

Reaction Kinetics of ZnO Dissociation for a Solar-Thermal Zn/ZnO Water-Splitting Cycle

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Abstract

Dissociation of fine zinc oxide particles ($<1 \mu\text{m}$) was explored at ultra-high temperatures (1700-2000 K) using a graphite aerosol reactor heated in a graphite tube furnace. The dissociation of ZnO is a critical reaction in a two-step water splitting process for the production of hydrogen, and the reaction can be performed in solar thermal reactors for sustainable hydrogen generation. Fundamental understanding of the reaction is critical to solar reactor design, and so the dissociation must be explored at residence times typical to these reactors (0.05s to 1.5s). An experimental test apparatus was designed to study the kinetics of this reaction, and test points were run using this reactor. Conversions between 30% and 70% were obtained at temperatures ranging between 2000 K and 2300 K and residence times scattered about 1.2 s. With this apparatus, a complete experimental campaign can be performed to determine the kinetic rate law for the ZnO dissociation reaction.

I. Introduction and Background

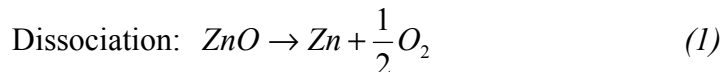
The energy needs of the world are rapidly expanding, while concerns over the supply duration and environmental impacts of fossil fuels are ever increasing. In order to sate the industrial world's energy appetite while alleviating the problems inherent to fossil fuel usage, a renewable, clean, and sustainable source of energy must be developed. Hydrogen produced via solar thermal water splitting can fulfill this need. Hydrogen produced in this way would take advantage of the major sustainable source of energy, the sun, and the product of its use would be clean water.

Direct thermal water splitting is extremely technically challenging, as the temperatures required for acceptable equilibrium conversions would exceed 4000 K. This temperature is well beyond even the most optimistic projections for the capabilities of concentrated solar energy arrays. The infeasibility of direct water splitting with current or near future technology has led to research in the development of multi-step cycles with the same net effect, i.e. the dissociation of water into its constituent elements. The advantages of this process approach are many and varied. First, the temperature of the decomposition reaction in the cycle is much lower than the temperature required to carry out the direct thermolysis of water. As high temperature is one of the two major limiting factors in direct water splitting in terms of efficiency, materials, and economic benefits, the reduction of this temperature can lead to significant gains on each of the aforementioned fronts. Second, as all of these multi-step processes remove hydrogen and oxygen gas in separate steps, there is no need to perform a high temperature gas separation of these elements, and there is no chance of the formation of an explosive (and thus dangerous) gas mixture. [1-3]

These advantages come at a price, though. First and foremost is that as the number of process steps increases, the maximum theoretical process efficiency decreases due to the irreversibility of each stage and of material and energy transfer between stages. With decreased efficiency comes poorer theoretical economics, overall conversion concerns, and bottom line reductions in overall energy production. In addition to decreased efficiency, multi-stage processes require the separation of reaction products at moderate temperatures, transportation of products/reagents between reaction stages, and, for high temperature reactions, the problem of recombination of dissociated compounds as temperature is reduced. [2, 4, 5]

After a thorough literature review and thermodynamic simulations, the class of multi-step cycles collectively known as the “metal oxide” cycles was chosen for study. These cycles met a number of important criteria, including temperature of operation, number of cycle steps, availability of reagents, and possible environmental impacts, all of which were factors in determining the future commercial feasibility of the cycles. At their core, the cycles are essentially the same. A metal oxide is thermally reduced at extremely high temperatures ($T > 1800$ K) in an initial step, and in a series of following steps the reduced metal oxide is combined with water to yield the original metal oxide and a hydrogen product. Of the metal-oxide cycles, one in particular was singled out for study, the ZnO/Zn process.

The ZnO/Zn process consists of two process steps:



This cycle has been the one most explored in the literature, due to the relatively low temperatures required for the dissociation reaction and the relatively quick kinetics of its water splitting reaction.

The ZnO decomposition reaction was simulated using the computer program Facility for the Analysis of Chemical Thermodynamics (FACT) and the equilibrium compositions for this reaction at 1 atm were determined, with a 1:1 ratio of inert Ar carrier gas to ZnO. Under these conditions, FACT predicts the start of ZnO dissociation at 1800 K, with complete dissociation occurring just under 2200 K. The addition of more inert to carry the ZnO particles reduces the necessary temperature for complete conversion of the ZnO predicted by FACT. This is a result of the reduced partial pressure of the product gases, shifting the reaction equilibrium toward the products. FACT predicts that the necessary temperature for complete conversion dips below 2100 K for a feed ratio of 3:1 (Ar to ZnO). The decreased temperature makes the entire process more efficient, and thus more feasible as a commercial energy solution.

