250 mm length; water cooled electric furnace.

Balance: Cahn RG Electrobalance

Maximum weight change: 1000 milligrams
Ultimate sensitivity: 0.1 microgram
Precision: 0.2 micrograms

Strip-chart Recorder: Hewlett-Packard Model H45-7100B frame with Model 17504A input module/dual channels)
Chart Speeds: 2 in/sec to 1 in./hr
Chart Span: 5-10 millivolts weight, 0°-1000°C type K thermocouple

Rotameters: Matheson tube 602 - N₂
            Matheson tube 610 - NO₂
            Matheson tube 610A - O₂
given in Figure IV-2. Further details of the apparatus are provided in the instruction manuals [2,3,4,5] and by Gibson [6].

The solid reactant (CaO) was suspended inside the reactor via a nichrome hang down wire attached to the electrobalance. Powdered samples were contained in a 9 mm diameter platinum pan. Pellet samples were held in a platinum wire cage designed to have a minimal effect on solid-gas mass transfer. Temperature measurement was provided by three shielded chromel-alumel thermocouples placed directly below the solid sample. One thermocouple was connected to the temperature programmer, one to the strip chart recorder, and one to a limit switch which would shut down the furnace if the temperature exceeded a preselected value. The temperature programmer and recorder thermocouples were each calibrated with a high temperature thermometer and a fourth thermocouple independent of the TGA. For each experimental run, the "true" temperature was taken as the calibrated programmer set point temperature.

The bulk of the nitrogen flow (80%) entered through the upper portion of the TGA to protect the balance mechanism from the corrosive reactant gases which entered through a side port above the solid sample. Also, a teflon baffle was placed between the upper balance mechanism and the reactant gas port to further reduce any back diffusion of reactant gases. The flow of $N_2$ from the upper balance mixed with the reactant gases and the mixture then flowed downward past the
Figure IV-2. TGA Reactor System
CaO suspended in the reactor. All gases exiting the TGA were vented to a hood for safety purposes.

Two modifications to the TGA reactor system were made for the present research. The first was the installation of a thermocouple positioner located beneath the hang down tube and attached to the TGA support stand. The need for exact and reproducible positioning of the thermocouples became apparent when after several early kinetic runs it was discovered that the thermocouples were not located beneath the solid sample. In fact for one run the thermocouples were actually closer to the reactor wall than to the solid sample. To prevent this, a thermocouple positioner which allowed accurate placement of the thermocouples via four adjusting screws was fabricated and installed.

The second modification was necessitated by the physical properties of NO₂. NO₂ is stored in cylinders as a liquid under its own vapor pressure of about one atmosphere at 70°F (21.2°C). Thus, in order to obtain gaseous NO₂, the NO₂ cylinder was wrapped with electric heat tracing and the cylinder pressure was maintained at 15 psig. The temperature was controlled by a variac connected to the electric heat tracing. Thus gaseous NO₂ was removed from the cylinder. However, since pure NO₂ condenses to a liquid at 21.2°C and 1 atm pressure, liquid NO₂ began to collect in the 316 stainless steel tubing and in the rotameter used to measure NO₂ flow. To prevent NO₂ condensation, the stainless steel tubing (from the NO₂ cylinder to the NO₂
rotameter) and the NO\textsubscript{2} rotameter were wrapped with electric heat tracing (connected to another variac) and were preheated to 56°C prior to each run. Upon exiting the rotameter, the NO\textsubscript{2} was diluted (with N\textsubscript{2} and O\textsubscript{2}) thereby reducing its partial pressure and lowering its condensation temperature. Thus, the electric heat tracing was required only to the gas mixing point.

C) Materials

Nitrogen (99.99% pure) and oxygen (99.9%) were obtained from Louisiana State University plant stores. Chemical grade nitric oxide (99.0%) and nitrogen dioxide (99.5%) were purchased from Matheson Gas Products Company. Typical contaminants of the Matheson gases are given in Table IV-2.

Analytical grade CaO powder obtained from Mallinckrodt Chemical Works were used in this study. The impurities in the CaO powder provided by Mallinckrodt appear in Table IV-3. The 100 to 200 mesh cut of the powder was used for all runs. The BET specific surface area of this powder was found to be 20.52 m\textsuperscript{2}/gr.

CaO pellets utilized in the present study were manufactured in this laboratory from the CaO powder described above. The manufacturing process involved mixing distilled water with the powder to form a moist paste of Ca(OH)\textsubscript{2}. This paste was rolled into small spherical pellets by hand. These pellets were then dried and stored in a laboratory oven maintained at 110°C. The dried pellets were composed
### TABLE IV-2

**Typical Contaminants of Matheson Gases [7]**

<table>
<thead>
<tr>
<th>Gas</th>
<th>Contaminant</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO₂</td>
<td>Chloride (as NOCl) - nil</td>
</tr>
<tr>
<td></td>
<td>H₂O - .06 mole %</td>
</tr>
<tr>
<td></td>
<td>Particulate - 1.0 milligram per liter</td>
</tr>
<tr>
<td>NO</td>
<td>CO₂ - .20 mole %</td>
</tr>
<tr>
<td></td>
<td>N₂ - .50 mole %</td>
</tr>
<tr>
<td></td>
<td>N₂O - .05 mole %</td>
</tr>
<tr>
<td></td>
<td>NO₂ - .05 mole %</td>
</tr>
</tbody>
</table>
### TABLE IV-3

**Maximum Limits of Impurities in Mallinckrodt CaO Powder**

<table>
<thead>
<tr>
<th>Impurity</th>
<th>Mole Per Cent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloride (Cl)</td>
<td>.005</td>
</tr>
<tr>
<td>Heavy metals (as Pb)</td>
<td>.010</td>
</tr>
<tr>
<td>Iron (Fe)</td>
<td>.100</td>
</tr>
<tr>
<td>Magnesium and Alkali salts (as MgO)</td>
<td>1.000</td>
</tr>
<tr>
<td>Nitrate (NO₃⁻)</td>
<td>0.50</td>
</tr>
<tr>
<td>Sulfur Compounds (as SO₄²⁻)</td>
<td>.100</td>
</tr>
<tr>
<td>Insoluble in HCl and NH₄OH Ppt.</td>
<td>1.5</td>
</tr>
<tr>
<td>Loss on Ignition</td>
<td>5.0</td>
</tr>
</tbody>
</table>
of \( \text{Ca(OH)}_2 \) since the oven temperature of 110°C was not sufficient to cause dehydration to \( \text{CaO} \). This dehydration step was carried out in the TGA. As will be pointed out in the procedure section, the dehydration step was carried out for each run (pellet and powder) since the \( \text{CaO} \) sorbed water from the atmosphere. The specific surface area of the untreated pellets (that is, \( \text{Ca(OH)}_2 \) pellets) was determined to be 10.85 \( \text{m}^2/\text{gr} \). The surface area of these pellets following dehydration to \( \text{CaO} \) was found to be 25.52 \( \text{m}^2/\text{gr} \).

D) Procedure

Prior to each TGA run, the electrobalance was recalibrated according to the method prescribed in the operating manual [2]. During the recalibration period, the \( \text{NO}_2 \) cylinder pressure was raised and maintained at 15 psig by heating in the manner discussed earlier. Also during the calibration period, the \( \text{NO}_2 \) stainless steel tubing (through which approximately 30 cc/min of nitrogen was flowing) and the \( \text{NO}_2 \) rotameter were preheated at 56°C.

Following the calibration, a solid previously weighed on a Mettler balance was placed in the TGA. (The diameter of pellet samples was measured to the nearest ten thousandth of an inch with an Ames thickness meter prior to placement in the TGA - true diameter was taken as the average of four measurements.) After placing the solid sample in the TGA, the TGA reactor system was sealed and the solid (powder or pellet) was weighed to the nearest one hundredth of a
milligram on the electrobalance. The TGA weight was assumed to be the "true" initial weight of the sample.

The Mettler and TGA weight measurements agreed closely. Typically this agreement was within ± 0.10 milligrams. Differences of this magnitude were considered attributable due to losses during transport of the pellet from the Mettler balance to the TGA sample holder. (When differences much greater than ± 0.10 milligrams occurred, the TGA was recalibrated and the two measurements were repeated).

The thermocouples were positioned and held in place beneath the solid sample via the thermocouple positioner described earlier. The system was then flushed with N₂ for 30 minutes; during this period the flows of the other gases were set and bypassed to a vented hood.

For powder runs, the sample was heated at 20°C/min to 600°C (Ca(OH)₂ decomposition begins at 580°C) and the sample was allowed to attain constant weight at 600°C. The CaO powder did not contain significant quantities of Ca(OH)₂ since the total weight loss experienced by the powder during dehydration was less than that for conversion of Ca(OH)₂ to CaO (24.3%). Thus, a majority of the water is believed to be bound moisture. Weight loss began at 95°C and was complete by 225°C.

For pellet runs, practically all of the sample was Ca(OH)₂, initially. Early dehydration runs revealed that at 600°C the dehydration of Ca(OH)₂ proceeded at a slow but constant rate and long times (40-60 minutes) were required
to attain constant weight. Thus, in subsequent pellet runs, the dehydration step consisted of heating at \( \approx 180^\circ C/\text{min} \) to 720°C at which temperature the sample attained constant weight in approximately 15-25 minutes depending on the sample size. For pellet samples, weight change began at around 200°C; a rapid weight change occurred near 600°C; the total weight change was complete after several minutes at 720°C. Most pellet runs averaged a 30-33% weight loss during dehydration indicating that some of the weight loss may be attributed to loss of bound water.

Upon completion of the dehydration step, the temperature programmer was dialed to the desired set point and time was allowed for the system to reach the desired temperature. When thermal equilibrium was reached, the reactive gases were switched from the vented hood to the TGA reactant gas port. A delay of 30 seconds to a minute occurred before the reactant gases reached the solid sample. The correct "time zero" for the reaction was apparent from the onset of mass change of the solid sample signifying that the reaction had begun. A typical TGA trace of mass change versus time is shown in Figure IV-3.

Due to aerodynamic drag effects, the true weight of the sample could not be read directly from the TGA trace during the course of the reaction. The sample weight at any time was the "true" TGA initial weight measured earlier under no flow plus the weight change indicated on the TGA trace.
Figure IV-3. Typical Thermobalance Response Curve
The experimental run was considered complete when the solid weight ceased to change with time. The reactant gases were then switched to vent and shut off. The temperature programmer was set to zero and the reactor cooled to ambient temperature. All reactant gas rotameters and the NO2 stainless steel tubing were purged with N2 during the cool down period. When the reactor had cooled to ambient temperature, the solid sample was removed from the TGA and placed in a sealed vial. Preparations for the next run were made. A small flow of N2 (30 to 40 cc/min) was passed through the TGA system continuously between runs.

The overall temperature range studied was 150° to 550°C. The weight of the dehydrated powdered samples ranged from 1.30 mg to 38.56 mg. The weight of the dehydrated pellet samples ranged from 6.68 mg to 46.04 mg. The partial pressure of NO2 was varied from .005 atm to .018 atm. The reactor was always operated at a pressure of one atmosphere. The total volumetric flow rate of combined gas past the solid varied from 225 cc/min to 1440 cc/min (STP).

E) Auxiliary Equipment

It was necessary to know the surface area of the solid reactant (CaO) to complete the kinetic study of the CaO-NO2-O2 reaction system. A Perkin-Elmer Model 212 D sorptometer was used to provide the specific surface area of the CaO reactant (powder and pellet) used in this research.
This sorptometer uses the continuous flow method in which the quantity of a gas \((N_2)\) adsorbed by a solid (at liquid nitrogen temperature) from a carrier gas (He) is measured as a function of the partial pressure of \(N_2\). From this information, the specific surface area of the solid is calculated from the Brunauer-Emmett-Teller (BET) equation, modified for present research:

\[
\frac{P}{V_{ads} (P_o - P)} = \left[ \frac{C^{-1}}{V_m c} \right] \frac{P}{P_o} + \frac{1}{V_m c} \quad \text{(IV-3)}
\]

where

\[
p = \text{partial pressure of nitrogen, force} \ 1^{-2}
\]

\[
P_o = \text{saturation pressure of nitrogen over the solid sample at the temperature of the liquid nitrogen, force} \ 1^{-2}
\]

\[
V_{ads} = \text{total volume of nitrogen at standard temperature and pressure on the surface of the solid sample,} \ 1^3
\]

\[
c = \text{constant expressing net adsorption energy}
\]

\[
V_m = \text{volume of nitrogen at standard temperature and pressure adsorbed when the entire adsorbent surface is covered with a monomolecular layer,} \ 1^3
\]

Since parameters \(V_m\) and \(c\) are constant for a given system, Equation (IV-3) may be rewritten as

\[
\frac{P}{V_{ads} (P_o - P)} = \alpha \left( \frac{P}{P_o} \right) + \beta \quad \text{(IV-4)}
\]

where

\[
\alpha = \frac{C^{-1}}{V_m c} \quad \text{(IV-5)}
\]

\[
\beta = \frac{1}{V_m c} \quad \text{(IV-6)}
\]
α and β were determined by using a linear least squares method to find the best straight line through three data points in a specific experiment. Utilizing the definition of α and β, it follows that

\[ V_m = \frac{1}{\alpha + \beta} \]

Once \( V_m \) was known, the total surface area of the sample was determined from:

\[ S_T = V_m S_o \]  

(IV-7)

where

- \( S_T \) = total surface area of sample, \( 1^3 \)
- \( S_o \) = cross-sectional area covered by a monolayer of nitrogen per unit volume at standard temperature and pressure, \( 1^2 1^{-3} \)

In the present study, \( p_o \) was assumed constant at 101.3 kPa so that \( S_o \) was constant at 4.3721 m²/ml (STP). The specific surface area was then given by:

\[ A_s = \frac{S_T}{m} = \frac{V_m (4.3721)}{m} \]  

(IV-8)

where

- \( A_s \) = specific surface area of sample, \( m^2/\text{gr} \)
- \( m \) = mass of sample, \( \text{gr} \)
- \( V_m \) = ml (STP)

The results of the surface area measurements for CaO powder, Ca(OH)₂ pellets, and CaO pellets appear in Table IV-4.

F) Experimental Difficulties

The corrosive nature of NO₂ causes several problems. As mentioned earlier, it was necessary to heat trace all
<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface Area (m²/gr)</th>
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</thead>
<tbody>
<tr>
<td>CaO Powder</td>
<td>20.52</td>
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<tr>
<td>Ca(OH)₂ Pellets</td>
<td>10.85</td>
</tr>
<tr>
<td>CaO Pellets</td>
<td>25.62</td>
</tr>
</tbody>
</table>
equipment (stainless steel tubing and rotameter) through which pure NO₂ flowed. Prior to the use of heat tracing, liquid NO₂ (N₂O₄) collected in the tubing and rotameter. The corrosive liquid NO₂(N₂O₄) dissolved the Viton packing in the rotameter and thus required repacking of the rotameter. Care was taken thereafter to ensure that the rotameter was preheated to approximately 56°C prior to passing NO₂ through it.

The high temperature corrosive nature of gaseous NO₂ resulted in deterioration of two thermocouples during the course of this research. The loss of the programmer thermocouple became apparent when temperature control became poor (that is, the furnace voltage oscillated wildly). Failure of the recorder thermocouple was recognized when the temperature indicated on the recorder failed to respond to changes in the programmer set point. In both cases, visual inspection of the tip of the malfunctioning thermocouple revealed severe corrosion. New thermocouples were installed and calibrated, and the experimental program was continued.

The reactor furnace failed twice during the experimental phase of this research due to melted electrical connections. The furnace was dismantled, repaired with high temperature electrical connectors, reassembled and put back in service.

In an effort to decrease external mass transfer resistance, the total gas flow rate past the solid sample was increased. However, at high flow rates, turbulence caused
the solid sample to swing violently in the reaction chamber (which in turn produced severe noise on the recorder mass trace). Thus, turbulence placed an upper limit on the permissible flow rate past the solid sample.
Literature Cited


CHAPTER V
EXPERIMENTAL RESULTS

Collection of data for the reaction between spherical CaO particles and NO\textsubscript{2} and O\textsubscript{2} constituted the bulk of the experimental work for this research. The reaction studied was

\[
\text{CaO(s)} + 2\text{NO}_2(g) + \frac{1}{2}\text{O}_2(g) + \text{Ca(NO}_3)_2(s)
\]  
(V-1)

Pellet data for this reaction will be presented first. The modelling efforts discussed in a later chapter were all based on these experimental results.

Next, the data for reaction (V-1) between CaO powder and NO\textsubscript{2} and O\textsubscript{2} will be presented. This work was an unsuccessful attempt to measure the intrinsic chemical reaction rate for this reaction. It is included here to further illustrate the phenomenon of reaction "die-off".

All reaction data was collected on the thermogravimetric analyzer (TGA) described in Chapter IV. Due to a difference in molecular weights, conversion of CaO to Ca(NO\textsubscript{3})\textsubscript{2} results in a weight increase. The TGA monitors this weight increase which is directly proportional to the fractional conversion. Fractional conversion of CaO to Ca(NO\textsubscript{3})\textsubscript{2} is calculated from the following equation:

\[
\bar{X}_t = \frac{W_t - W_0}{W_0} \left[ \frac{\text{MW}_S}{a_P \text{MW}_P - a_S \text{MW}_S} \right] 
\]  
(V-2)

where

\[
\bar{X}_t = \text{overall fractional conversion of time } t
\]
\[ W_t = \text{weight of sample on TGA at time } t \ (\text{mg}) \]
\[ W_0 = \text{weight of sample on TGA at beginning of run (mg)} \]
\[ W_0^* = \text{true initial weight of sample on TGA, measured before TGA is brought to reaction conditions (mg)} \]
\[ MW_s, MW_p = \text{molecular weights of solid reactant and solid product, respectively (56.08 mg CaO/mg mole CaO, 164.09 mg Ca(NO}_3)_2/mg mole Ca(NO}_3)_2 \]
\[ a_s, a_p = \text{stoichiometric coefficients for solid reactant and solid product, respectively (} a_s = a_p = 1.0 \]

Substitution of numerical values into equation (V-2) yields

\[ R_t = 0.5192 \left( \frac{W_t - W_0}{W_0^*} \right) \quad (V-3) \]

A typical TGA trace is shown in Figure V-1. The slope of this curve at any time is directly proportional to the global (overall) rate of reaction. Application of reaction models requires that as many as four resistances be considered. These include transport of reactant gas from the bulk gas phase to the surface of the solid (external mass transfer), diffusion of the reactant gas through the pores of the solid reactant (pore diffusion), diffusion of reactant gas through the product layer (product layer diffusion), and the intrinsic chemical reaction. The product layer diffusion resistance can be considered negligible if only initial global rates are used since under these conditions the amount of product material present is small.

If only the initial, approximately linear, portion of the curve in Figure V-1 is used, the initial global rate of reaction \( R_{G_i} \) may be calculated from...
Figure V-1. Typical TGA Response Curve.
where

\[ R_{gi} = \frac{(\frac{a_G}{a_s})(\frac{d w}{d t})_0}{w_o A_s \left[ \frac{a_p}{a_s} (MW_p - MW_s) \right]} \]

(V-4)

\( R_{gi} \) = initial global rate of reaction based on the total available surface area of solid reactant (mg moles NO\(_2\)/cm\(^2\) min)

\( a_G \) = stoichiometric coefficient for reactant gas from equation (V-1) \((a_G = a_{NO_2} = 2.0)\)

\( (\frac{d w}{d t})_0 \) = initial rate of change of mass - initial slope of curve in Figure V-1 (mg/min)

\( A_s \) = initial specific surface area of solid reactant CaO \((A_s = 205.2 \text{ cm}^2/\text{mg for CaO powder, } A_s = 255.2 \text{ cm}^2/\text{mg for CaO pellets})\).

Another reason for concentrating upon the initial global rates is that rates calculated via equation (V-4) are based on unit surface area of the reactant solid; this surface area decreases with time as the solid reactant is converted to product. Thus, the only realistic rate per unit surface area which can be obtained from experiment is the initial global rate since the surface area of the solid is known accurately only at the beginning of the reaction.

A) Experimental Results for CaO Pellets

The results of the experimental runs with spherical CaO particles and NO\(_2\) and O\(_2\) are presented in this section. The effect of temperature, concentration of gas species, total
gas flow rate, and pellet size on conversion are reported. The separate effects of mass transfer, pore diffusion, and intrinsic surface reaction are analyzed using the initial rate data. Arrhenius constants for the intrinsic surface reaction are reported. At all temperatures, the system is initially strongly influenced by external mass transfer resistance but as the reaction proceeds it is believed that the controlling resistance is shifted to product layer. At higher temperatures (350°C and above) pore diffusion resistance is also important and is believed to become the controlling resistance at later times. Product volume becomes so great -due to the large difference in the molar volumes of the solid reactant (CaO) and solid product (Ca(NO₃)₂) - that porosity approaches zero and the reaction effectively "dies-off" at conversions less than 100%.

Pellet data was collected in the temperature range 150° to 550°C. The concentration of NO₂ was varied from 0.5 to 1.8 mole percent while O₂ concentration was maintained constant at 8.7 mole percent. Radii of the pellets used ranged from a low of 0.121 cm to a high of 0.228 cm. Three total gas flow rates were used - 225 cc/min, 450 cc/min, and 924 cc/min (STP).

The experimental rate data for CaO pellets are summarized in Table V-1. Complete results may be found in Appendix A. Fractional conversions of CaO at selected times are given along with the maximum conversion when the reaction was terminated. Since the rate of conversion
<table>
<thead>
<tr>
<th>T(°C)</th>
<th>Run#</th>
<th>%NO₂</th>
<th>(r_s) (cm)</th>
<th>(W_0) (mg)</th>
<th>(\bar{x}) at Selected Times</th>
<th>Final Conversion, (\bar{x}_f) (Time)</th>
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</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1m 2m 40m 60m 90m</td>
<td></td>
</tr>
<tr>
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<td>241</td>
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<td>.126</td>
<td>8.03</td>
<td>2.7 3.7 5.61 6.02 6.52</td>
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</tr>
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<td>246</td>
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<td>.127</td>
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<td>247</td>
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<tr>
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<td>.189</td>
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<td>22.99</td>
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<td>.199</td>
<td>27.74</td>
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<td>20.7 (102m)</td>
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<td>.193</td>
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<td>1.4 2.8 11.7</td>
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**TABLE V-1**

Reaction Rate Data for the Reaction Between CaO Particles
and NO₂ and O₂
TABLE V-1 (continued)

Reaction Rate Data for the Reaction Between CaO Particles and NO₂ and O₂

<table>
<thead>
<tr>
<th>T(°C)</th>
<th>Run#</th>
<th>%NO₂</th>
<th>r₀(cm)</th>
<th>W₀*(mg)</th>
<th>%X at Selected Times</th>
<th>Final Conversion, %Xₐₙₑ₁</th>
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</thead>
<tbody>
<tr>
<td></td>
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<td>2m</td>
</tr>
<tr>
<td>250°</td>
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(STP)
### TABLE V-1 (continued)

Reaction Rate Data for the Reaction Between CaO Particles and NO$_2$ and O$_2$

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<th>%NO$_2$</th>
<th>$r_s$(cm)</th>
<th>$w_0$*(mg)</th>
<th>$\chi^X$ at Selected Times</th>
<th>Final Conversion, $\bar{\chi}^X_f$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1m</td>
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</tr>
<tr>
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<td>.206</td>
<td>31.5</td>
<td>1.1</td>
<td>2.4</td>
</tr>
<tr>
<td>(STP)</td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
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<td>13.5</td>
</tr>
<tr>
<td>550°18%O$_2$</td>
<td>223</td>
<td>1.8</td>
<td>.209</td>
<td>34.54</td>
<td>1.9</td>
<td>3.8</td>
</tr>
<tr>
<td>214</td>
<td>1.8</td>
<td>.130</td>
<td>7.84</td>
<td>2.9</td>
<td>6.6</td>
<td>35.1</td>
</tr>
<tr>
<td>213</td>
<td>1.8</td>
<td>.192</td>
<td>24.80</td>
<td>2.6</td>
<td>5.44</td>
<td>38.1</td>
</tr>
<tr>
<td>232</td>
<td>1.8</td>
<td>.200</td>
<td>25.84</td>
<td>3.01</td>
<td>5.83</td>
<td>34.6</td>
</tr>
<tr>
<td>233</td>
<td>1.8</td>
<td>.212</td>
<td>32.39</td>
<td>2.81</td>
<td>5.54</td>
<td>30.1</td>
</tr>
<tr>
<td>234</td>
<td>1.8</td>
<td>.158</td>
<td>14.64</td>
<td>3.01</td>
<td>6.56</td>
<td>35.6</td>
</tr>
<tr>
<td>18%O$_2$</td>
<td>238</td>
<td>1.8</td>
<td>.205</td>
<td>33.72</td>
<td>2.77</td>
<td>5.7</td>
</tr>
<tr>
<td>215</td>
<td>1.0</td>
<td>.127</td>
<td>8.16</td>
<td>1.78</td>
<td>3.7</td>
<td>35.0</td>
</tr>
<tr>
<td>218</td>
<td>1.0</td>
<td>.213</td>
<td>33.80</td>
<td>1.1</td>
<td>2.4</td>
<td>20.23</td>
</tr>
<tr>
<td>216</td>
<td>0.5</td>
<td>.128</td>
<td>7.32</td>
<td>.85</td>
<td>1.7</td>
<td>17.3</td>
</tr>
<tr>
<td>217</td>
<td>0.5</td>
<td>.219</td>
<td>39.59</td>
<td>.47</td>
<td>1.04</td>
<td></td>
</tr>
</tbody>
</table>

145
becomes small well before 100% conversion is reached, not all runs were carried out to the point of complete "die-off". Therefore, no special significance should be made of differences in maximum conversions listed since in some cases the time at which the run was terminated was arbitrary. Also, included in Table V-1 are values for the pellet radius and mass.

Reaction Reproducibility

Figure V-2 presents the time-conversion data for three pellets whose properties were similar and which were reacted under identical conditions (T=350°C; 1.8 mole percent NO₂). The purpose of these three runs was to determine the reproducibility of the reaction system. As shown in Figure V-2 the data for all three runs exhibit similar behavior - an initial rapid rise in conversion followed by reaction "die-off". The reproducibility is excellent with Runs 229 and 230 achieving a slightly high "die-off" conversion than Run 211.

Figure V-3 presents time-conversion data for three pellets reacted at a lower temperature (250°C). The data for these runs exhibit behavior similar to that observed for all runs at 150° and 250°C - an initial rapid rise in conversion followed by a regime in which the rate of conversion proceeds at a much slower, albeit, steady rate. The reproducibility is excellent for Runs Ca-192 and 193 at all times, but not as good for Run Ca-191. While processing
Figure V-2. A Test of Reaction Reproducibility

Fractional Conversion of CaO, $X$

<table>
<thead>
<tr>
<th>Run</th>
<th>$r_s$ (cm)</th>
<th>$\epsilon_o$</th>
</tr>
</thead>
<tbody>
<tr>
<td>#211</td>
<td>0.213</td>
<td>0.76</td>
</tr>
<tr>
<td>#229</td>
<td>0.213</td>
<td>0.75</td>
</tr>
<tr>
<td>#230</td>
<td>0.207</td>
<td>0.72</td>
</tr>
</tbody>
</table>

All Cases: $T=350^\circ$C
1.8 mole % NO$_2$
Fractional Conversion of CaO, \( \chi \)

All Cases: \( T=250^\circ C \)
1.8 mole % NO\(_2\)

<table>
<thead>
<tr>
<th>Run</th>
<th>( r_g ) (cm)</th>
<th>( \epsilon )</th>
</tr>
</thead>
<tbody>
<tr>
<td>#191</td>
<td>0.1925</td>
<td>0.75</td>
</tr>
<tr>
<td>#192</td>
<td>0.1888</td>
<td>0.76</td>
</tr>
<tr>
<td>#193</td>
<td>0.1904</td>
<td>0.77</td>
</tr>
</tbody>
</table>

Figure V-3. A Test of Reaction Reproducibility
good initial agreement with Runs Ca-192 and 193, Run Ca-191 proceeds to a high level of conversion before the slow reaction period begins.

This discrepancy may be explained by the fact that although efforts were made to select similar pellets for these runs, the pellets were not in fact identical. The pellet used for Run Ca-191 was somewhat larger and had a lower porosity than those used in Ca-192 and 193. It is therefore recognized that a certain amount of scatter will be present in the data due to variations in the physical properties of the CaO pellets.

Effect of Temperature

Pellet data was collected at five temperatures - 150°, 250°, 350°, 450°, and 550°C. Figure V-4 compares the typical time-conversion behavior for pellets reacted at various temperatures with a fixed gas composition of 1.8 mole percent NO₂. As shown in the figure, the reaction at 150° and 250°C proceeded at a slow but steady rate at later times in contrast to the "die-off" exhibited at 350°C and above. Final conversions were strongly affected by temperature. With the exception of 550°C, the final conversions increased with temperature.

The 550°C data is unique in that the final conversion level is somewhere between that observed for 350° and 450°C. Also, closer inspection of the data in Figure V-4 in the early stages of reaction (2 - 4 minutes) shows that the
Figure V-4. The Effect of Temperature on Time-Conversion Behavior of the Reaction Between CaO Particles and NO₂ and O₂
conversion at 550°C lags behind that for 350° and 450°C. The 550°C data will be discussed in more detail later.

Another important piece of information depicted in Figure V-4 is that the rate of conversion is a relatively weak function of temperature prior to the point where the effect of die-off becomes noticeable. It must be remembered, however, that these runs were made at a constant mole percent NO\textsubscript{2} (1.8%), and as such the concentration of NO\textsubscript{2} decreased from 5.18 x 10\textsuperscript{-4} mgmoles NO\textsubscript{2}/cm\textsuperscript{3} at 150°C to 2.66 x 10\textsuperscript{-4} mgmoles NO\textsubscript{2}/cm\textsuperscript{3} at 550°C. Notwithstanding this fact, the temperature dependence of the initial rate of conversion is smaller than that expected due to a smaller NO\textsubscript{2} concentration and is taken as an indication that the reaction system is strongly influenced by external mass transfer resistance at early times - a finding discussed in more detail later.

Referring to Table V-1, the final fractional conversion of CaO (R\textsubscript{f}) at 150°C was found to be in the range 6.0 to 9.0%; at 250°C, R\textsubscript{f} was in the range 15.0 to 20.0%; at 350°C, the final R\textsubscript{f} was in the range 30.0 to 35.0%; at 450°C, the final R\textsubscript{f} occurred between 40. and 45.%; at 550°C, the final R\textsubscript{f} occurred in the range 35. to 45.%. No reaction was found at a temperature near 600°C.

Isolated instances in which R\textsubscript{f} was higher than the aforementioned ranges did occur. However, these were found to occur under unusual circumstances. One such case was Run Ca-250 (T=350°C) in which R\textsubscript{f} was 48.7%. Post-reaction inspection of the pellet revealed that the pellet had cracked - presumably this occurred during the dehydration
step since the initial global reaction rate was also unusually high - exposing interior portions of the solid reactant which would normally have been much more inaccessible to the reactant gas. Therefore, the overall $R_f$ was much higher than that expected for a typical 350°C run.

The behavior of $R_f$ with respect to temperature was not totally unexpected. The tendency for the reaction to "die-off" is believed to be caused by a combination of pore closure and product layer diffusion resistance. Due to the large difference between the molar volumes of the solid reactant (16.6 cm$^3$/mgmole CaO) and solid product (65.8 cm$^3$/mgmole Ca(NO$_3$)$_2$), pores close as the solid product builds up near the pore mouth. Microscopic examination of the reacted pellets showed that the solid product was very dense. Thus, product layer diffusion for the present study is believed to be occurring via the mechanism of solid state diffusion [1]. Solid state diffusion coefficients, $D'_s$, are often represented by an Arrhenius-type equation such as

$$D'_s = D'_s_0 e^{-\frac{E_s}{RT}}$$

(V-5)

which (depending on the value of $E_s$) allows for large variations in $D'_s$ with temperature [2]. Therefore, it is not surprising that the level of final conversion increased with temperature (as shown in Figure V-4) since the rate of solid state diffusion in the product layer would be higher.

In an effort to test for the importance of kinetic or diffusion control in the die-off regime, two special runs
were made to determine the effects that NO₂ concentration and temperature, respectively, have on the rate of conversion in the die-off regime. Figure V-5 presents the time-conversion results of a run carried out at 150°C using 0.5 mole % NO₂. After sixty minutes of reaction, the rate of conversion is seen to be very slow. After ninety minutes, the concentration of NO₂ was raised from 0.5% to 1.8 mole % NO₂. As shown in Figure V-5, the increase in NO₂ concentration had no effect on the rate of conversion. This lack of dependence on NO₂ concentration suggests that the controlling resistance is not due to kinetics.

Figure V-6 illustrates the response of a pellet reacted with 1.8 mole % NO₂ at different temperature levels. Note that in this figure the time scale is discontinuous in order to include the pertinent portions of this run on a single plot. The initial temperature for this run was 150°C. The rate of conversion became very slow after approximately five minutes at a value of $\bar{X} = 0.04$. The fractional conversion at this temperature was 9% after five hours of reaction time. After five hours and ten minutes, the temperature was raised from 150°C to 250°C. The rate of reaction immediately increased but soon slowed and approached a conversion of 26%. Upon raising the temperature from 250°C to 350°C, the fractional conversion increased to 46.5%. An increase in temperature from 350°C to 450°C, increased the fractional conversion from 46.5% to 54% while raising the temperature to 550°C resulted in a small increase in the final fractional conversion from 54% to 55.5%.
Figure V-5. The Response of the Fractional Conversion of CaO in the Die-Off Regime to an Increase in the Concentration of NO₂.
Figure V-6. The Response of the Conversion of CaO in the Die-Off Regime to Successive Increases in Temperature.
The initial rate of change in conversion becomes slower with each successive temperature increase. This may result from the fact that while the solid state diffusivity, $D'_s$, is increasing with temperature, the thickness of the product layer is also greater due to the high level of overall fractional conversion at the time of each successive temperature increase. Also, some pores may have already become closed off due to the build-up of solid product. The important fact shown in Figure V-6 is that the conversion increased with each temperature increase.

The die-off conversions at 250°, 350°, 450°, and 550°C shown in Figure V-6 are higher than those typical of these temperatures as listed in Table V-2. The higher $X_f$'s for this special run may be the result of the added conversion which occurred at the interior portion of the pellet at 150°C - a portion of the pellet which may have remained unconverted had the run commenced at a higher temperature since at the higher temperature pore diffusion resistance would have been greater. This effect may be cumulative since the difference in the final conversions shown in Table V-2 increased with temperature up to 350°C.

Considering Figures V-5 and V-6 together offers evidence that the mechanism occurring in the "die-off" regime is probably a combination of pore diffusion and solid-state diffusion, not chemical reaction, since the die-off conversion increased with temperature but was found to be independent of the concentration of reactant gas NO$_2$. 
TABLE V-2

Comparison of Typical Die-Off Fractional Conversions With Those of Run 251

<table>
<thead>
<tr>
<th>Final Fractional Conversion $X_f$</th>
<th>Typical $X_f$</th>
<th>Run 251 $X_f$</th>
<th>($X_f^{Typical} - X_f^{Run 251}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T(^\circ C)$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>150°</td>
<td>6.-9.</td>
<td>9.</td>
<td>0</td>
</tr>
<tr>
<td>350°</td>
<td>30.-35.</td>
<td>46.5</td>
<td>11.5</td>
</tr>
<tr>
<td>450°</td>
<td>40.-45.</td>
<td>54.</td>
<td>9.</td>
</tr>
<tr>
<td>550°</td>
<td>35.-45.</td>
<td>55.5</td>
<td>10.5</td>
</tr>
</tbody>
</table>
The experimental anomalies at 550°C - ie, slower initial rates and earlier onset of reaction die-off - have been established previously. The cause of these anomalies is not known but experimental evidence has shown that no reaction occurs near 600°C.

Thermodynamic calculations for reaction (V-1) based on conditions similar to those used in the TGA (2% NO₂ - 8% O₂ - 90% Inert (N₂)) predicted that the reaction should proceed up to 475°C with no reaction occurring at temperatures above 475°C. It appears at this point that the 550°C experimental results are in conflict with thermodynamics.

Equilibrium calculations were based on the technique outlined in Smith and Van Ness [3] and made use of the following form of the free energy equation

\[ \Delta F^\circ(T) = \Delta H_0 - \Delta a T \ln T - \frac{\Delta b}{2} T^2 + \frac{\Delta v}{2T} - IT \]

(V-6)

where \( T \) is the absolute temperature (°K); the other terms are derived from thermodynamic data as described in Smith and Van Ness [3]. The thermodynamic data and the subsequent \( \Delta F^\circ(T) \) equation used in the calculations are given in Table V-3.

The discrepancy between thermodynamic calculations and experimental evidence at 550°C could be caused by one or both of two reasons. First, the temperature measurements could be in error and second, the thermodynamic data used in calculating the free energy change for the reaction could be incorrect. The TGA thermocouples were recalibrated several
### TABLE V-3

Thermodynamic Data Used in $\Delta F^\circ(T)$ Equation

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\Delta H_f$ (kcal/gram mole)</th>
<th>$S^\circ$ (cal/gram mole K)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>-151.73</td>
<td>9.48</td>
<td>Radian Corporation[4]</td>
</tr>
<tr>
<td>NO$_2$</td>
<td>7.91</td>
<td>57.34</td>
<td>Radian Corporation[4]</td>
</tr>
<tr>
<td>O$_2$</td>
<td>0.0</td>
<td>48.97</td>
<td>Radian Corporation[4]</td>
</tr>
<tr>
<td>Ca(NO$_3$)$_2$</td>
<td>-224.28</td>
<td>46.20</td>
<td>Radian Corporation[4]</td>
</tr>
</tbody>
</table>

Heat Capacity Data

Equation Form: $C_p = \alpha + \beta T - \frac{\gamma}{T^2} \left( \frac{\text{cal}}{\text{gram mole}} \right) \ T[=]^{\circ}K$

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\alpha$ (cal/gram mole)</th>
<th>$\beta \times 10^3$ (cal/gram mole$^o$K)</th>
<th>$\gamma \times 10^{-5}$ (cal$^o$K/gram mole)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>11.67</td>
<td>1.08</td>
<td>1.56</td>
<td>Kelley[5]</td>
</tr>
<tr>
<td>NO$_2$</td>
<td>10.07</td>
<td>2.28</td>
<td>1.67</td>
<td>Kelley[5]</td>
</tr>
<tr>
<td>O$_2$</td>
<td>7.16</td>
<td>1.0</td>
<td>0.40</td>
<td>Kelley[5]</td>
</tr>
<tr>
<td>Ca(NO$_3$)$_2$</td>
<td>29.37</td>
<td>36.8</td>
<td>4.13</td>
<td>Kelley[5]</td>
</tr>
</tbody>
</table>

$\Delta F^\circ(T) = -87612 - (-6.02)T \ln T - \left( \frac{30.66 \times 10^{-3}}{2} \right)T^2 + \left( \frac{-0.97 \times 10^5}{2T} \right) - (-70.72)$
times and no error in the temperature measurement was re­
vealed. A unique characteristic of gas-solid reactions in
which products and reactants do not mix in the gas phase is
that the reaction either goes to completion or doesn't occur
at all. There are no intermediate fractional conversions
but rather the reaction ceases abruptly at that temperature
where the equilibrium decomposition pressure is greater than
the actual partial pressure of the gas component. As such
any error in the thermodynamic data used in the calculations
can significantly change the predicted maximum temperature
\( T_m \) at which the reaction is still thermodynamically feasi­
ble. Therefore the calculations were repeated to determine
the sensitivity of \( T_m \) to small changes in the thermodynamic
calculations.

Increases in \( \Delta H_0, \Delta \beta, \) and \( \Delta \gamma \) resulted in an increase in
\( T_m \), while decreases in \( \Delta \sigma \) and \( I \) caused an increase in \( T_m \).
It was possible to extend \( T_m \) to 550°C with only a 4% increase
in \( \Delta H_0, \Delta \beta, \) and \( \Delta \gamma \) combined with a 4% decrease in \( \Delta \sigma \) and \( I \).
Therefore, allowing for small errors in thermodynamic data,
the experimental results at 550°C can be reconciled with
thermodynamics.

**Effect of Reactant Gas Concentration**

The response of the reaction system at various reactive
gas concentrations at 350° and 450°C is shown in Figures V-7
and V-8, respectively. Three reactant gas compositions were
used - 1.8%, 1.0%, and 0.5 mole % \( \text{NO}_2 \). For all results
Figure V-7. The Effect of NO₂ Concentration on the Fractional Conversion of CaO Particles at 350°C.

All Cases: T=350°C

<table>
<thead>
<tr>
<th>Run</th>
<th>NO₂ Concentration</th>
<th>r₀ (cm)</th>
<th>ε₀</th>
</tr>
</thead>
<tbody>
<tr>
<td>#207</td>
<td>1.8 mole%NO₂</td>
<td>0.2084</td>
<td>0.74</td>
</tr>
<tr>
<td>#205</td>
<td>1.0 mole%NO₂</td>
<td>0.2136</td>
<td>0.74</td>
</tr>
<tr>
<td>#208</td>
<td>0.5 mole%NO₂</td>
<td>0.2136</td>
<td>0.75</td>
</tr>
</tbody>
</table>
shown the total gas flow rate was 924 cc/min (STP) and oxygen was maintained at 8.7 mole % with nitrogen serving as an inert. Each figure represents the time-conversion behavior of pellets of similar size and properties.

For the cases shown in Figures V-7 and V-8 the initial rate of conversion was found to increase with an increase in NO₂ concentration. This behavior was observed at all temperatures of this study. However, by extrapolating the curves we see that increasing the reactant gas concentration also leads to earlier reaction die-off. Qualitatively, this effect is not unexpected since the faster the initial reaction occurs, the faster the product layer develops on the pellet surface, thereby, inhibiting the diffusion of reactant gases into the pellet. In the case of the 350°C runs presented in Figure V-7, the early die-off of the 1.8% NO₂ run was so pronounced that the level of conversion for the 1.0% NO₂ run eventually exceeded the conversion for the 1.8% NO₂ run. This crossing of the 1.8% and 1.0% NO₂ curves was observed also at 250° and 150°C. Extrapolating the data for 450°C runs appearing in Figure V-8 shows that the 1.8% NO₂ run dies off earliest followed by the run at 1.0% NO₂ but the curves never cross.

The 0.5% NO₂ runs achieved the lowest final fractional conversions in all runs presented thus far. However, in some instances (Figure V-9), the time-conversion curves for each of the three concentrations crossed. Initial reaction rate increased with increasing concentration while ultimate
Fractional Conversion of CaO

All Cases: T=450°C

- Run #211 (1.8 mole% NO₂)  0.213  0.76
- Run #219 (1.0 mole% NO₂)  0.212  0.75
- Run #222 (0.5 mole% NO₂)  0.213  0.75

Figure V-8. The Effect of NO₂ Concentration on the Fractional Conversion of CaO Particles at 450°C.
conversion was inversely related to concentration. This effect was noted only at 250°C and 350°C, and at these temperatures only for smaller pellets.

**Effect of Oxygen Concentration**

As discussed in Chapter II thermodynamics suggest that the NO₂ might undergo decomposition to NO and O₂ above 200°C. However, no data on the kinetics of the following decomposition reaction

\[
\text{NO}_2 \rightarrow \text{NO} + \frac{1}{2} \text{O}_2 \quad (V-7)
\]

was available. Therefore, two special experimental runs were made to test the importance of this reaction. The concentration of O₂ was increased from 8.7 mole % to 18 mole % - thus decreasing the tendency for NO₂ decomposition - for runs at 450° and 550°C. Figures V-10 and V-11 compare the time-conversion behavior of these two special runs to data collected using 8.7 mole % O₂. Allowing for differences in pellet properties, the data agree reasonably well especially during the initial period of the reaction. Comparison of the initial global rate of reaction, \( R_\text{G1} \), listed in Figures V-10 and V-11 - shows that the addition of O₂ had a negligible effect at 450° and 550°C. We conclude, although the evidence is indirect, that NO₂ decomposition is not important even at 550°C.

The die-off conversions for the 18% O₂ runs shown in Figures V-10 and V-11 are somewhat lower than for the 8.7 % O₂ data. However, this difference may not be significant
Fractional Conversion of CaO

All Cases; T=250°C

<table>
<thead>
<tr>
<th>Run #</th>
<th>NO₂ Concentration</th>
<th>r_s (cm)</th>
<th>ε_o</th>
</tr>
</thead>
<tbody>
<tr>
<td>#192</td>
<td>1.8 mole%NO₂</td>
<td>0.1888</td>
<td>0.76</td>
</tr>
<tr>
<td>#198</td>
<td>1.0 mole%NO₂</td>
<td>0.1768</td>
<td>0.76</td>
</tr>
<tr>
<td>#202</td>
<td>0.5 mole%NO₂</td>
<td>0.1824</td>
<td>0.75</td>
</tr>
</tbody>
</table>

Figure V-9. The Effect of NO₂ Concentration on the Fractional Conversion of CaO Particles at 250°C.
Fractional Conversion of CaO

![Graph showing the effect of O\textsubscript{2} on the conversion of CaO at 450°C.](image)

**Equations:**

\[
R_G = 3.34 \times 10^{-6} \frac{\text{mg moles NO}_2}{\text{cm}^2 \text{ min}} \quad \text{(Run #229)}
\]

\[
R_G' = 3.36 \times 10^{-6} \frac{\text{mg moles NO}_2}{\text{cm}^2 \text{ min}} \quad \text{(Run #212)}
\]

**Conditions:**

- All Cases: \( T = 450^\circ \text{C} \)
- \( \text{NO}_2 = 1.8 \) mole%
- \( r_s (\text{cm}) \) and \( \varepsilon \)

<table>
<thead>
<tr>
<th>Run #</th>
<th>( \text{NO}_2 ) (mole%)</th>
<th>( r_s ) (cm)</th>
<th>( \varepsilon )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca-229</td>
<td>8.7</td>
<td>0.2129</td>
<td>0.75</td>
</tr>
<tr>
<td>Ca-212</td>
<td>18</td>
<td>0.2195</td>
<td>0.76</td>
</tr>
</tbody>
</table>

Figure V-10. The Effect of \( \text{O}_2 \) on the Conversion of CaO at 450°C
**Fractional Conversion of CaO**

**Figure V-11. The Effect of $O_2$ on the Conversion of CaO at 550°C**

\[ R_G = 4.242 \times 10^{-6} \text{ (Run#213)} \]
\[ R_G = 4.196 \times 10^{-6} \text{ (Run#238)} \]

All Cases:  $T=550°C$

$NO_2=1.8$ mole%

- Run #Ca-213 8.7 mole% $O_2$  
  \( r_s \text{ (cm)} \quad \epsilon_o \)
  \( 0.2093 \quad 0.75 \)

- Run #Ca-238 18 mole% $O_2$
  \( r_s \text{ (cm)} \quad \epsilon_o \)
  \( 0.2052 \quad 0.72 \)

- Run #Ca-238 18 mole% $O_2$
  \( r_s \text{ (cm)} \quad \epsilon_o \)
  \( 0.2052 \quad 0.72 \)
since the final conversions lie within the range typical for both 450°C and 550°C runs.

**Effect of Total Gas Flowrate**

The importance of total gas flow rate on the time-conversion behavior of the reaction system was investigated at 450°C using 1.8 mole % NO₂ with results shown in Figure V-12. Three flow rates were studied - 924 cc/min)ₚ, 450 cc/min)ₚ, and 225 cc/min)ₚ. The maximum flow rate permissible was 924 cc/min)ₚ; higher flows induced excessive aerodynamic drag on the sample and excessive noise on the recorder trace.

Since the mass transfer coefficient (kₘₐ) is a monotonically increasing function of total gas flow rate past the solid sample, increasing the flow rate should increase the initial rate of conversion if external mass transfer resistance is important. The results depicted in Figure V-12 are typical of a system in which external mass transfer resistance is appreciable. The initial rate of conversion clearly increases with increases in total gas flow rate. All of the other data was collected using the highest flow permissible - 924 cc/min)ₚ.

**The Effect of Pellet Properties**

Pellet properties such as the initial pellet porosity (εₒ), solid reactant concentration (Cₛₒ), and specific surface area (Aₛ) could not be controlled. εₒ ranged from .68 to .78 with a majority of values in the range .74 to .76.
All Cases: \( T = 450^\circ C \) \( \text{NO}_2 = 1.8 \text{ mole \%} \)

- Run #211 Flow=924 (cc/min) STP 350
- Run #224 Flow=450 (cc/min) STP 305
- Run #225 Flow=225 (cc/min) STP 267

Figure V-12. Flow rate Effects on the Fractional Conversion of CaO Particles at 450\(^\circ\)C
Cs0 depends, among other things, on the purity of the solid reactant which was assumed to be 100%. This assumption was based upon infrared analysis of several dehydrated, unreacted pellets which showed the presence of only CaO and a small amount of Ca(OH)2. (Ca(OH)2 was thought to have been formed between the time the pellet was dehydrated and its subsequent I. R. analysis.) Cs0 depends on porosity, as well, via equation III-28.

A similar uncertainty existed with respect to the specific surface area (As) of individual pellets. Due to equipment limitations, As of individual pellets could not be measured. The value of 25.52 m²/gr used for As in this study is the average of two measurements using approximately 20-25 pellets for each measurement. Therefore, any variations in As from pellet to pellet was not accounted for. As such, scatter in the data may be attributable to variations in As for each pellet.

The only pellet property over which independent control existed was the pellet size (radius). Since pellets of various sizes were made, a pellet in a desired size range could usually be selected. (The true pellet diameter was accepted as the average of four measurements across random diameters. Pellet radius, rs, was taken as one-half the average diameter. Since rs is involved in calculating εo and εo is used to calculate Cs0, any errors in rs measurements will be propagated as errors in the values used for εo and Cs0.)
In theory decreasing pellet size should increase the initial rate of conversion for the present reaction system since smaller pellets tend to reduce external mass transfer resistance owing to a larger mass transfer coefficient. This effect was observed for several runs including those shown in Figure V-13 reacted at 450°C with 1.0 mole % NO₂. At lower temperatures this effect should not be as severe since the slower kinetic rate reduces the relative importance of external mass transfer resistance. This fact is depicted in Figure V-14 for runs carried out at 250°C with 1.0 mole % NO₂. In this figure we see that the smaller pellet exhibits a slightly faster initial rate of conversion but its level of conversion is exceeded after 30 minutes by that of the larger pellet. A majority of the runs behaved in a manner similar to the 450° and 250° runs just described.

Examples were observed, however, in which just the opposite effect as described above occurred. Figure V-15 presents the X-t results for a large and small pellet reacted at 450°C with 1.8 mole % NO₂. In this figure, the small pellet required a longer time to reach a given conversion than did the large pellet up to 80 minutes, at which time the curves crossed. Similar behavior was observed at 350°C using 1.8 mole % NO₂ but the curves never crossed. Thus, no distinct pattern could be discerned with respect to the effect pellet size had on the final conversion.
Fractional Conversion of CaO

All Cases: \( \text{NO}_2 = 1.0 \text{ mole \%} \)

- Small Run $\#$Ca-220  \( r_s (\text{cm}) \) 0.1208  0.73
- Large Run $\#$Ca-219  0.2122  0.74

Figure V-13. The Effect of Pellet Size on the Fractional Conversion of CaO Particles.
All Cases: \( NO_2 = 1.0 \text{ mole }\% \)

\[
\begin{array}{ccc}
\text{Small Run \#Ca-200} & r_S (\text{cm}) & \varepsilon_0 \\
0.1363 & 0.746 \\
\text{Large Run \#Ca-197} & 0.2277 & 0.750
\end{array}
\]

Figure V-14. The Effect of Pellet Size on the Fractional Conversion of CaO Particles.
Figure V-15. The Effect of Pellet Size on the Fractional Conversion of CaO Particles.

All Cases: $\text{NO}_2 = 1.8 \text{ mole \%}$

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<td>Large Run #Ca-211</td>
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Reaction Parameter Analysis

In this section initial rate data will be used to evaluate the reaction order with respect to NO\textsubscript{2} and the intrinsic reaction rate constant, k'. The initial rates are used for this purpose since no product layer diffusion resistance can be present and since the initial properties of the reacting pellet are known. Consider a single pellet undergoing reaction with a gas A. Assuming first order behavior with respect to A (an assumption verified later), the initial reaction rate may be expressed as

\[ R_{G_i} = a_G k' C_{S_o} \bar{C}_A \]  \hspace{1cm} (V-8)

\[ = k' \bar{C}_A \]  \hspace{1cm} (V-9)

where

\[ R_{G_i} = \] initial global rate of reaction, measured experimentally via equation V-4 (moles/1^2 time)
\[ a_G = \] stoichiometric coefficient for reactant gas
\[ C_{S_o} = \] initial concentration of solid reactant (moles/1^3)
\[ k' = \] intrinsic reaction rate constant (1^4/mole time)
\[ k' = \] combined constant = \( a_A k_s C_{S_o} \) (1/time)
\[ C_A = \] effective concentration of reactant gas A within the pellet (moles/1^3), this concentration is less than the surface concentration \( C_{A_s} \) when pore diffusion resistance is present

Proof of first order behavior with respect to A requires linearity of \( R_{G_i} \) with \( \bar{C}_A \). Direct measurement of
\( \bar{c}_A \) was not possible in the present study. Therefore, the relationship was sought between \( \bar{c}_A \) and \( C_{A_s} \) which in turn could be related to the measured bulk concentration \( (C_{A_o}) \). \( \bar{c}_A \) can be related to \( C_{A_s} \) through the effectiveness factor, \( EF \). \( EF \) accounts for the reduction in the reaction rate caused by pore diffusion resistance and is defined as follows:

\[
EF = \frac{\text{actual global reaction rate within the pellet}}{\text{global reaction rate if not slowed by pore diffusion}} \tag{V-10}
\]

\[
= \frac{R_{Gi}', \text{ with pore diffusion}}{R_{Gi}', \text{ without pore diffusion}} \tag{V-11}
\]

The denominator in (V-11) may be interpreted as the global reaction rate if surface conditions - ie, temperature and reactant gas concentration - prevailed throughout the pellet.

\( EF \) is a function of the Thiele modulus, \( \phi_s \), which for a spherical pellet is [6]

\[
\phi_s = \frac{r_s^2}{3} \left( \frac{a_G k_s' C_{S_o} \rho_p A_s}{D \varepsilon_o^2} \right) \tag{V-12}
\]

where

- \( \rho_p \) = pellet density (mass/l^3)
- \( A_s \) = specific surface area of pellet (l^2/mass)
- \( D \) = diffusivity of gas in pores - combination of molecular and Knudsen diffusivities - (l^2/time)
- \( \varepsilon_o \) = initial pellet porosity

Once a value of \( \phi_s \) is known the effectiveness factor may be calculated using the following expression [6]
Since the reaction rate is proportional to concentration, we see from equation (V-11) that the relationship between $\bar{c}_A$ and $C_{As}$ for a first order reaction is

$$\bar{c}_A = EF \cdot C_{As}$$

which when substituted into equation (V-8) allows the global reaction rate to be written in terms of $C_{As}$

$$R_{Gi} = a_G \cdot k'_s \cdot C_{So} \cdot EF \cdot C_{As}$$

Attention may now be turned to relating $C_{As}$ to the measured bulk gas concentration ($C_{Ao}$). $C_{Ao}$ may be used to calculate $C_{As}$ from experimental data via the following equation

$$C_{As} = C_{Ao} - \frac{R_{mi}}{k_{mA}}$$

where

$$R_{mi} = \text{initial rate of external mass transfer per unit external surface area of pellet (moles/time)}$$

$$k_{mA} = \text{mass transfer coefficient (1/time)}$$

$R_{mi}$ was calculated by converting the initial global rate of reaction ($R_{Gi}$) from a total surface area (external and internal) basis to an external surface area basis as shown here

$$R_{mi} = R_{Gi} \left( \frac{A_{tot}}{A_{ext}} \right)$$
where

\[ A_{tot} = \text{total available surface area of solid reactant (} \text{m}^2) \]
\[ = (\text{initial pellet mass}) \times \text{(specific surface area of solid reactant)} \]

\[ A_{ext} = \text{external surface area of pellet}^2 \text{ (m}^2 \text{)} \]
\[ = 4 \pi r_s^2 \]

The mass transfer coefficient \( k_{m} \) was estimated by the Froessling method [7]

\[ N_{Sh} = 2.0 + 0.60 \left( \frac{N_{Re}^{0.5} N_{Sc}^{3.3}}{N_{Sh}} \right) \quad (V-18) \]

where

\[ N_{Sh} = \text{Sherwood Number, } \left( \frac{2 k_{m}}{D_m} \right) r_s \]
\[ N_{Re} = \text{Reynolds Number, } \left( \frac{2 r_s G}{\mu_G} \right) \]
\[ N_{Sc} = \text{Schmidt Number, } \left( \frac{\mu_G}{\rho_G D_m} \right) \]
\[ D_m = \text{molecular diffusion coefficient for reactant gas through bulk gas stream (m}^2/\text{time}) \]
\[ G = \text{mass flux of gas (mass/m}^2\text{time}) \]
\[ \mu_G = \text{bulk gas viscosity (mass/m}^2\text{time}) \]
\[ \rho_G = \text{bulk gas density (mass/m}^3\text{)} \]

The range for \( N_{Sh}, N_{Re}, \) and \( N_{Sc} \) was 3.6 to 4.1, 8.0 to 12.0, and 1.10 to 1.14, respectively.

Equations (V-15) for \( R_{G_1} \) and (V-13) for EF represent a system of two equations in two unknowns - \( k_s \) and EF. Determination of the unique values requires their simultaneous solution. An iterative method used to solve for \( k_s \) and EF from experimental data is outlined below:
1) Calculate $C_{As}$ from equation (V-16).

2) Assume $EF = 1.0$ initially.

3) Calculate $k'_s$ from the measured $R_{Gi}$ using equation (V-19) below (obtained by rearranging equation (V-15)).

$$k'_s = R_{Gi} / \left( \frac{C_{So}}{C_{As}} \right)$$  \hspace{1cm} (V-19)

4) Use $k'_s$ from step 3) to find a value for $\phi_s$ from equation (V-12).

5) Calculate $EF$ from equation (V-13).

6) Compare EF calculated in step 5) with the value assumed in step 3). If EF from step 5) is not the same as that used in step 3), then return to step 3) with the current value of EF and repeat the procedure until EF used in step 3) agrees with the value of EF calculated in step 5) to within some tolerance (.0001).

The results of the initial rate calculations appear in Table V-4. The entries under the heading "Relative Resistance" represent the fraction of the total resistance offered by external mass transfer, $\left( \frac{C_{As} - C_{A_0}}{C_{A_0}} \right)$, pore diffusion resistance, $\left( \frac{C_{As} - \bar{C}_{A}}{C_{A_0}} \right)$, and chemical reaction resistance, $\frac{\bar{C}_{A}}{C_{A_0}}$. Inspection of the relative resistance due to external mass transfer in Table V-4 shows that a significant drop in the reactant gas concentration occurred from the bulk gas stream to the pellet surface. Also, the drop in surface gas concentration was found to increase as pellet radius increased. This latter trend is expected since $k_m$ is inversely proportional to pellet radius as given by equation (V-18). Based on the magnitude of the drop in reactant gas concentration, it may be concluded that
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<th>T(°C)</th>
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<th>Bulk Reactant Gas Concentration $C_A O \times 10^4$ (mgmoles NO$_2$/cm$^3$)</th>
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<th>Initial Global Rate of Reaction $R_G i \times 10^6$ (mgmoles NO$_2$ cm$^2$/min)</th>
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TABLE V-4 (continued)

Initial Rate Data (Analysis Based on Spherical Pellet Geometry)

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<th>$\bar{C}_A \times 10^4$ (mgmoles NO$_2$ / cm$^3$)</th>
<th>$k'_s \times 10^3$ (cm$^3$/mgmole-sec)</th>
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TABLE V-4 (continued)

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<th>(C_A \times 10^4) mgmole NO₂</th>
<th>Intrinsic Reaction Rate Constant (k'_s \times 10^3) cm³/mgmole/min</th>
<th>Relative Reaction Resistance Mass Transfer Pore Diffusion Reaction</th>
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<td>19.9</td>
<td>(\frac{C_A - C}{C_{A_0}})</td>
</tr>
<tr>
<td></td>
<td>229</td>
<td>0.201</td>
<td>6.61</td>
<td>(\frac{C_A - C}{C_{A_0}})</td>
</tr>
<tr>
<td></td>
<td>230</td>
<td>0.11</td>
<td>13.2</td>
<td>(\frac{C_A - C}{C_{A_0}})</td>
</tr>
<tr>
<td></td>
<td>220</td>
<td>0.257</td>
<td>5.14</td>
<td>(\frac{C_A - C}{C_{A_0}})</td>
</tr>
<tr>
<td>550°</td>
<td>214</td>
<td>0.554</td>
<td>3.81</td>
<td>(\frac{C_A - C}{C_{A_0}})</td>
</tr>
<tr>
<td></td>
<td>234</td>
<td>0.288</td>
<td>6.4</td>
<td>(\frac{C_A - C}{C_{A_0}})</td>
</tr>
<tr>
<td></td>
<td>215</td>
<td>0.284</td>
<td>3.46</td>
<td>(\frac{C_A - C}{C_{A_0}})</td>
</tr>
<tr>
<td></td>
<td>218</td>
<td>0.16</td>
<td>4.22</td>
<td>(\frac{C_A - C}{C_{A_0}})</td>
</tr>
<tr>
<td></td>
<td>216</td>
<td>0.248</td>
<td>1.96</td>
<td>(\frac{C_A - C}{C_{A_0}})</td>
</tr>
<tr>
<td></td>
<td>217</td>
<td>0.084</td>
<td>3.34</td>
<td>(\frac{C_A - C}{C_{A_0}})</td>
</tr>
</tbody>
</table>
the initial global rate of reaction is strongly influenced by external mass transfer.

As discussed earlier, proof of first order behavior with respect to NO₂ concentration requires linearity between \( R_{G_i} \) and \( \bar{C}_A \). \( R_{G_i} \) was found to be linear with \( \bar{C}_A \) between 150°C and 450°C as depicted in Figure V-16. Therefore, the dependence on \( \bar{C}_A \) in the rate expression (V-8) assumed earlier in the development of the equations used to calculate \( k'_s \) and EF is valid.

The results of the effectiveness factor calculations appear in Table V-4. Values for the relative resistance due to pore diffusion show that this resistance is significant for all runs. The general nature of effectiveness factor calculations is illustrated by the fact that at a constant temperature values for EF (allowing for scatter in the data) were found to be relatively independent of pellet size and mole percent of reactant gas used. A minimum in the average EF occurs at 450°C. This indicates that pore diffusion resistance is less at 550°C than at 450°C, a result not readily explainable.

The rate constants \( (k'_s) \) appearing in Table V-4 were found to obey the classical Arrhenius relationship over the temperature range 150°C to 450°C.

\[
k'_s = k_{s_0} e^{-\frac{E_A}{RT}} \tag{V-20}
\]
Figure V-16. Reaction Order with Respect to NO* Concentration.

Initial Global Reaction Rate, $R_{G1}$ (mg moles NO$_2$ cm$^3$ min$^{-1}$)
where

\[ k_{s_0} = \text{frequency factor (cm}^4/\text{mg mole min)} \]
\[ E_A = \text{activation energy (cal/gr mole)} \]
\[ R = \text{gas constant (1.987 cal/gr mole °K)} \]
\[ T = \text{absolute temperature (°K)} \]

In many cases above 150°C, the relative resistance due to chemical reaction was small compared to that for external mass transfer and pore diffusion. In these cases, it would be difficult to obtain an accurate measurement of \( k'_s \). For the sake of accuracy those runs whose relative chemical reaction resistance was less than .02 were arbitrarily dropped from the analysis to determine the Arrhenius constants and thus, do not appear in Table V-4.

Determination of \( k_{s_0} \) and \( E_A \) for the remaining 32 data points from 150° to 450°C was accomplished by use of a non-linear least squares analysis. The Arrhenius expression is:

\[ k'_s = 0.4172 e^{-5297/RT} \]

Equation (V-21) along with the data appear in Figure V-17. Also appearing in the figure is the data at 550°C. There is no ready explanation for the lower intrinsic rate constant at 550°C. The scatter in the data is believed caused by experimental measurement errors and the inherent variation in physical properties from pellet to pellet.
Figure V-17. Arrhenius Plot of $k_g$
(Spherical Pellet Geometry)

\[ k_g = 0.4172e^{-\frac{5297}{RT}} \]
Post Reaction Analyses

Infrared Analysis: Selected samples reacted at 150°, 250°, 350°, 450°, and 550°C with 1.0 or 1.8 mole % NO₂ were analyzed by infrared spectroscopy to identify species present in the solid product to verify reaction stoichiometry. Reaction product material was mixed with KBr and made into wafers by application of pressure (15,000 to 20,000 psi) via a hydraulic press.

IR spectrographs of standard samples of Ca(OH)₂ pellets, dehydrated Ca(OH)₂ pellets (ie, CaO), reagent grade Ca(NO₃)₂·4H₂O, and - due to the lack of a Ca(NO₂)₂ sample - reagent grade NaN₂O₂ were generated. IR spectrographs for Ca(OH)₂, Ca(NO₃)₂·4H₂O and NaN₂O₂ were available from the Sadtler Index [8] and these compared well with the spectrographs for the standard samples generated.

The IR spectroscopic analysis of the reaction product for runs 240, 196, 235, 212, 219, and 214 showed the existence of only Ca(NO₃)₂·4H₂O, Ca(OH)₂, and CaO. Presence of Ca(OH)₂ resulted from absorption of atmospheric moisture during post reaction preparation of the samples for IR analysis. The conspicuous absence of Ca(NO₂)₂ verifies that only reaction V-1 is occurring.

Microscopic Examination of Reacted CaO Pellets: Reacted pellets chosen for examination were mounted in a quick setting epoxy plastic to facilitate handling. The mounted samples were sanded until the equatorial cross section of the pellet was exposed. Photographs of the
pellet cross sections were taken and these appear in Figures V-18 and V-19.

Figure V-18 is a photograph of the pellet used in Run 211 which was reacted at 450°C with 1.8 mole % NO\textsubscript{2}. The final fractional conversion for Run 211 was 42%. Inspection of the photograph reveals the presence of a thick outer layer of material surrounding a more porous interior core. Calculating the overall fractional conversion based on the values of the radii of the pellet and the interior core using the unreacted core model according to equation III-24 yields $\bar{X} \approx 70\%$ compared to the experimental value for $\bar{X}$ of 42%. The difference between these values for $\bar{X}$ indicates that some unreacted CaO may be present in the outer layer depicted in Figure V-18.

Figure V-19 is a photograph of the pellet used in Run 232 which was reacted at 550°C with 1.8 mole percent NO\textsubscript{2}. The final fractional conversion for this run was 39.6%. A thick outer layer can be observed. The reaction appears to have been limited to a region near the pellet surface which suggests that the "die-off" observed may have resulted from pore diffusion limitations - perhaps due to surface porosity approaching zero.

Effect of Reaction on Pellet Radius: The effect of reaction on the pellet radius was negligible. Comparison of the measured radius before and after reaction showed little change had occurred. This is not surprising since in most cases the fractional conversions were 30% or less. However,
Figure V-18. Microscopic Photograph of Pellet Used in Run 211 (T=450°C, 1.8 mole of NO₂). Magnification = 20x.
Figure V-19. Microscopic Photograph of Pellet Used in Run #232 (T=550°C, 1.8 mole % NO₂). Magnification = (a) 10x, (b) 37.5x.
in those instances in which conversion was appreciable (i.e., \( > 40\% \)), the measurement of pellet radius was difficult due to the hygroscopic nature of the reaction product - \( \text{Ca(NO}_3\text{)}_2 \). The surface of these pellets became soft during measurement of the diameters and as such erroneously small values for the pellet diameters results.

B) CaO Powder Data

A sizeable amount of time was spent collecting kinetic data for the reaction between CaO powder and \( \text{NO}_2 \) and \( \text{O}_2 \). This work was an unsuccessful attempt to measure the global reaction rate for reaction (V-1) in the absence of external mass transfer thus producing a value for the intrinsic reaction rate. However, external mass transfer resistance could not be eliminated. Data will be presented showing that the measured \( k' \) has a weak temperature dependence. Time-conversion data will be presented illustrating the phenomenon of reaction "die-off".

Since no useful value for the reaction rate constant could be obtained, a reaction order study was not performed. Therefore, all powder data presented here was collected using a gas having a composition of 1.8 mole \% \( \text{NO}_2 \) - 8.7 mole \% \( \text{O}_2 \) - 89.5 mole \% \( \text{N}_2 \).

The solid sample size was reduced and the gas velocity past the sample was increased in the effort to eliminate mass transfer resistance [6,7]. However, balance sensitivity places a lower limit on the minimum sample size
permissible. Also, there is a practical upper limit to the allowable gas flow rate within the TGA reactor chamber before excessive swinging of the sample pan occurs. With the exception of two runs, all data was collected using a total gas flow rate of 924 cc/min (STP). Two runs (Run 151 and 152) were carried out using a total gas flow rate of 1108 cc/min (STP). Unfortunately, use of a larger recorder range (required to dampen the "noise" induced by the higher flow) reduced the accuracy of the data and use of this flow was discontinued.

Reaction data for CaO powder is summarized in Table V-5 which contains both initial global rate and time-conversion data. The effect of temperature on the fractional conversion of CaO powder is shown in Figure V-20. As in the case of the pellet data (see Figures V-4 and V-7), the most significant feature in this plot is the apparent reaction "die-off" whose level increases with temperature. Also, similar to the pellet data is the behavior of the 550°C run. The explanation offered for 550°C pellet data behavior is applicable to the 550°C powder data as well. No reaction was found at 600°C.