Although the thermodynamics of the ZnO decomposition are favorable for application in a solar furnace, very little is known about the inherent reaction kinetics. Due to radiation losses, which are proportional to the area insulated, it is desired to have the smallest possible reactor to complete the ZnO decomposition. The reaction kinetics must be studied and a rate law formulated to complete this design. This paper presents an apparatus and method to experimentally study these high temperature reaction kinetics. Initial results are presented as verification of the concept and as a baseline for constructing a future experimental test matrix.

II. Experimental Apparatus

The basic objective in the kinetic experiments is the rapid heating of aerosol ZnO powders followed by rapid quench of the reaction products with appropriate measurements performed to determine conversion. The experiments were conducted in a graphite tube furnace at the University of Colorado (Figure 1). Sub-micron ZnO was loaded into a vibratory feeder reservoir mounted at the top of the furnace. The feeder shakes the particles into a Spinning Wheel Feeder (SWF), where the particles are entrained in an Argon gas stream. A spinning titanium wheel inside the SWF breaks agglomerates of the ZnO particles up and disperses these particles evenly in the gas flow.

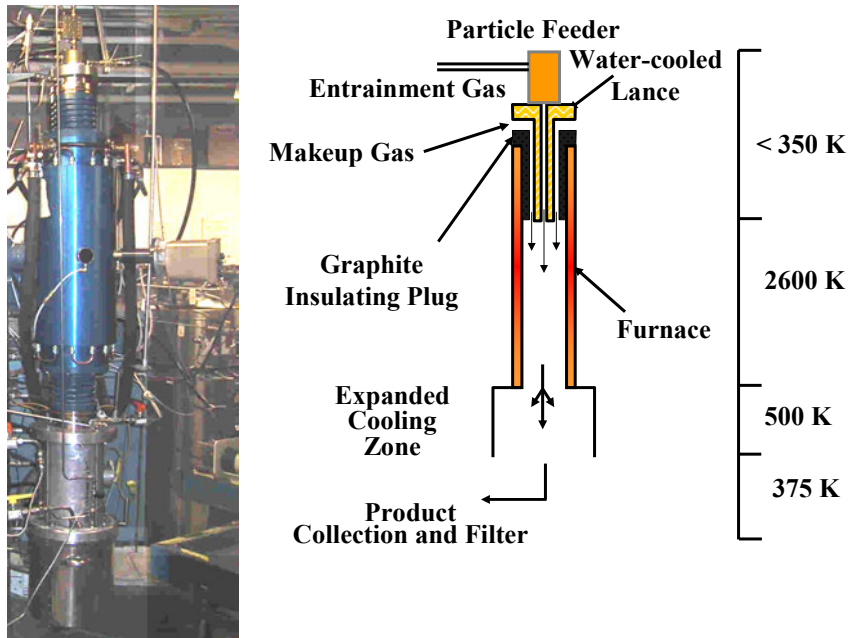


Figure 1: Transport Tube Apparatus

Leaving the SWF, the particles are fed into a water-cooled copper “lance.” In the graphite furnace, there is a central “hot zone” that is maintained at desired reaction temperature. Outside of this “hot zone,” the temperature is both lower and unknown. In order to avoid feeding the particles through this zone of unknown temperature, the lance is used to maintain room temperature of the particles until they reach the hot zone. At this point, the particles leave the lance and are heated by radiation at very fast rates ($>10^6$ K/s) to furnace wall temperature.

The lance is shown in Figures 2 and 3. It consists of three copper tubes, the outer 1” in OD and the inner 3/8” in OD, and the tubes are brazed to a copper connecting cap. A thin brass weir tube is employed, and is sealed into the water manifold (far left in top picture) with an o-ring. The copper tubes slide over and within the brass tube, and are sealed into the water manifold with an o-ring. A furnace cover piece (center of picture) slides over the lance and seals the top of the furnace with an o-ring. It is water cooled as well. A small metal clamp attaches to the portion of the lance extending into the furnace, and it is the connection piece for the space filling graphite insulation (top right, Figure 2).