It is interesting to compare the die-off conversions obtained using powder and pellet forms of CaO as shown in Table V-6. With the exception of 550°C, the die-off conversion for the powder is lower than that for the pellet. This behavior is to be expected due to the lower porosity for the powder samples.
<table>
<thead>
<tr>
<th>T(°C)</th>
<th>Run#</th>
<th>Sample Size (mg)</th>
<th>NO₂ Concentration C₉O₂ x 10^4 (mgmoles NO₂/cm³)</th>
<th>Initial Weight Change (dw/dt)</th>
<th>Initial Reaction Rate R_Gi x 10⁶ (mgmoles NO₂/cm²min)</th>
<th>Pseudo-Rate Constant k' x 10⁻² (cm/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>550°</td>
<td>129</td>
<td>1.6</td>
<td>2.664</td>
<td>.23</td>
<td>13.0</td>
<td>4.88</td>
</tr>
<tr>
<td></td>
<td>130</td>
<td>4.25</td>
<td>2.664</td>
<td>.375</td>
<td>7.962</td>
<td>2.99</td>
</tr>
<tr>
<td></td>
<td>131</td>
<td>5.71</td>
<td>2.664</td>
<td>.375</td>
<td>5.926</td>
<td>2.22</td>
</tr>
<tr>
<td></td>
<td>132</td>
<td>2.54</td>
<td>2.664</td>
<td>.320</td>
<td>11.37</td>
<td>4.27</td>
</tr>
<tr>
<td>600°</td>
<td>133</td>
<td>2.51</td>
<td>2.51</td>
<td></td>
<td></td>
<td>No Reaction occurred at this Temperature</td>
</tr>
<tr>
<td>500°</td>
<td>134</td>
<td>1.68</td>
<td>2.835</td>
<td>.293</td>
<td>15.74</td>
<td>5.55</td>
</tr>
<tr>
<td></td>
<td>135</td>
<td>2.44</td>
<td>2.835</td>
<td>.400</td>
<td>14.79</td>
<td>5.22</td>
</tr>
<tr>
<td></td>
<td>136</td>
<td>4.27</td>
<td>2.835</td>
<td>.500</td>
<td>10.57</td>
<td>3.73</td>
</tr>
<tr>
<td></td>
<td>137</td>
<td>6.01</td>
<td>2.835</td>
<td>.600</td>
<td>9.009</td>
<td>3.18</td>
</tr>
<tr>
<td>450°</td>
<td>138</td>
<td>1.52</td>
<td>3.003</td>
<td>.267</td>
<td>15.85</td>
<td>5.23</td>
</tr>
<tr>
<td></td>
<td>139</td>
<td>2.56</td>
<td>3.003</td>
<td>.440</td>
<td>15.51</td>
<td>5.11</td>
</tr>
<tr>
<td></td>
<td>140</td>
<td>4.56</td>
<td>3.003</td>
<td>.700</td>
<td>13.85</td>
<td>4.57</td>
</tr>
<tr>
<td></td>
<td>141</td>
<td>6.13</td>
<td>3.003</td>
<td>.750</td>
<td>11.04</td>
<td>3.64</td>
</tr>
<tr>
<td></td>
<td>142</td>
<td>7.54</td>
<td>3.003</td>
<td>.767</td>
<td>9.180</td>
<td>2.58</td>
</tr>
<tr>
<td></td>
<td>143</td>
<td>8.78</td>
<td>3.003</td>
<td>.80</td>
<td>8.22</td>
<td>2.71</td>
</tr>
<tr>
<td>400°</td>
<td>144</td>
<td>1.76</td>
<td>3.258</td>
<td>.40</td>
<td>20.51</td>
<td>6.30</td>
</tr>
<tr>
<td></td>
<td>145</td>
<td>3.04</td>
<td>3.258</td>
<td>.52</td>
<td>15.44</td>
<td>4.74</td>
</tr>
<tr>
<td></td>
<td>146</td>
<td>1.30</td>
<td>3.258</td>
<td>.40</td>
<td>27.77</td>
<td>8.52</td>
</tr>
<tr>
<td></td>
<td>147</td>
<td>4.57</td>
<td>3.258</td>
<td>.643</td>
<td>12.70</td>
<td>3.90</td>
</tr>
<tr>
<td></td>
<td>148</td>
<td>6.15</td>
<td>3.258</td>
<td>.833</td>
<td>12.22</td>
<td>3.75</td>
</tr>
<tr>
<td></td>
<td>149</td>
<td>1.63</td>
<td>3.258</td>
<td>.32</td>
<td>17.72</td>
<td>5.44</td>
</tr>
</tbody>
</table>
### TABLE V-5 (continued)

**Experimental Data for CaO Powder (200-100 mesh) Reacting with NO₂ and O₂**

| T(°C) | Run# | Sample Size (mg) | \( \frac{\text{mg} \text{moles} \text{NO}_2}{\text{cm}^3} \) | Initial Weight Change (mg/min) | Initial Reaction Rate \( \frac{\text{mg} \text{moles} \text{NO}_2}{\text{cm}^2 \text{min}} \) | Pseudo-Rate Constant \( \frac{R_{G_i}}{C_{A_i} \text{cm}^2/\text{min}} \) = \( \frac{k'}{10^{-2}} \) |
|-------|------|-----------------|----------------|-----------------|----------------|----------------|----------------|
| 400°  | 150  | 1.44            | 3.258          | .40             | 25.07          | 7.70           |
|       | 151  | 7.28            | 3.258          | 1.17            | 14.50          | 4.45           |
|       | 152  | 2.56            | 3.258          | 1.10            | 38.78          | 11.9           |
|       | 178  | 24.65           | 3.258          | 1.50            | 5.491          | 1.69           |
|       | 179  | 5.25            | 3.258          | .80             | 13.75          | 4.22           |
|       | 180  | 13.28           | 3.258          | 1.30            | 8.834          | 2.71           |
|       | 177  | 26.31           | 3.169          | 1.67            | 5.730          | 1.81           |
| 250°  | 173  | 38.56           | 3.775          | 1.80            | 4.212          | 1.12           |
|       | 174  | 23.95           | 3.775          | 1.75            | 6.594          | 1.75           |
|       | 175  | 4.15            | 3.775          | .958            | 20.83          | 5.52           |
TABLE V-5 (continued)

Experimental Data for CaO Powder (200-100 mesh) Reacting with NO\textsubscript{2} and O\textsubscript{2}

<table>
<thead>
<tr>
<th>T(°C)</th>
<th>Run#</th>
<th>Fractional Conversion at a Given Time</th>
<th>Maximum</th>
<th>Time</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(\bar{X}(t))</td>
<td>(X_{max})</td>
<td>(min)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1m</td>
<td>2m</td>
<td>20m</td>
</tr>
<tr>
<td>550°</td>
<td>129</td>
<td>0.065</td>
<td>0.104</td>
<td>0.532</td>
</tr>
<tr>
<td></td>
<td>130</td>
<td>0.046</td>
<td>0.079</td>
<td>0.513</td>
</tr>
<tr>
<td></td>
<td>131</td>
<td>0.027</td>
<td>0.057</td>
<td>0.460</td>
</tr>
<tr>
<td></td>
<td>132</td>
<td>0.057</td>
<td>0.103</td>
<td>0.554</td>
</tr>
<tr>
<td>600°</td>
<td>133</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>500°</td>
<td>134</td>
<td>0.063</td>
<td>0.111</td>
<td>0.433</td>
</tr>
<tr>
<td></td>
<td>135</td>
<td>0.054</td>
<td>0.102</td>
<td>0.487</td>
</tr>
<tr>
<td></td>
<td>136</td>
<td>0.050</td>
<td>0.092</td>
<td>0.412</td>
</tr>
<tr>
<td></td>
<td>137</td>
<td>0.048</td>
<td>0.086</td>
<td>0.439</td>
</tr>
<tr>
<td>450°</td>
<td>138</td>
<td>0.082</td>
<td>0.139</td>
<td>0.348</td>
</tr>
<tr>
<td></td>
<td>139</td>
<td>0.066</td>
<td>0.116</td>
<td>0.349</td>
</tr>
<tr>
<td></td>
<td>140</td>
<td>0.058</td>
<td>0.112</td>
<td>0.370</td>
</tr>
<tr>
<td></td>
<td>141</td>
<td>0.059</td>
<td>0.098</td>
<td>0.383</td>
</tr>
<tr>
<td></td>
<td>142</td>
<td>0.059</td>
<td>0.088</td>
<td>0.297</td>
</tr>
<tr>
<td></td>
<td>143</td>
<td>0.047</td>
<td>0.089</td>
<td>0.348</td>
</tr>
<tr>
<td>400°</td>
<td>144</td>
<td>0.059</td>
<td>0.177</td>
<td>0.286</td>
</tr>
<tr>
<td></td>
<td>145</td>
<td>0.077</td>
<td>0.142</td>
<td>0.289</td>
</tr>
<tr>
<td></td>
<td>146</td>
<td>0.120</td>
<td>0.179</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>147</td>
<td>0.064</td>
<td>0.134</td>
<td>0.277</td>
</tr>
<tr>
<td></td>
<td>148</td>
<td>0.057</td>
<td>0.100</td>
<td>0.262</td>
</tr>
<tr>
<td></td>
<td>149</td>
<td>0.093</td>
<td>0.158</td>
<td>0.325</td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>0.201</td>
<td>0.247</td>
<td>0.390</td>
</tr>
<tr>
<td></td>
<td>151</td>
<td>0.096</td>
<td>0.142</td>
<td>0.303</td>
</tr>
<tr>
<td></td>
<td>152</td>
<td>0.138</td>
<td>0.203</td>
<td>0.336</td>
</tr>
</tbody>
</table>
**TABLE V-5 (continued)**

Experimental Data for CaO Powder (200-100 mesh) Reacting with NO₂ and O₂

<table>
<thead>
<tr>
<th>T(°C)</th>
<th>Run#</th>
<th>Fractional Conversion at a Given Time</th>
<th>Maximum</th>
<th>Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>1m</td>
<td>2m</td>
<td>20m</td>
</tr>
<tr>
<td>450°</td>
<td>178</td>
<td>.026</td>
<td>.059</td>
<td></td>
</tr>
<tr>
<td></td>
<td>179</td>
<td>.073</td>
<td>.140</td>
<td></td>
</tr>
<tr>
<td></td>
<td>180</td>
<td>.046</td>
<td>.093</td>
<td></td>
</tr>
<tr>
<td>350°</td>
<td>176</td>
<td>.074</td>
<td>.149</td>
<td></td>
</tr>
<tr>
<td></td>
<td>177</td>
<td>.030</td>
<td>.062</td>
<td></td>
</tr>
<tr>
<td>250°</td>
<td>173</td>
<td>.059</td>
<td>.092</td>
<td></td>
</tr>
<tr>
<td></td>
<td>174</td>
<td>.037</td>
<td>.065</td>
<td></td>
</tr>
<tr>
<td></td>
<td>175</td>
<td>.098</td>
<td>.113</td>
<td></td>
</tr>
</tbody>
</table>
Figure V-20. The Conversion of CaO Powder as a Function of Temperature.
TABLE V-6

Comparison of Maximum Fractional Conversion For Powder and Pellet Forms of CaO

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>Powder</th>
<th>Pellet</th>
</tr>
</thead>
<tbody>
<tr>
<td>250°</td>
<td>.12</td>
<td>.15-.20</td>
</tr>
<tr>
<td>350°</td>
<td>.20</td>
<td>.30-.35</td>
</tr>
<tr>
<td>450°</td>
<td>.35</td>
<td>.40-.45</td>
</tr>
<tr>
<td>550°</td>
<td>.60</td>
<td>.45-.50</td>
</tr>
</tbody>
</table>
The initial global rate \( (R_{G_i}) \) was calculated from equation V-4. Values of \( R_{G_i} \), along with the values of the pseudo-rate constant \( (k' = \frac{a_G C_{S_o} k_s}{\epsilon_0}) \) calculated from (assuming no mass transfer resistance)

\[
k' = \frac{R_{G_i}}{C_{A_o}} \quad \text{(cm/min)} \quad \text{(V-22)}
\]

appear in Table V-5. \( R_{G_i} \) and \( k' \) were found to increase with decreasing sample size at constant temperature. The dependence on sample size is illustrated in Figure V-21 in which the time-conversion behavior of two runs of different initial sample size reacted at 350°C is shown. It is clear that the initial rate of conversion is strongly dependent on sample size. The final conversions are seen to be independent of initial sample size because \( \epsilon_0 \) for powder samples is presumably identical. The 350°C behavior is typical of the behavior observed at other temperatures.

Inspection of Table V-5 shows that a maximum in \( k' \) occurs at 400°C. Great significance should not be placed on this fact because of the severe scatter in the data. However, it is accepted that the data above 400°C may be influenced by more severe external mass transfer resistance. However, even the use of the limited data below 400°C produced one conclusion: The temperature dependence of the measured \( k_s \) is very weak - not at all characteristic of a kinetic rate constant.
Figure V-21. The Conversion of CaO Powder for a NO$_2$/O$_2$/CaO Reaction As a Function of Time and Solid Sample Size.
Strong dependence on sample size and weak temperature dependence exhibited by $k'$ strongly suggests that the dominant resistance initially in the powder data is external mass transfer resistance. It was concluded, therefore, that the intrinsic chemical reaction rate constant could not be measured using powder samples since external mass transfer resistance could not be eliminated within the limits of our reaction system.
Literature Cited


CHAPTER VI
COMPARISON OF EXPERIMENTAL DATA WITH A VARIABLE PROPERTY GRAIN MODEL

In this chapter, the experimental time-conversion data reported in Chapter V will be compared with a variable property grain model similar to that of Georgakis et al. [1]. The chapter will begin with a presentation of the dimensionless variable property grain model equations along with a discussion of the methods used to evaluate the required parameters. Before presenting predictions of this variable property grain model (VPGM), a brief presentation of the results of the constant property grain model (CPGM) will be given. The CPGM section is included to provide a benchmark against which the VPGM may be compared. In the CPGM section the importance of grain diffusion will be considered and the shortcomings of this model will be discussed.

Attention will then be focused on the predictive capabilities of the VPGM. It will be shown that the VPGM produces a much improved match with experimental time-conversion data for cases in which pore diffusion resistance is important. In particular, this model predicts reaction "die-off" while the CPGM can not.

A) The Model

The model of Georgakis, Chang, and Szekely [1] - discussed earlier in Chapter III - was modified for use in
the present research. This model was chosen due to its simple description of decline in pellet porosity with reaction which may lead to prediction of reaction "die-off". However, the model as presented by Georgakis et al [1] ignored external mass transfer, a resistance which was shown in Chapter V to be important in the present study. Georgakis et al. [1] also ignored the variation of the pore diffusion coefficient \(D_G\) and tortuosity factor \(\tau\) with solid structural changes. \(D_G\) and \(\tau\) are used in estimating the effective diffusivity via equation III-91. Thus, modifications to the model of Georgakis et al. [1] include the incorporation of external mass transfer resistance and the allowance for variation of the pore diffusion coefficient and the tortuosity factor with changes in porosity.

**Dimensionless Model Equations**

The gas phase and solid phase material balance equations for the VFGM, along with the appropriate boundary and initial conditions, were cast in dimensionless form for ease of numerical solution. The resultant gas phase material balance is:

\[
\frac{\partial^2 C}{\partial \xi^2} + \frac{2}{\xi} \left( \frac{\partial C}{\partial \xi} \right) + \frac{1}{\delta(r)} \left( \frac{\partial \delta(r)}{\partial \xi} \right) \left( \frac{\partial C}{\partial \xi} \right) = -3a_A r_s \Phi_G \xi C^2
\]

\[
= \frac{-3a_A r_s \Phi_G \xi C^2}{r_s' \delta(r) \left[ 1 - a_A \Phi_G \xi C \left( 1 - \frac{\xi C}{\xi} \right) \right]} \quad (VI-1)
\]

with the boundary conditions

\[
\left. \frac{\partial C}{\partial \xi} \right|_{\xi=1.0} = \frac{Bi M}{\delta} (1-C) \quad (VI-2)
\]
and
\[ \frac{\delta C}{\delta \xi} \bigg|_{\xi=0} = \frac{\delta \delta (r)}{\delta \xi} \bigg|_{\xi=0} = 0 \quad (VI-3) \]

The solid reactant material balance is
\[ \frac{\delta \xi' C}{\delta \theta} = \frac{a_{s} C}{[1 - a_A \phi_G \xi_C^C (1 - \frac{\xi_C^C}{\xi_C^C})]} \quad (VI-4) \]

with the initial condition
\[ \xi_C^C \bigg|_{\theta=0} = 1.0 \quad (VI-5) \]

The nomenclature introduced in equations VI-1 through VI-5 is defined below:

- \( C \) = dimensionless reactant gas concentration = \( C_A/C_{A_0} \)
- \( \xi \) = dimensionless radial coordinate for pellet = \( r/r_s \)
- \( \delta \) = dimensionless effective diffusivity within the pellet = \( D_e/D_{e_0} \)
- \( \phi_G \) = Thiele modulus for the pellet = \( k_s C_s r_s / D_{e_0} \)
- \( \xi' \) = dimensionless grain radius = \( r'/r_{s_0} \)
- \( \xi'_C \) = dimensionless unreacted-core radius within a grain = \( r'_C/r_{s_0} \)
- \( \phi'_C \) = Thiele modulus for an individual grain = \( k'_s C'_s r'_s / D'_s \)
- \( \text{Bi}_M \) = Biot number for mass transfer = \( k_M r_s / D_{e_0} \)
- \( \theta \) = dimensionless time = \( k_s C_{A_0} t/r_{s_0} \)

Parameters used in the above dimensionless variables were defined previously in Chapter III.

It is worth noting the differences between the model given above and other variable property models discussed in
Chapter III. The term accounting for radial variation in the pellet effective diffusivity has been retained in this development whereas it was assumed negligible in the development of Hartman and Coughlin [2] as well as Ranade and Harrison [3] and Ramachandran and Smith [4]. It may prove to be negligible in practical situations but is included here for the sake of completeness. The expression giving local fractional conversion in terms of the grain unreacted core radius — equation III-24 — must be replaced with

\[ X = 1 - \left( \frac{r_c'}{r_s} \right)^3 \]  

(VI-6)

in which \( r_s' \) is replaced by the initial grain radius, \( r_{so} \). This change is necessary since in this model grain radius varies and conversion must be based upon the amount of solid reactant present initially. This effect was considered negligible by Ranade and Harrison [3].

Evaluation of Model Parameters

In order to solve the model equations, various parameters must be evaluated. It is desired that the dependence on both radial position and time be considered. Values of the physical constants specific to the present reaction system will be listed at the end of this section.

Grain radius. The relationship suggested by Wen [5] can be used to estimate the initial grain radius:

\[ r_{so}' = \frac{3}{A_{so} \rho s_o} \]  

(III-30)
where $A'_{so}$ is the measured initial surface area of the pellets and $\rho'_{go}$ is the initial grain density - assumed equal to the crystalline density of pure solid reactant, $\rho_s$. Grain radius varies with local fractional conversion as follows:

$$r'_s = r'_{s_0} \left[ 1 + X (\gamma - 1) \right]^{1/3} \quad \text{(VI-7)}$$

In the above equation $\gamma$ is an expansion factor defined in Chapter III as

$$\gamma = \left( \frac{a_P}{a_S} \right) \frac{V_P}{V_S} \quad \text{(III-53)}$$

where $V_S$ and $V_P$ are the molar volumes for the reactant and product solids, respectively. $\gamma$ is a key parameter in this model. If $\gamma < 1$, the grains will shrink and the pore structure opens. If $\gamma > 1$, the grains will expand and the pellet porosity will decrease since solid product will take up volume previously occupied by pores. For the case of $\gamma > 1$, the pellet porosity can become so low that reaction "die-off" occurs. For the present reaction system $\gamma$ has a value of 3.96.

**Grain density.** Grain density may also be expressed as a function of local fractional conversion

$$\rho'_g = \frac{[(1-X)\rho_S + X \rho_P \rho (1-\varepsilon_P)]}{[1 + X (\gamma-1)]} \quad \text{(VI-8)}$$

where $\rho_S$ and $\rho_P$ are the crystalline density of solid product and reactant, respectively. $\varepsilon_p$ is the porosity of the solid product. Since the unreacted grain is assumed non-porous and reaction results in a product requiring more volume than the reactant, $\varepsilon_p$ is assumed zero.
Pellet porosity. Local values of the pellet porosity may be calculated with

\[ \varepsilon = 1 - (1-\varepsilon_o) (1+X(\gamma-1)) \]  

(VI-9)

This expression may be obtained by manipulation of the expressions for porosity of Hartman et al. [2] or Georgakis et al. [1].

Equation VI-9 may also be used to determine the maximum initial porosity (\( \varepsilon_o \)) such that local porosity (\( \varepsilon \)) remains nonzero when the local fractional conversion (\( X \)) becomes 1.0. Using \( \gamma = 3.96 \), setting \( \varepsilon = 0 \) and \( X = 1.0 \) and solving equation VI-9 for \( \varepsilon_o \) yields a value of 0.747. \( \varepsilon_o \) for the pellets used in this research ranged from 0.68 to 0.78 with a majority in the range 0.74 to 0.76. Thus, zero values for the local porosity are predicted by the VPGM at local values of \( X<1.0 \) for those pellets whose initial porosity is less than 0.747.

Thus, the radial profile of local fractional conversion obtained by solving the model equations permits calculation of the radial profiles for grain radius, grain density, and pellet porosity.

Knudsen diffusivity. The following relation for the Knudsen diffusivity was used [6]

\[ D_K = 19400 \frac{\varepsilon}{A_S \rho_P} \sqrt{T/M} \]  

(VI-10)

In this equation, \( T \) is the absolute temperature (°K), \( M \) is the molecular weight of the diffusing gas, \( \rho_P \) is the bulk density of the pellet, and \( A_S \) is the specific surface area. Rearrangement of equation III-30 provides an expression for the local specific surface area.
which when used with VI-9 for $\varepsilon$, permits calculation of the radial profile for the Knudsen diffusivity via equation VI-10.

**Molecular diffusivity.** The Chapman-Enskog equation [7] was used to estimate binary molecular diffusivities for the gas components of this reaction system. The technique given by Satterfield [6] was used to estimate the diffusion coefficient ($D_m$) for a single gas through a mixture of $n$ components.

**Pellet effective diffusivity.** A well accepted correlation for pellet effective diffusivity ($D_e$) and the one used by Georgakis et al. [1] is

$$D_e = D_G \frac{\varepsilon}{\tau}$$  \hspace{1cm} (VI-12)

where $\tau$ is the tortuosity factor and $D_G$ is given by

$$D_G = \frac{1}{\frac{1}{D_m} + \frac{1}{D_K}}$$  \hspace{1cm} (VI-13)

Georgakis et al. [1] assumed $\tau$ to be constant. The random pore model of Wakao and Smith [9] was used in this work since a more realistic approach is to allow $\tau$ to vary with solid structural changes.

Wakao and Smith [9] concluded that $\tau = 1/\varepsilon$ which transforms VI-12 to

$$D_e = D_G \varepsilon^2$$  \hspace{1cm} (VI-14)

Wen [10] has suggested that the exponent in VI-14 varied between 2.0 and 3.0. A value of 2.0 has been assumed for the present modelling work. Thus, using equations VI-9, 10,
13 and 14, the radial profile for pellet effective diffusivity may be generated.

**External mass transfer coefficient.** The method of Froessling [11] was chosen to estimate the mass transfer coefficient, $k_m$. The appropriate expression was given in Chapter V as equation V-18.

**Grain diffusivity.** Grain diffusion is assumed to occur by the mechanism of solid state diffusion, as grain porosity ($\varepsilon_p$) is assumed zero. There exists no method to estimate *a priori* a value for the grain solid state diffusivity, $D_s'$. Determination of this parameter will be by "best fit" to the data by a trial-and-error procedure. Solid state diffusion is an activated process and as such the temperature dependence may be modelled by an Arrhenius-type relationship [12].

**Reaction rate constant.** An Arrhenius-type relationship for the rate constant based on experimental initial rate data was given in Chapter V as

$$k_s' = 0.4172 \ e^{-\frac{5297}{RT}}$$

(V-24)

Due to the small value of the relative reaction resistance (See Table V-4) it is conceded that considerable uncertainty exists in the value of $k_s'$. However, equation V-24 is the best expression based on available data. Unless stated otherwise, V-24 will be used in the modelling work for rate constant predictions and will henceforth be referred to as the base case value for $k_s'$. Whenever a value of $k_s'$ other than that predicted by V-24 is used, this fact will be clearly pointed out.
Values for constants pertinent to the present reaction system used in the modelling work are listed below:

\[ a_G = \text{stoichiometric coefficient for reactant gas NO}_2 = -2.0 \]
\[ a_S = \text{stoichiometric coefficient for reactant solid CaO} = -1.0 \]
\[ a_P = \text{stoichiometric coefficient for product solid Ca(NO}_3)_2 = 1.0 \]
\[ A_{S_O} = \text{initial specific surface area of solid reactant} = 2.55.2 \text{ cm}^2/\text{mg} \]
\[ \rho_S = \text{true crystalline density of CaO} = 3380 \text{ mg/cm}^3 \]
\[ \rho_P = \text{true crystalline density of Ca(NO}_3)_2 = 2504 \text{ mg/cm}^3 \]
\[ M_G = \text{molecular weight of NO}_2 = 46.01 \text{ mg/mgmole} \]
\[ M_S = \text{molecular weight of CaO} = 56.08 \text{ mg/mgmole} \]
\[ M_P = \text{molecular weight of Ca(NO}_3)_2 = 164.08 \text{ mg/mgmole} \]
\[ \gamma = \text{expansion factor} = 3.96 \]
\[ r_{S_O}' = \text{initial grain radius} = 3.478 \times 10^{-6} \text{ cm} \]

**Numerical Solution Procedure**

The numerical solution procedure used by Gibson [13] was adapted for this work. The gas phase material balance was solved using finite difference approximations and a modification of Gaussian elimination which made use of the Thomas algorithm. The solid phase material balance equation (which is used to increment in time) was solved by Hamming's predictor-corrector method with a fourth-order Runge-Kutta initiator. Detailed discussion of these numerical methods can be found in Carnahan et al. [14].
The general numerical procedure is outlined below:

1) Utilizing the appropriate boundary conditions, the gas phase material balance is solved at initial conditions to give the initial reactant gas concentration versus pellet radial position profile.

2) The solid phase material balance is solved with the current values for the model parameters, thereby incrementing in time. The result of this calculation is the radial profile for the grain unreacted-core radius (at the new time step) from which the radial profile of the local fractional conversion is obtained.

3) The model parameters are updated as a function of radial position.

4) The overall fractional conversion is obtained by integrating the local fractional conversion profile with respect to pellet volume using Simpson's rule.

5) If the desired overall fractional conversion is reached the numerical procedure is stopped. If not, the gas phase material balance is solved using the new values obtained in steps 2), 3), and 4). Steps 2) and 5) are repeated until the desired overall fractional conversion is reached.

Complete program listings, including sample input and output, can be found in Appendix C.
B) Model Results Using the Constant Property Grain Model

Runs at 150° and 350°C were chosen for comparison with the constant property grain model (CPGM). A more exhaustive study was not warranted since the CPGM has limited applicability for the present system in which changes in solid properties are significant.

As discussed in an earlier section, all model parameters except the grain diffusion coefficient (D_g) may be estimated or measured a priori. For initial analysis of the experimental data with the CPGM, grain diffusion resistance was rendered negligible in the model by making D_g large (10^{-3} \text{ cm}^2/\text{min}). This permitted examination of how well the CPGM could match experimental data when only three resistances were allowed - namely, external mass transfer, pore diffusion, and intrinsic chemical reaction. As shown in Figure VI-1, the agreement at both 150° and 350°C is extremely poor. The CPGM grossly overpredicts the time-conversion behavior. Failure of this model to predict experimental reaction data may be due in part to the absence of grain diffusion resistance and suggests that this resistance is important. Also, solid property variations due to reaction are not considered.

Inclusion of grain diffusion in the CPGM was undertaken next. In this model and the variable property grain model presented in the next section, grain diffusion is assumed to occur by solid state diffusion. Solid state diffusion is an activated process and as such the diffusion coefficient
Figure VI-1. Comparison of Experimental Data to Constant Property Grain Model Predictions (No Grain Diffusion Resistance) \( T=150^\circ C, T=350^\circ C \)
exhibits an Arrhenius relationship with temperature. Thus, at lower temperatures, the grain diffusion coefficient would conceivably be small and the grain diffusion resistance large.

Since no method exists to estimate \textit{a priori} a value for the grain diffusion coefficient, the determination of the most suitable value was by trial-and-error. The best value for a given run was chosen to be that which resulted in good correlation of predicted time-conversion behavior with experimental. At 150°C this was accomplished by matching the conversion at later times and accepting a poorer early agreement. At 350°C this approach was not possible since the CPGM can not predict reaction "die-off". Instead "good" correlation at 350°C was taken as matching the early time-conversion behavior.

Typical results when grain diffusion resistance is included at 350°C and 150°C are given in Figures VI-2 and 3, respectively. Inclusion of grain diffusion resistance clearly improves the match between model and experimental data when compared to the case of negligible grain diffusion resistance (\(D'_s = 10^{-3} \text{ cm}^2/\text{min}\)). Best values for the grain diffusion coefficient in these figures were determined to be 1.0 \(\times 10^{-11} \text{ cm}^2/\text{min}\) at 150°C and 2.0 \(\times 10^{-9} \text{ cm}^2/\text{min}\) at 350°C. The fit at 350°C is seen to be excellent at low times (0-15 minutes); however, the fit becomes less satisfactory as time goes on. In particular, the model fails to predict the reaction "die-off" observed. The results at 450°C and 550°C are similar to that at 350°C.
Figure VI-2. Comparison of Experimental Data to Constant Property Grain Model, Effect of Grain Diffusion Resistance, T=350°C
Fractional Conversion of CaO

- Run 241, T=150°C, 1.8% NO₂

Grain Model Predictions

$D_s' = 10^{-3} \frac{cm^2}{min}$

$D_s' = 1.0 \times 10^{-1} \frac{cm^2}{min}$

Figure VI-3. Comparison of Experimental Data to Constant Property Grain Model, Effect of Grain Diffusion Resistance, T=150°C
The results at 150°C shown in Figure VI-3 are more promising. Although initial agreement is not perfect, the agreement improves at later times. Similar behavior was observed at 250°C. Better overall agreement with lower temperature data may be the result of the lower overall conversions (less than ten percent) which suggests no significant variations in solid properties have yet occurred. Also, at the lower temperatures, grain diffusion resistance is conceivably very important, perhaps even controlling, which implies uniform solid property profiles within the pellet.

In general it may be concluded that the constant property grain model can be tuned to give an acceptable match to the experimental data only when the overall conversion is low enough that significant solid property changes have not occurred. However, when the above conditions are not met there is no possibility the CPGM can match the experimental results observed. Therefore, a need exists for a better model; one that can adequately predict the reaction "die-off" encountered in this study. In the next section the results of the variable property grain model will be presented.

C) Predictions of the Variable Property Grain Model

The variable property grain model (VPGM) was applied to experimental data obtained at 150°, 250°, 350°, 450° and 550°C. The value for the grain diffusivity \(D'_g\) was
adjusted - by a trial and error procedure - until a good correlation of the model with experimental time-conversion data was obtained. Agreement of individual runs at 350°, 450°, and 550°C was superior to that at 150° and 250°C. Thus, in the ensuing presentation an alternate method of fitting the model to the data at 150° and 250°C by adjusting $k_s$ will also be discussed.

VPGM Predictions at 150°C. Figures VI-4 and VI-5 present the predictions of the VPGM-with and without grain diffusion resistance-as compared to experimental data collected at 150°C. Included in both figures are the predictions of the CPGM when grain diffusion resistance is negligible. Three observations may be made from Figures VI-4 and VI-5. First, in the absence of grain diffusion resistance, the VPGM comes closer to matching the experimental data than does the CPGM. The abrupt horizontal section in the VPGM curve ($D_s' = 10^{-3}$ cm²/min) in Figure VI-4 is predicted as a result of zero values for the local porosity at the pellet surface. The low initial porosity for this run ($\epsilon_o = 0.719$) indicates that the local porosity will become zero at local conversions less than 1.0. The critical (minimum) value for $\epsilon_o$ to prevent this is 0.747 as discussed previously. The abrupt break in the VPGM curve in Figure VI-4 may be contrasted to the gradual "die-off" depicted in Figure VI-5 for the VPGM curve ($D_s' = 10^{-3}$ cm²/min). The initial porosity for this latter run is 0.748. Thus, local values of porosity never become zero but become small
Figure VI-4. Comparison of Experimental Data with VPGM Predictions, Effect of Grain Diffusion Resistance $T=150^\circ C$
Fractional Conversion of CaO, $X$

$D_s^* = 10^{-3} \text{ cm}^2/\text{min}$

$D_s^* = 3.0 \times 10^{-11} \text{ cm}^2/\text{min}$

Run #249 $\varepsilon_o = .748$, 0.5%NO$_2$

VPGM Predictions
CPGM Predictions

Figure VI-5. Comparison of Experimental Data with VPGM Predictions, Effect of Grain Diffusion Resistance, T=150°C
enough at the pellet surface to significantly retard diffusion of reactant gas into the pellet. More will be said of this phenomenon later in this section where the profiles of structural properties predicted by the VPGM will be discussed. Secondly, inclusion of grain diffusion resistance in the VPGM is necessary to predict adequately the experimental data. Note the much improved agreement in both Figures VI-4 and VI-5 when grain diffusion resistance is included. Thirdly, the quality of the overall fit for the VPGM at 150°C is very similar to that of the CPGM—poor agreement initially with better agreement at later times. The similar behavior for the CPGM and VPGM at 150°C may be attributed to the low overall conversions (less than ten percent) which suggests relatively small variations in solid properties to distinguish the two models. Also, at this temperature, grain diffusion resistance is very important, perhaps even controlling, which implies uniform solid profiles within the pellet.

As part of the computer output of the VPGM, radial profiles of key system variables including local fractional conversion, dimensionless gas concentration, local porosity, and dimensionless grain radius were tabulated at selected overall conversion level increments. These profiles were valuable in interpreting the actual reaction behavior observed.

Figure VI-6 shows the radial fractional conversion profile predicted by the VPGM at 150°C (Run 241) at an
Figure VI-6. Local Fractional Conversion Profiles at an Overall Conversion of .08 - Effect of Grain Diffusion Resistance. $T=150^\circ C$
overall conversion level of 0.08 when grain diffusion is negligible \( (D'_g = 10^{-3} \, \text{cm}^2/\text{min}) \) and when grain diffusion is important \( (D'_g = 3.5 \times 10^{-11} \, \text{cm}^2/\text{min}) \). The time-conversion results (experimental and model predictions) for this run were given previously in Figure VI-4. When grain diffusion resistance is made negligible in the model, the VPGM predicts a steep conversion profile in which the bulk of the reaction occurs very near the surface of the pellet and the local porosity there becomes zero. This is shown in Figure VI-7 where predicted radial porosity profiles at selected overall conversion levels are depicted. The fractional conversion profile shown in Figure VI-6 when \( D'_g = 3.5 \times 10^{-11} \, \text{cm}^2/\text{min} \) is very flat. The porosity profiles in this case are also flat with porosity decreasing from 0.719 (initial value) to 0.66 throughout the pellet at a value of \( \bar{X} = 0.08 \). Since better match between model predictions and data occurred when \( D'_g = 3.5 \times 10^{-11} \, \text{cm}^2/\text{min} \), the flat profiles predicted should be more realistic of actual behavior.

Comparing the "best" values of the grain diffusivity \( (D'_g) \) for Run 241 using the CPGM and the VPGM \( (1.0 \times 10^{-11} \, \text{and} \, 3.5 \times 10^{-11} \, \text{cm}^2/\text{min}, \, \text{respectively}) \), one sees that the VPGM requires a larger value for \( D'_g \). Grain diffusion resistance is dependent on diffusion path length as well as the diffusion coefficient. In the present system, this length is the thickness of the product layer about each grain. For the VPGM this thickness is greater than for the CPGM due to grain expansion with reaction. It is logical
Figure VI-7. Local Porosity Profiles at Various Overall Conversions Predicted by the VPGE - Negligible Grain Diffusion Resistance T=150°C
therefore, that in order to match the same experimental data the VPGM would require a larger value for D' than the CPGM. A total of six runs at 150°C were examined with the best value of D' determined for each. Individual best values are summarized in Table VI-1. Excepting Run 240, the scatter in D' is relatively small at 150°C.

The "best" value for D' at a given temperature was chosen as the average of the individual "best" values at that temperature. The value of D' at 150°C was determined to be $4.58 \times 10^{-11}$ cm$^2$/min. Predictions of the VPGM for two runs when this value of D' is used appear in Figure VI-8 a) and b), respectively. For comparison the curves for the individual best D' are also given. The closeness of the two curves in Figure VI-8a is a reflection of the closeness of the value for individual best D' and the average D'. Figure VI-8b, on the other hand, represents the case where the deviation between individual best and the average value is maximum. Using the average D' the VPGM underpredicts the best fit curve ($D'_s = 8.5 \times 10^{-11}$ cm$^2$/min) and the experimental data at all times.

VPGM Predictions at 250°C. Qualitatively, the predictions of the VPGM at 250°C were similar to those at 150°C. The results for a 250°C run appear in Figure VI-9. The "best" value of D' for this run was determined to be $2.50 \times 10^{-10}$ cm$^2$/min. Using this value for D', the model underpredicts initially but the model and experimental curves coincide at later times. (This behavior was observed for all runs at 250°C except one which will be discussed.
TABLE VI-1
Best Values for $D_s'$ at 150°C

<table>
<thead>
<tr>
<th>Run Number</th>
<th>$%$NO$_2$</th>
<th>$D_s'$ (cm$^2$/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>241</td>
<td>1.8</td>
<td>$3.5 \times 10^{-11}$</td>
</tr>
<tr>
<td>246</td>
<td>1.8</td>
<td>$3.5 \times 10^{-11}$</td>
</tr>
<tr>
<td>247</td>
<td>1.8</td>
<td>$3.5 \times 10^{-11}$</td>
</tr>
<tr>
<td>240</td>
<td>1.0</td>
<td>$8.5 \times 10^{-11}$</td>
</tr>
<tr>
<td>248</td>
<td>1.0</td>
<td>$5.5 \times 10^{-11}$</td>
</tr>
<tr>
<td>249</td>
<td>0.5</td>
<td>$3.0 \times 10^{-11}$</td>
</tr>
</tbody>
</table>

Average = $4.58 \times 10^{-11}$ cm$^2$/min
Standard Deviation = $2.11 \times 10^{-11}$ cm$^2$/min
Fractional Conversion of CaO

- Run 246 $e_0 = 0.759$, 1.8% NO$_2$
- Run 240 $e_0 = 0.683$, 1.0% NO$_2$

**VPGM Predictions**

- $D_s' = 4.58 \times 10^{-11} \text{ cm}^2/\text{min}$
- $D_s' = 3.5 \times 10^{-11} \text{ cm}^2/\text{min}$
- $D_s' = 8.5 \times 10^{-11} \text{ cm}^2/\text{min}$
- $D_s' = 4.58 \times 10^{-11} \text{ cm}^2/\text{min}$

Figure VI-8. Comparison of Experimental Data with Predictions of the VPGM - Use of Average Grain Diffusion Coefficient $T=150^\circ C$
shortly.) Agreement is not perfect but it is an improvement over the case of negligible grain diffusion resistance \( (D'_g = 10^{-3} \text{ cm}^2/\text{min}) \) for either VPGM or CPGM, also shown in Figure VI-9. In the absence of grain diffusion resistance, both the VPGM and CPGM overpredicted initially but in the case of VPGM this was followed by reaction "die-off" at a conversion of 0.145, once again the predicted die-off occurred when the surface porosity became very small.

A total of 13 runs at 250°C were analyzed with the best value of \( D'_g \) determined for each. Individual best values are listed in Table VI-2. With the exception of Run 243, the values of \( D'_g \) are grouped on either side of \( 3.0 \times 10^{-10} \text{ cm}^2/\text{min} \). Thus, the values of \( D'_g \) observed at 250°C are approximately one order of magnitude greater than those reported at 150°C.

The unusually high value of \( D'_g \) for Run 243 occurs because of the atypical nature of the experimental data for Run 243. This run exhibited reaction "die-off" experimentally while other runs at 250°C did not. Also, the final conversion for Run 243 (0.20) was well above the conversion for other 250°C runs. The VPGM was able to match this behavior (See Figure VI-10) but required a value for \( D'_g \) two orders of magnitude greater than the typical value observed at 250°C. The reason for this anomalous behavior is unknown but the value for \( D'_g \) from Run 243 was not included when the individual best values were averaged.
Fractional Conversion of CaO,

- Run #201, $c_o = 0.763$, 0.5% NO$_2$
- VPGM Predictions

Figure VI-9. Comparison of Experimental Data with VPGM Predictions, Using Average Value of $D_s^\prime$, $T=250^\circ$C

$D_s^\prime = 10^{-3}$ cm$^2$/min

$D_s^\prime = 2.50 \times 10^{-10}$
### TABLE VI-2

Best Values for $D'$ at 250°C

<table>
<thead>
<tr>
<th>Run Number</th>
<th>$%$NO₂</th>
<th>$D'$ (cm²/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>194</td>
<td>1.8</td>
<td>$1.25 \times 10^{-10}$</td>
</tr>
<tr>
<td>195</td>
<td>1.8</td>
<td>$0.50 \times 10^{-10}$</td>
</tr>
<tr>
<td>196</td>
<td>1.8</td>
<td>$3.0 \times 10^{-10}$</td>
</tr>
<tr>
<td>191</td>
<td>1.8</td>
<td>$2.0 \times 10^{-10}$</td>
</tr>
<tr>
<td>192</td>
<td>1.8</td>
<td>$2.0 \times 10^{-10}$</td>
</tr>
<tr>
<td>193</td>
<td>1.8</td>
<td>$1.25 \times 10^{-10}$</td>
</tr>
<tr>
<td>243*</td>
<td>1.8</td>
<td>$5.0 \times 10^{-8}$</td>
</tr>
<tr>
<td>200</td>
<td>1.0</td>
<td>$3.0 \times 10^{-10}$</td>
</tr>
<tr>
<td>198</td>
<td>1.0</td>
<td>$2.5 \times 10^{-10}$</td>
</tr>
<tr>
<td>197</td>
<td>1.0</td>
<td>$6.0 \times 10^{-10}$</td>
</tr>
<tr>
<td>201</td>
<td>0.5</td>
<td>$2.5 \times 10^{-10}$</td>
</tr>
<tr>
<td>202</td>
<td>0.5</td>
<td>$9.5 \times 10^{-10}$</td>
</tr>
<tr>
<td>203</td>
<td>0.5</td>
<td>$9.5 \times 10^{-10}$</td>
</tr>
</tbody>
</table>

Average = $3.58 \times 10^{-10}$ cm²/min

Standard Deviation = $3.08 \times 10^{-10}$

*Not included when calculating the average $D'$ at 250°C.*
The "best" value was chosen as the average of the individual best values determined for the runs at 250°C. Neglecting Run 243, the best value for \( D' \) at 250°C was determined to be \( 3.58 \times 10^{-10} \text{ cm}^2/\text{min} \).

Utilization of an average \( D' \) worked well for many runs at 250°C. A typical run is shown in Figure VI-11 which includes the best curve for the run for comparison. However, there were some runs in which the use of the average \( D' \) at 250°C (\( 3.58 \times 10^{-10} \text{ cm}^2/\text{min} \)) resulted in a less satisfactory match between model predictions and experimental data. The results for one such run are depicted in Figure VI-12. The model and experimental curves cross at 15 minutes with model overprediction increasing with time thereafter. The best curve (\( D'=1.25 \times 10^{-10} \text{ cm}^2/\text{min} \)) for this run is included for comparison.

The predicted profiles for local conversion at 250°C were similar to those observed at 150°C. Figure VI-13 shows for \( \bar{x}=.08 \) that at 250°C (Run 201) when grain diffusion resistance is made negligible in the model (\( D'=10^{-3} \text{ cm}^2/\text{min} \)), a steep conversion profile near the pellet surface is predicted. A flat conversion profile is predicted when \( D'=2.5 \times 10^{-10} \text{ cm}^2/\text{min} \) as shown in Figure VI-13. Since better agreement between model predictions and experimental time-conversion data occurred when a small \( D' \) is used, the flat conversion profile is believed to be more realistic.
Fractional Conversion of CaO

Run 243 $\varepsilon_o = 0.752, 1.8\% \text{ NO}_2$

$D' = 5.0 \times 10^{-8} \text{ cm}^2/\text{min}$

Figure VI-10. Comparison of Experimental Data with Predictions of the VPGM - $T=250^\circ\text{C}$
Figure VI-11. Comparison of Experimental Data with VPGM Predictions - Use of Average Grain Diffusion Coefficient. $T=250 \degree C$. 

- Run 200, $\varepsilon_o = 0.747$, 1.0% NO$_2$

$D_s' = 3.58 \times 10^{-10} \text{ cm}^2 / \text{min}$

$D_s' = 3.0 \times 10^{-10} \text{ cm}^2 / \text{min}$
Figure VI-12. Comparison of Experimental Data to VPGM Predictions, T=250°C

- Run #193 $\epsilon_o = .765$, 1.8% NO$_2$

VPGM Predictions

$D_S^- = 3.58 \times 10^{-10}$ cm$^2$/min

$D_S^- = 1.25 \times 10^{-10}$ cm$^2$/min
Run 201
\( e_0 = 0.763 \)

0.5% NO\(_2\)

\( X = 0.08 \)

\[ D_s' = 10^{-3} \frac{\text{cm}^2}{\text{min}} \]

\[ D_s' = 2.5 \times 10^{-10} \frac{\text{cm}^2}{\text{min}} \]

Figure VI-13. Local Fractional Conversion Profiles of an Overall Conversion of 0.08 - Effect of Grain Diffusion Resistance. 

\( T = 250\, ^\circ\text{C} \)
Alternate Approaches to Matching the VPGM to Experimental Data at 150° and 250°C. The VPGM results at 150°C and 250°C have all suffered from poor initial agreement. The magnitude of $D'_s$ required for good match at later times has made grain diffusion the controlling resistance. In an effort to improve the overall agreement of the VPGM at these temperatures, two alternate approaches of matching the VPGM to experimental data were explored.

At low temperatures the activated processes (chemical reaction or grain diffusion) would be expected to contribute significant resistance. The previous presentation addressed the case when grain diffusion controls. A similar approach was taken with respect to chemical reaction. For selected runs at 150° and 250°C grain diffusion resistance was made negligible in the model ($D'_s=10^{-3}$ cm²/min) and the value for the rate constant ($k'_s$) was adjusted - by trial and error procedure - until a good match between model predictions and data occurred.

Two methods were used. First, $k'_s$ was decreased with respect to the base case $k'_s$ in an effort to match the final conversion; secondly, $k'_s$ was increased. The ability to improve fit by altering $k'_s$ in both directions is unique to the VPGM as will be discussed later.

Typical results at 150° and 250°C for the first method appear in curve (1) of Figures VI-14 and 15, respectively. The results are very poor with severe underprediction at early times followed by increasing overprediction as time
Fractional Conversion of CaO

- Run 248 $e_o = 0.747$, 1.0% NO$_2$

VPGM Predictions ($D_s^* = 10^{-3}$ cm$^2$/min)

1. $k_s^* = 5.0 \times 10^{-6}$ cm$^4$/mgmole min
2. $k_s^* = 1600. \times 10^{-4}$ cm$^4$/mgmole min

Figure VI-14. Comparison of Experimental Data with Predictions of the VPGM -
Use of $k_s^*$ to Match Data, $T=150^\circ$C
Run 198 \( e_o = 0.756, 1.0\% \text{ NO}_2 \)

VPGM Predictions \((D' = 10^{-3} \text{ cm}^2 \text{ min})\)

- \((1) k'_s = 1.0 \times 10^{-5} \frac{\text{ cm}^4}{\text{ mgmole min}}\)
- \((2) k'_s = 50. \times 10^{-4} \frac{\text{ cm}^4}{\text{ mgmole min}}\)

Figure VI-15. Comparison of Experimental Data with Predictions of the VPGM - Use of \(k'_s\) to Match Data, \(T=250^\circ \text{C}\)
goes on. This method is clearly inferior to the match obtained by fitting on the grain diffusion coefficient. Decreasing $k_s'$ to improve agreement at later times increases the already unacceptable underprediction at early times.

The second method - increasing $k_s'$ - is demonstrated in curve (2) of Figures VI-14 and 15 at 150°C and 250°C, respectively. In this case, the VPGM overpredicts initially followed by prediction of reaction "die-off." (It is important to recognize that this approach is possible only for the VPGM due to its ability to predict zero surface porosity. While agreement is better than for curve (1), the method of increasing $k_s'$ has two major drawbacks. First, the method is based on prediction on reaction "die-off". Typical results in Figures VI-14 and 15 show that the experimental data at 150°C and 250°C never really dies off but instead increases steadily (albeit slowly). Secondly, and more importantly, the required value of $k_s'$ at 150°C is inconsistent with that at 250°C. $k_s'$ for these runs was determined to be $1600 \times 10^{-4} \text{ cm}^4/\text{mg mole min}$ and $50.0 \times 10^{-4} \text{ cm}^4/\text{mg mole min}$ at 150°C and 250°C, respectively. In addition when this method was applied at 350°C, the best $k_s'$, shown in Figure VI-16, was smaller ($k_s'=4.15 \times 10^{-4} \text{ cm}^4/\text{mg mole min}$) than that at 250°C. A decreasing $k_s'$ with temperature is totally unrealistic and consequently this method was abandoned.

Thus, we conclude that the slow but steady reaction observed at 150°C and 250°C is best described by the small grain diffusion coefficients.
Figure VI-16. Comparison of Experimental Data with Predictions of the VPGM - Use of $k_s^*$ to Match Data, T=350°C

$k_s^* = 4.15 \times 10^{-4} \frac{cm^4}{mgmole \text{ min}}$

$\triangle$ - Run 204, $\varepsilon_o = 0.768$, 1.0% NO$_2$

VPGM Predictions ($D_s^* = 10^{-3} \frac{cm^2}{\text{min}}$)
The Importance of Chemical Reaction Resistance at 150° and 250°C. The small values for the average $D_\text{s}$ at 150° and 250°C (4.5 $\times$ 10$^{-11}$ cm$^2$/min and 3.5 $\times$ 10$^{-10}$ cm$^2$/min, respectively) suggest that grain diffusion resistance is very important. However, at low temperatures other "activated" processes such as chemical reaction may also offer significant resistance. Determination of the sensitivity of the VPGM predictions to changes in $k'_s$ provides insight into the importance of chemical reaction resistance at 150°C and 250°C. If changes in $k'_s$ result in significant changes in the predicted time-conversion behavior, then chemical reaction resistance is important. Likewise, if the predicted time-conversion behavior is insensitive to changes in $k'_s$ then it may be concluded that chemical reaction resistance is very small.

Figures VI-17 and 18 show the results when $k'_s$ is varied by two orders of magnitude from its base case value at 150° and 250°C, respectively. (The base case value is taken as the value predicted by the Arrhenius expression given as equation V-24.) The predictions are not very sensitive to a two order of magnitude increase in $k'_s$. Larger effects are seen when $k'_s$ is reduced by two orders of magnitude. These results are offered as additional evidence that grain diffusion resistance is much more important than chemical reaction resistance at 150° and 250°C.

The unique capability of the VPGM to predict experimentally observed reaction "die-off" will be demonstrated in
Fractional Conversion of CaO, X

- Run 241
- VPGM Predictions ($D_s = 4.26 \times 10^{-11} \text{ cm}^2 / \text{min}$)

$$k_s^* = 7.644 \times 10^{-4} \text{ cm}^4 / \text{mgmole min}$$

Figure VI-17. Comparison of Experimental Data with Predictions of the VPGM - Effect of $k_s^*$, T=150°C
Fractional Conversion of CaO, X

- Run 201
- VPGM Predictions ($D_s = 2.87 \times 10^{-10} \text{ cm}^2 \text{ min}^{-1}$)

$$k_s = 25.51 \times 10^{-4} \frac{\text{cm}^4}{\text{mg mole min}}$$

Figure VI-18. Comparison of Experimental Data with Predictions of the VPGM - Effect of $k_s$, $T=250^\circ C$
the next two sections in which the results of the model at 350°C, 450°C, and 550°C are presented.

**VPGM Predictions at 350°C.** The experimental results at 350°C and above differed from those observed at the lower temperatures. In particular, at the lower temperatures the phenomenon of reaction "die-off" was not observed. Instead the reaction proceeded at a slow but steady rate. As shown in earlier sections of this chapter, it was possible to match this behavior by fitting on \( D_s' \) alone. The best match between model predictions and experimental data at 150° and 250° occurred with small values of \( D_s' \), thereby making grain diffusion resistance controlling. In contrast, the experimental data at 350°, 450°, and 550°C exhibited reaction "die-off" believed to be caused by surface porosity approaching zero, thus making pore diffusion resistance very important. However, the only means of matching the experimental behavior at these temperatures required fitting on \( D_s' \) also. Thus, grain diffusion resistance was also found to be significant at 350°C and above. This parameter determined to a large extent the overall conversion at which die-off occurred.

Figures VI-19 and 20 compare the results of the VPGM, the CPGM, and experimental data. The CPGM and VPGM exhibit similar predictive capability at early times but the CPGM fails completely at later times to match the experimental data. In particular, the CPGM can not predict reaction "die-off". The predictions of the VPGM are superior to
Figure VI-19. Comparison of Experimental Data with Predictions of the VPGM and CPGM. T=350 °C

\[ D_s^* = 0.35 \times 10^{-9} \text{ cm}^2/\text{min} \]

\[ D_s^* = 3.0 \times 10^{-8} \text{ cm}^2/\text{min} \]
Figure VI-20. Comparison of Experimental Data with Predictions of VPGM and CPGM. T=350°C
those of the CPGM. In both figures the VPGM does a good job of predicting the experimentally observed die-off conversion. In fact the agreement shown in Figure VI-19 is excellent at all times; the agreement in Figure VI-20 is good with only minor underprediction occurring at intermediate times (5 to 12 minutes).

Included in Figure VI-20 are the predictions of the VPGM with a large $D'_s$ ($10^{-3}$ cm$^2$/min). Small overprediction at early times followed by premature "die-off" was typical of all VPGM results observed at 350°C when grain diffusion resistance was made negligible. Thus, inclusion of grain diffusion resistance in the VPGM is necessary to predict adequately the experimental data.

The VPGM predicts reaction "die-off" by virtue of the surface porosity approaching zero thereby preventing diffusion of reactant gas into the pellet. If reaction "die-off" occurs at an overall conversion much less than one, the predicted radial conversion profiles should be steep and reaction should be largely restricted to a region near the pellet surface. Also, the profiles should become steeper in time owing to the increased importance of pore diffusion resistance. Such behavior is depicted in Figure VI-21 in which the local fractional conversion profiles predicted by the VPGM are plotted. The time-conversion results for this run were presented previously in Figure VI-19. The conversion profiles in Figure VI-21 are steep and become steeper as overall conversion and time increase. At the die-off
Figure VI-21. Local Fractional Conversion Profiles at Various Overall Conversion Levels as Predicted by the VPGM. $T=350^\circ$C.
conversion (overall) of 0.30, the VPGM predicts all of the solid has been converted at the surface but local fractional conversion is less than 0.45 at a distance ten per cent from the surface with the inner 40% of the pellet remaining virtually unreacted.

The steep predicted conversion profiles also produce large radial gradients in the profiles of solid properties (for example, porosity). As shown in Figure VI-22, most of the change occurs in the outer 30% of the pellet. As porosity decreases, pore diffusion resistance increases. The porosity at "die-off" in Figure VI-22 is 0.036. While this is not zero ($\varepsilon_0$ for this run is greater than 0.747), it is small enough to effectively stop the reaction by significantly retarding diffusion of reactant gas into the pellet.

Figure VI-23 presents the predicted dimensionless reactant gas concentration at various overall conversions for the same run. This figure provides insight as to the relative importance of external mass transfer and pore diffusion resistance. The dimensionless reactant reactant gas concentration ($C$) at the pellet surface ($\xi=1.0$) is a measure of the relative mass transfer resistance. As $C$ approaches 1.0, the external mass transfer resistance approaches zero. In Figure VI-23, $C$ at the surface is 0.23, 0.71, 0.85, and 0.97 at overall conversions of 0.0, 0.10, 0.20, and 0.30, respectively.
Figure VI-22. Local Porosity Profiles at Various Overall Conversions as Predicted by VPGM. T=350°C

Run 189
\[ \varepsilon_0 = 0.756 \]
1.8% NO₂

\[ D_s' = 3.0 \times 10^{-8} \text{ cm}^2 \text{ min}^{-1} \]
Run 189
\[ \varepsilon_0 = 0.756 \]
1.8% NO₂

\[ D_s^* = 3.0 \times 10^{-8} \, \text{cm}^2/\text{min} \]

Figure VI-23. Dimensionless NO₂ Concentration at Various Overall Conversion Levels as Predicted by the VPGM. T=350°C
The slope of the profiles shown in Figure VI-23 is a measure of the relative importance of pore diffusion resistance. A small slope (flat profiles) implies small pore diffusion resistance. In contrast, a large slope implies a large pore diffusion resistance. The slopes depicted are clearly steep and become steeper with time which emphasizes that pore diffusion resistance is important and becomes more important as time goes on. This behavior is due to the decline in surface porosity with conversion (and thus, with time) as depicted in Figure VI-22.

The time-conversion results given previously in Figure VI-20 \((D' = 4.5 \times 10^{-8} \text{ cm}^2/\text{min})\) are typical of the quality of fit the VPGM yielded at 350°C - good early agreement, under-prediction at intermediate times, and excellent prediction of "die-off" conversion. (Reduction and, in some cases, elimination of the underprediction at intermediate times can be accomplished by relaxing one of the assumptions made in the development of the VPGM. This will be discussed and results presented at the end of this chapter.) In only one of eleven runs at 350°C was the VPGM not able to match the experimental data. For that case the experimental time-conversion results were significantly high than for the remaining ten runs. There is no ready explanation for this single run anomaly.

Eleven runs at 350°C were analyzed with the best value of \(D'_s\) determined for each. Individual best values appear in Table VI-3. The scatter in \(D'_s\) is within one order of
TABLE VI-3

Best Values for $D'_s$ at 350°C

<table>
<thead>
<tr>
<th>Run Number</th>
<th>$%$NO$_2$</th>
<th>$D'_s$ (cm$^2$/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>189</td>
<td>1.8</td>
<td>$3.0 \times 10^{-8}$</td>
</tr>
<tr>
<td>190</td>
<td>1.8</td>
<td>$4.5 \times 10^{-8}$</td>
</tr>
<tr>
<td>207</td>
<td>1.8</td>
<td>$1.10 \times 10^{-8}$</td>
</tr>
<tr>
<td>231</td>
<td>1.8</td>
<td>$1.25 \times 10^{-8}$</td>
</tr>
<tr>
<td>204</td>
<td>1.0</td>
<td>$5.50 \times 10^{-8}$</td>
</tr>
<tr>
<td>205</td>
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<td>$1.0 \times 10^{-8}$</td>
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<tr>
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<td>1.0</td>
<td>$1.50 \times 10^{-8}$</td>
</tr>
<tr>
<td>235</td>
<td>1.0</td>
<td>$0.45 \times 10^{-8}$</td>
</tr>
<tr>
<td>236</td>
<td>1.0</td>
<td>$0.55 \times 10^{-8}$</td>
</tr>
<tr>
<td>208</td>
<td>0.5</td>
<td>$2.0 \times 10^{-8}$</td>
</tr>
<tr>
<td>209</td>
<td>0.5</td>
<td>$1.0 \times 10^{-8}$</td>
</tr>
</tbody>
</table>
magnitude, approximately. The "best" value of $D_s'$ at 350°C was taken as the arithmetic average of the values shown in Table VI-3, that is, $2.08 \times 10^{-8} \text{ cm}^2/\text{min}$.

Figures VI-24 and 25 compare the VPGM predictions using the individual best $D_s'$ with the average $D_s'$. In Figure VI-24, the average $D_s'$ is somewhat larger than the individual best ($1.25 \times 10^{-8} \text{ cm}^2/\text{min}$) and the predicted die-off conversion for the average $D_s'$ is lower by 5% (absolute) than the experimental and "best" curve. Figure VI-25 shows a case when the average $D_s'$ is less than the "best" $D_s'$ ($5.50 \times 10^{-8} \text{ cm}^2/\text{min}$). Using the average $D_s'$, the VPGM underpredicts at early times, crosses the "best" curve at 25 minutes with increasing overprediction of the experimental data after 32 minutes. The sensitivity of the VPGM predictions at 350°C with respect to $D_s'$ suggests that both grain diffusion resistance and pore diffusion resistance are important at this temperature.

The importance of chemical reaction resistance is shown in Figure VI-26. A two order of magnitude increase in $k_s'$ increases the predicted conversion slightly at early times as compared to the base case curve ($k_s'$). The two curves cross at 10 minutes with the larger $k_s'$ slightly underpredicting the "die-off" conversion. Crossing of the curves occurs when pore diffusion resistance is large since a larger $k_s'$ increases the rate of conversion at the pellet surface, thereby, increasing the rate of decline in surface porosity. Larger effects are observed as $k_s'$ is decreased.
Figure VI-24. Comparison of Experimental Data with Predictions of the VPGM - Use of Average Grain Diffusion Coefficient. T=350°C
Fractional Conversion of CaO, $X$

$D_s^* = 2.08 \times 10^{-8} \frac{cm^2}{min}$

$D_s^* = 5.50 \times 10^{-8} \frac{cm^2}{min}$

Figure VI-25. Comparison of Experimental Data with Predictions of the VPGM - Use of Average Grain Diffusion Coefficient.

$T=350^\circ C.$
Fractional Conversion of CaO

Run 204, $\varepsilon_0 = 0.768$, 1.0% NO$_2$

VPGM Predictions ($D_s' = 5.50 \times 10^{-8}$ cm$^2$/min)

Time Scale Change

$k_s' \times 100$

$k_s'/100$

Time (mins) 0 1 2 3 4 5 10 15 20 25 30 35 40 45 50 55 60

Figure VI-26. Comparison of Experimental Data with Predictions of the VPGM - Effect of $k_s'$. $T=350$°C
with gross underprediction occurring throughout most of the reaction time. The small effect noted with increases in $k'_s$ suggests that chemical reaction offers a minor resistance at 350°C.

**VPGM Results at 450°C.** The predictions of the VPGM and the CPGM are shown in Figure VI-27 for a 450°C run. In a fashion similar to the 350°C results, the CPGM and VPGM exhibit similar predictive capability at early times (0-10 minutes) but the CPGM totally fails to predict the "die-off" observed experimentally. The VPGM by contrast does an excellent job of matching the experimental data for this run at all times. All results at 450°C were not as favorable as those shown in Figure VI-27. In some cases the VPGM had difficulty matching experimental conversions at intermediate times. A typical case is given in Figure VI-28 ($D'_s = 0.80 \times 10^{-8} \, \text{cm}^2/\text{min}$). (As pointed out earlier in the 350°C results section, this problem of matching intermediate time-conversion results can be reduced by relaxing one of the assumptions made in VPGM development and results will be presented in a later section.)

The effect of grain diffusion resistance is also shown in Figure VI-28. Overprediction at early times followed closely by premature reaction "die-off" was typical of all runs at 450°C when grain diffusion resistance was made negligible in the model ($D'_s = 10^{-3} \, \text{cm}^2/\text{min}$).
Figure VI-27. Comparison of Experimental Data with Predictions of the VPGM and CPGM. $T=450^\circ C$

- VPGM Predictions
- CPGM Predictions

$D_s^* = 0.20 \times 10^{-8} \text{ cm}^2 \text{ min}^{-1}$

$D_s^* = 1.0 \times 10^{-8} \text{ cm}^2 \text{ min}^{-1}$

Run 187, $\epsilon_o = 0.754$, 1.8% NO$_2$
Figure VI-28. Comparison of Experimental Data with Predictions of the VPGM -
Effect of Grain Diffusion Coefficient. T=450°C

Fractional Conversion of CaO, X

Time

Scale Change

$D_s' = 0.80 \times 10^{-8} \text{ cm}^2/\text{min}$

$D_s' = 10^{-3} \text{ cm}^2/\text{min}$

$\Delta$ - Run 219, $\epsilon_o = 0.746$, 1.0% NO$_2$

- VPGM Predictions

Time (mins)
Chemical reaction resistance at 450°C had less of an effect than at 350°C but the behavior was similar qualitatively - a two order of magnitude increase in $k'_s$ increased predicted conversions at early times with "die-off" conversion slightly lower than for the base case $k'_s$; decreasing $k'_s$ two orders of magnitude resulted in underprediction throughout most of the reaction time.

The local porosity profiles at various overall conversions for a typical run at 450°C appear in Figure VI-29. The predicted surface porosity for this run becomes zero at an overall conversion of 0.38. (The initial porosity for this run (.746) was less than the critical porosity (.747).) The greatest changes in porosity occurred in the outer 40% of the pellet. The predicted dimensionless gas concentration profiles for this run (#219) are steep and become steeper with overall conversion as depicted in Figure VI-30. Thus, pore diffusion resistance becomes more important as reaction time increases. Also discernible in Figure VI-30 is the decreasing importance of external mass transfer resistance with overall conversion - C at $\xi = 1.0$ (pellet surface) approaches 1.0 as overall conversion (and thus, reaction time) increase.

The steepness of the porosity profiles shown in Figure VI-29 suggests that other structural properties (such as grain radius) should exhibit steep profiles as well. This is shown in Figure VI-31 where the predicted grain radius at the pellet surface has increases 60% at die-off conversion
Figure VI-29. Local Porosity Profiles at Various Overall Conversions as Predicted by the VPGM. T=450°C

Run 219

$\varepsilon_0 = 0.746$

1.0% NO₂

Local Porosity, $\varepsilon$

Dimensionless Radial Position, $\bar{\xi}$
Figure VI-30. Dimensionless NO$_2$ Concentration at Various Overall Conversions as Predicted by the VPGM. $T=450^\circ C$
Figure VI-31. Dimensionless Grain Radius Profile at Various Overall Conversions as Predicted by the VPGM. T=450°C
(0.42) while the corresponding change at the pellet center is only 4%.

A total of nine runs were analyzed at 450°C with the best value for $D'_S$ determined for each by a trial-and-error procedure. The "best" values are summarized in Table VI-4. With the exception of Run 230, the scatter in the values is less than a factor of two. The average of the "best" individual values, $0.79 \times 10^{-8} \text{ cm}^2/\text{min}$, was taken as the "best" value for $D'_S$ at 450°C. Use of the average $D'_S$ and the "best" individual $D'_S$ for a run at 450°C are compared in Figure VI-32. Use of the average $D'_S$ (which is less than the individual "best" $1.20 \times 10^{-8} \text{ cm}^2/\text{min}$) resulted in under-prediction with respect to the best curve at all times. The sensitivity of VPGM predictions to the value of $D'_S$ used indicates that grain diffusion resistance is still quite important at 450°C.

**VPGM Results at 550°C.** The predictions of the VPGM at 550°C were very similar to those observed at 350° and 450°C. Likewise, fitting on $D'_S$ yielded good match between experimental data and VPGM predictions. Typical results appear in Figure VI-33. Agreement is good at early times and prediction of "die-off" is excellent. However, the same under-prediction at intermediate times which was observed at 350° and 450°C also occurred at 550°C. Included in Figure VI-33 are the predictions of the CFGM which are clearly inferior to the VPGM predictions. The best fit for the CFGM is seen
TABLE VI-4

Best Values for \( D' \) at 450°C

<table>
<thead>
<tr>
<th>Run Number</th>
<th>( % \text{NO}_2 )</th>
<th>( D' ) (cm(^2)/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>187</td>
<td>1.8</td>
<td>( 1.0 \times 10^{-8} )</td>
</tr>
<tr>
<td>188</td>
<td>1.8</td>
<td>( 1.0 \times 10^{-8} )</td>
</tr>
<tr>
<td>211</td>
<td>1.8</td>
<td>( 0.75 \times 10^{-8} )</td>
</tr>
<tr>
<td>229</td>
<td>1.8</td>
<td>( 0.50 \times 10^{-8} )</td>
</tr>
<tr>
<td>230</td>
<td>1.8</td>
<td>( 0.25 \times 10^{-8} )</td>
</tr>
<tr>
<td>219</td>
<td>1.0</td>
<td>( 0.80 \times 10^{-8} )</td>
</tr>
<tr>
<td>220</td>
<td>1.0</td>
<td>( 0.70 \times 10^{-8} )</td>
</tr>
<tr>
<td>221</td>
<td>0.5</td>
<td>( 1.20 \times 10^{-8} )</td>
</tr>
<tr>
<td>222</td>
<td>0.5</td>
<td>( 0.90 \times 10^{-8} )</td>
</tr>
</tbody>
</table>

Average Value = \( 0.79 \times 10^{-8} \) cm\(^2\)/min

Standard Deviation = \( 0.29 \times 10^{-8} \)
Figure VI-32. Comparison of Experimental Data with Predictions of the VPGM -
Use of Average Grain Diffusion Coefficient.  T=450°C
Figure VI-33. Comparison of Experimental Data with Predictions of the VPGM and CPGM. $T=550^{\circ}C$. 

- Run 233, $e_o = 0.761$, 1.8% NO$_2$
- VPGM Predictions ($D_s^* = 1.8 \times 10^{-8}$ cm$^2$ min$^{-1}$)
- CPGM Predictions ($D_s^* = 1.0 \times 10^{-8}$ cm$^2$ min$^{-1}$)
to match the experimental data at early times only. Lower values of $D'_s$ result in poorer early match with little improvement at later times since the CPGM cannot predict "die-off".

The experimental results for two runs at 550°C could not be matched by the VPGM with underprediction occurring at all but early times. However, for several runs (3) the agreement was excellent as shown by the example in Figure VI-34 ($D'_s = 4.5 \times 10^{-8} \text{ cm}^2/\text{min}$). The case when $D'_s$ is small ($10^{-3} \text{ cm}^2/\text{min}$) is also shown in Figure VI-34. The extremely poor fit - overprediction followed by the premature die-off - emphasizes the necessity of inclusion of grain diffusion resistance at 550°C.

A total of nine runs were analyzed at 550°C with individual "best" values for $D'_s$ determined for each by a trial-and-error procedure. These "best" values are summarized in Table VI-5. The scatter in $D'_s$ is approximately one order of magnitude. The "best" value for $D'_s$ at 550°C was taken as the average of the individual "best" values, $1.41 \times 10^{-8} \text{ cm}^2/\text{min}$. Use of this average value in the VPGM yielded results similar to those observed at 350° and 450°C.

In summary, the VPGM has been shown to be much superior to the CPGM at 350°, 450°, and 550°C due to the ability of the VPGM to predict reaction "die-off". However, it has been shown that additional improvements in the VPGM are desirable. In particular, the underprediction of the VPGM at intermediate times needs to be reduced. In the next
Fractional Conversion of CaO, X

- Run 218, $\varepsilon_0 = 0.754, 1.0\%$ NO$_2$
- VPGM Predictions

$D_s = 4.5 \times 10^{-8} \frac{cm^2}{min}$

$D_s' = 10^{-3} \frac{cm^2}{min}$

Figure VI-34. Comparison of Experimental Data with Predictions of VPGM - Effect of Grain Diffusion Resistance. T=550°C.
### TABLE VI-5

Best Values for $D_s'$ at 550°C

<table>
<thead>
<tr>
<th>Run Number</th>
<th>$% NO_2$</th>
<th>$D_s$ (cm²/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>214</td>
<td>1.8</td>
<td>$0.50 \times 10^{-8}$</td>
</tr>
<tr>
<td>213</td>
<td>1.8</td>
<td>$1.0 \times 10^{-8}$</td>
</tr>
<tr>
<td>232</td>
<td>1.8</td>
<td>$2.0 \times 10^{-8}$</td>
</tr>
<tr>
<td>233</td>
<td>1.8</td>
<td>$1.8 \times 10^{-8}$</td>
</tr>
<tr>
<td>234</td>
<td>1.8</td>
<td>$1.0 \times 10^{-8}$</td>
</tr>
<tr>
<td>215</td>
<td>1.0</td>
<td>$1.0 \times 10^{-8}$</td>
</tr>
<tr>
<td>218</td>
<td>1.0</td>
<td>$4.5 \times 10^{-8}$</td>
</tr>
<tr>
<td>216</td>
<td>0.5</td>
<td>$0.50 \times 10^{-8}$</td>
</tr>
<tr>
<td>217</td>
<td>0.5</td>
<td>$0.35 \times 10^{-8}$</td>
</tr>
</tbody>
</table>

**Average Value** = $1.41 \times 10^{-8}$

**Standard Deviation** = $1.29 \times 10^{-8}$
section a means of improving the VPGM predictions at 350°, 450°, and 550°C will be discussed.

Improvement in VPGM Predictions at 350°C, 450°C, and 550°C. Pore diffusion resistance has been shown to be important at 350°, 450°, and 550°C. Predictions of zero (or near zero) surface porosities have enabled the VPGM to match the experimentally observed "die-off" conversion. However, in many instances the VPGM underpredicted the experimental time-conversion data at intermediate times.

Pore diffusion in the VPGM utilizes an effective diffusivity \( D_e \) which depends on a pore diffusion coefficient \( D_g \) and the local porosity (\( \varepsilon \)) as given by equation \( VI-14 \)

\[
D_e = D_g \varepsilon^2 \quad (VI-14)
\]

Therefore, to change the pore diffusion resistance predicted by the VPGM one must modify the expression for \( D_e \).

Previously, \( D_G \) has been allowed to vary due to changes in the Knudsen diffusivity \( D_K \) which is a function of porosity as given in equation VI-10. However, it was found that an improved match with experimental time-conversion data could be obtained if \( D_K \) was maintained constant at its initial value. This, it should be noted, is in accord with the original Georgakis et al. [1] model. Thus, the effective diffusivity was modelled as

\[
D_e = D_G \varepsilon^2 \quad (VI-25)
\]

The variable property grain model with a constant \( D_G \) (that is, with \( D_e \) modelled as VI-25) will henceforth be referred to as VPGMC.
Experimental data at 350°, 450°, and 550°C were analyzed using VPGMC and the results fit on D'\textsubscript{s}. The results depicted in Figures VI-35, 36, and 37 are typical of the improved fit obtained by using VPGMC. Use of VPGMC improved the results of approximately 70% of the runs at 350°, 450°, and 550°C. In 15% of the runs VPGM did a better job while there was no difference between VPGM and VPGMC in the remaining 15% of the runs at 350°, 450°, and 550°C. At 150° and 250°C predictions of the VPGM and VPGMC were identical since $\epsilon$ and $D_K$ changed little at these temperatures due to the low overall and local conversions observed. Also, at these temperatures, pore diffusion resistance was small. Therefore, the values for the individual "best" and average $D'_s$ at 150°C and 250°C reported earlier (see Tables VI-1 and 2) for the VPGM are identical to those for VPGMC.

Table VI-6 gives the values for the individual "best" and average $D'_s$ at 350°, 450°, and 550°C when using the VPGMC. The scatter at 350° and 450°C is less than one order of magnitude. With the exception of the two 0.5% NO\textsubscript{2} runs at 550°C, the scatter at this temperature is also less than one order of magnitude. The values for $D'_s$ in Table VI-6 are roughly two to three times larger than the corresponding values determined using the VPGM (see Tables VI-3, 4, and 5). However, the scatter in the values for $D'_s$ is approximately the same for the VPGMC and VPGM. The average values shown at 350°, 450°, and 550°C ($5.6 \times 10^{-8}$, $2.07 \times 10^{-8}$, and $4.05 \times 10^{-8}$ cm\textsuperscript{2}/min, respectively) are taken as the best
Figure VI-35. Comparison of Experimental Data with Predictions of the VPGM and VPGMC. T=350°C.

- Run 232 $\epsilon_o = .740$, 1.8% NO$_2$
- VPGM Predictions ($D^-_s = 1.0 \times 10^{-8}$ cm$^2$/min)
- VPGMC Predictions ($D^-_s = 2.5 \times 10^{-8}$ cm$^2$/min)
Figure VI-36. Comparison of Experimental Data with Predictions of VPGM and VPGMC. $T=450^\circ C$. 

- Run 188, $\varepsilon_0 = .748$, 1.8% NO$_2$
- VPGM Predictions ($D_s^*=1.0 \times 10^{-8}$ cm$^2$/min)
- VPGMC Predictions ($D_s^*=3.0 \times 10^{-8}$ cm$^2$/min)
Fractional Conversion of CaO, $X$

- Run 232, $x_0 = 0.772$, 1.8% NO₂
- VPGM Predictions ($D_s^i = 2.0 \times 10^{-8}$ cm²/min)
- VPGMC Predictions ($D_s^i = 10.0 \times 10^{-8}$ cm²/min)

Figure VI-37. Comparison of Experimental Data with Predictions of VPGM and VPGMC. $T=550°C$. 