The graphite slides over the clamp, and is held into place with molybdenum pins.



Figure 2: Lance exploded view



Figure 3: Lance assembled view

In the reaction zone, the lance gas flow and entrained particles are joined by a “sweep” flow that enters the top of the reactor and flows around the lance. This flow is employed to obtain a desired reaction zone residence time without incurring the high pressures that would arise from flowing all reactor gas through the lance. At the end of the reaction “hot zone,” the reaction products enter a water cooled quench tube. The purpose of this tube is to essentially freeze the reaction at a given residence time,

avoiding further reaction or recombination of reaction products in the furnace cooling zone.

Figure 4 shows the disassembled quench tube. It consists of a 1" OD copper tube mounted within a 2" OD copper tube (top of picture). These are both brazed to a connecting copper cap. The two-tube assembly then slides over a 1.5" OD brass tube, which screws into the quench tube manifold piece (far left). The copper tubes are sealed within the manifold by o-rings, and screws hold the two manifold pieces together. Water enters the quench tube manifold and moves into the annular space between the 1" copper and 1.5" brass tubes, travels up to the top of the tube, spills over a weir, and flows out through the annular space between the 1.5" brass tube and the 2" copper tube. This effectively provides water cooling to the inside of the 1" copper tube, where the reaction products are to be quenched. To protect the top copper cap of the quench tube and to direct products into the quench tube, a sloped zirconia cap (upper right corner) has been machined to fit on the top of the quench tube.



Figure 4: Disassembled quench tube

Upon leaving the quench tube, heavy product powders were collected by gravity in a stainless steel vessel, and fine entrained product powders were collected in a downstream HEPA filter. Product gases were then passed through an OMEGA mass flowmeter, an Advanced Micro Instruments O₂ analyzer, and a California Analytical Instruments CO/CO₂ detector. With measurements from these devices, a gas based value for the total oxygen generated by ZnO dissociation can be calculated, and the conversion can be determined. The measurements from the detectors were integrated using a Simpson's Rule numerical technique, and the conversions can be coupled with temperature and residence time information to formulate a kinetic rate law for the reaction.

Necessary to the analysis of the data from these experiments is a way to determine the hot zone residence time given wall temperature, gas flow, and lance entry point. Due to the extremely high temperatures encountered in these experiments, direct measurement

of gas flow in the furnace during experimentation is impractical. Instead, the authors decided to model gas flow in the reactor by solving the basic transport equations for the system over the hot zone geometry. A finite element model for this problem was built using the commercial software FEMLAB™.

The geometry to be modeled and associated boundary conditions are shown in Figures 4-6. The geometry is symmetric about the z-axis (no azimuthal dependence), so only one half of the hot zone is seen here. The top left hand corner is the lance entry, and the make-up gas entry is in the top right hand corner. At the bottom left hand corner is the quench tube entry, and the bottom right hand corner is the small “sweep” gas exit. A temperature boundary condition is set at the tube wall, and entry gas velocities are determined from set flow rates and laminar tube or annular flow solutions.