278
TABLE VI-6

Best Values for $D'_s$ at 350°, 450°, and 550°C for VPGMC

<table>
<thead>
<tr>
<th>$T(°C)$</th>
<th>Run Number</th>
<th>$%NO_2$</th>
<th>$D'_s$ (cm$^2$/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>350°</td>
<td>189</td>
<td>1.8</td>
<td>$8.5 \times 10^{-8}$</td>
</tr>
<tr>
<td></td>
<td>190</td>
<td>1.8</td>
<td>$12.5 \times 10^{-8}$</td>
</tr>
<tr>
<td></td>
<td>207</td>
<td>1.8</td>
<td>$2.5 \times 10^{-8}$</td>
</tr>
<tr>
<td></td>
<td>231</td>
<td>1.8</td>
<td>$3.75 \times 10^{-8}$</td>
</tr>
<tr>
<td></td>
<td>204</td>
<td>1.0</td>
<td>$17.5 \times 10^{-8}$</td>
</tr>
<tr>
<td></td>
<td>205</td>
<td>1.0</td>
<td>$1.90 \times 10^{-8}$</td>
</tr>
<tr>
<td></td>
<td>206</td>
<td>1.0</td>
<td>$5.0 \times 10^{-8}$</td>
</tr>
<tr>
<td></td>
<td>235</td>
<td>1.0</td>
<td>$1.25 \times 10^{-8}$</td>
</tr>
<tr>
<td></td>
<td>236</td>
<td>1.0</td>
<td>$1.25 \times 10^{-8}$</td>
</tr>
<tr>
<td></td>
<td>208</td>
<td>0.5</td>
<td>$5.0 \times 10^{-8}$</td>
</tr>
<tr>
<td></td>
<td>209</td>
<td>0.5</td>
<td>$2.5 \times 10^{-8}$</td>
</tr>
</tbody>
</table>

Average = $5.60 \times 10^{-8}$

Standard Deviation = $5.22 \times 10^{-8}$

<table>
<thead>
<tr>
<th>$T(°C)$</th>
<th>Run Number</th>
<th>$%NO_2$</th>
<th>$D'_s$ (cm$^2$/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>450°</td>
<td>187</td>
<td>1.8</td>
<td>$3.0 \times 10^{-8}$</td>
</tr>
<tr>
<td></td>
<td>188</td>
<td>1.8</td>
<td>$3.0 \times 10^{-8}$</td>
</tr>
<tr>
<td></td>
<td>211</td>
<td>1.8</td>
<td>$2.4 \times 10^{-8}$</td>
</tr>
<tr>
<td></td>
<td>229</td>
<td>1.8</td>
<td>$1.3 \times 10^{-8}$</td>
</tr>
<tr>
<td></td>
<td>230</td>
<td>1.8</td>
<td>$0.65 \times 10^{-8}$</td>
</tr>
<tr>
<td></td>
<td>219</td>
<td>1.0</td>
<td>$2.2 \times 10^{-8}$</td>
</tr>
<tr>
<td></td>
<td>220</td>
<td>1.0</td>
<td>$2.1 \times 10^{-8}$</td>
</tr>
<tr>
<td></td>
<td>221</td>
<td>0.5</td>
<td>$0.9 \times 10^{-8}$</td>
</tr>
<tr>
<td></td>
<td>222</td>
<td>0.5</td>
<td>$0.9 \times 10^{-8}$</td>
</tr>
</tbody>
</table>

Average = $1.83 \times 10^{-8}$

Standard Deviation = $0.913 \times 10^{-8}$
TABLE VI-6 (continued)

Best Values for $D'_s$ at 350°, 450°, and 550°C for VPGMC

<table>
<thead>
<tr>
<th>$T$(°C)</th>
<th>Run Number</th>
<th>$%NO_2$</th>
<th>$D'_s$ (cm$^2$/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>550°</td>
<td>214</td>
<td>1.8</td>
<td>$1.75 \times 10^{-8}$</td>
</tr>
<tr>
<td></td>
<td>213</td>
<td>1.8</td>
<td>$2.0 \times 10^{-8}$</td>
</tr>
<tr>
<td></td>
<td>232</td>
<td>1.8</td>
<td>$10.0 \times 10^{-8}$</td>
</tr>
<tr>
<td></td>
<td>233</td>
<td>1.8</td>
<td>$5.0 \times 10^{-8}$</td>
</tr>
<tr>
<td></td>
<td>234</td>
<td>1.8</td>
<td>$2.75 \times 10^{-8}$</td>
</tr>
<tr>
<td></td>
<td>215</td>
<td>1.0</td>
<td>$1.60 \times 10^{-8}$</td>
</tr>
<tr>
<td></td>
<td>218</td>
<td>1.0</td>
<td>$12.5 \times 10^{-8}$</td>
</tr>
<tr>
<td></td>
<td>216</td>
<td>0.5</td>
<td>$0.50 \times 10^{-8}$</td>
</tr>
<tr>
<td></td>
<td>217</td>
<td>0.5</td>
<td>$0.35 \times 10^{-8}$</td>
</tr>
</tbody>
</table>

Average = $4.05 \times 10^{-8}$

Standard Deviation = $4.35 \times 10^{-8}$
estimate for $D'_s$ at these temperatures. The effect of using the average $D'_s$ in VPGMC showed the same behavior as observed for the VPGM.

A possible explanation for improved fit when $D_K$ is held constant follows. When $D_K$ becomes small in VPGM (that is, $D_K \ll D_m$), $D_e$ becomes

$$D_e = D_K \varepsilon^2 \quad (VI-26)$$

Since $D_K$ is a function of $\varepsilon$,

$$D_e \propto \varepsilon^3 \quad (VI-27)$$

In contrast VPGMC maintains $D_K$ constant and therefore allows $D_e$ to vary with $\varepsilon^2$. It appears that variation of $D_e$ with $\varepsilon^3$ for the present reaction system results in an exaggerated pore diffusion resistance at intermediate times. A better match to time-conversion data occurred when $D_e \propto \varepsilon^2$ as observed with VPGMC. Since the pore diffusion resistance is different for VPGMC, a larger value for $D'_s$ is required to predict approximately the same "die-off" conversion as VPGM.

C) Quantitative Relative Resistance Analysis

Previously, the importance of the four resistances - external mass transfer, pore diffusion, grain diffusion, and chemical reaction - has been dealt with only qualitatively via inspection of surface concentrations and the shape of the predicted concentration profiles. In this section a method of quantifying the four resistances will be developed and typical results will be presented.
Transport of gas occurs due to a difference in concentration as the driving force. As the driving force goes to zero, the resistance also goes to zero. Thus, external mass transfer (MT), pore diffusion (PD), and grain diffusion (GD) resistance may be quantified with the following expressions:

\[
\text{MT} = \frac{C_{A_0} - C_{A_S}}{C_{A_0}} \quad (VI-28)
\]

\[
\text{PD} = \frac{C_{A_S} - \bar{C}_A}{C_{A_0}} \quad (VI-29)
\]

\[
\text{GD} = \frac{\bar{C}_A - \bar{C}_A}{C_{A_0}} \quad (VI-30)
\]

The corresponding relationship for the resistance due to chemical reaction is

\[
\text{CR} = \frac{\bar{C}_{A_C}}{\bar{C}_{A_0}} \quad (VI-31)
\]

where

\[
C_{A_0} = \text{bulk reactant gas concentration (moles/} l^3) \]

\[
C_{A_S} = \text{surface concentration of reactant gas (moles/l}^3) \]

\[
\bar{C}_A = \text{average concentration of reactant gas within pores (moles/} l) \]

\[
\bar{C}_{A_C} = \text{average concentration of reactant gas at surface of unreacted core associated with each grain (moles/l}^3) \]

\(
\bar{C}_A \text{ and } \bar{C}_{A_C} \text{ are obtained by integrating the predicted profiles for } C_A \text{ and } C_{A_C} \text{ with respect to pellet volume.}
\)
It should be noted that MT, PD, GD, and CR have been normalized with respect to $C_{A_o}$. Thus, we know that

$$MT + PD + GD + CR = 1.0$$  \hspace{1cm} (VI-32)

Normalization simplifies comparison of the individual relative resistances. As a given resistance approaches 1.0, it becomes the controlling resistance.

Figure VI-38 shows the results of the relative resistance analysis via VPGMC for a typical run carried out at 250°C. Values for the individual relative resistances are plotted versus overall fractional conversion of CaO. The distance between the curves at a given overall fractional conversion is a quantitative measure of the importance of the individual resistances. External mass transfer is seen to be very important initially (MT is 64% of the total resistance at $\bar{x}=0.0$) but the importance of external mass transfer resistance diminishes rapidly with conversion (MT is 2% at $\bar{x}=.08$). Pore diffusion resistance behaves similarly with PD decreasing from 29.5% initially to 4.5% at an overall conversion of 0.08. Chemical reaction offers a small resistance initially (6.5%) which becomes negligible (0.5%) by 2.0 per cent overall conversion. The dominant resistance is clearly grain diffusion. It is zero initially since no product layer is present but grows rapidly with fractional conversion. The behavior for this 250°C run is representative of the relative resistance results observed at 150°C and 250°C. These findings support the qualitative
Figure VI-38. Quantitative Relative Resistance Analysis Using VPGMC. \( T=250^\circ C \)
conclusions drawn earlier based on the slopes of the predicted concentration profiles - at the lower temperatures, grain diffusion is the dominant resistant shortly after the reaction commences.

Figure VI-39 presents the relative resistance analysis using VPGMC for a typical 450°C run. Comparison between the experimental and predicted time-conversion data for this run (#188) was presented earlier in Figure VI-36. External mass transfer resistance is seen to decline with overall conversion (and, hence with time) but not as abruptly as was observed at 250°C. For the present case, MT decreased from 73.5% of total resistance initially to 1.2% at the final overall conversion of 0.47. As pointed out earlier, grain diffusion resistance is zero at the start of the reaction but increases with product layer growth. However, in contrast to the 250°C run presented previously (See Figure VI-38), grain diffusion resistance in Figure VI-39 reaches a maximum (28% at \( \bar{x} = 0.21 \)) and declines thereafter, becoming zero by \( \bar{x} = 0.047 \). Pore diffusion resistance for this run is approximately 25% of the total resistance when the reaction commences. Due to a decrease in surface porosity - brought about by grain expansion - pore diffusion resistance increases. Although the surface porosity never becomes zero, it becomes small enough (\( \varepsilon = 0.006 \) at pellet surface) to make PD 97% of the total resistance at \( \bar{x} = 0.47 \). Thus, pore diffusion resistance is clearly the dominant resistance.
Figure VI-39. Quantitative Relative Resistance Analysis Using VPGMC. T=450°C.
Chemical reaction resistance (CR) in Figure VI-39, which is less than 2.5% of the total initially, decreases to a minimum of 0.22% near $\bar{X}=0.45$ and becomes 2.0% at $\bar{X}=0.47$. The important fact is that CR is small throughout the reaction, again suggesting that the value used for $k'_A$ is of minor importance. It is interesting to note that CR exhibits a minimum while GD possesses a maximum. This behavior is linked to the ever-increasing pore diffusion resistance. Shortly after the reaction begins, a concentration difference $(\bar{c}_A - \bar{c}_A^{\text{c}})$ develops across the product layer associated with the grains. This concentration difference represents the grain diffusion resistance as given by equation (VI-30) and increases as the product layer grows. Simultaneously, however, the surface porosity decreases which eventually leads to a drop in $\bar{c}_A$. Eventually the gas concentration within the pellet approaches zero and the only non-zero values for $c_A$ exist at the pellet surface. However, at $\bar{X}=0.47$ the surface grains have been completely reacted and $\bar{c}_A=\bar{c}_A^{\text{c}}$ which makes GD zero. CR, on the other hand, depends only on the value of $\bar{c}_A^{\text{c}}$ (which is at the very center of a completely reacted grain). For $\bar{X}=0.47$, $\bar{c}_A^{\text{c}}$ is zero everywhere within the pellet but non-zero for the grains at the pellet surface. Thus, the increase in CR as the die-off conversion is approached results solely from the reactant gases within the product layer associated with the grains at the pellet surface.
In summary, analysis of relative resistances quantitatively has been shown to be useful in supporting the qualitative conclusions drawn earlier:

a) Grain diffusion resistance is important at all temperatures of this study.

b) At the lower temperatures (150° and 250°C), grain diffusion resistance controls shortly after the reaction commences.

c) At the higher temperatures, grain diffusion and pore diffusion resistances are both significant during the reaction but the controlling resistance shifts to pore diffusion as surface porosity approaches zero.

d) External mass transfer resistance is important for all runs initially but this resistance declines with fractional conversion and, hence, with time.

e) Chemical reaction resistance is of minor importance at all temperatures of this study.

D) The Temperature Dependence of $D'_s$

As pointed out previously in this chapter, transport of gases through the product layer about each grain is assumed to occur through the mechanism of solid state diffusion. Solid state diffusion is an activated process and as such the diffusion coefficient ($D'_s$) should exhibit an Arrhenius relationship with temperature [12].

The individual "best" values for $D'_s$ obtained by fitting the experimental data with the VPAGM were given in Tables VI-1, 2, 3, 4, and 5 for runs made at 150°, 250°, 350°, 450°, and 550°C, respectively. These are plotted in Figure VI-40 with the numbers adjacent to the triangles denoting replicates. The average value at each temperature is
Figure VI-40. Arrhenius Plot. Grain Diffusion Coefficient, $D'_S$ (VPGM)
separately noted. The two lines in Figure VI-40 represent a least square fit to different portions of the data and will be discussed in more detail later. The 350°C results seem out of place - exhibiting a higher value than at 450° and 550°C. The data at 150°, 250°, 450°, and 550°C appear to correlate well with temperature on the semi-log scale of Figure VI-40. Similar behavior of D'_s with temperature was observed when fitting the experimental data with VPGMC - the values for D'_s at 350°C were larger than expected with D'_s correlating well at the other four temperatures. (See Figure VI-41).

It is not easy to justify a higher value of D'_s at 350°C than at 450° and 550°C. In an effort to reconcile this discrepancy the value of D'_s at 350°C was arbitrarily fixed at 2.0 x 10^{-9} \text{ cm}^2/\text{min} (this value was obtained from the least squares line through the average values at the other four temperatures) and the rate constant k'_s was varied to match the experimental time-conversion behavior. However, the model predictions were relatively insensitive to changes in k'_s at 350°C and consequently, the match with the data was extremely poor with underprediction at early times followed by overprediction and failure to predict "die-off". This approach was abandoned.

Another attempt to improve the temperature behavior of D'_s involved using the least squares line through the data at 150°, 250°, and 350°C to obtain a new value for D'_s at 450°C. This new value of D'_s at 450°C (1.25 x 10^{-7} \text{ cm}^2/\text{min}) was used
Figure VI-41. Arrhenius Plot. Grain Diffusion Coefficient, $D_s'$ (VPGMC).

$D_s' \left( \frac{\text{cm}^2}{\text{min}} \right) = 7.02 \times 10^{-5} e^{-\frac{12,180}{RT}}$

$D_s' \left( \frac{\text{cm}^2}{\text{min}} \right) = 1.99 \times 10^{-4} e^{-\frac{12,770}{RT}}$

- "Best" Individual Values
- Average Value
in VPGMC and $k'_s$ was varied to match the experimental data at 450°C. However, the values of the "best" fit $k'_s$ at 450°C were two orders of magnitude less than the experimental value of $k'_s$ at 350°C. This method was also rejected.

Notwithstanding the anomalous behavior at 350°C it is instructive to determine $D'_s$ as a function of temperature via an Arrhenius-type relationship

$$D'_s = D'_s e^{-\frac{E}{RT}} \quad (V-5)$$

The following equations were determined for the VPGM and VPGMC, respectively, when the 350°C data was excluded.

$$D'_s = 7.96 \times 10^{-6} e^{-\frac{RT}{10,210}} \text{ (cm}^2/\text{min}) \quad (VI-33)$$

and

$$D'_s = 7.02 \times 10^{-5} e^{-\frac{RT}{12,810}} \text{ (cm}^2/\text{min}) \quad (VI-34)$$

The correlation coefficients for equations VI-A and B are 0.998 and 0.995, respectively. A plot of equations VI-33 and 34 is given as curve (1) in Figure VI-40 and 41, respectively.

The activation energies determined above are approximately one half those reported by Ranade [3] (22,000 cal/grmole) for the reaction of ZnO with H$_2$S. No data on $D'_s$ was available in the literature for the nitration reaction of the present study.

When the 350°C data was included in the analysis, the following Arrhenius-type equation was determined for the VPGM and VPGMC, respectively,
\[ D_s' = 1.93 \times 10^{-5} e^{-\frac{RT}{cm^2/min}} \] (VI-35)

and

\[ D_s' = 1.99 \times 10^{-4} e^{-\frac{RT}{cm^2/min}} \] (VI-36)

The activation energies are similar to those of equations VI-33 and 34. However, the frequency factors are roughly twice those determined previously. The correlation coefficients for VI-35 and 36 are also smaller (0.922 and 0.921, respectively). Equations VI-35 and 36 appear as curve (2) in Figures VI-40 and 41, respectively. The fit is less satisfactory with respect to the average values at 150°, 250°, 450°, and 550°C than when the 350°C data is neglected (curve 1).

E) Summary

Throughout this chapter model predictions have been compared to experimental time-conversion data for single runs only. It is instructive to conclude this chapter with a look at how well VPGMC matches experimental data for several runs under various conditions on the same plot.

Figure VI-42 compares the predictions of VPGMC (when using the individual "best" values for \(D_s'\)) with experimental data collected at 150°, 350°, 450°, and 550°C. With the exception of the small underprediction initially at 150°C, the agreement between model predictions and experimental data is excellent. In particular, the model predicts the
Figure VI-42. Comparison of Experimental Data with the Predictions at VPGMC at 150°, 350°, 450°, and 550°C.
actual "die-off" observed for the 350°C ($\varepsilon_o < 0.747$) due to pore closure. The initial porosity for the 450°C run is such that the porosity never goes to zero but it becomes small enough at the pellet surface to effectively stop the reaction. The model predicts this behavior in an excellent fashion. The predictions at 550°C could not be better. (The 550°C run lies below the 450°C run due to a difference in pellet properties. In particular, the 550°C pellet is much larger ($r_s = 0.200$ cm) than the 450°C pellet ($r_s = 0.142$ cm).) Since the initial porosity is significantly larger than 0.747, the surface porosity never closes and the reaction does not "die-off". As shown, the model predicts this as well. At 150°C, the initial underprediction is offset by the good agreement at later times.

Figures VI-43 and VI-44 compare the model and experimental results for different NO$_2$ concentrations at 350° and 450°C, respectively. In Figure VI-43 the "best" values for $D'_g$ are used. Agreement is excellent at all three gas concentrations. Two points are worth noting. First, the experimentally observed reaction "die-off" at 1.8% NO$_2$ is matched perfectly by VPGMC. Secondly, the crossing of the 1.8% and 1.0% NO$_2$ curves - as discussed earlier in Chapter V - is also predicted by the model.

Figure VI-44 shows the ability of VPGMC to predict experimental data at 450°C and various NO$_2$ concentrations when using an average value for $D'_g$ ($1.83 \times 10^{-8}$ cm$^2$/min). The model overpredicts slightly at all times for the 0.5%
Figure VI-43. Comparison of Experimental Data with Predictions of VPGMC, Effect of NO₂ Concentration. T=350°C.
Figure VI-44. Comparison of Experimental Data with Predictions of VPGMC. Effect of NO$_2$ Concentration. Use of Average Value for D'$_s$ T=450°C.
NO\textsubscript{2} curve. Agreement is much better for the 1.0% NO\textsubscript{2} curve with only small overprediction of the "die-off" conversion. VPGMC does a good job for most of the 1.8% NO\textsubscript{2} curve but substantially overpredicts the final conversion. Nonetheless, considering that an average value for D\textsubscript{s}' was used in Figure VI-44 the quality of agreement between model and experimental data is quite good. It should be pointed out, however, that the use of an average value for D\textsubscript{s}' did not produce as good agreement as that depicted in Figure VI-44 for every run.
Literature Cited


Recalling that the overall objective of this work was to study the effect of variable solid properties upon the kinetics of the gas-solid reaction system (CaO/NO₂/O₂) and to modify and/or extend existing gas-solid reaction models to analyze these effects, the following overall conclusions were drawn:

(A) CaO has been shown to react with NO₂ in the presence of oxygen. However, due to low overall fractional conversions ("die-off"), the NO₂ capacity of the reactant solid is severely curtailed. As such, use of CaO pellets to remove NO₂ would be feasible only for highly porous forms of CaO.

(B) To avoid erroneous predictions of conversion-time behavior, variable property gas-solid reaction models should be used since property changes occur in most systems and can affect reaction behavior appreciably.

(C) A noncatalytic gas-solid reaction model (VPGM), originally proposed by Georgakis et al, which allowed for solid property changes due to reaction and which predicted radial profiles of these property changes was modified for this study. This model - an extension of the grain model (CPGM) - was capable of matching the experimental behavior for the CaO/ NO₂/O₂ reaction system in the temperature range of this study - 150° to 550°C.
(D) The predictive capability of the VPGM and CPGM were similar in matching the slow but steady reaction observed at 150° and 250°C. However, VPGM was vastly superior to the CPGM at 350°C and above, at which temperatures reaction "die-off" was observed. CPGM can not predict "die-off", whereas, VPGM did so quite well.

(E) Changes in solid properties due to reaction were found to be strongly dependent on the difference between the solid product molar volume and solid reactant molar volume. If the initial porosity was below a critical value, reaction "die-off" occurred as the surface porosity approached zero.

(F) A technique to evaluate relative resistances was developed and applied to the data to determine quantitatively the importance of the four resistances - external mass transfer, pore diffusion, grain diffusion, and chemical reaction - at each point in the reaction. The controlling resistance at 150° and 250°C was clearly grain diffusion shortly after the reaction commenced. At 350°C and above, the analysis indicated that grain diffusion and pore diffusion are both important at intermediate times with the controlling resistance shifting to pore diffusion as surface porosity approached zero. At all temperatures, external mass transfer was important initially, decreasing in importance with conversion. Intrinsic chemical reaction exerted only a minor resistance at all temperatures and at all conversions.
(G) It was found that the predictive capabilities of VPGM could be improved by holding constant the diffusion coefficient, $D_G$ (combined molecular and Knudsen), used to calculate the effective diffusivity within the pellet.

(H) It was possible to match experimental data with model predictions (VPGM and VPGMC) at all temperatures by fitting on a single parameter - the grain diffusion coefficient, $D'_g$. $D'_g$ at 150°, 250°, 450°, and 550°C correlated well with temperature. Values for $D'_g$ at 350°C, however, were somewhat higher than expected and did not correlate with the values determined at the other four temperatures.

Recommendations for future work in this area include:

(A) Experimental measurement of porosity and pore size distribution for the solid reactant. VPGM considered a uniform distribution throughout the pellet for these properties. Such information when incorporated in the model might help to reduce the scatter in $D'_g$ at each temperature.

(B) Further study is needed in the correlation of the particle effective diffusivity ($D_e$). In particular, a correlation for the variation of the Knudsen diffusion coefficient ($D_K$) with changes in local porosity is warranted. The correlation for $D_K$ used in VPGM (Equation VI-10) was developed from kinetic theory and is applicable to a cylindrical pore of unchanging radius. While such theory may be reasonably applicable to solid catalyst particles having constant properties, there is a clear need for a $D_K$ correlation more applicable to the varying structure assumed in VPGM and in other such extensions of the grain model.
(C) VPGM should be applied to data for a reaction system in which the solid becomes more porous with conversion. A timely example would be application of the model to the gasification of coal of lignite particles.

(D) Incorporation of VPGM into a design package for fixed-bed reactors for noncatalytic gas-solid reactions should be useful.

(E) Use of a porous, high surface area support upon which CaO is deposited may provide a viable method of NO_x removal from flue gases. However, much more work is required, including a complete study of reactant regeneration and the effect of competing reactions from, for example, CO_2 and SO_2.
**NOMENCLATURE**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
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<tbody>
<tr>
<td>$A_e$</td>
<td>equilibrium surface area of solid, $1^2$/mass</td>
</tr>
<tr>
<td>$A_{ext}$</td>
<td>external surface area of pellet, $1^2$</td>
</tr>
<tr>
<td>$A_S$</td>
<td>specific surface area, $1^2$/mass</td>
</tr>
<tr>
<td>$A'_S$</td>
<td>measured initial surface area of pellet</td>
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<td>$A_S(X,t)$</td>
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<tr>
<td>$A(t)$</td>
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<td>$A_{tot}$</td>
<td>total available surface area of solid reactant, $1^2$</td>
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<tr>
<td>$A(X)$</td>
<td>specific surface area of reacting, nonsintering solid at fractional conversion of solid reactant, $X$, $1^2$/mass</td>
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<td>constants used in free energy equation (II-5)</td>
</tr>
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<td>$a_{D,P}$</td>
<td>stoichiometric coefficients for the product gas D and solid P, respectively (positive)</td>
</tr>
<tr>
<td>$a_{G,S}$</td>
<td>stoichiometric coefficients for the reactant gas G and solid S, respectively (negative)</td>
</tr>
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<td>$a_{ij}$</td>
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</tr>
<tr>
<td>$B_i$</td>
<td>number of gram-atoms of each element</td>
</tr>
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<td>constant in equations (III-87) and (III-88)</td>
</tr>
<tr>
<td>$b(T)$</td>
<td>exponent in equations (III-87) and (III-88)</td>
</tr>
<tr>
<td>$C$</td>
<td>dimensionless reactant gas concentration, $C_A/C_A^o$</td>
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<tr>
<td>$\bar{C}_A$</td>
<td>average concentration of reactant gas within pores, moles/1$^3$, as used in equations (VI-29) and (VI-30)</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
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<tr>
<td>--------</td>
<td>------------</td>
</tr>
<tr>
<td>( \bar{c}_{A_c} )</td>
<td>average concentration of reactant gas at surface of unreacted core associated with each grain, moles/1³</td>
</tr>
<tr>
<td>( c_{A_o} )</td>
<td>bulk reactant gas concentration, moles/1³</td>
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<tr>
<td>( c_{A_s} )</td>
<td>surface concentration of reactant gas, moles/1³</td>
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<td>concentration of gaseous reactant ( G ) at unreacted core surface, moles/1³</td>
</tr>
<tr>
<td>( c'_{G_c} )</td>
<td>concentration of reactant gas ( G ) at the surface of the unreacted core of each grain, moles/1³</td>
</tr>
<tr>
<td>( c_{G_o} )</td>
<td>molar concentration of the reactant gas ( G ) in the bulk gas stream, moles/1³</td>
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<tr>
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<td>the reactant gas concentration at the surface of the pellet, moles/1³</td>
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<tr>
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</tr>
<tr>
<td>( c'_{S_o} )</td>
<td>initial reactant solid concentration in each grain, moles/1³</td>
</tr>
<tr>
<td>( c )</td>
<td>constant expressing net adsorption energy</td>
</tr>
<tr>
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</tr>
<tr>
<td>( D_e )</td>
<td>effective diffusivity of gaseous reactant ( G ), 1²/t</td>
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<td>( D'_{e} )</td>
<td>grain diffusion coefficient used in the constant property grain model</td>
</tr>
<tr>
<td>( D_{G} )</td>
<td>combination of molecular (( D_M )) and Knudsen (( D_K )) diffusion coefficients as given by equation (III-27), 1²/t</td>
</tr>
<tr>
<td>( D_K )</td>
<td>Knudsen diffusivity</td>
</tr>
<tr>
<td>( D_M )</td>
<td>molecular diffusivity of gas reactant, 1²</td>
</tr>
</tbody>
</table>
\( D_S \) - solid state diffusion coefficient

\( D'_S \) - solid state diffusion coefficient for each grain

\( D_{So} \) - pre-exponential term found in equation (V-5)

\( \left( \frac{dw}{dt} \right)_0 \) - initial rate of weight change due to reaction, mass/time

\( E \) - expansion factor, ratio of molar densities and stoichiometric coefficients of solid reactant and product, defined by equation (III-41)

\( E_A \) - activation energy, cal/gr mole

\( E_F \) - effectiveness factor

\( E_S \) - activation energy for sintering, cal/gr mole

\( F \) - total free energy of a system, cal

\( F^o \) - standard free energy per mole, cal/mole

\( \Delta F^o \) - free energy change, cal/mole

\( G_D \) - relative grain diffusion resistance

\( g \) - local acceleration due to gravity, 1/t^2

\( g(\phi) \) - relative tortuosity factor = \( \tau_f(\phi)/\tau_f(0) \)

\( \Delta H_0 \) - constant used in free energy equation (V-6)

\( I \) - integration constant in equation (V-6)

\( K \) - constant used in Froessling equation (III-26)

\( k \) - reaction rate constant, ( moles \( S/1^3 \) s-sec ), used in equation (III-31) moles G/\( 1^3 \) gas

\( k_m \) - mass transfer coefficient for gaseous reactant G from the bulk gas phase to the exterior surface of the solid, 1/t

\( k_m^A \) - mass transfer coefficient, 1/time

\( k_S \) - intrinsic reaction rate constant based on the surface area of the unreacted core 1^4/mole t
\(k'_s\) - intrinsic reaction rate constant based on the surface area of the unreacted core of each grain, \(1^6/\text{mole t}\)

\(k_{so}\) - frequency factor, \(\text{cm}^4/\text{mg mole min}\)

\(L\) - pore length (single pore model)

\(M_{CC}\) - molecular weight of CaCO_3, mass/ moles

\(M_P\) - molecular weight of solid product \(P\), mass/ moles

\(M_S\) - molecular weight of solid reactant \(S\), mass/ moles

\(MT\) - relative mass transfer resistance

\(MW_P\) - molecular weight of solid product, mass/ moles

\(MW_S\) - molecular weight of solid reactant, mass/ moles

\(m\) - total number of elements as used in equation (II-4)

\(m\) - exponent in equation (III-26)

\(N_{Re}\) - Reynolds number, \(2 r_s G/\mu_G\)

\(N_{Sc}\) - Schmidt number, \(\mu_G/\rho_G D_m\)

\(N_{Sh}\) - Sherwood number, \(2 k_m A r_s/D_m\)

\(n\) - number of gaseous species in a system used in equation (II-3)

\(n\) - exponent used in equation (III-26)

\(P\) - total pressure, atm

\(PD\) - relative pore diffusion resistance

\(p\) - partial pressure of nitrogen, force/1^2

\(P_0\) - saturation pressure of nitrogen over the solid sample at the temperature of the liquid nitrogen, force/1^2

\(R\) - universal gas constant, 1.987 cal/gr mole °K
\( R_G \) - rate of production of G per unit surface area by chemical reaction, moles/l^2 time

\( \dot{R}_G \) - rate of production of gaseous reactant G by chemical reaction per unit volume, moles/l^3 time

\( R_{G_i} \) - initial global rate of reaction, measured experimentally via equation (V-4), moles/l^2 time

\( R_{m_i} \) - initial rate of external mass transfer per unit external surface area of pellet, moles/l^2 time

\( \dot{R}_S \) - rate of production of solid reactant S by chemical reaction per unit volume, moles/l^3 time

\( r \) - radial position within the pellet, l

\( r \) - initial pore radius in the single pore model, l

\( r_c \) - radius of unreacted core of spherical solid pellet, l

\( r'_c \) - radius of the unreacted core within each grain, l

\( r_s \) - radius of spherical solid pellet, l

\( r'_s \) - grain radius, l

\( r'_s_0 \) - initial value of the grain radius within the pellet, l

\( S \) - specific surface area, l^2/mass

\( S_o \) - cross-sectional area covered by a monolayer of nitrogen per unit volume, at standard temperature and pressure, l^2/l^3

\( S_p \) - specific surface area of the solid product, l^2/mass

\( S_s \) - specific surface area of the solid reactant, l^2/mass

\( S_T \) - total surface area of sample, l^3

\( T \) - temperature of the system

\( t \) - time, min
\( V_{\text{ads}} \) - total volume at standard temperature and pressure of nitrogen on the surface of the solid sample, \( 1^3 \)

\( V_{\text{CO}}, V_{\text{CS}} \) - molar volumes of void-free \( \text{CaO} \) and \( \text{CaSO}_4 \), respectively, \( 1^3/\text{mole} \)

\( V_m \) - volume at standard temperature and pressure of nitrogen absorbed when the entire adsorbent surface is covered with a monomolecular layer, \( 1^3 \)

\( V_p \) - molar volume of solid product

\( V_s \) - molar volume of solid reactant

\( w_o \) - initial pellet mass, \( \text{mg} \)

\( w^*_o \) - true initial pellet mass, \( \text{mg} \)

\( w_t \) - weight of sample on TGA at time \( t \)

\( x \) - local fractional conversion of solid reactant

\( \dot{x} \) - overall fractional conversion of solid reactant

\( x \) - spatial coordinate in direction of pores, length

\( \bar{x} \) - total gram-moles of gaseous species, \( \frac{n}{i=1} x_i \)

\( x_i \) - number of gram-moles of species \( i \)

\( y \) - weight fraction of \( \text{CaCO}_3 \) in limestone

\( z \) - axial coordinate in single pore model
GREEK LETTERS

\( \alpha \) - slope of BET plot
\( \Delta \alpha, \Delta \beta, \Delta \gamma \) - constants used in free energy equation (V-6)
\( \beta \) - y-intercept of BET plot
\( \gamma \) - expansion factor similar to E
\( \delta \) - total thickness of product layer in single pore model \((\delta_1 + \delta_2)\) - Single Pore Model
\( \delta(r) \) - dimensionless effective diffusivity within the pellet \(= \frac{D_e}{D_{e_o}}\)
\( \delta_1 \) - the distance between the original pore wall (at time = 0) and the current pore wall (at time = t) - Single Pore Model
\( \delta_2 \) - the distance between the original pore wall and the current reaction interface - Single Pore Model
\( \varepsilon \) - particle porosity
\( \varepsilon_{LS} \) - porosity of natural limestone
\( \varepsilon_o \) - initial pellet porosity
\( \varepsilon_p \) - porosity of the solid product P
\( \varepsilon_s \) - the porosity after sintering of the pellet at the given time and temperature
\( \varepsilon_{so}, \varepsilon_{po} \) - initial volume fractions for S and P, respectively
\( \lambda \) - radius of the solid in the single pore model
\( \mu_g \) - bulk gas viscosity, mass/1² time
\( \Phi \) - fraction of pores removed during sintering
\( \Phi_G \) - Thiele modulus for pellet in the grain model, \( r_s k_s c_{so}/D_{eA} \)
\( \Phi'_G \) - Thiele modulus for grain in the grain model, \( r'_s k'_s c'_{so}/D'_eA \)
\( \phi_s \) - pellet Thiele modulus, for use in equation (V-12)

\[
\phi_s = \frac{r_s}{3} \left[ \frac{a_G k_s C_{S_0} \rho_p A_s}{D \varepsilon_o^2} \right]^{1/3}
\]

\( \rho_{CC} \) - density of CaCO\(_3\), mass/\(l^3\)
\( \rho_G \) - bulk gas density, mass/\(l^3\)
\( \rho_g' \) - grain density, mass/\(l^3\)
\( \rho_p \) - crystalline density of solid product P.
\( \rho_s \) - crystalline density of solid reactant S.
\( \rho_s' \) - true crystalline density of solid reactant, mass/\(l^3\)

\( \xi \) - dimensionless radial coordinate for the pellet = \( r/r_s \)

\( \xi' \) - dimensionless grain radius, \( r_s'/r_s' \)

\( \xi_c' \) - dimensionless unreacted-core radius within a grain = \( r_c'/r_s' \)

\( \tau \) - pellet tortuosity

\( \theta \) - dimensionless time = \( k_s' C_{A_o} t/r_s' \)
APPENDICES
APPENDIX A

CaO Pellet Reaction Data
The following nomenclature is used in Appendix A for the CaO Pellet Reaction Data:

\[ W_0 = \text{Initial Mass (mg)} \]
\[ r = \text{Initial Particle Radius (cm)} \]
\[ \varepsilon = \text{Initial Porosity} \]
\[ T = \text{Reaction Temperature (°C)} \]
\[ \chi = \text{Overall Fractional Conversion of CaO} \]
\[ t = \text{Time (min)} \]
Run #187

\[ W_0 = 22.31 \text{ mg} \quad \tau = 0.754 \quad \text{Gas Flows (cm}^3/\text{min})_{\text{STP}} \]
\[ r = 0.1857 \text{ cm} \quad T = 450^\circ \text{C} \quad \begin{array}{c} \text{N}_2 \ 826.5 \\ \text{O}_2 \ 80.0 \\ \text{NO}_2 \ 16.6 \end{array} \]

Time-Conversion Data

<table>
<thead>
<tr>
<th>( t )</th>
<th>( \bar{t} )</th>
<th>( t )</th>
<th>( \bar{t} )</th>
<th>( t )</th>
<th>( \bar{t} )</th>
<th>( t )</th>
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Run #188

\[ W_0 = 10.20 \text{ mg} \quad \tau = 0.748 \quad \text{Gas Flows (cm}^3/\text{min})_{\text{STP}} \]
\[ r = 0.1420 \text{ cm} \quad T = 450^\circ \text{C} \quad \begin{array}{c} \text{N}_2 \ 826.5 \\ \text{O}_2 \ 80.0 \\ \text{NO}_2 \ 16.6 \end{array} \]

Time-Conversion Data

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Run #189

\[ W_0 = 16.21 \text{ mg} \quad \tau = 0.756 \quad \text{Gas Flows (cm}^3/\text{min})_{\text{STP}} \]
\[ r = 0.1674 \text{ cm} \quad T = 350^\circ \text{C} \quad \begin{array}{c} \text{N}_2 \ 826.5 \\ \text{O}_2 \ 80.0 \\ \text{NO}_2 \ 16.6 \end{array} \]

Time-Conversion Data

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</table>
### Run #190

\[ W_0 = 10.93 \text{ mg} \quad \epsilon = 0.739 \quad \text{Gas Flows (cm}^3/\text{min})_{\text{STP}} \]

\[ r = 0.1435 \text{ cm} \quad T = 350^\circ \text{C} \quad \begin{array}{c}
\text{N}_2 \quad 826.5 \\
\text{O}_2 \quad 80.0 \\
\text{NO}_2 \quad 16.6
\end{array} \]

**Time-Conversion Data**

| t | \( \frac{\epsilon}{\epsilon} | t | \( \frac{\epsilon}{\epsilon} | t | \( \frac{\epsilon}{\epsilon} | t | \( \frac{\epsilon}{\epsilon} |
|---|---|---|---|---|---|
| 0.0 | 0.0 | 8.0 | 0.192 | 14.0 | 0.233 | 20.0 | 0.238 |
| 2.0 | 0.076 | 10.0 | 0.212 | 16.0 | 0.234 | 22.0 | 0.238 |
| 4.0 | 0.129 | 12.0 | 0.227 | 18.0 | 0.235 | 24.0 | 0.238 |
| 6.0 | 0.166 | | | | | | |

### Run #191

\[ W_0 = 25.77 \text{ mg} \quad \epsilon = 0.745 \quad \text{Gas Flows (cm}^3/\text{min})_{\text{STP}} \]

\[ r = 0.1925 \text{ cm} \quad T = 250^\circ \text{C} \quad \begin{array}{c}
\text{N}_2 \quad 826.5 \\
\text{O}_2 \quad 80.0 \\
\text{NO}_2 \quad 16.6
\end{array} \]

**Time-Conversion Data**

| t | \( \frac{\epsilon}{\epsilon} | t | \( \frac{\epsilon}{\epsilon} | t | \( \frac{\epsilon}{\epsilon} | t | \( \frac{\epsilon}{\epsilon} |
|---|---|---|---|---|---|
| 0.0 | 0.0 | 4.0 | 0.077 | 20.0 | 0.092 | 40.0 | 0.108 |
| 1.0 | 0.036 | 5.0 | 0.080 | 25.0 | 0.097 | 45.0 | 0.110 |
| 2.0 | 0.056 | 10.0 | 0.085 | 30.0 | 0.101 | 49.0 | 0.113 |
| 3.0 | 0.069 | 15.0 | 0.090 | 35.0 | 0.104 | | |

### Run #192

\[ W_0 = 22.55 \text{ mg} \quad \epsilon = 0.763 \quad \text{Gas Flows (cm}^3/\text{min})_{\text{STP}} \]

\[ r = 0.1888 \text{ cm} \quad T = 250^\circ \text{C} \quad \begin{array}{c}
\text{N}_2 \quad 826.5 \\
\text{O}_2 \quad 80.0 \\
\text{NO}_2 \quad 16.6
\end{array} \]

**Time-Conversion Data**

| t | \( \frac{\epsilon}{\epsilon} | t | \( \frac{\epsilon}{\epsilon} | t | \( \frac{\epsilon}{\epsilon} | t | \( \frac{\epsilon}{\epsilon} |
|---|---|---|---|---|---|
| 0.0 | 0.0 | 4.0 | 0.064 | 15.0 | 0.075 | 30.0 | 0.085 |
| 1.0 | 0.032 | 5.0 | 0.065 | 20.0 | 0.078 | 35.0 | 0.087 |
| 2.0 | 0.050 | 10.0 | 0.071 | 25.0 | 0.082 | 37.0 | 0.088 |
| 3.0 | 0.060 | | | | | | |
Run #193

$W_0 = 22.99 \text{ mg}$  \quad $\varepsilon = 0.765$  \quad Gas Flows (cm$^3$/min)$_{STP}$

$r = 0.1904 \text{ cm}$  \quad $T = 250^\circ \text{C}$  \quad \begin{align*}
\text{N}_2 &= 826.2 \\
\text{O}_2 &= 80.0 \\
\text{NO}_2 &= 16.6
\end{align*}

Time-Conversion Data

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Run #194

$W_0 = 9.38 \text{ mg}$  \quad $\varepsilon = 0.735$  \quad Gas Flows (cm$^3$/min)$_{STP}$

$r = 0.1356 \text{ cm}$  \quad $T = 250^\circ \text{C}$  \quad \begin{align*}
\text{N}_2 &= 826.2 \\
\text{O}_2 &= 80.0 \\
\text{NO}_2 &= 16.6
\end{align*}

Time-Conversion Data

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Run #195

$W_0 = 11.71 \text{ mg}$  \quad $\varepsilon = 0.735$  \quad Gas Flows (cm$^3$/min)$_{STP}$

$r = 0.1460 \text{ cm}$  \quad $T = 250^\circ \text{C}$  \quad \begin{align*}
\text{N}_2 &= 826.2 \\
\text{O}_2 &= 80.0 \\
\text{NO}_2 &= 16.6
\end{align*}

Time-Conversion Data

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Run #196

\[ W_0 = 46.04 \text{ mg} \quad \epsilon = 0.721 \quad \text{Gas Flows (cm}^3/\text{min})_{\text{STP}} \]
\[ r = 0.2268 \text{ cm} \quad T = 250^\circ \text{C} \]
\[ N_2 = 826.2 \]
\[ O_2 = 80.0 \]
\[ NO_2 = 16.6 \]

Time-Conversion Data

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Run #197

\[ W_0 = 41.87 \text{ mg} \quad \epsilon = 0.750 \quad \text{Gas Flows (cm}^3/\text{min})_{\text{STP}} \]
\[ r = 0.2277 \text{ cm} \quad T = 250^\circ \text{C} \]
\[ N_2 = 833.6 \]
\[ O_2 = 80.0 \]
\[ NO_2 = 9.23 \]

Time-Conversion Data

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Run #198

\[ W_0 = 19.07 \text{ mg} \quad \epsilon = 0.756 \quad \text{Gas Flows (cm}^3/\text{min})_{\text{STP}} \]
\[ r = 0.1768 \text{ cm} \quad T = 250^\circ \text{C} \]
\[ N_2 = 833.6 \]
\[ O_2 = 80.0 \]
\[ NO_2 = 9.23 \]

Time-Conversion Data

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### Run #200

\[ W_0 = 9.07 \text{ mg} \quad \epsilon = 0.747 \quad \text{Gas Flows (cm}^3/\text{min})_{\text{STP}} \]

\[ r = 0.1363 \text{ cm} \quad T = 250^\circ \text{C} \]

\[
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\text{Time-Conversion Data} \\
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1.0 & 0.025 & 10.0 & 0.083 & 30.0 & 0.098 \\
2.0 & 0.042 & 15.0 & 0.089 & 35.0 & 0.101 \\
3.0 & 0.055 & 20.0 & 0.092 & 40.0 & 0.103 \\
4.0 & 0.065 & & & & \\
\end{array}
\]

### Run #201

\[ W_0 = 8.25 \text{ mg} \quad \epsilon = 0.763 \quad \text{Gas Flows (cm}^3/\text{min})_{\text{STP}} \]

\[ r = 0.1350 \text{ cm} \quad T = 250^\circ \text{C} \]

\[
\begin{array}{cccccc}
\text{Time-Conversion Data} \\
\hline
\text{t} & \frac{\text{X}}{t} & \text{t} & \frac{\text{X}}{t} & \text{t} & \frac{\text{X}}{t} \\
0.0 & 0.0 & 5.0 & 0.038 & 25.0 & 0.058 \\
1.0 & 0.013 & 10.0 & 0.047 & 30.0 & 0.060 \\
2.0 & 0.023 & 15.0 & 0.050 & 35.0 & 0.062 \\
3.0 & 0.029 & 20.0 & 0.055 & 40.0 & 0.065 \\
4.0 & 0.035 & & & & \\
\end{array}
\]

### Run #202

\[ W_0 = 21.87 \text{ mg} \quad \epsilon = 0.746 \quad \text{Gas Flows (cm}^3/\text{min})_{\text{STP}} \]

\[ r = 0.1824 \text{ cm} \quad T = 250^\circ \text{C} \]

\[
\begin{array}{cccccc}
\text{Time-Conversion Data} \\
\hline
\text{t} & \frac{\text{X}}{t} & \text{t} & \frac{\text{X}}{t} & \text{t} & \frac{\text{X}}{t} \\
0.0 & 0.0 & 5.0 & 0.046 & 30.0 & 0.103 \\
1.0 & 0.013 & 10.0 & 0.072 & 35.0 & 0.107 \\
2.0 & 0.023 & 15.0 & 0.088 & 40.0 & 0.110 \\
3.0 & 0.032 & 20.0 & 0.095 & 45.0 & 0.113 \\
4.0 & 0.040 & 25.0 & 0.099 & 50.0 & 0.115 \\
\end{array}
\]
Run #203

\( W_0 = 31.92 \text{ mg} \quad \varepsilon = 0.776 \quad \text{Gas Flows (cm}^3/\text{min})_{STP} \)

\( r = 0.2160 \text{ cm} \quad T = 250^\circ \text{C} \)

\[ \begin{array}{cccccccc}
0.0 & 0.0 & 5.0 & \ 0.040 & 25.0 & \ 0.096 & 45.0 & \ 0.108 \\
1.0 & 0.009 & 10.0 & \ 0.066 & 30.0 & \ 0.099 & 50.0 & \ 0.111 \\
2.0 & 0.018 & 15.0 & \ 0.083 & 35.0 & \ 0.102 & 55.0 & \ 0.113 \\
3.0 & 0.026 & 20.0 & \ 0.091 & 40.0 & \ 0.105 & 57.0 & \ 0.114 \\
4.0 & \ & \ & \ & \ & \ & \ & \\
\end{array} \]

Run #204

\( W_0 = 10.40 \text{ mg} \quad \varepsilon = 0.768 \quad \text{Gas Flows (cm}^3/\text{min})_{STP} \)

\( r = 0.1469 \text{ cm} \quad T = 350^\circ \text{C} \)

\[ \begin{array}{cccccccc}
0.0 & 0.0 & 5.0 & \ 0.138 & 25.0 & \ 0.300 & 45.0 & \ 0.310 \\
1.0 & 0.030 & 10.0 & \ 0.223 & 30.0 & \ 0.303 & 50.0 & \ 0.311 \\
2.0 & 0.060 & 15.0 & \ 0.269 & 35.0 & \ 0.305 & 55.0 & \ 0.314 \\
3.0 & 0.090 & 20.0 & \ 0.294 & 40.0 & \ 0.308 & 60.0 & \ 0.314 \\
4.0 & \ & \ & \ & \ & \ & \ & \\
\end{array} \]

Run #205

\( W_0 = 35.74 \text{ mg} \quad \varepsilon = 0.741 \quad \text{Gas Flows (cm}^3/\text{min})_{STP} \)

\( r = 0.2136 \text{ cm} \quad T = 350^\circ \text{C} \)

\[ \begin{array}{cccccccc}
0.0 & 0.0 & 4.0 & \ 0.071 & 20.0 & \ 0.211 & 40.0 & \ 0.293 \\
1.0 & 0.017 & 5.0 & \ 0.084 & 25.0 & \ 0.237 & 45.0 & \ 0.307 \\
2.0 & 0.037 & 10.0 & \ 0.141 & 30.0 & \ 0.259 & 50.0 & \ 0.319 \\
3.0 & 0.056 & 15.0 & \ 0.179 & 35.0 & \ 0.277 & 54.0 & \ 0.326 \\
\end{array} \]
Run #206

\[ W_0 = 17.81 \text{ mg} \quad \epsilon = 0.750 \quad \text{Gas Flow} \ (\text{cm}^3/\text{min})_{\text{STP}} \]

\[ r = 0.1713 \text{ cm} \quad T = 350^\circ \text{C} \]

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Run #207

\[ W_0 = 33.34 \text{ mg} \quad \epsilon = 0.740 \quad \text{Gas Flow} \ (\text{cm}^3/\text{min})_{\text{STP}} \]

\[ r = 0.2084 \text{ cm} \quad T = 350^\circ \text{C} \]

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Run #208

\[ W_0 = 34.40 \text{ mg} \quad \epsilon = 0.751 \quad \text{Gas Flow} \ (\text{cm}^3/\text{min})_{\text{STP}} \]

\[ r = 0.2136 \text{ cm} \quad T = 350^\circ \text{C} \]

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Run #209

\( W_0 = 22.95 \text{ mg} \) \( \varepsilon = 0.738 \) \( \text{Gas Flows (cm}^3/\text{min})_{\text{STP}} \)

\( r = 0.1835 \text{ cm} \) \( T = 350^\circ \text{C} \)

\( \begin{array}{ccccccc}
N_2 & 838.0 \\
O_2 & 80.0 \\
NO_2 & 4.62 \\
\end{array} \)

**Time-Conversion Data**

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Run #210

\( W_0 = 13.28 \text{ mg} \) \( \varepsilon = 0.759 \) \( \text{Gas Flows (cm}^3/\text{min})_{\text{STP}} \)

\( r = 0.1570 \text{ cm} \) \( T = 350^\circ \text{C} \)

\( \begin{array}{ccccccc}
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O_2 & 80.0 \\
NO_2 & 4.62 \\
\end{array} \)

**Time-Conversion Data**

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Run #211

\( W_0 = 33.42 \text{ mg} \) \( \varepsilon = 0.757 \) \( \text{Gas Flows (cm}^3/\text{min})_{\text{STP}} \)

\( r = 0.2134 \text{ cm} \) \( T = 450^\circ \text{C} \)

\( \begin{array}{ccccccc}
N_2 & 826.5 \\
O_2 & 80.0 \\
NO_2 & 16.6 \\
\end{array} \)

**Time-Conversion Data**

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Run #212

\[ W_0 = 36.47 \text{ mg} \quad e = 0.757 \quad \text{Gas Flows (cm}^3/\text{min})_{\text{STP}} \]
\[ r = 0.2195 \text{ cm} \quad T = 350^\circ C \]
\[ \text{Gas Flows (cm}^3/\text{min})_{\text{STP}} \]
\[ \text{N}_2 \quad 741.0 \]
\[ \text{O}_2 \quad 165.0 \]
\[ \text{NO}_2 \quad 16.6 \]

Time-Conversion Data

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Run #213

\[ W_0 = 24.80 \text{ mg} \quad e = 0.752 \quad \text{Gas Flows (cm}^3/\text{min})_{\text{STP}} \]
\[ r = 0.1919 \text{ cm} \quad T = 550^\circ C \]
\[ \text{Gas Flows (cm}^3/\text{min})_{\text{STP}} \]
\[ \text{N}_2 \quad 826.5 \]
\[ \text{O}_2 \quad 80.0 \]
\[ \text{NO}_2 \quad 16.6 \]

Time-Conversion Data

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Run #214

\[ W_0 = 7.84 \text{ mg} \quad e = 0.747 \quad \text{Gas Flows (cm}^3/\text{min})_{\text{STP}} \]
\[ r = 0.1299 \text{ cm} \quad T = 550^\circ C \]
\[ \text{Gas Flows (cm}^3/\text{min})_{\text{STP}} \]
\[ \text{N}_2 \quad 826.5 \]
\[ \text{O}_2 \quad 80.0 \]
\[ \text{NO}_2 \quad 16.6 \]

Time-Conversion Data

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Run #215

\[ W_0 = 8.16 \text{ mg} \quad \epsilon = 0.720 \quad \text{Gas Flows (cm}^3/\text{min})_{\text{STP}} \]

\[ r = 0.1267 \text{ cm} \quad T = 550^\circ \text{C} \]

\[ \begin{array}{cccccccc}
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2.0 & 0.037 & 15.0 & 0.200 & 35.0 & 0.325 & 55.0 & 0.406 \\
3.0 & 0.056 & 20.0 & 0.238 & 40.0 & 0.350 & 60.0 & 0.422 \\
4.0 & 0.073 & & & & & & \\
\end{array} \]

Run #216

\[ W_0 = 7.32 \text{ mg} \quad \epsilon = 0.755 \quad \text{Gas Flows (cm}^3/\text{min})_{\text{STP}} \]

\[ r = 0.1283 \text{ cm} \quad T = 550^\circ \text{C} \]

\[ \begin{array}{cccccccc}
\text{Time-Conversion Data} \\
0.0 & 0.0 & 5.0 & 0.042 & 25.0 & 0.146 & 45.0 & 0.192 \\
1.0 & 0.009 & 10.0 & 0.073 & 30.0 & 0.161 & 50.0 & 0.200 \\
2.0 & 0.017 & 15.0 & 0.096 & 35.0 & 0.173 & 55.0 & 0.208 \\
3.0 & 0.026 & 20.0 & 0.115 & 40.0 & 0.182 & 60.0 & 0.216 \\
4.0 & 0.034 & 25.0 & 0.132 & & & & \\
\end{array} \]

Run #217

\[ W_0 = 39.59 \text{ mg} \quad \epsilon = 0.735 \quad \text{Gas Flows (cm}^3/\text{min})_{\text{STP}} \]

\[ r = 0.2193 \text{ cm} \quad T = 550^\circ \text{C} \]

\[ \begin{array}{cccccccc}
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1.0 & 0.005 & 4.0 & 0.021 & 15.0 & 0.056 & 28.0 & 0.071 \\
2.0 & 0.010 & 5.0 & 0.026 & 20.0 & 0.062 & & & \\
\end{array} \]
Run #218

\[ W_0 = 33.80 \text{ mg} \quad \epsilon = 0.754 \quad \text{Gas Flows (cm}^3/\text{min})_{\text{STP}} \]
\[ r = 0.2134 \text{ cm} \quad T = 550^\circ\text{C} \quad N_2 \ 833.6 \quad O_2 \ 80.0 \quad NO_2 \ 9.23 \]

Time-Conversion Data

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Run #219

\[ W_0 = 34.30 \text{ mg} \quad \epsilon = 0.747 \quad \text{Gas Flows (cm}^3/\text{min})_{\text{STP}} \]
\[ r = 0.2122 \text{ cm} \quad T = 450^\circ\text{C} \quad N_2 \ 833.6 \quad O_2 \ 80.0 \quad NO_2 \ 9.23 \]

Time-Conversion Data

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Run #220

\[ W_0 = 6.68 \text{ mg} \quad \epsilon = 0.732 \quad \text{Gas Flows (cm}^3/\text{min})_{\text{STP}} \]
\[ r = 0.1208 \text{ cm} \quad T = 450^\circ\text{C} \quad N_2 \ 833.6 \quad O_2 \ 80.0 \quad NO_2 \ 9.23 \]

Time-Conversion Data

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| X  | 5.0  | .113 |      |       | 5.0  | .113 |      |       |
### Run #221

\[ W_o = 7.90 \text{ mg} \quad \varepsilon = 0.748 \quad \text{Gas Flows (cm}^3/\text{min})_{\text{STP}} \]

\[ r = 0.1304 \text{ cm} \quad T = 450^\circ \text{C} \]

\[ \begin{align*}
\text{Time-Conversion Data} \\
\begin{array}{cccccccccc}
t & X & t & X & t & X & t & X \\
0.0 & 0.0 & 10.0 & .084 & 60.0 & .283 & 110.0 & .385 \\
1.0 & .008 & 20.0 & .144 & 70.0 & .308 & 120.0 & .400 \\
2.0 & .017 & 30.0 & .189 & 80.0 & .331 & 130.0 & .413 \\
3.0 & .027 & 40.0 & .225 & 90.0 & .351 & 140.0 & .425 \\
4.0 & .036 & 50.0 & .257 & 100.0 & .370 & 150.0 & .434 \\
5.0 & .044 & & & & & & \\
\end{array}
\end{align*} \]

### Run #222

\[ W_o = 34.42 \text{ mg} \quad \varepsilon = 0.747 \quad \text{Gas Flows (cm}^3/\text{min})_{\text{STP}} \]

\[ r = 0.2125 \text{ cm} \quad T = 450^\circ \text{C} \]

\[ \begin{align*}
\text{Time-Conversion Data} \\
\begin{array}{cccccccccc}
t & X & t & X & t & X & t & X \\
0.0 & 0.0 & 4.0 & .019 & 20.0 & .076 & 80.0 & .220 \\
1.0 & .005 & 5.0 & .024 & 40.0 & .135 & 100.0 & .255 \\
2.0 & .009 & 10.0 & .038 & 60.0 & .180 & 103.0 & .263 \\
3.0 & .014 & & & & & & \\
\end{array}
\end{align*} \]

### Run #223

\[ W_o = 34.54 \text{ mg} \quad \varepsilon = 0.734 \quad \text{Gas Flows (cm}^3/\text{min})_{\text{STP}} \]

\[ r = 0.2093 \text{ cm} \quad T = 550^\circ \text{C} \]

\[ \begin{align*}
\text{Time-Conversion Data} \\
\begin{array}{cccccccccc}
t & X & t & X & t & X & t & X \\
0.0 & 0.0 & 4.0 & .059 & 30.0 & .100 & 70.0 & .118 \\
1.0 & .019 & 5.0 & .066 & 40.0 & .107 & 80.0 & .123 \\
2.0 & .038 & 10.0 & .079 & 50.0 & .111 & 90.0 & .124 \\
3.0 & .051 & 20.0 & .093 & 60.0 & .116 & & & \\
\end{array}
\end{align*} \]
### Run #224

\( W_0 = 32.74 \text{ mg} \quad \varepsilon = 0.734 \quad \text{Gas Flows (cm}^3/\text{min})_{\text{STP}} \)

\( r = 0.2057 \text{ cm} \quad T = 450^\circ\text{C} \quad \begin{align*}
\text{N}_2 & : 403.0 \\
\text{O}_2 & : 39.2 \\
\text{NO}_2 & : 8.1
\end{align*} \)

#### Time-Conversion Data

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### Run #225

\( W_0 = 31.50 \text{ mg} \quad \varepsilon = 0.746 \quad \text{Gas Flows (cm}^3/\text{min})_{\text{STP}} \)

\( r = 0.2061 \text{ cm} \quad T = 450^\circ\text{C} \quad \begin{align*}
\text{N}_2 & : 201.5 \\
\text{O}_2 & : 19.6 \\
\text{NO}_2 & : 4.1
\end{align*} \)

#### Time-Conversion Data

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### Run #229

\( W_0 = 34.82 \text{ mg} \quad \varepsilon = 0.745 \quad \text{Gas Flows (cm}^3/\text{min})_{\text{STP}} \)

\( r = 0.2129 \text{ cm} \quad T = 450^\circ\text{C} \quad \begin{align*}
\text{N}_2 & : 826.5 \\
\text{O}_2 & : 80.0 \\
\text{NO}_2 & : 16.6
\end{align*} \)

#### Time-Conversion Data

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Run #230

\[ W_0 = 34.72 \text{ mg} \quad \epsilon = 0.722 \quad \text{Gas Flows (cm}^3/\text{min})_{\text{STP}} \]
\[ r = 0.2066 \text{ cm} \quad T = 450^\circ C \]
\[ \begin{array}{cccccc}
    t & \bar{X} & \bar{t} & \bar{X} & \bar{t} & \bar{X} \\
    0.0 & 0.0 & 4.0 & 0.099 & 20.0 & 0.267 & 80.0 & 0.440 \\
    1.0 & 0.032 & 5.0 & 0.117 & 40.0 & 0.367 & 100.0 & 0.443 \\
    2.0 & 0.057 & 10.0 & 0.184 & 60.0 & 0.423 & 105.0 & 0.444 \\
    3.0 & 0.080 & \\
\end{array} \]

Run #231

\[ W_0 = 35.00 \text{ mg} \quad \epsilon = 0.760 \quad \text{Gas Flows (cm}^3/\text{min})_{\text{STP}} \]
\[ r = 0.2177 \text{ cm} \quad T = 350^\circ C \]
\[ \begin{array}{cccccc}
    t & \bar{X} & \bar{t} & \bar{X} & \bar{t} & \bar{X} \\
    0.0 & 0.0 & 4.0 & 0.104 & 40.0 & 0.330 & 120.0 & 0.360 \\
    1.0 & 0.031 & 5.0 & 0.121 & 60.0 & 0.343 & 140.0 & 0.365 \\
    2.0 & 0.060 & 10.0 & 0.185 & 80.0 & 0.349 & 160.0 & 0.368 \\
    3.0 & 0.084 & 20.0 & 0.265 & 100.0 & 0.355 & 167.0 & 0.370 \\
\end{array} \]

Run #232

\[ W_0 = 25.84 \text{ mg} \quad \epsilon = 0.772 \quad \text{Gas Flows (cm}^3/\text{min})_{\text{STP}} \]
\[ r = 0.1999 \text{ cm} \quad T = 550^\circ C \]
\[ \begin{array}{cccccc}
    t & \bar{X} & \bar{t} & \bar{X} & \bar{t} & \bar{X} \\
    0.0 & 0.0 & 4.0 & 0.108 & 20.0 & 0.291 & 80.0 & 0.380 \\
    1.0 & 0.030 & 5.0 & 0.133 & 40.0 & 0.346 & 100.0 & 0.391 \\
    2.0 & 0.058 & 10.0 & 0.219 & 60.0 & 0.367 & 120.0 & 0.396 \\
    3.0 & 0.084 & \\
\end{array} \]
Run #233

\[ W_0 = 32.29 \text{ mg} \quad \varepsilon = 0.761 \quad \text{Gas Flows (cm}^3/\text{min)}_{\text{STP}} \]

\[ r = 0.2121 \text{ cm} \quad T = 550^\circ\text{C} \quad \begin{align*} 
N_2 & \quad 826.5 \\
O_2 & \quad 80.0 \\
NO_2 & \quad 16.6
\end{align*} \]

Time-Conversion Data

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Run #234

\[ W_0 = 14.64 \text{ mg} \quad \varepsilon = 0.738 \quad \text{Gas Flows (cm}^3/\text{min)}_{\text{STP}} \]

\[ r = 0.1580 \text{ cm} \quad T = 550^\circ\text{C} \quad \begin{align*} 
N_2 & \quad 826.5 \\
O_2 & \quad 80.0 \\
NO_2 & \quad 16.6
\end{align*} \]

Time-Conversion Data

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Run #235

\[ W_0 = 20.35 \text{ mg} \quad \varepsilon = 0.704 \quad \text{Gas Flows (cm}^3/\text{min)}_{\text{STP}} \]

\[ r = 0.1694 \text{ cm} \quad T = 350^\circ\text{C} \quad \begin{align*} 
N_2 & \quad 833.6 \\
O_2 & \quad 80.0 \\
NO_2 & \quad 9.23
\end{align*} \]

Time-Conversion Data

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Run #236

$W_0 = 11.91 \text{ mg}$  $\varepsilon = 0.711$  Gas Flows (cm$^3$/min)$_{STP}$

$r = 0.1427 \text{ cm}$  $T = 350^\circ C$

$N_2$  833.6

$O_2$  80.0

$NO_2$  9.23

Time-Conversion Data

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Run #238

$W_0 = 33.72 \text{ mg}$  $\varepsilon = 0.724$  Gas Flows (cm$^3$/min)$_{STP}$

$r = 0.2052 \text{ cm}$  $T = 550^\circ C$

$N_2$  741.0

$O_2$  165.0

$NO_2$  16.6

Time-Conversion Data

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Run #240

$W_0 = 9.55 \text{ mg}$  $\varepsilon = 0.683$  Gas Flows (cm$^3$/min)$_{STP}$

$r = 0.1288 \text{ cm}$  $T = 150^\circ C$

$N_2$  833.6

$O_2$  80.0

$NO_2$  9.23

Time-Conversion Data

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### Run #241

\[ W_0 = 8.03 \text{ mg} \quad \epsilon = 0.719 \quad \text{Gas Flows (cm}^3/\text{min})_{\text{STP}} \]

\[ r = 0.1264 \text{ cm} \quad T = 150^\circ \text{C} \]

\[
\begin{array}{cccccccc}
 t & \Delta t & t & \Delta t & t & \Delta t & t & \Delta t \\
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 1.0 & 0.027 & 5.0 & 0.047 & 40.0 & 0.056 & 80.0 & 0.064 \\
 2.0 & 0.037 & 10.0 & 0.046 & 50.0 & 0.059 & 90.0 & 0.065 \\
 3.0 & 0.039 & 20.0 & 0.051 & 60.0 & 0.060 & &  \\
\end{array}
\]

### Run #243

\[ W_0 = 27.74 \text{ mg} \quad \epsilon = 0.752 \quad \text{Gas Flows (cm}^3/\text{min})_{\text{STP}} \]

\[ r = 0.1991 \text{ cm} \quad T = 250^\circ \text{C} \]

\[
\begin{array}{cccccccc}
 t & \Delta t & t & \Delta t & t & \Delta t & t & \Delta t \\
 0.0 & 0.0 & 5.0 & 0.018 & 40.0 & 0.193 & 80.0 & 0.202 \\
 1.0 & 0.033 & 10.0 & 0.164 & 50.0 & 0.195 & 90.0 & 0.204 \\
 2.0 & 0.063 & 20.0 & 0.186 & 60.0 & 0.197 & 100.0 & 0.207 \\
 3.0 & 0.086 & 30.0 & 0.189 & 70.0 & 0.199 & 102.0 & 0.207 \\
 4.0 & 0.104 & & & & & &  \\
\end{array}
\]

### Run #244

\[ W_0 = 25.14 \text{ mg} \quad \epsilon = 0.768 \quad \text{Gas Flows (cm}^3/\text{min})_{\text{STP}} \]

\[ r = 0.1970 \text{ cm} \quad T = 250^\circ \text{C} \]

\[
\begin{array}{cccccccc}
 t & \Delta t & t & \Delta t & t & \Delta t & t & \Delta t \\
 0.0 & 0.0 & 5.0 & 0.125 & 25.0 & 0.305 & 45.0 & 0.313 \\
 1.0 & 0.022 & 10.0 & 0.202 & 30.0 & 0.309 & 50.0 & 0.314 \\
 2.0 & 0.051 & 15.0 & 0.251 & 35.0 & 0.311 & 55.0 & 0.316 \\
 3.0 & 0.078 & 20.0 & 0.284 & 40.0 & 0.312 & 60.0 & 0.317 \\
 4.0 & 0.103 & & & & & &  \\
\end{array}
\]
### Run #245

\[ W_0 = 23.15 \text{ mg} \quad \varepsilon = 0.774 \quad \text{Gas Flows (cm}^3/\text{min})_{\text{STP}} \]

\[ r = 0.1930 \text{ cm} \quad T = 250^\circ\text{C} \]

**N₂** 741.0  
**O₂** 165.0  
**NO₂** 16.6  

#### Time-Conversion Data

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### Run #246

\[ W_0 = 6.95 \text{ mg} \quad \varepsilon = 0.759 \quad \text{Gas Flows (cm}^3/\text{min})_{\text{STP}} \]

\[ r = 0.1267 \text{ cm} \quad T = 150^\circ\text{C} \]

**N₂** 826.5  
**O₂** 80.0  
**NO₂** 16.6  

#### Time-Conversion Data

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### Run #247

\[ W_0 = 25.70 \text{ mg} \quad \varepsilon = 0.760 \quad \text{Gas Flows (cm}^3/\text{min})_{\text{STP}} \]

\[ r = 0.1953 \text{ cm} \quad T = 150^\circ\text{C} \]

**N₂** 826.5  
**O₂** 80.0  
**NO₂** 16.6  

#### Time-Conversion Data

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Run #248

\[
W_o = 26.07 \text{ mg} \quad \epsilon = 0.747 \quad \text{Gas Flows (cm}^3/\text{min)}_{\text{STP}}
\]

\[
r = 0.1939 \text{ cm} \quad T = 150°C
\]

\[
\begin{array}{cccccccc}
\text{Time-Conversion Data} \\
0.0 & 5.0 & .034 & 50.0 & .051 & 100.0 & .060 \\
1.0 & 10.0 & .037 & 60.0 & .053 & 110.0 & .061 \\
2.0 & 20.0 & .042 & 70.0 & .055 & 120.0 & .062 \\
3.0 & 30.0 & .045 & 80.0 & .057 & 130.0 & .063 \\
4.0 & 40.0 & .048 & 90.0 & .058 & 140.0 & .064 \\
\end{array}
\]

Run #249

\[
W_o = 7.20 \text{ mg} \quad \epsilon = 0.748 \quad \text{Gas Flows (cm}^3/\text{min)}_{\text{STP}}
\]

\[
r = 0.1264 \text{ cm} \quad T = 150°C
\]

\[
\begin{array}{cccccccc}
\text{Time-Conversion Data} \\
0.0 & 5.0 & .014 & 50.0 & .027 & 90.0 & .032 \\
1.0 & 10.0 & .017 & 60.0 & .029 & 100.0 & .033 \\
2.0 & 20.0 & .020 & 70.0 & .030 & 110.0 & .033 \\
3.0 & 30.0 & .023 & 80.0 & .032 & 120.0 & .034 \\
4.0 & 40.0 & .026 & & & & \\
\end{array}
\]

Run #250

\[
W_o = 9.06 \text{ mg} \quad \epsilon = 0.740 \quad \text{Gas Flows (cm}^3/\text{min)}_{\text{STP}}
\]

\[
r = 0.1344 \text{ cm} \quad T = 350°C
\]

\[
\begin{array}{cccccccc}
\text{Time-Conversion Data} \\
0.0 & 80.0 & .446 & 200.0 & .479 & 320.0 & .546 \\
5.0 & 100.0 & .453 & 220.0 & .481 & 340.0 & .548 \\
10.0 & 120.0 & .458 & 240.0 & .485 & 360.0 & .565 \\
20.0 & 140.0 & .465 & 260.0 & .488 & 380.0 & .569 \\
40.0 & 160.0 & .470 & 280.0 & .535 & 390.0 & .569 \\
60.0 & 180.0 & .474 & 300.0 & .542 & & \\
\end{array}
\]
Run #251

\( W_0 = 29.44 \text{ mg} \quad \epsilon = 0.749 \quad \text{Gas Flows (cm}^3/\text{min})_{\text{STP}} \)

\( r = 0.2023 \text{ cm} \quad T = 150^\circ, 250^\circ, \quad \text{N}_2 \quad 826.5 \)

\( 350^\circ, 450^\circ, \quad \text{O}_2 \quad 80.0 \)

\( 550^\circ \text{C} \quad \text{NO}_2 \quad 16.6 \)

Time-Conversion Data

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APPENDIX B

CaO Powder Reaction Data
The following nomenclature is used in Appendix B for the CaO Powder Reaction Data:

- $W_0$ = Initial Mass (mg)
- $T$ = Temperature (°C)
Run #129

\[ W_0 = 1.60 \text{ mg} \quad T = 550^\circ \text{C} \]

Gas Flows \((\text{cm}^3/\text{min})_{\text{STP}}\)  
\[
\begin{align*}
&N_2 & 824.0 \\
&O_2 & 80.0 \\
&NO_2 & 16.6 \\
\end{align*}
\]

Time-Conversion Data

\[
\begin{array}{cccccccc}
t & R & t & R & t & R & t & R \\
0.0 & 0.0 & 10.0 & 0.376 & 18.0 & 0.518 & 26.0 & 0.595 \\
2.0 & 0.103 & 12.0 & 0.416 & 20.0 & 0.533 & 28.0 & 0.610 \\
4.0 & 0.142 & 14.0 & 0.457 & 22.0 & 0.551 & 30.0 & 0.612 \\
6.0 & 0.248 & 16.0 & 0.493 & 24.0 & 0.574 & 32.0 & 0.620 \\
8.0 & 0.312 & & & & & & \\
\end{array}
\]

Run #130

\[ W_0 = 5.34 \text{ mg} \quad T = 550^\circ \text{C} \]

Gas Flows \((\text{cm}^3/\text{min})_{\text{STP}}\)  
\[
\begin{align*}
&N_2 & 900.0 \\
&O_2 & 80.0 \\
&NO_2 & 20.0 \\
\end{align*}
\]

Time-Conversion Data

\[
\begin{array}{cccccccc}
t & R & t & R & t & R & t & R \\
0.0 & 0.0 & 4.0 & 0.147 & 15.0 & 0.439 & 30.0 & 0.585 \\
1.0 & 0.046 & 5.0 & 0.176 & 20.0 & 0.513 & 35.0 & 0.600 \\
2.0 & 0.079 & 10.0 & 0.319 & 25.0 & 0.557 & 40.0 & 0.611 \\
3.0 & 0.114 & & & & & & \\
\end{array}
\]

Run #131

\[ W_0 = 5.71 \text{ mg} \quad T = 550^\circ \text{C} \]

Gas Flows \((\text{cm}^3/\text{min})_{\text{STP}}\)  
\[
\begin{align*}
&N_2 & 900.0 \\
&O_2 & 80.0 \\
&NO_2 & 20.0 \\
\end{align*}
\]

Time-Conversion Data

\[
\begin{array}{cccccccc}
t & R & t & R & t & R & t & R \\
0.0 & 0.0 & 4.0 & 0.114 & 15.0 & 0.381 & 30.0 & 0.564 \\
1.0 & 0.027 & 5.0 & 0.141 & 20.0 & 0.460 & 35.0 & 0.584 \\
2.0 & 0.057 & 10.0 & 0.282 & 25.0 & 0.523 & 39.5 & 0.600 \\
3.0 & 0.086 & & & & & & \\
\end{array}
\]
### Run #132

\[ W_0 = 2.54 \text{ mg} \quad T = 550°C \quad \text{Gas Flows (cm}^3/\text{min})_{\text{STP}} \]

\[ \begin{array}{cccccccc}
N_2 & 900.0 \\
O_2 & 80.0 \\
NO_2 & 20.0 \\
\end{array} \]

**Time-Conversion Data**

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### Run #133

\[ W_0 = 2.51 \text{ mg} \quad T = 600°C \quad \text{Gas Flows (cm}^3/\text{min})_{\text{STP}} \]

\[ \begin{array}{cccccccc}
N_2 & 900.0 \\
O_2 & 80.0 \\
NO_2 & 20.0 \\
\end{array} \]

**Time-Conversion Data**

No reaction occurred at 600°C.