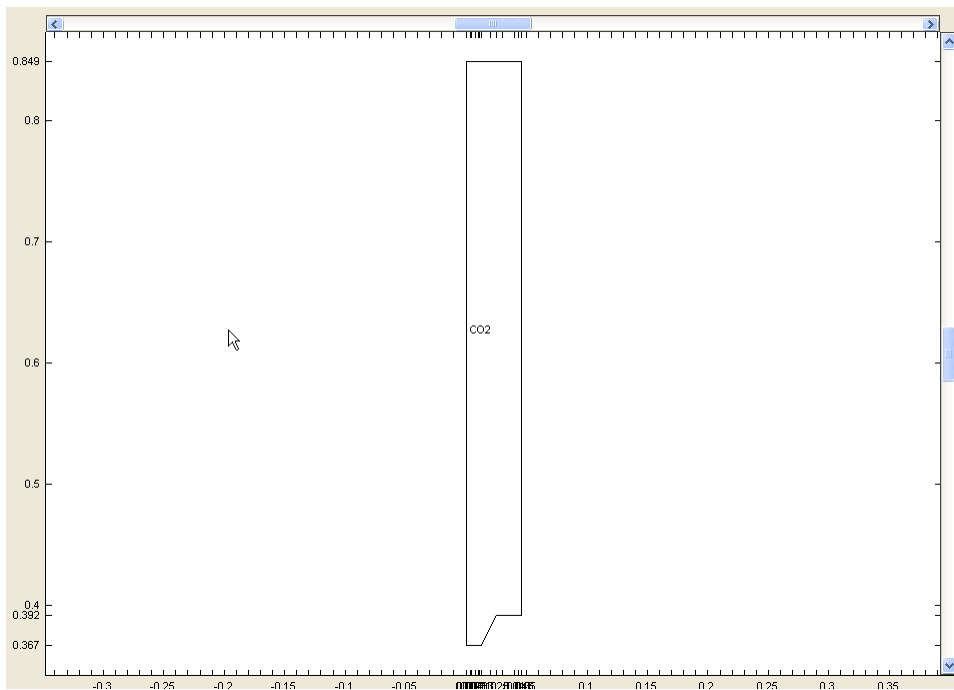


Figure 5: FEMLAB model geometry

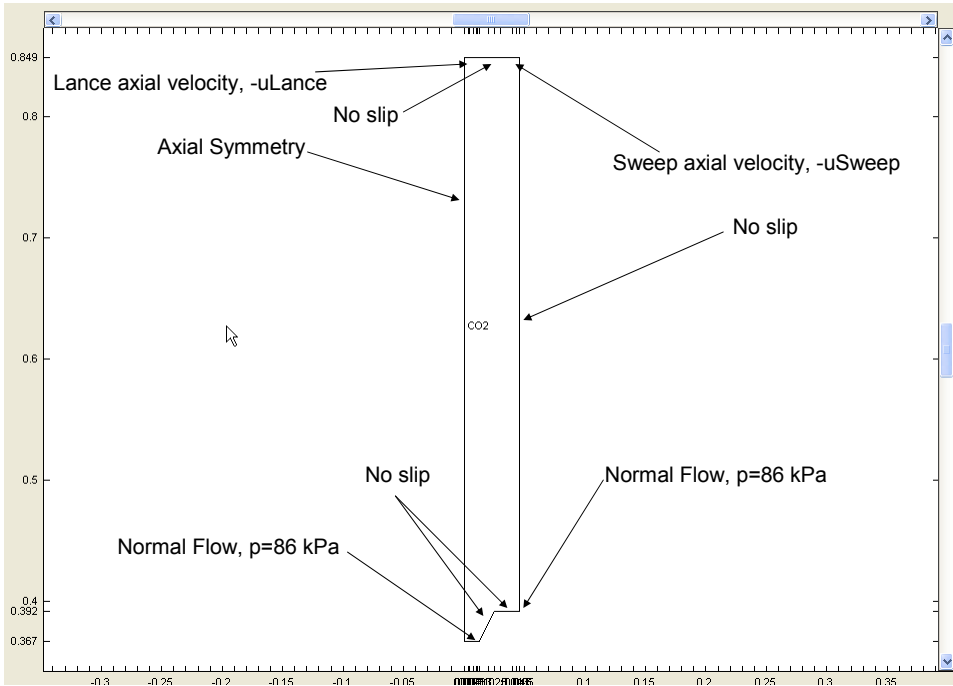


Figure 6: FEMLAB model flow boundary conditions

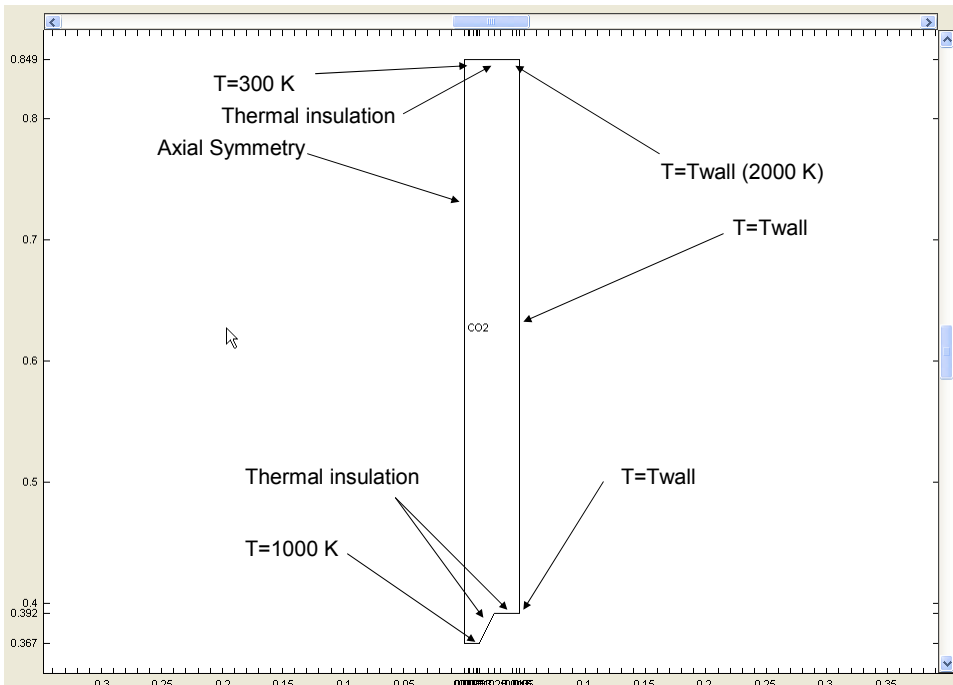


Figure 7: FEMLAB model temperature boundary conditions.

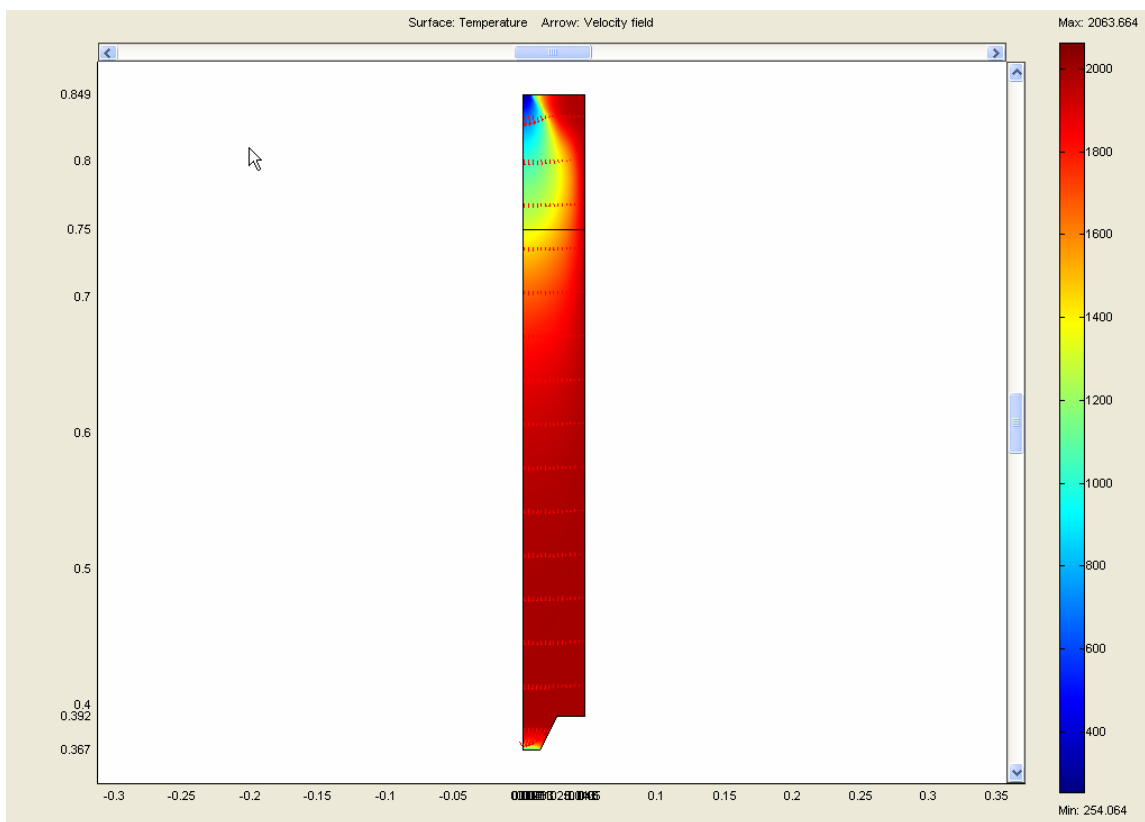


Figure 8: Sample FEMLAB simulation result (color is temperature, arrows velocity)

Due to the extreme temperature fluctuations in the system, large density variations exist over the reactor geometry. These density variations lead to pockets of instability in the finite element solution, and can inhibit convergence of this solution. In order to overcome this problem, the first approach was to decrease the mesh size; theoretically, there exists a mesh size small enough to resolve the instabilities arising from the density fluctuation. However, memory limitations prevented the software from solving the problem. The solution of the problem required the addition of some artificial diffusion, stabilizing the solution in the problem areas and allowing for convergence. The first of such solutions is seen in Figure 8.