### Run #134

\[ W_0 = 1.68 \text{ mg} \quad T = 500°C \quad \text{Gas Flows (cm}^3/\text{min})_{\text{STP}} \]

\[ \begin{array}{cccccccc}
N_2 & 900.0 \\
O_2 & 80.0 \\
NO_2 & 20.0 \\
\end{array} \]

**Time-Conversion Data**

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### Run #135

\( W_0 = 2.44 \text{ mg} \) \( T = 500^\circ \text{C} \) \( \text{Gas Flows (cm}^3/\text{min})_{\text{STP}} \)

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### Run #136

\( W_0 = 4.27 \text{ mg} \) \( T = 500^\circ \text{C} \) \( \text{Gas Flows (cm}^3/\text{min})_{\text{STP}} \)

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<th>( t )</th>
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### Run #137

\( W_0 = 6.01 \text{ mg} \) \( T = 500^\circ \text{C} \) \( \text{Gas Flows (cm}^3/\text{min})_{\text{STP}} \)

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### Run #138

$W_o = 1.52 \text{ mg}$  
$T = 450^\circ \text{C}$  
Gas Flows $(\text{cm}^3/\text{min})_{\text{STP}}$

<table>
<thead>
<tr>
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<tbody>
<tr>
<td>0.0</td>
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<td>8.0</td>
<td>0.314</td>
<td>14.0</td>
<td>0.328</td>
<td>20.0</td>
<td>0.348</td>
</tr>
<tr>
<td>2.0</td>
<td>0.139</td>
<td>10.0</td>
<td>0.328</td>
<td>16.0</td>
<td>0.335</td>
<td>22.0</td>
<td>0.348</td>
</tr>
<tr>
<td>4.0</td>
<td>0.229</td>
<td>12.0</td>
<td>0.328</td>
<td>18.0</td>
<td>0.342</td>
<td>24.0</td>
<td>0.348</td>
</tr>
<tr>
<td>6.0</td>
<td>0.280</td>
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</table>

### Run #139

$W_o = 2.56 \text{ mg}$  
$T = 450^\circ \text{C}$  
Gas Flows $(\text{cm}^3/\text{min})_{\text{STP}}$

<table>
<thead>
<tr>
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<tbody>
<tr>
<td>0.0</td>
<td>0.0</td>
<td>3.0</td>
<td>0.161</td>
<td>10.0</td>
<td>0.325</td>
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<td>0.349</td>
</tr>
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<td>1.0</td>
<td>0.066</td>
<td>4.0</td>
<td>0.203</td>
<td>15.0</td>
<td>0.341</td>
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<td>5.0</td>
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<td></td>
</tr>
</tbody>
</table>

### Run #140

$W_o = 4.56 \text{ mg}$  
$T = 450^\circ \text{C}$  
Gas Flows $(\text{cm}^3/\text{min})_{\text{STP}}$

<table>
<thead>
<tr>
<th>$t$</th>
<th>$X$</th>
<th>$t$</th>
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</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.0</td>
<td>3.0</td>
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<td>10.0</td>
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</tr>
<tr>
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<td>0.058</td>
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<td>0.186</td>
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<td>0.360</td>
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<td>0.432</td>
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</tbody>
</table>
Run #141

$W_0 = 6.13 \text{ mg}$ $T = 450^\circ C$ Gas Flows (cm$^3$/min)$_{STP}$

<table>
<thead>
<tr>
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</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.0</td>
<td>3.0</td>
<td>.137</td>
</tr>
<tr>
<td>1.0</td>
<td>.059</td>
<td>4.0</td>
<td>.171</td>
</tr>
<tr>
<td>2.0</td>
<td>.098</td>
<td>5.0</td>
<td>.198</td>
</tr>
</tbody>
</table>

Run #142

$W_0 = 7.54 \text{ mg}$ $T = 450^\circ C$ Gas Flows (cm$^3$/min)$_{STP}$

<table>
<thead>
<tr>
<th>$t$</th>
<th>$X$</th>
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</thead>
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<tr>
<td>0.0</td>
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<td>3.0</td>
<td>.126</td>
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<tr>
<td>1.0</td>
<td>.050</td>
<td>4.0</td>
<td>.159</td>
</tr>
<tr>
<td>2.0</td>
<td>.088</td>
<td>5.0</td>
<td>.187</td>
</tr>
</tbody>
</table>

Run #143

$W_0 = 8.78 \text{ mg}$ $T = 450^\circ C$ Gas Flows (cm$^3$/min)$_{STP}$

<table>
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<tr>
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<th>$X$</th>
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</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.0</td>
<td>3.0</td>
<td>.131</td>
</tr>
<tr>
<td>1.0</td>
<td>.047</td>
<td>4.0</td>
<td>.171</td>
</tr>
<tr>
<td>2.0</td>
<td>.089</td>
<td>5.0</td>
<td>.202</td>
</tr>
</tbody>
</table>
### Run #144

*W*₀ = 1.76 mg  \( T = 400^\circ C \)  

<table>
<thead>
<tr>
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<th>( \frac{X}{t} )</th>
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<tr>
<td>0.0</td>
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<td>.240</td>
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<td>.281</td>
<td>25.0</td>
</tr>
<tr>
<td>2.0</td>
<td>.177</td>
<td>5.0</td>
<td>.254</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Run #145

*W*₀ = 3.04 mg  \( T = 400^\circ C \)  

<table>
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</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.0</td>
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<td>.279</td>
<td>20.0</td>
</tr>
<tr>
<td>1.0</td>
<td>.077</td>
<td>4.0</td>
<td>.228</td>
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<td>.286</td>
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</tr>
<tr>
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<td>5.0</td>
<td>.255</td>
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### Run #146

*W*₀ = 1.30 mg  \( T = 400^\circ C \)  

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<th>( \frac{X}{t} )</th>
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<tr>
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<tr>
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<td>.120</td>
<td>4.0</td>
<td>.240</td>
<td>8.0</td>
<td>.260</td>
<td>12.0</td>
</tr>
<tr>
<td>2.0</td>
<td>.179</td>
<td>5.0</td>
<td>.254</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Run #147

\[ W_0 = 4.57 \text{ mg} \quad T = 400^\circ \text{C} \quad \text{Gas Flows (cm}^3/\text{min})_{\text{STP}} \]
\[ \begin{align*}
\text{N}_2 & \quad 900.0 \\
\text{O}_2 & \quad 80.0 \\
\text{NO}_2 & \quad 20.0
\end{align*} \]

Time-Conversion Data

<table>
<thead>
<tr>
<th>t</th>
<th>( \bar{R} )</th>
<th>t</th>
<th>( \bar{R} )</th>
<th>t</th>
<th>( \bar{R} )</th>
<th>t</th>
<th>( \bar{R} )</th>
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<tbody>
<tr>
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<td>0.267</td>
<td>20.0</td>
<td>0.277</td>
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<tr>
<td>2.0</td>
<td>0.134</td>
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</tr>
</tbody>
</table>

Run #148

\[ W_0 = 6.15 \text{ mg} \quad T = 400^\circ \text{C} \quad \text{Gas Flows (cm}^3/\text{min})_{\text{STP}} \]
\[ \begin{align*}
\text{N}_2 & \quad 900.0 \\
\text{O}_2 & \quad 80.0 \\
\text{NO}_2 & \quad 20.0
\end{align*} \]

Time-Conversion Data

<table>
<thead>
<tr>
<th>t</th>
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<th>t</th>
<th>( \bar{R} )</th>
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<tr>
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<td>0.265</td>
</tr>
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<td>0.196</td>
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</table>

Run #149

\[ W_0 = 1.63 \text{ mg} \quad T = 400^\circ \text{C} \quad \text{Gas Flows (cm}^3/\text{min})_{\text{STP}} \]
\[ \begin{align*}
\text{N}_2 & \quad 900.0 \\
\text{O}_2 & \quad 80.0 \\
\text{NO}_2 & \quad 20.0
\end{align*} \]

Time-Conversion Data

<table>
<thead>
<tr>
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<th>( \bar{R} )</th>
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<td>3.0</td>
<td>0.206</td>
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<td>0.321</td>
</tr>
<tr>
<td>1.0</td>
<td>0.093</td>
<td>4.0</td>
<td>0.243</td>
<td>10.0</td>
<td>0.317</td>
<td>20.0</td>
<td>0.325</td>
</tr>
<tr>
<td>2.0</td>
<td>0.158</td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
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</table>
### Run #150

\[ W_0 = 1.44 \text{ mg} \quad T = 400^\circ \text{C} \]

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<th>( t )</th>
<th>( \bar{R} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
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<tr>
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<td>0.319</td>
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<td>20.0</td>
<td>0.390</td>
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<tr>
<td>2.0</td>
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</tr>
</tbody>
</table>

### Run #151

\[ W_0 = 7.28 \text{ mg} \quad T = 400^\circ \text{C} \]

<table>
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<tr>
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<th>( t )</th>
<th>( \bar{R} )</th>
</tr>
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<tr>
<td>0.0</td>
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<td>0.298</td>
<td>16.0</td>
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<tr>
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<td>0.096</td>
<td>5.0</td>
<td>0.235</td>
<td>12.0</td>
<td>0.299</td>
<td>18.0</td>
<td>0.303</td>
</tr>
<tr>
<td>2.0</td>
<td>0.141</td>
<td>6.0</td>
<td>0.257</td>
<td>14.0</td>
<td>0.300</td>
<td>20.0</td>
<td>0.303</td>
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<tr>
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<td>0.286</td>
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</table>

### Run #152

\[ W_0 = 2.56 \text{ mg} \quad T = 400^\circ \text{C} \]

<table>
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<tr>
<th>( t )</th>
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<th>( \bar{R} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.0</td>
<td>4.0</td>
<td>0.279</td>
<td>10.0</td>
<td>0.328</td>
<td>16.0</td>
<td>0.336</td>
</tr>
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<td>0.301</td>
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<td>18.0</td>
<td>0.336</td>
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<td>0.336</td>
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<tr>
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<td>0.324</td>
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</table>
### Run #173

$W_0 = 38.56 \text{ mg } \quad T = 250^\circ C \quad \text{Gas Flows (cm}^3/\text{min})_{\text{STP}}$

<table>
<thead>
<tr>
<th>$t$</th>
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<tbody>
<tr>
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<tr>
<td>1.0</td>
<td>0.059</td>
</tr>
</tbody>
</table>

### Run #174

$W_0 = 23.95 \text{ mg } \quad T = 250^\circ C \quad \text{Gas Flows (cm}^3/\text{min})_{\text{STP}}$

<table>
<thead>
<tr>
<th>$t$</th>
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</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>1.0</td>
<td>0.037</td>
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</tbody>
</table>

### Run #175

$W_0 = 4.15 \text{ mg } \quad T = 250^\circ C \quad \text{Gas Flows (cm}^3/\text{min})_{\text{STP}}$

<table>
<thead>
<tr>
<th>$t$</th>
<th>$\bar{x}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>1.0</td>
<td>0.098</td>
</tr>
<tr>
<td>2.0</td>
<td>0.113</td>
</tr>
</tbody>
</table>
Run #176

$W_0 = 4.58 \text{ mg}$  \hspace{1cm} $T = 350^\circ \text{C}$  \hspace{1cm} Gas Flows (cm$^3$/min)$_{\text{STP}}$

- $N_2 \hspace{1cm} 900.0$
- $O_2 \hspace{1cm} 80.0$
- $N_2O_2 \hspace{1cm} 20.0$

<table>
<thead>
<tr>
<th>$t$</th>
<th>$X$</th>
<th>$t$</th>
<th>$X$</th>
<th>$t$</th>
<th>$X$</th>
<th>$t$</th>
<th>$X$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.0</td>
<td>3.0</td>
<td>0.193</td>
<td>5.0</td>
<td>0.202</td>
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<td>0.210</td>
</tr>
<tr>
<td>1.0</td>
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<td>0.195</td>
<td>6.0</td>
<td>0.204</td>
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<td>0.210</td>
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<td>2.0</td>
<td>0.149</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Run #177

$W_0 = 26.31 \text{ mg}$  \hspace{1cm} $T = 350^\circ \text{C}$  \hspace{1cm} Gas Flows (cm$^3$/min)$_{\text{STP}}$

- $N_2 \hspace{1cm} 900.0$
- $O_2 \hspace{1cm} 80.0$
- $N_2O_2 \hspace{1cm} 20.0$

<table>
<thead>
<tr>
<th>$t$</th>
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<th>$X$</th>
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</thead>
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<td>7.0</td>
<td>0.171</td>
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<td>0.202</td>
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<td>0.030</td>
<td>4.0</td>
<td>0.116</td>
<td>9.0</td>
<td>0.191</td>
<td>15.0</td>
<td>0.203</td>
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<td>0.138</td>
<td>11.0</td>
<td>0.200</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Run #178

$W_0 = 24.65 \text{ mg}$  \hspace{1cm} $T = 400^\circ \text{C}$  \hspace{1cm} Gas Flows (cm$^3$/min)$_{\text{STP}}$

- $N_2 \hspace{1cm} 900.0$
- $O_2 \hspace{1cm} 80.0$
- $N_2O_2 \hspace{1cm} 20.0$

<table>
<thead>
<tr>
<th>$t$</th>
<th>$X$</th>
<th>$t$</th>
<th>$X$</th>
<th>$t$</th>
<th>$X$</th>
<th>$t$</th>
<th>$X$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.0</td>
<td>3.0</td>
<td>0.087</td>
<td>5.0</td>
<td>0.135</td>
<td>15.0</td>
<td>0.236</td>
</tr>
<tr>
<td>1.0</td>
<td>0.026</td>
<td>4.0</td>
<td>0.112</td>
<td>10.0</td>
<td>0.211</td>
<td>18.0</td>
<td>0.243</td>
</tr>
<tr>
<td>2.0</td>
<td>0.059</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Run #179

\(W_0 = 5.25 \text{ mg}\)  \(T = 400^\circ\text{C}\)  \(\text{Gas Flows (cm}^3/\text{min})_{\text{STP}}\)

\[
\begin{array}{ccc}
N_2 & 900.0 \\
O_2 & 80.0 \\
NO_2 & 20.0 \\
\end{array}
\]

**Time-Conversion Data**

<table>
<thead>
<tr>
<th>(t)</th>
<th>(\chi)</th>
<th>(t)</th>
<th>(\chi)</th>
<th>(t)</th>
<th>(\chi)</th>
<th>(t)</th>
<th>(\chi)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.0</td>
<td>2.0</td>
<td>0.140</td>
<td>4.0</td>
<td>0.212</td>
<td>10.0</td>
<td>0.236</td>
</tr>
<tr>
<td>1.0</td>
<td>0.073</td>
<td>3.0</td>
<td>0.186</td>
<td>5.0</td>
<td>0.228</td>
<td>15.0</td>
<td>0.241</td>
</tr>
</tbody>
</table>

Run #180

\(W_0 = 13.28 \text{ mg}\)  \(T = 400^\circ\text{C}\)  \(\text{Gas Flows (cm}^3/\text{min})_{\text{STP}}\)

\[
\begin{array}{ccc}
N_2 & 900.0 \\
O_2 & 80.0 \\
NO_2 & 20.0 \\
\end{array}
\]

**Time-Conversion Data**

<table>
<thead>
<tr>
<th>(t)</th>
<th>(\chi)</th>
<th>(t)</th>
<th>(\chi)</th>
<th>(t)</th>
<th>(\chi)</th>
<th>(t)</th>
<th>(\chi)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.0</td>
<td>2.0</td>
<td>0.093</td>
<td>4.0</td>
<td>0.162</td>
<td>10.0</td>
<td>0.241</td>
</tr>
<tr>
<td>1.0</td>
<td>0.046</td>
<td>3.0</td>
<td>0.131</td>
<td>5.0</td>
<td>0.187</td>
<td>15.0</td>
<td>0.245</td>
</tr>
</tbody>
</table>
APPENDIX C

Computer Programs

VPGM

VPGMC

CPGM
The program listing and sample input data for the noncatalytic gas-solid reaction models used in this study are presented here. VPGM and VPGMC have been consolidated into a single program - MODGRNA. MODGRNA becomes VPGM when the logical IF parameter ON1 is FALSE. When ON1 is TRUE, MODGRNA becomes VPGMC. ON1 is fixed at the beginning of the program, as shown at the bottom of the second page of the printout.
VARIABLE PROPERTY GRAIN MODEL

(VPGM/VPGMC)

COMPUTER PROGRAM
THE VARIABLE PROPERTY GRAIN MODEL: VPMA AND VPMMC

MODGMA

KEN REIBERT'S MODIFIED GRAIN MODEL (THIS WILL BE THE MODGMA)

THIS PROGRAM WILL ACCOUNT FOR VARIABLE SOLID PROPERTY CHANGES
DUE TO REACTION.
THE FOLLOWING ASSUMPTIONS ARE USED:
1. POROSITY VARIES WITH CONVERSION VIA AN EXPANSION
FACTOR (E).
2. GRAIN RADIUS WILL BE ALLOWED TO VARY WITH CONVERSION.
3. THE NUMBER OF GRAINS REMAINS CONSTANT.
4. THE PELLET RADIUS REMAINS CONSTANT.
5. EFFECTIVE DIFFUSIVITY (DE(I)) WILL VARY WITH POROSITY
   \[ DE(I) = DG(I) \times EPSP(I)^{\text{**BETA}} \]

NOTE: WITH VPMA \[ DE(I) = DG(I) \times EPSP(I)^{\text{**BETA}} \]
      WHERE \[ DG(I) = FW(JK,DM) \]
      WITH VPMMC \[ DE(I) = DGo \times EPSP(I)^{\text{**BETA}} \]
      WHERE DGo = CONSTANT AT INITIAL VALUE.

6. ISOTHERMAL REACTION.
7. IRREVERSIBLE REACTION.
8. PSUEDO STEADY STATE ASSUMPTION.
9. ACCOUNTS FOR EXTERNAL MASS TRANSFER FROM BULK TO
    PELLET SURFACE.
**BELRES**

```fortran
DIMENSION C(101), CLEN(101), CTEMP(101), X(101), RC(101),
       RCD(101), RAGD(101), RADGD(101), RHOME(101),
       DIMDE(101), DE(101), DK(101), DG(101), EPSP(101),
       LPCRE(101), SSA(101),
       SESEP(11), SSS1(11), SEPME(11), STIME(11), SXBAR(11),
       IX(40), PROFL1(11,21), PROFL2(11,21), PROFL3(11,21),
       PROFL4(11,21), PROFL5(11,21), PROFL6(11,21),
       PROFL7(11,21), PROFL8(11,21),
       PROFL9(11,21), PROFL10(11,21), PROFL11(11,21), PROFL12(11,21)
REAL KNA, KSC, KS, MWC, MWR, MWP
```

**BELRES**

```fortran
REAL MT(10), MTFP
DIMENSION CAC(101), PD(10), GD(10), CH(10), CB(10), CACB(10),
       SUMREL(10)
```

**BELRES**

```fortran
SET FLAG ON1 TO MAKE MODGRNA = VPGR ON VPGRNC
```

**BELRES**

```fortran
LOGICAL ON1
```

**BELRES**

```fortran
IF ON1 IS TRUE, THEN MODGRNC
```

**BELRES**

```fortran
IF ON1 IS FALSE, THEN MODGRNA
```

```fortran
ON1 = .FALSE.
```

**BELRES**

```fortran
COMMON / A11 / M, MP1, H, M2
COMMON / B11 / RDP, RSO
COMMON / D11 / CAO, KS
```
INPUT DATA

CARD NO. 1
  I8UN = RUN NUMBER

CARD NO. 2
  W0 = INITIAL PELLET MASS (MG)
  RADP = PELLET RADIUS (CM)
  CAO = INITIAL REACTANT GAS CONC. (MG/NOLES/CM**3)
  CS0 = INITIAL SOLID REACTANT CONC. (MG/NOLES/CM**3)
  TEMP = REACTION TEMP (DEG. K)

CARD NO. 3
  DM = MOLECULAR DIFFUSIVITY (CM**2/MIN)
  DGRM = SOLID STATE DIFFUSIVITY IN THE GRAIN (CM**2/MIN)
  EPSG = GRAIN POROSITY - ASSUMED ZERO
  BETA = POWER TO WHICH PELLET POROSITY IS RAISED TO CALC.
  DE (EFFECTIVE DIFFUSIVITY). USUALLY 2.0 TO 3.0.

CARD NO. 4
  AA = STOIC. COEFF. FOR REACTANT GAS (-2.0 FOR NO2)
  AS = STOIC. COEFF. FOR REACTANT SOLID (-1.0 FOR CA0)
  AP = STOIC. COEFF. FOR PRODUCT SOLID (1.0 FOR CA(NO3)2)
  AMG = MW OF REACTANT GAS (46.01 FOR NO2)
  AMR = MW OF REACTANT SOLID (58.08 FOR CA0)
  AMW = MW OF PRODUCT SOLID (164.06 FOR CA(NO3)2)
  EFLAG = EXPANSION FACTOR FLAG (IF EFLAG.EQ.0.0, THEN E IS
          CALCULATED BY PROGRAM).
  IF EFLAG.NE.0.0 THEN E=EFLAG
  IF EFLAG.EQ.1.0 THEN HOMOGNA BECOMES THE GRAIN
  MODEL.

CARD NO. 5
  KBA = MASS TRANSFER COEFF. FOR REACTANT GAS (CM/MIN)
  KSO = KINETIC FREQUENCY (CM**4/MG/NOLES MIN)
  EA = ACTIVATION ENERGY (CAL / GM/NOLE)
  LH01 = CRYSTALLINE DENSITY OF REACTANT SOLID (MG/CM**3)
          (3800 MG/CM**3 FOR CA0)
  LH02 = CRYSTALLINE DENSITY OF PRODUCT SOLID (MG/CM**3)
          (2504 MG/CM**3 FOR CA(NO3)2)
SSAO = INITIAL SPECIFIC SURFACE AREA FOR REACTANT SOLID
(255.2 cm²/mg FOR CAO PELLETS)
TRUKIN= MEASURED RATE CONSTANT (cm³/mg MOLE MIN)
(IF ZERO READ THEN ARRHENIUS VALUE IS USED IN CALCS)

CARD NO. 6
N = NUMBER OF INTERVALS THE SOLID RADIUS WILL BE DIVIDED
INTO FOR INTEGRATION
ITER = MAXIMUM NUMBER OF TIME STEPS
DTIME = TIME STEP=DN
XFNAL = DESIRED FINAL CONVERSION
DELPRT = PRINT INTERVAL.

BEGIN INPUT OF DATA

READ(5,*) IRUN
10 FORMAT(15)
IF (IRUN.EQ.0) GO TO 998

IF (ON1) GO TO 333
WRITE(6,10)
10 FORMAT(I18,2X,'********** MODGNA (VPGM) THE MODIFIED GRAIN MODEL ***
************* ***')
WRITE(6,10)
16 FORMAT(/,2X,'************** CASE A. DG = FN(DK,DM) ',
'**/2X, '************** DE(I)=DG(I)*EPSP(I)**BETA
' THIS IS MODGNA) VPGM **********/',)
GO TO 3033

333 WRITE (6,3030)
3030 FORMAT(I18,2X,'******** ON1 IS TRUE **** MODGNC (VPGMC) ***
************* ***')
WRITE(6,3031)
3031 FORMAT(/,2X,'************** CASE C. DG = CONSTANT ',
'**/2X, '************** DE(I)=DG0*EPSP(I)**BETA
' THIS IS VPGMC ) ************/',)
3033 WRITE (6,11) IBUN
   11 FORMAT (8I1, 'BUN NUMBER ', 19)

   READ (5,*), W0, RADP, CAO, CSO, TEMP
   FORMAT (8G10.0)
   WRITE (6,31) W0, RADP, CAO, CSO, TEMP
31 FORMAT (/10X, 'INITIAL VOLUME MASS (g) = ',1PE12.4,5X,'RADP (cm) = ',
         - P10.4,5X,'INITIAL GAS CONC. muk (MGMOLE/CM**3) = ',1PE12.4,5X,
         - /10X, 'CSO (MGMOLE/CM**3) = ',0PF10.4,5X,'TEMP (DEG.K) = ',F10.2,//)

   READ (5,*), DHI, DGRN, EPSG, BETA
   WRITE (6,32) DHI, DGRN, EPSG, BETA
32 FORMAT (10X, 'DHI (CM**2/MIN) = ',1PE12.4,5X,'DGRN (CM**2/MIN) = ',
         - 1PE12.4,5X,'EPSG (CM**2/CM**2) = ',1PE12.4,5X,'BETA = ',0PF10.2)

   READ (5,*), AA, AS, AP, H2O, WA, IH2O, EFLAG
   WRITE (6,33) AA, AS, AP, H2O, WA, IH2O, EFLAG
33 FORMAT (/10X, 'AA = ',5F2.5X,'AS = ',5F2.5X,'AP = ',5F2.5X,'10X,
         - 'H2O (MG) = ',F10.2,5X,'WA (CM) = ',F10.2,5X,'IH2O = ',
         - 'EFLAG (CM**2/CM**2) = ',F10.2,'/6X, EFLAG = ',F10.3,' ****',//)

   READ (5,*), KHA, KSO, EA, ka1, H2O, SSAO, TRUKIN
   WRITE (6,34) KHA, KSO, EA, ka1, H2O, SSAO, TRUKIN
34 FORMAT (10X, 'KHA (CM/MIN) = ',1PE12.4,5X,'KSO (CM**4/MGMOLE MIN) = ',
         - 1PE12.4,5X,'EA (CM/CM**3) = ',1PE12.4,'/10X,'RHO1 (MG/CM**3) = ',
         - 0PF10.2,5X,'RHO2 (MG/CM**3) = ',F10.2,5X,'SSAO (CM**2/MG) = ',F10.2,
         - '//6X, TRUKIN = ',1PE12.4,' ****',//)

   READ (5,*), NITER, DTME, AFINAL, DELPRT
   WRITE (6,35) NITER, DTME, AFINAL, DELPRT
35 FORMAT (10X, 'NITER = ',15,5X,'NITER = ',15,5X,'DTME = ',1PE12.4,5X,
         - 'AFINAL = ',F10.2,5X,'DELPRT = ',F10.5)
DGO = (DP1+LC*9700.0*(T/RH)*(*.5))*.0.
DGO = (DGO+DH)/(DGO+DH)

C PAC ALLOWS US TO VARY DGO BY ANY FACTOR IE., 10,-10,Etc.
PAC = 1.0
DGO = DGO*PAC

C
DGO = 0.0
DGO = DH
DGO = DGO*EPSPO**BETA
VOLR = MVR/RHO1
VOLP = MVR/RHO2

C ******** CHECK EFLAG ********
IF(EFLAG.EQ.0.0)
  E = AP*VOLR/(-AS*VOLR*(1.0-EPSP))
IF(EFLAG.EQ.0.0) E = EFLAG

C
KSO = 3.0/(SSSO*RHO)

C
TIMEPT =0.0

C
******** CHECK TRUKIN ********
KS = TRUKIN
IF(TRUKIN.EQ.0.0)
  KS = KSO*EXP(-EA/(1.907*TEMP))

C

C INITIALIZE PARAMETERS USED IN MODEL.
EPSPO = 1.0 - WO/(4.186*RHO1*ADP**3)
EPSBAR = EPSPO
SSABAR = SSAO
RPOREO = 2.*EPSPO/(SSSO*(1.-EPSPO)*RHO1)
RPBAR = RPOREO
2004 FORMAT (/10X,'DT = ',IPE12.5,'PH = ',IPE12.5,5X,'PHIG = ',IPE12.5)
C
WRITE(6,2005) DT,DT,DT
2005 FORMAT (/10X,'DT = ',IPE12.5)
C
C
WRITE (6,45)
45 FORMAT (//// 6X,'TIME', 3X,'CONV')/
C
C
N = 1./FLOAT(N)
N2=N*N
NP1=N+1
NPRINT = N/10
IX=0
ICNT=0
ISTART=0
ISTEP1=0.0
ISTEP2=0.50
TIME=0.
IXBAR=0.
DO 60 I=1,NP1
X(I) = 0.0
DCD(I) = 1.
RHOMIX(I) = RH01
RADGD(I) = 1.0
RADG(I) = RS0
DIMDE(I) = 1.0
EPSF(I) = EPSPO
RPORE(I) = RPOREQ
DK(I) = DKQ
DG(I) = DGO
DB(I)=DG(I)*EPSPO*BE*GA
SSA(I) = 3./(RADG(I)*RHOMIX(I))
C
C
60 C(I) = ((FLOAT(I)-1.)/FLOAT(M))**3.
   C(I)=C(2)
   DO 80 I=1,MP1
   80 CTEMP(I) = C(I)
C
************** PAX THIS FOR MODGRN **************
C
   CALL GASBLN(ECN,CTEMP,CMH,AA,PHIG,PHIP,BI,
       .DINDE,RADGD,EPSP,EPSPQ,E,
C
C
**************BEGIN CALCULATIONS FOR MOD GRN******************
   DO 90 I=1,MP1
   90 C(I) = CMH(I)
   100 CONTINUE
C
BEGIN CALCULATIONS FOR MODAL RESULTS
C
   IWRITE =0
8200 ICNT = ICNT+1
   IF(DTIME.GT.0.05) GO TO 8201
   IF((TIME+DTIME).LT.TIMPT) GO TO 8100
   GO TO 8202
8201 IF(TIME.LT.TIMPT) GO TO 8100
8202 IWRITE = IWRITE + 1
   TX(1,IWRITE)=TIME
   TX(2,IWRITE)=IXBAR
   TX(3,IWRITE) = EPSBAR
   TX(4,IWRITE) = SSABAR
   IF(IWRITE.EQ.6) GO TO 8300
   TIMPT = TIMPT + DELMAT
C
8100 IF(IXBAR.LT.ISTEP1) GO TO 120
C
C **RELRES**
DO 1101 JJ=1,MP1
1101 CAC(JJ) = C(JJ)/(1.0 - AA*PHI*BCD(JJ)/(1.0 - ACD(JJ)/RADGD(JJ)))
  
C
C
I=0
IX=IX+1
DO 110 IKEEP=1,MP1,MP1+1
I=I+1
PROPL1(IX,I) = I(IKEEP)
PROPL2(IX,I) = C(IKEEP)
PROPL3(IX,I) = RADGD(IKEEP)
PROPL4(IX,I) = ACD(IKEEP)
PROPL5(IX,I) = EPSP(IKEEP)
PROPL6(IX,I) = DHME(IKEEP)
PROPL7(IX,I) = SSHA(IKEEP)
PROPL8(IX,I) = KHOMIX(IKEEP)
PROPL9(IX,I) = DK(IKEEP)
PROPL10(IX,I) = DG(IKEEP)
PROPL11(IX,I) = DE(IKEEP)
PROPL12(IX,I) = BPOKE(IKEEP)
110 CONTINUE
C
C
*************
C
C
**BELRES**
C
C
CALL SIMPS(C,CABAR)
C
C
C
CALL SIMPS(CAC,CACBAR)
MT(IX) = 1.0 - C(MP1)
PD(IX) = C(MP1) - CABAR
GD(IX) = CABAR - CACBAR
CR(IX) = CACBAR
CB(IX) = CABAR
CACB(IX) = CAQBAR
SUMREL(IX) = MT(IX) + V(IX) * GD(IX) + CR(IX)

***********************************************************************

SIXBAR(IX) = XBAR
STIME(IX) = TIME
SEPSP(IX) = EPSBAR
SSSA(IX) = SSabar
SPORRE(IX) = PRBAR

DISTEP = 0.10
XSTEP1 = XSTEP1 + DISTEP
XSTEP1 = XSTEP1 + 0.10

CALL SLOBL1 (ISTART, RCD, CMEX, AA, AS, PHI, IPH, BI, DTHETA, DIMX, BADGD, EPS, EPSP, EPSO, BADP, RSO, E)

***********************************************************************

TIME = TIME + DTIM

UPDATE PARAMETERS

DO 130 I=1, MFI
IF (RCD(I) .LT. 0.0) RCD(I) = 0.0
X(I) = 1. - RCD(I)**0.
IF (X(I) .LT. 0.0) X(I) = 0.0
IF (X(I) .GE. 1.0) X(I) = 1.0
EPSP(I) = 1. - ((1. - EPSP)*E + (1. - E)*X(I))
BADGD(I) = (1. + X(I)*Z(I))**3333
IF (E .NE. 1.0)


```plaintext
- RHOMIX(I) = ( (1. - A(I)) * W1 + E*I(I) * W2 * (1 - EPSG) ) /
  ( A(I) + E*I(I) * (E-1))
  RADG(I) = RADGD(I) * ESO
  IF(E.NE.1.0)
  - SSA(I) = 3./RADG(I) * RHOMIX(I))

C 130 CONTINUE
  CALL SIMPS (X, XMB)
  CALL SIMPS (SSA, SSBAB)
C
C ********** IF LOCAL POROSITY GOES TO ZERO THEN TERMINATE PROGRAM*********
C
   DO 135 I=1, NP1
C   IF(EPSPI(I) .LE. 0.0) GO TO 201
C   IF(EPSPI(I) .LE. 0.0) GO TO 170
C   IF(EPSPI(I) .LE. 0.0) EPSPI(I) = E12.4
C   WRITE(6,173) I, EPSPI(I), I, X(I), I, C(I)
173 FORMAT (5X, 'EPSPI(', 'I3,2X) = ', E12.4, 5X, 'X(', 'I3,2X) = ', E12.4,
  8X, 'C(', 'I3,2X) = ', E12.4)
   RPOBE(I) = 2.*EPSPI(I)/(SSA(I) * RHOMIX(I) * (1. - EPSPI(I)))
C
C
C IF(ON1) GO TO 444
D1(I) = 9700.*RPOBE(I) * SWAT(I) / (EMP/MHG) * E0.
D1(I) = DK(I) * DM/(D1(I) + DM)
D1(I) = DG(I) * FAC
DE(I) = DG(I) * EPSPI(I) ** BETA
444 CONTINUE
IF(ON1) DE(I) = DG0 * EPSPI(I) ** BETA
DIMDE(I) = DE(I) / DE0
135 CONTINUE
  CALL SIMPS (EPSPI, EPSBAA)
  CALL SIMPS (RPOBE, RBBAA)
C ********** AND POROSITY CHECK **********
```
C
DO 140 I=1,MP1
140 CTEMP(I) = C(I)
C
C
CALL GASBLH(BCD,CTEMP,CNEW,AA,PHIG,PHIF,BI,
       .DINDE,RADGD,EPSP,EPSP0,E)
C
C
*******************************************************************************
DO 150 I=1,MP1
C
150 C(I) = CNEW(I)
IF(XBAR.LT.XSTEP2) GO TO 170
DTIME = 2.*DINDE
DTHETA = 2.*DTHETA
XSTEP2 = 2.*XSTEP2
ISTART = 0
C
C
170 CONTINUE
C
**RELRES**
CALL SIMPS(C,CABAR)
DO 1111 JJ=1,MP1
1111 CAC(JJ) = C(JJ)/((1.0 - A*PHIG*BCD(JJ)*(1.0 - BCD(JJ)/RADGD(JJ))
       - )
CALL SIMPS(CAC,CACBAR)
MTIF = 1.0 - C(MP1)
PDXF = C(MP1) - CABAR
GDXF = CABAR - CACBAR
CRIF = CACBAR
CBIF = CABAR
CACCBIF = CACBAR
SUBRES = MTIF + PDXF + GDXF + CRIF
DO 2900 I=1,MP1
IF(EPSP(I) .LE. 1.0E-4) GO TO 201
2900 CONTINUE
C IF(EPS2(NP1) .LE. 0.0) GO TO 201
C
C ********************************************
C C170 IF(XBAR.GE.XFINAL) GO TO 210
IF(XBAR.GE.XFINAL) GO TO 1940
IF (ICMT.GT.ITER) GO TO 190
GO TO 8200
8300 WRITE(6,190) (TX(1,i),TX(2,i), i=1,6)
190 FORMAT (5X,6(F7.3,2X,F5.3,3X))
TIMRT = TIMRT + DELRT
GO TO 100
C
C ******************************************** COME HERE IF XBAR .GE. XFINAL ***************
1940 WRITE(6,1941)
1941 FORMAT (//,25X,'** XBAR IS GREATER THAN OR EQUAL TO XFINAL **/*)
GO TO 210
C
C ******************************************** COME HERE IF MAX NUMBER OF ITERATIONS IS EXCEEDED ********
195 WRITE(6,199)
199 FORMAT (//,25X,'********** ITERATIONS EXCEEDED ************',//)
WRITE (6,200) ICMT
200 FORMAT (///10X,'MAXIMUM NUMBER OF ITERATIONS TO REACH XFINAL HAS ',
. ' BEEN EXCEEDED.',/10X, 'PROGRAM WILL OUTPUT REMAINING',
. ' INFORMATION AND TERMINATE THIS CASE.',/10X, 'ITERATIONS',
. ' USED = ', I6)
GO TO 210
C