III. Experimental Procedure

The basic procedure of the kinetics experiments was as follows. ZnO feed was sifted in a 45 micron sieve to break up any large agglomerates that may have existed in the powder. This material was then loaded into the reservoir of a vibratory tray feeder, which was massed before installing it into the feeder tray. The furnace was purged with argon and heated to the desired reaction temperature.

Once reaction temperature was reached, the spinning wheel feeder was turned on and set to the optimal angular speed, determined from experiments run by the authors. The gases were set to appropriate flows to obtain the desired residence time condition, and the feeder was started. At this point, the experimenters observed the detectors for the

presence of product gases. The amounts of these gases were recorded and later integrated to get a gas-based number for the reaction conversion.

After approximately 10 grams of reactant powder was fed, the feeder was stopped and the furnace cooled. At room temperature, product powders were collected from the large gravity collection vessel, the HEPA filter, and the inside of the quench tube. These products were massed and analyzed in a LECO TC600 machine for oxygen content. The oxygen content in these samples gave a second number for conversion, this one based on powder measurements.

IV. Results

In order to test the experimental apparatus and to determine the residence time and temperature regimes in which the ZnO dissociation reaction would have ideal conversions for kinetic rate law determination, a number of test points were run. Temperature conditions between 2000 K and 2300 K were run, as well as residence times ranging from 1.0 s to 1.5 s. The results for a few of these points are shown below. Figures 9 and 10 show raw and integrated gas product traces for reaction at 2000 K and 1.13 s. The generation of O₂, CO, and CO₂ demonstrates dissociation of ZnO, the only oxygen source in the reactor. The carbon products are generated by reaction of oxygen with the graphite tube wall. While in an industrially operating reactor this would be undesirable, it makes little difference in the reaction kinetics, as the reaction is operating outside of the thermodynamically controlled regime.

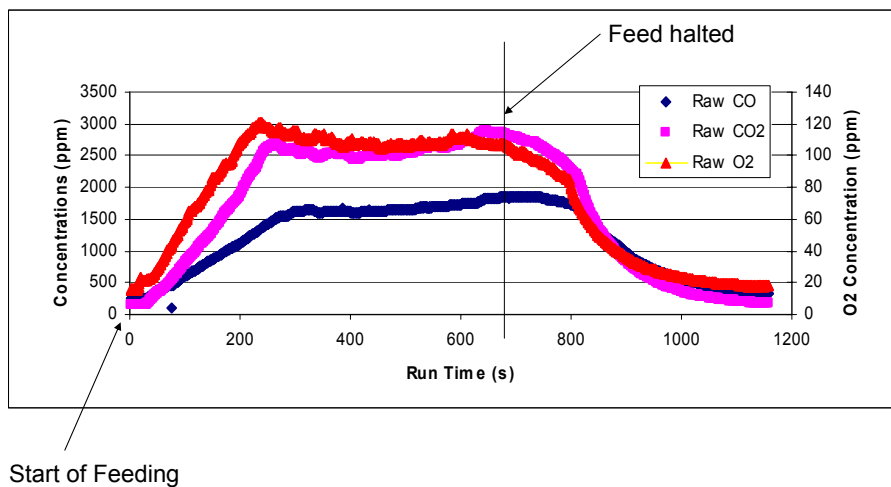


Figure 9: Reaction Product Concentrations for ZnO Dissociation (1.0 s, 2300 K)