*************** COME HERE IF LOCAL POROSITY GOES TO ZERO ***************
201  WRITE(6,202)
202  FORMAT(//,'****** THIS RUN PREMATURELY TERMINATED ******,'//)
   WRITE(6,203) TIME,I, EPS(I), X(I), XBAR
203  FORMAT(//,'A VALUE FOR THE LOCAL POROSITY IS LESS THAN OR
   EQUAL TO ZERO.  
   'F10.4,'11d= ',F10.4,'EPS(',I,')=',E12.4,
   'F10.4,'X(',I,')=',E12.4,'XBAR=',E12.4,'/10X,'PROGRAM WILL
   OUTPUT REMAINING INFORMATION AND TERMINATE THIS CASE.\')
   WRITE(6,204)
204  FORMAT(//,'****** deterrent
   II=WRITE+1
   TX(1,II) = TIME
   TX(2,II) = XBAR
   WRITE (6,190) (TX(1,II),II(4,I), I=1,II)

C
C

WRITE(6,219)
219  FORMAT(//,'THE SPATIAL PROFILES OF LOCAL FRACTIONAL CONVERSION'
   ' AND GAS REACTANT',//, 'CONCENTRATION FOR VARIOUS',
   ' TIMES AND OVERALL CONVERSION ARE')
C

DO 240 I=1,IX
C
   WRITE (6,230) TIME(I), XBAR(I), PROFIL(I,II), II=1,II
230  FORMAT(//, 'AT TIME = ',F7.3,' MIN AND FRACTIONAL CONVERSION'
   ' = ',F7.3,' LOCAL FRACTIONAL CONVERSION ',
   ' PROFILE IS ',//10X, 1F9.4)
C
C
   WRITE(6,300) (PROFL(I,II),II=1,II)
300  FORMAT(//, 'GRAIN MAJOR PROFILE (DIMENSIONLESS) IS',
   ' //10X, 1F9.4, //10X, 1F9.4)
C

WRITE (6,301) (PROFL (1,II),II=1,11)
301 FORMAT (/7X,'THE (CORE RADIUS/INITIAL GRAIN RADIUS) PROFILE IS',
- '15',//10X,11F14.4)
C

WRITE (6,250) (PROFL (1,II),II=1,11)
250 FORMAT (/7X,'GAS REACTANT PROFILE (DIMENSIONLESS) IS',//10X,
- '11F9.4,5X,'PELLET SURFACE')
C

WRITE (6,302) (PROFL (1,II),II=1,11)
302 FORMAT (/7X,'POROSITY PROFILE FOR PELLET IS ',
- '//10X,9E12.4,10X,2E12.4)
C

WRITE (6,303) (PROFL (1,II),II=1,11)
303 FORMAT (/7X,'EFFECTIVE DIFFUSIVITY PROFILE IS (DIMENSIONLESS) IS',
- '//10X,1P9E12.5,10X,2E12.5)
C

WRITE (6,304) (PROFL (1,II),II=1,11)
304 FORMAT (/7X,'SPECIFIC SURFACE AREA PROFILE IS (CM**2/MG)'//10X,
- '1P9E12.5,10X,2E12.5)
C

WRITE (6,305) (PROFL (1,II),II=1,11)
305 FORMAT (/7X,'GRAIN DENSITY PROFILE IS (MG/CM**3)'//10X,
- '1P9E12.5,10X,2E12.5)
C

WRITE (6,306) (PROFL (1,II),II=1,11)
306 FORMAT (/7X,'DK PROFILE IS (CM**2/CM)'//10X,
- '1P9E12.5,10X,2E12.5)
C

WRITE (6,307) (PROFL (1,II),II=1,11)
307 FORMAT (/7X,'DG PROFILE IS - DK & DM COMBINED -(CM**2/CM)'//10X,
- '1P9E12.5,10X,2E12.5)
C

WRITE (6,308) (PROFL (1,II),II=1,11)
308 FORMAT (/7X,'DE PROFILE IS (CM**2/CM)'//10X,
C

WRITE(6, 309)     (PMPLZ(L,LI), LI=1,11)
309 FORMAT(/, 'PORE RADIUS PROFILE IS', //10X,
         . /19E12.5,/,10X,2E12.5)
C

WRITE (6, 1500) SEBSP(I), SMPOW(EI), SSSA(I)
1500 FORMAT(/, 'THE OVERALL PELLET POROSITY IS', 1PE12.5,
         . /10X, 'THE PRESENT AVG POROS RADIUS IS', 1PE12.5,
         . /10X, 'THE OVERALL SURFACE AREA IS', 1PE12.5)
C

**RELRES**
C

WRITE(6, 1505)
1505 FORMAT(/, '**** RELATIVE RESISTANCES ****', //)
WRITE(6, 1503) CB(I), CACB(I)
1503 FORMAT(/, '5X, 'CABAR = ', F10.4, '5X, 'CACHAR = ', F10.4, //)
WRITE(6, 1504) HT(I), PD(I), C(I), SUMET(I)
1504 FORMAT(/, '5X, 'HT = ', F10.4, '5X, 'PD = ', F10.4, '5X, 'CM = ', F10.4,
         . 'CM = ', F10.4, '5X, 'SUMET = ', F10.4, //)
C

**************
C

WRITE(6, 1501)
1501 FORMAT(/, '5X, '**************', //)
240 CONTINUE
C

WRITE (6, 230) TIME, ADAL, (X(I), I=1, M, NPRINT)
WRITE (6, 300) (RADGW(I), I=1, M, NPRINT)
C
WRITE(6,301) ( RCD(i), i=1,MP1,NPRINT)
WRITE (6,250) ( C(i), i=1,MP1,NPRINT)
WRITE (6,302) ( EPS2(i), i=1,MP1,NPRINT)
WRITE (6,303) ( DIME(i), i=1,MP1,NPRINT)
WRITE (6,304) ( SSA(i), i=1,MP1,NPRINT)
WRITE (6,305) ( MHOA4A(i), i=1,MP1,NPRINT)
WRITE (6,306) ( DK1(i), i=1,MP1,NPRINT)
WRITE (6,307) ( DO(i), i=1,MP1,NPRINT)
WRITE (6,308) ( DQ(i), i=1,MP1,NPRINT)
WRITE (6,309) ( HPOME(i), i=1,MP1,NPRINT)
WRITE (6,1500) EPSBAK, WPBAK, SSABAK

**RELRES**
WRITE (6,1505)
WRITE (6,1503) CBXF,CACB XF
WRITE (6,1504) MTXF,PD XF, GLMF, CRXF, SUMREL

***************
WRITE (6,1501)
GO TO 1

998 WRITE (6,999)
999 FORMAT (V///10X, 'LAST CASE HAS BEEN RUN')
STOP
END

SUBROUTINE FOR SOLVING SOLID PHASE MATERIAL BALANCE

--ONE REACTIVE GAS--

SUBROUTINE SLDB1(ISTART,Y,C,AA,AS,PHIG,PHIP,BI,DINBA,
DIMDE,RADGD,EPSP,EPSP0,KADP,MSO,E)
DIMENSION Y(101), C(101), CTEMP(101)
DIMENSION DINDE(101),RADGD(101),EPSP(101)
COMMON /A11/ N,NP1,NH,SH2
COMMON/C11/ K1,K2,K3,K4,YM1(101),YM2(101),YM3(101),P(101),PH1(101)
           ,PH2(101)
REAL K1(101), K2(101), K3(101), K4(101)

FCT1(I1,I2,I3,I4) = AS*X2*(1. - X4)/
               - (X3*3*(1. - AA*PHIG*X1*(1. - X1/X3))*(1. - EPSPO))

DO 5 I=1,NP1
 5 F(I) = FCT1(X(I),C(I),RADGD(I),EPSP(I))
IF (ISTART.GE.1) GO TO 20
DO 10 I=1,NP1
  YM3(I) = 0.
  YM2(I) = 0.
  YM1(I) = 0.
  FM2(I) = 0.
  PH1(I) = 0.
10   FM1(I) = 0.
20   IF (ISTART.GE.3) GO TO 100
DO 30 I=1,MP1
  30 K1(I) = F(I)
  DO 40 I=1,MP1
  40 K2(I) = Y(I) + 0.5 * DTHETA * K1(I)
  CALL GASBLN(K2,C,CTEMP,AA,PHIG,PHIP,BI,DINDE,BADGD,EPSP,EPSP0,E)
  DO 50 I=1,MP1
  50 K2(I) = FCT(K2(I),CTEMP(I),BADGD(I),EPSP(I))
  DO 60 I=1,MP1
  60 K3(I) = Y(I) + 0.5*DTHETA * K2(I)
  CALL GASBLN(K3,C,CTEMP,AA,PHIG,PHIP,BI,DINDE,BADGD,EPSP,EPSP0,E)
  DO 70 I=1,MP1
  70 K3(I) = FCT(K3(I),CTEMP(I),BADGD(I),EPSP(I))
  DO 80 I=1,MP1
  80 K4(I) = Y(I) + DTHETA * K3(I)
  CALL GASBLN(K4,C,CTEMP,AA,PHIG,PHIP,BI,DINDE,BADGD,EPSP,EPSP0,E)
  DO 90 I=1,MP1
  90 K4(I) = FCT(K4(I),CTEMP(I),BADGD(I),EPSP(I))
  YM3(I) = YM2(I)
  YM2(I) = YM1(I)
  YM1(I) = Y(I)
  Y(I) = Y(I) + 0.1666666 * DTHETA * (K1(I) + 2.*K2(I) + 2.*K3(I) + K4(I))
C *************** CHECK TO ENSURE THAT ECD(I) IS NEVER LESS THAN 0.0********
  IF(Y(I).LE.0.0) Y(I) = 0.0
C *********************************************************
  PM2(I) = PM1(I)
  90 PM1(I) = F(I)
  ISTART = ISTART + 1
  RETURN
  DO 110 I=1,MP1
  110 K1(I) = YM3(I) + 1.3333333 * DTHETA * (2.*F(I)-PM1(I)+2.*PM2(I))
  IF(ISTART.GT.3) GO TO 110
  DO 120 I=1,MP1
  120 K4(I) = 0.
  130 DO 140 I=1,MP1
  140 CONTINUE
K2(I) = K1(I) + 0.925*YH3(I)*K4(I)
CALL GASBLN(K2,C,CTEMP,AA,PH1,P,H1,DIHDE,RADGD,ESP,EPSP,EA)
DO 150 I=1,NP1
K3(I) = 0.125*(9.*Y(I)-YN2(I)) + 3.*DTHETA*FCT1(K2(I),CTEMP(I),
  RADGD(I),ESP(I)) + 2.*F(I)-PH1(I))
K4(I) = K3(I) - K1(I)
YN3(I) = YN2(I)
YN2(I) = YN1(I)
YN1(I) = Y(I)
Y(I) = K3(I) - 7.4380108-02*K4(I)
C *****************************************************************************
C CHECK TO ENSURE THAT RCD(I) IS NEVER LESS THAN 0.
IF (Y(I) .LE. 0.0) Y(I) = 0.0
C *****************************************************************************
FM2(I) = FM1(I)
150 FM1(I) = F(I)
ISTART = ISTART + 1
RETURN
END

SUBROUTINE FOR SOLVING GAS PHASE MATERIAL BALANCE

SUBROUTINE GASBLN(Y,C, CNM,AA,PH1,P,H1,DIHDE,RADGD,ESP,EPSP,EA)
  COMMON /AIN/N,NP1,H2
  COMMON/B1/RADG,RSO
  DIMENSION Y(101), C(101), CNM(101), D(101), U(101), KBE(101)
  REAL L(101)
  DIMENSION DIHDE(101), RADGD(101), ESP(101)
  DO 10 I=1,NP1
IF(Y(I) .LT. 0.0) Y(I) = 0.0

10  CMEV(I) = C(I)
    DO 20 I=2,N
        L(I) = FLOAT(I-2)/(FLOAT(I-1)*H2) - (DIMDE(I+1) - DIMDE(I-1))/
        (DIMDE(I)*N*H2)
    20  U(I) = FLOAT(I)/(FLOAT(I-1)*H2) + (DIMDE(I+1) - DIMDE(I-1))/
        (DIMDE(I)*N*H2)
    U(1) = 2./H2
    L(I) = 0.0

C

***********************************************************************

***********************************************************************

C

DO 40 I=1,NP1
    D(I) = 3. * AA * PHIG * MADI * Y(I) **2 * (1. - EPSPI(I))/
        (B50 * DIMDE(I) * HADGD(I) **2 * (1. - EPSPO) *)
        (1. - AA * PHIGY(I) * (I - Y(I))/HADGD(I))) - 2./H2
40  RHS(I) = 0.

C

*********************************************************************** BEGIN NEW NP1 EXPRESSIONS ***************

C

A = D(NP1) + 2./H2
    L(NP1) = 1./H2 - 2./(N*H2) + DIMDE(N)/(DIMDE(NP1)*H2)
    D(NP1) = (-2.0*BI)/(d*DIMDE(NP1)) - 1./H2 + 2./(N*H2)
    -DIMDE(N)/(DIMDE(NP1)*H2) + A
    RHS(NP1) = -2.0*BI/(d*DIMDE(NP1))

C

*********************************************************************** END OF NEW NP1 EXPRESSIONS ******************
U(NP1) = 0.0
CALL TRIDAG (1,NP1,L,U,J,MHS,CNEW)
DO 50 I=1,NP1
   IF(CNEW(I)*LE.0.) CNEW(I) = 1.E-30
   RETURN
END

SIMPSON'S RULE INTEGRATION

SUBROUTINE SIMPS (X,XBAR)
COMMON /A11/ N,NP1,H,W2
DIMENSION F(101),X(101)
NCHECK = (NP1/2)*2
IF(NCHECK.EQ.NP1) GO TO 30
   WM1 = N-1
   DO 10 I=1,NP1
      10   F(I) = X(I) * (((FLOAT(I)-1.)*W)**2.)
   XBAR = F(1) + 4.*F(2) + F(NP1)
   DO 20 I=3,WM1,2
      20   XBAR = XBAR + 2.*F(I) + 4.*F(I+1)
   XBAR = H * XBAR
   RETURN
30   WRITE(6,40)
   40   FORMAT(/'SIMPSON'S RULE REQUIRES AN EVEN NUMBER OF INTERVALS'/)
   STOP
END
SUBROUTINE FOR SOLVING A SYSTEM OF LINEAR SIMULTANEOUS EQUATIONS HAVING A TRIDIAGONAL COEFFICIENT MATRIX.


SUBROUTINE TRIDAG(IF,L,A,B,C,D,V)
DIMENSION A(101),B(101),C(101),D(101),V(101),BETA(101),GAMMA(101)

...COMPUTE INTERMEDIATE ARRAYS BETA AND GAMMA......

BETA(IF) = B(IF)
GAMMA(IF) = D(IF)/BETA(IF)
IPPI = IF + 1
DO 1 I = IPPI, L
BETA(I) = B(I) - A(I)*C(I-1)/BETA(I-1)
1 GAMMA(I) = (D(I) - A(I)*GAMMA(I-1))/BETA(I)

...COMPUTE FINAL SOLUTION VECTOR V......

V(L) = GAMMA(L)
LAST = L - IF
DO 2 K = 1, LAST
I = L - K
2 V(I) = GAMMA(I) - C(I)*V(I+1)/BETA(I)
RETURN
END
SAMPLE INPUT DATA TO

VARIABLE PROPERTY GRAIN MODEL (VPGM/VPGMC)
22.31 1.002-08 3.038-04 4.84 7.24
36.6 -1.0 1.0 4.0 5.0 3.0 1.0 3.30 1.0
388 0.0 1.77 5.297 3.04 2.02 2.02 50.2 0.0 0.0002-04
50 500 .25 -.98 0 0
EXAMPLE PROGRAM OUTPUT FOR VPGM
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<th>MASS (G)</th>
<th>TIME (MIN)</th>
<th>MASS (G)</th>
<th>TIME (MIN)</th>
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<td>8.0</td>
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>>>>>>>> ITERATIONS EXCEEDED <<<<<<<<<<<

CALCULATION NUMBER OF ITERATIONS TO REACH FLUX HAS BEEN EXCEEDED.
PROCEED WILL CONTACT RELEVANT INFORMATIONS AND TERMINATE THIS CASE.

ITERATIONS EXCEEDED = 150
120,000 0.415 120,000 0.415

<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<

THE SPATIAL PROFILES OF LOCAL FRACTIONAL CONVERSION AND GAS REACTANT
CONCENTRATION FOR VARIOUS TIMES AND OVERALL CONVERSION ARE

AT TIME = 0.0 0.999 AND FRACTIONAL CONVERSION = 0.0

LOCAL FRACTIONAL CONVERSION PROFILE IS

0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0

GAS REACTANT PROFILE (BASIS KINETICS) IS

1.0000 1.0000 1.0000 1.0000 1.0000 1.0000 1.0000 1.0000 1.0000 1.0000
1.0000 1.0000 1.0000 1.0000 1.0000 1.0000 1.0000 1.0000 1.0000 1.0000

THE GAS REACTANT/INITIAL GAS RATIO PROFILE IS

1.0000 1.0000 1.0000 1.0000 1.0000 1.0000 1.0000 1.0000 1.0000 1.0000

380
**AT TIME = 6.000 ALE AND FRACTIONAL CONVERSION = 0.992**

**LOCAL FRACTIONAL CONVERSION PROFILE IS**

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**CHAIN RADIUS PROFILE (DIMENSIONLESS) IS**

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**THE (CORE RADIUS/INITIAL CHAIN RADIUS) PROFILES IS**

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**CHAIN RADIUS PROFILE (DIMENSIONLESS) IS**

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**PROPERTY PROFILES FOR PULLEY IS**

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**EFFICIENT SPECIFIC SURFACES PROFILES IS (DIMENSIONLESS)**

|------------|------------|------------|------------|------------|------------|------------|------------|------------|

**SPECIFIC SURFACE AREA PROFILES IS (CD++/A)**

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**CHAIN RADIUS PROFILE IS (CD++/C)**

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**CD PROFILES IS (CD++/CD)**

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1.412924*91 9.1*4974*44

**DG PROFILE IS**

- 1.056923*91 5.141492*91 1.129015*91 1.411741*91 1.069112*91 1.050368*91 9.296092*91 1.223521*91 2.216688*91 2.64885*91 4.2144*91 7.31412*91

**DG PROFILE IS**

- 6.032468*91 6.123496*91 6.031356*91 6.118232*91 6.227732*91 6.945792*91 7.597984*91 8.796024*91 9.044064*91 2.214242*91 3.902364*91 2.531059*91

**PORE RADII PROFILE IS**

- 7.802310*91 7.168246*91 7.101192*91 7.000850*91 6.975288*91 6.746318*91 6.305788*91 5.928468*91 5.375076*91 4.737238*91 3.904118*91

**THE OVERALL PELLET POROSITY IS** 0.679939*91
**THE PRESENT TOTAL PORE RADII IS** 5.406712*91
**THE OVERALL SURFACE AREA IS** 2.33722*91

*** RELATIVE RESISTANCES ***

- **CABAL** = 0.4926  **CACHAL** = 0.0047
- **RT** = 0.1029  **R** = 0.0016  **GR** = 0.0009  **CR** = 0.0047

**SUMMER** = 5.0000

***********************
CONSTANT PROPERTY GRAIN MODEL (CPGM)

COMPUTER PROGRAM
THE CONSTANT PROPERTY GRAIN MODEL (CPGB)

GRAIN MODEL--FOR ONE REACTIVE GAS

DIMENSION C(2,101), CNEX(101), CTETP(101), R(101), A(101),
- TI(2,6), P(201,11,21), PROPL2(2,11,21), STXH(11),
- SIBAB(11), D(2), DEAP(2), BI(2), PHIP(2), PHIg(2),
- AA(2), AS(2)

REAL KMA(2), KS
COMMON /A11/ N, NP1, h, d2
COMMON/B11/RADG, RAPP
COMMON /D11/ CAO(2), KS(2), DEAG(2), CSOG

INPUT

IRUN = RUN NUMBER
MREACT = NUMBER OF REACTIVE GAS SPECIES
EPSP = PARTICLE POROSITY--FRACTIONAL VOLUME
DGRN = GRAIN EFFECTIVE DIFFUSIVITY
RADP = PARTICLE RADIUS--CM
RADG = GRAIN RADIUS--CM
CSO = BULK SOLID CONCENTRATION--MG MOLE/CC
BETA = CONSTANT USED IN THE DETERMINATION OF EFFECTIVE DIFFUSIVITY--USUALLY 2.0
DG = GASEOUS DIFFUSION CONSTANT--COMBINED KNUDSEN AND MOLECULAR
- (CM**2)/SEC
KMA = MASS TRANSFER CONSTANT--CM/SEC
CAO = BULK REACTIVE GAS CONCENTRATION--MG MOLE/CC
KS = REACTION RATE CONSTANT--(CM**4)/(MG MOLE*MIN)
AA = STOICHIOMETRIC COEFFICIENT--GAS PHASE
AS = STOICHIOMETRIC COEFFICIENT--SOLID PHASE
C
N = NUMBER OF INTERVALS THE SOLID RADIUS WILL BE DIVIDED
C
INTO FOR INTEGRATION
C
ITER = MAXIMUM NUMBER OF TIME STEPS
C
DTIME = TIME STEP--MIN
C
XFINAL = DESIRED FINAL CONVERSION
1
READ(5, *) IRUN, NREA, EPS, DGRM, RADP, RADG, CSO, BETA
10 FORMAT (215, F10.6, E10.3, F10.4, E10.3, 2F10.4)
IF (IRUN.EQ.0) GO TO 990
WRITE (6, 15)
15 FORMAT (1H1, 10X, 'GAULD MODEL')
WRITE (6, 10) IRUN, NREA, EPS, DGRM, RADP, RADG, CSO, BETA
DO 20 I = 1, NREA
READ(5, *) DG(I), KMA(I), CAO(I), KS(I), AA(I), AS(I)
30 FORMAT (4E12.5, 4F10.5)
WRITE (6, 30) DG(I), KMA(I), CAO(I), KS(I), AA(I), AS(I)
20 CONTINUE
READ(5, *) N, ITER, DTIME, XFINAL
WRITE (6, 40) N, ITER, DTIME, XFINAL
40 FORMAT (215, 2F10.4)
WRITE (6, 45)
45 FORMAT (//, 6X, 'TIME', 3X, 'CONV')/
CSOG = CSO/ (1. - EPS)
DO 50 I = 1, NREA
DEAP(I) = DG(I)*EPS**BETA
DEAG(I) = DGRM
B1(I) = KMA(I)*RADP/DEAP(I)
PH1P(I) = RADP*KS(I)*CSOG/(DEAP(I)**60.)
PH1G(I) = RADG*KS(I)*CSOG/(DEAG(I)**60.)
50 CONTINUE
H = 1./FLOAT(N)
M2 = H**2
DTHETA = KS(1)*CAO(1)*DTIME/RADG
NP1 = N + 1
NPRINT = N/10
IX = 0
ICNT=0
ISTART=0
XSTEP1=0.0
XSTEP2=0.50
TIME=0.
XBAR=0.
DO 60 I=1,MP1
X(I) = 0.0
R(I) = 1.
DO 60 II=1,WPACT
60 C(II,1) = ((FLOAT(I)-1.0)/FLOAT(N))**3.
DO 70 II=1,WPACT
70 C(II,1)=C(II,2)
DO 90 II=1,WPACT
DO 80 I=1,MP1
80 CTMP(I) = C(II,1)
CALL GASBLM(B,CTMP,CNEW,AA,II),PH1G(II),PHIP(II),BI(II))
DO 90 I=1,MP1
90 C(II,1) = CNEW(I)
100 CONTINUE
DO 180 IWRITE=1,6
ICNT = ICNT+1
TX(1,IWRITE) = TIME
TX(2,IWRITE) = XBAR
IF[XBAR.LT.XSTEP1] GO TO 120
I=0
IX=IX+1
DO 110 IKEEP=1,MP1,WPMLT
I=I+1
PROPL1(IX,I) = X(IKEEP)
DO 110 II=1,WPACT
110 PROPL2(II,IX,I) = C(II, IKEEP)
SIBAR(IX)=XBAR
SIME(IX)=TIME
XSTEP1=XSTEP1+0.10
120 IF(MREA=aY.1) CALL S:\1)1(1,START,AA,AA(i),AS(i),PHEG(1),
PHIP(1),B1(1),DTHETA)
TIME = TIME + DTIIIE
DO 130 I=1, NPI
IF (X(I) LT. 0.0) X(I) = 0.0
X(I) = 1. - X(I) * 3.
CALL SIMPS (I, IBAR)
DO 160 II=1, MREA:o
DO 160 I=1,IP1
160 CNEW(I) = C(I1, I)
CALL GASL(LH(A,CTEMP,CH,AA(I),PHIG(II),PHIP(II),B1(I)))
DO 150 I=1,II1
150 CUE (I) = CUES (1)
160 CONTINUE
IF (XBAR, LT. XSTEP2) GO TO 170
DTIME = 2.*DTIME
DTHETA = 2.*DTHETA
XSTEP2 = 2.*XSTEP2
ISTART = 0
170 IF (XBAR, GE. XFINAL) GO TO 210
IF (ICNT, GT. ITER) GO TO 193
180 CONTINUE
WRITE(6,190) (TX(1, I), TX(2, I), I=1,6)
190 FORMAT (5X,6(F7.3,2X,F5.3,3X))
GO TO 100
195 WRITE(6,200) ICNT
200 FORMAT (/10X,'MAXIMUM NUMBER OF ITERATIONS TO REACH XFINAL HAS ',
. 'BEEN EXCEEDED. '/10X,'PROGRAM WILL OUTPUT REMAINING ',
. 'INFORMATION AND TERMINATE THIS CASE. ',/10X,'ITERATIONS',
. 'USED = ', I6)
210 I1=I1+1
TX(1, I1) = TIME
TX(2, I1) = XBAR
WRITE(6,190) (TX(1, I), TX(2, I), I=1,II)
WRITE(6,220)
SUBROUTINE FOR SOLVING SOLID PHASE MATERIAL BALANCE

SUBROUTINE SLDRL1(LSTART,Y,C,AA,AS,PHIG,PHIP,B1,DTHETA)
DIMENSION Y(101), C(101), CTLAP(101)
COMMON /A11/ N,NPI,H2
COMMON/C11/ K1,K2,K3,K4,YH1(101),YH2(101),YH3(101),P(101),PM1(101)
C
REAL K1(101), K2(101), K3(101), K4(101)
C
FCT1(X1,X2) = AS*X2/(1. - AA*PHIG*X1* (1. - X1))
DO 5 I=1,NP1
5 F(I) = FCT1(Y(I),C(I))
IF (LSTART.GE.1) GO TO 20
DO 10 I=1,NP1
YM3(I) = 0.
YM2(I) = 0.
YM1(I) = 0.
FM2(I) = 0.
10 FM1(I) = 0.
10 IF(ISSTART.GE.3) GO TO 100

DO 30 I=1,NP1
30 K1(I) = P(I)
DO 40 I=1,NP1
40 K2(I) = Y(I) + 0.5 * DTHETA * K1(I)
CALL GASBLN(K2,C,CTEMP,AA,PHIG,PHIP,BI)
DO 50 I=1,NP1
50 K2(I) = FCT1(K2(I),CTEMP(I))
DO 60 I=1,NP1
60 K3(I) = Y(I) + 0.5*DTHETA * K2(I)
CALL GASBLN(K3,C,CTEMP,AA,PHIG,PHIP,BI)
DO 70 I=1,NP1
70 K3(I) = FCT1(K3(I),CTEMP(I))
DO 80 I=1,NP1
80 K4(I) = Y(I) + DTHETA * K3(I)
CALL GASBLN(K4,C,CTEMP,AA,PHIG,PHIP,BI)
DO 90 I=1,NP1
90 K4(I) = FCT1(K4(I),CTEMP(I))
YM3(I) = YM2(I)
YM2(I) = YM1(I)
YM1(I) = Y(I)
Y(I) = Y(I) + 0.1000006 * DTHETA * (K1(I) + 2.*K2(I) + 2.*K3(I))
   + K4(I))
FM2(I) = FM1(I)
90 FM1(I) = P(I)
ISTART = ISTART + 1
RETURN
100 DO 110 I=1,NP1
110  
K1(I) = YM3(I) + 1.333333 * DTHERA = (2. * F(I) - PM1(I) + 2. * PM2(I))
IF (ISTART .GT. 1) GO TO 130
DO 120 I = 1, MP1
120  
K4(I) = 0.
130  
DO 140 I = 1, MP1
140  
K2(I) = K1(I) + 0.925*19.3 * K4(I)
CALL GASBLN(K2, C, CTEMP, AA, 2, M, PHI, BI)
DO 150 I = 1, MP1
150  
K3(I) = 0.125*(Y2(I) - Y2(I) + 3.* DTHERA*(FCT1(K2(I), CTEMP(I)))
K6(I) = K3(I) - K1(I)
YM3(I) = YM2(I)
YM2(I) = YM1(I)
YM1(I) = Y(I)
Y(I) = K3(I) - 7.438016-02 * K4(I)
PM2(I) = PM1(I)
150  
PH1(I) = P(I)
ISTART = ISTART + 1
RETURN
END

SUBROUTINE FOR SOLVING GAS PHASE MATERIAL BALANCE

SUBROUTINE GASBLN(Y, C, CMW, AA, PH1, PH1, BI)
COMMON /A11/ W, MP1, M, H2
COMMON/B11/K4DG, RA0P
DIMENSION Y(101), C(101), CMW(101), D(101), U(101), RMS(101)
REAL L(101)
DO 10 I = 1, MP1
10  
IF (Y(I) .LT. 0.0) Y(I) = 0.0
10  
CMW(I) = C(I)
DO 20 I = 2, MP1
20  
L(I) = FLOAT(I-2)/(FLOAT(I-1)*H2)
U(I) = FLOAT(I)/(FLOAT(I-1)*H2)
U(I) = 2. / H2
L(NP1) = 2. / \sqrt{2}

DO 40 I=1,NP1
D(I) = 3. * AA * PHI2 * MAD2 * Y(I) ** 2. / (MADG * (1. - AA * PHI2 * Y(I) * (1. - I(I)))) - 2. / \sqrt{2}

40 RHS(I) = 0.
RHS(NP1) = -2.0 * R * BL * W(NP1)
D(NP1) = D(NP1) + RHS(NP1)

C WRITE(6,888) (L(I),D(I),U(I),MHS(I),I=1,NP1)
C 888 FORMAT(1X,8E12.5)
CALL TRIDAG (1,NP1,L,D,U,MHS,CNEW)
DO 50 I=1,NP1
50 IF(CNEW(I).LE.0.) CNEW(I) = 1.0 * 30
C WRITE(6,888) (C(I),CNEW(I),I=1,NP1)
RETURN
END

C SIMPSON'S RULE INTEGRATION

SUBROUTINE SIMPS (A,XBAR)
COMMON /A1/ W,NP1,H,n2
DIMENSION F(101),X(101)
NCHECK = (NP1/2) ** 2
IF (NCHECK.EQ.NP1) GO TO 30
MM1 = H-1
DO 10 I=1,NP1
10 F(I) = X(I) * (((FLOAT(I)-1.) * H) ** 2.)
XBAR = F(I) + 4. * F(I+2) + F(NP1)
DO 20 I=3,nM1,2
XBAR = XBAR + 2. * F(I) + 4. * F(I+1)
XBAR = H * XBAR
RETURN
30 WRITE(6,40)
40 FORMAT(/,5X,'SIMPSON'S RULE REQUIRES AN EVEN NUMBER OF INTERVALS')
STOP
END
SAMPLE INPUT DATA TO CONSTANT PROPERTY GRAIN MODEL (CPGM)
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EXAMPLE PROGRAM OUTPUT FOR CPGM
THE SPATIAL PROFILES OF LOCAL FRACTIONAL CONVERSION AND GAS REACTANT CONCENTRATION FOR VARIOUS TIMES AND OVERALL CONVERSION ARE

AT TIME = 0.0 R.H. AND FRACTIONAL CONVERSION = 0.0

THE LOCAL FRACTIONAL CONVERSION PROFILE IS
0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0

THE PROFILE FOR GAS REACTANT IS
0.0000 0.0000 0.0000 0.0001 0.0003 0.0006 0.0027 0.0092 0.0316 0.1197 0.3926

AT TIME = 4.000 R.H. AND FRACTIONAL CONVERSION = 0.106

THE LOCAL FRACTIONAL CONVERSION PROFILE IS
0.0000 0.0000 0.0001 0.0003 0.0004 0.0013 0.0042 0.0140 0.0373 0.1579 0.6622

THE PROFILE FOR GAS REACTANT IS
0.0000 0.0000 0.0000 0.0001 0.0003 0.0010 0.0034 0.0115 0.0392 0.1334 0.4446

AT TIME = 8.000 R.H. AND FRACTIONAL CONVERSION = 0.205

THE LOCAL FRACTIONAL CONVERSION PROFILE IS
0.0001 0.0001 0.0001 0.0003 0.0004 0.0029 0.0094 0.0315 0.1008 0.3249 0.7756

THE PROFILE FOR GAS REACTANT IS
0.0000 0.0000 0.0000 0.0001 0.0003 0.0013 0.0044 0.0144 0.0501 0.1643 0.4730

AT TIME = 12.250 R.H. AND FRACTIONAL CONVERSION = 0.301

THE LOCAL FRACTIONAL CONVERSION PROFILE IS
0.0001 0.0001 0.0002 0.0004 0.0017 0.0052 0.0169 0.0559 0.1880 0.5121 0.8518

THE PROFILE FOR GAS REACTANT IS
0.0000 0.0000 0.0001 0.0002 0.0006 0.0010 0.0030 0.0282 0.0672 0.2161 0.5361

AT TIME = 17.500 R.H. AND FRACTIONAL CONVERSION = 0.403

THE LOCAL FRACTIONAL CONVERSION PROFILE IS
0.0002 0.0002 0.0004 0.0010 0.0030 0.0093 0.0362 0.0945 0.3025 0.7280 1.0000

THE PROFILE FOR GAS REACTANT IS
0.0000 0.0000 0.0001 0.0003 0.0005 0.0029 0.0093 0.0309 0.1004 0.2990 0.6056
Kenneth Charles Reibert, the son of Kenneth H. and June Reibert, was born in Great Lakes, Illinois, on July 1, 1952. Since his father was a career Navy man, he attended elementary school in many parts of the United States including Kodiak, Alaska, Willow Grove, Pennsylvania, Milwaukee, Wisconsin, and Belle Chasse, Louisiana. He graduated from River Oaks Academy (Belle Chasse, Louisiana) in May, 1970. Upon graduation he was awarded an LSU Centennial Award Scholarship.

He graduated cum laude from LSU in May, 1974, receiving a Bachelor of Science degree in Chemical Engineering. He was awarded the Jesse Coates Award that same year. In August, 1976, he received his Master of Science degree in Chemical Engineering.

His industrial experience includes summer engineering jobs with Kaiser, Monsanto, Allied Chemical, and the Department of Energy.

The author is a member of Tau Beta Pi, Phi Kappa Phi, Phi Lambda Upsilon, Phi Eta Sigma, and A.I.Ch.E. He has been the recipient of numerous scholarships including the Charles B. Tidwell Award, Tenneco Scholarship, and an Exxon Fellowship.

Presently the author is employed as a Senior Research Engineer with Dow Chemical in Plaquemine, Louisiana. He is married to the former Pamela Foerster of Belle Chasse,
Louisiana, and they reside with their five month old son, Jason, in Baton Rouge, Louisiana.
Candidate: Kenneth Charles Reibert

Major Field: Chemical Engineering

Title of Thesis: The Reaction Between Calcium Oxide and Nitrogen Dioxide in the Presence of Oxygen: A Variable Solid Property Grain Model

Approved:

[Signature]
Major Professor and Chairman

[Signature]
Dean of the Graduate School

EXAMINING COMMITTEE:

[Signature]

[Signature]

[Signature]

Date of Examination:

March 29, 1982