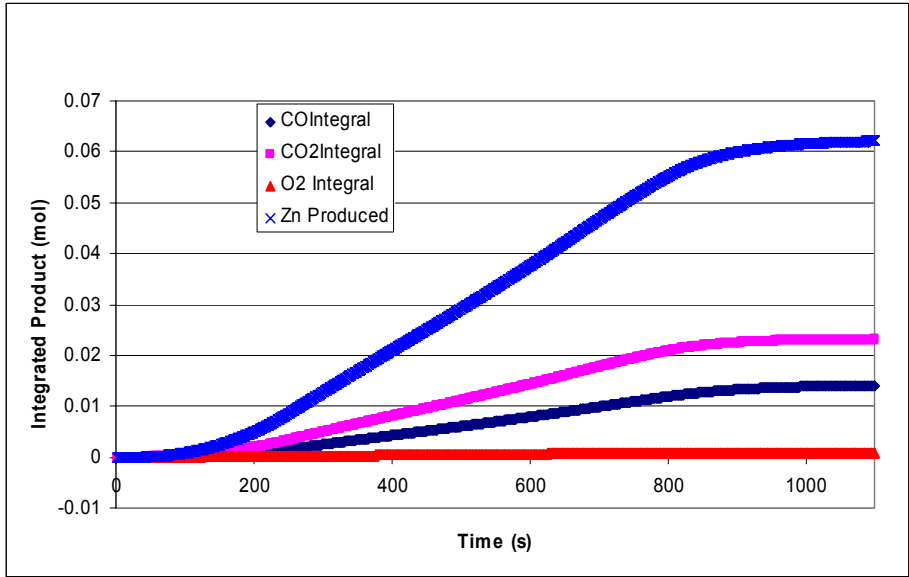


Figure 10: Cumulative Production of Reaction Products in ZnO Dissociation (1.13 s, 2300 K)

Figure 11 shows some test points for this kinetic reactor. The goal of these test points was to demonstrate the reactor's ability to take mid-range conversion kinetic data at temperatures between 2000 K and 2300 K. As can be seen in this rather sparse chart, higher temperature or longer residence time both lead to greater conversion.

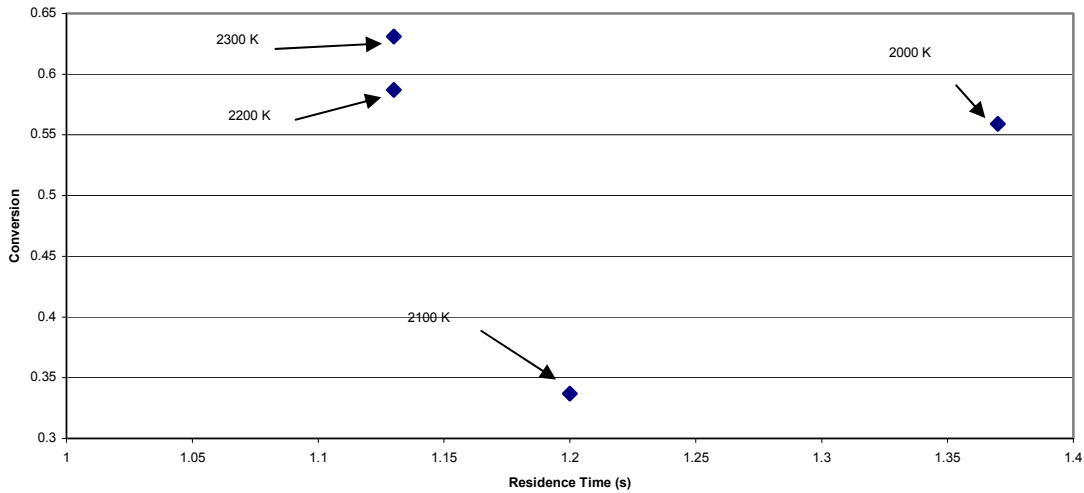


Figure 11: Test Points for Kinetic Experiments

These experiments demonstrate that ZnO can be dissociated in the kinetics reactor, and kinetics results fit qualitatively with expectations for the test points tried. From the results of the test points, an experimental matrix focused on determining the rate law for

the ZnO dissociation reaction should concentrate on temperatures between 2000 K and 2300 K and on residence times between 0.7 s and 1.5 s.

V. Conclusions and future work

An experimental design and apparatus was presented for the determination of ZnO dissociation reaction kinetics. This apparatus was tested at a variety of temperature and residence time conditions, and satisfactory results were achieved. Conversions ranging between 35% and 75% were achieved for temperatures between 2000 K and 2300 K and residence times scattered about 1.25 s. It was determined that an effective kinetic experimental design would focus on these temperatures and residence times between 0.7 s and 1.5 s. In the near future the authors plan on running this experimental matrix and determining a kinetic rate law for the ZnO dissociation reaction.

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