Aerospace Thermodynamics

Subject Area(s)  Thermodynamics, redox
Associated Unit  Advanced Placement Topic Review
Associated Lesson  Engaging Selected topic Review
Activity Title  Aerospace Thermodynamics
Grade Level  11-12
Activity Dependency  This activity is designed for advanced placement classes.
Time Required  130 (two 45 min periods)
Time Required Note  n/a

Group Size  2-3 Students
Expendable Cost per Group  none

Summary
This activity involves reinforcing concepts in thermodynamics with a very interesting, REAL, application that involves current materials research on next generation aerospace vehicles. Students will get introduced to next generation wing design and practical reasons for using Ultra High Temperature Ceramic Materials (UHTC’s). UHTC’s are introduced to familiarize students then oxidation of such materials is discussed. The relation to basic chemistry concepts is realized through a thermodynamic description of oxidation process with presentation of applicable thermodynamic and chemical equilibrium equations and how they are implemented. To finalize the presentation a Jeopardy activity has been prepared with a series of thermodynamic questions for students to interactively answer. Handouts and salient data tables are provided with the activity. Students should be able to understand chemical equilibrium, Gibb’s free energy and it temperature dependence, entropy and enthalpy. A final Jeopardy question is included to incorporate graphing calculators or computers (if available).

Engineering Connection

Oxidation is a common issue of all materials. Metals and certain ceramics tend to oxidize rapidly when exposed to air at elevated temperatures. This is a fundamental problem with hypersonic aircraft wing design. Wing leading edges are exposed to ultra-high temperatures while being exposed to a harsh oxidizing environment. The goal for materials engineers is to design materials that have ultra-high melting points while maintaining chemical stability when oxygen is introduced. Shape change due to material degradation and eventual material failure will affect hypersonic maneuverability and possibly lead to wing failure. One of the first processes to designing such materials is to investigate material systems that qualify for such operating environments. This selection process is aided by a thermodynamic analysis to understand various reactions that might take place under varying temperature and pressure. Incorporated are chemical and phase equilibrium. Understanding these concepts provides engineers with a screening process that reduces costly experimentation by focusing experiments to the most stable material system. Such materials have been selected and include Group IV diborides (MeBₓ). These UHTC’s can either be monolithic or composite with typical reinforcements of various carbides (MeC)

Engineering Category = #1,2
Choose the category that best describes this activity’s amount/depth of engineering content:
1. Relating science and/or math concept(s) to engineering
2. Engineering analysis or partial design
3. Engineering design process

Keywords
Thermodynamics, ceramics, composites, zirconium diboride, hafnium diboride, oxidation, UHTC, high temperature, aerospace, hypersonic vehicles

Educational Standards


Standard 11: Science concepts. The student understands the energy changes that occur in chemical reactions.
C. Use thermochemical equations to calculate energy changes that occur in chemical reactions and classify reactions as exothermic or endothermic.

Standard 9: Science concepts. The student understands the principles of ideal gas behavior, kinetic molecular theory, and the conditions that influence the behavior of gases.

Standard 8: Science concepts. The student can quantify the changes that occur during chemical reactions.

D. Use the law of conservation of mass to write and balance chemical equations

**AP Requirements (North Shore Senior High School 2010-2011)**
1) Unit 1 Chemistry Fundamentals:
   - Manipulate Chemical Quantities
   - Solve Problems using Dimensional Analysis
   - Demonstrate safe laboratory practices
2) Unit 6 & 7 Thermochemistry, Thermodynamics & Equilibria

Pre-Requisite Knowledge
Students must have been introduced to concepts in thermodynamics, reaction types, and oxidation reduction.

Learning Objectives
After this activity, students should be able to:
- Identify reaction products from a reaction description.
- Calculate and determine whether a reaction is spontaneous using standard thermodynamic data.
- Infer reaction spontaneity by applying definitions of enthalpy, entropy, and Gibb’s Free Energy.
- Understand what is meant by spontaneous reaction and how this relates to reactivity when multiple elements are involved.
- Understand how vapor pressure influences material phase change
- Calculate equilibrium partial pressures from chemical equilibrium concepts.
- Implement graphical representations of thermodynamic data to solve oxidation problems
- Identify the importance of oxidizers and reducers in high intensity reactions.

Materials List
For Teacher Introductory presentation and Jeopardy activity:
- Projector
- Computer
- Laser pointer – optional
- Personal size white boards
- Dry erase markers and erasers
- Graphing calculator or computers (laptop if applicable)

Introduction / Motivation
The attached presentation should be sufficient for an adequate introduction and motivation sequence. The instructor can start off with a discussion if desired. However, the presentation includes questions throughout to constantly engage students. Instructor may choose to use such questions in a discussion format before diving into specific introductory material.

Vocabulary / Definitions

<table>
<thead>
<tr>
<th>Word</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>UHTC</td>
<td>Ultra High Temperature Ceramics for aerospace applications. Group IV Diboride ceramic and ceramic composites</td>
</tr>
<tr>
<td>Ceramic</td>
<td>Classification of material which describes strong, directionally covalent bonded materials with exceptionally high melting points and brittleness.</td>
</tr>
<tr>
<td>Composite</td>
<td>Classification of material which incorporates two different materials or constituents. Typically involves a matrix phase (continuous) and reinforcement (discontinuous or fiber)</td>
</tr>
<tr>
<td>Hypersonic</td>
<td>Speeds relating more than 5 times the speed of sound (Mach 5).</td>
</tr>
<tr>
<td>Volatility</td>
<td>Stability of a liquid or solid phase from transforming into a gaseous phase</td>
</tr>
<tr>
<td>Vapor Pressure</td>
<td>The pressure a solution (solid or liquid) exerts on its surroundings</td>
</tr>
<tr>
<td>Partial Pressure</td>
<td>Pressure of individual gas components when summed equal the total external pressure</td>
</tr>
<tr>
<td>Thermodynamics</td>
<td>Study of energy and its conversions.</td>
</tr>
<tr>
<td>----------------</td>
<td>------------------------------------</td>
</tr>
<tr>
<td>REDOX</td>
<td>Reduction (receives electron) and Oxidation (loses electron) Reactions</td>
</tr>
<tr>
<td>Gibb’s Free Energy (G)</td>
<td>Thermodynamic energy functions with independent variables of Enthalpy (H), Entropy (S) and Temperature (T (K)). Change in energy under constant volume and entropy conditions with varying pressure and temperature.</td>
</tr>
<tr>
<td>Entropy (S)</td>
<td>Thermodynamic function that measures randomness or disorder</td>
</tr>
<tr>
<td>Enthalpy (H)</td>
<td>Thermodynamic function that measures the energy flow as heat in a constant pressure system</td>
</tr>
<tr>
<td>Exothermic</td>
<td>Reaction is said to be exothermic when a release of heat is created upon completion</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>A state where the net (average) flow of matter and energy is equal or approximately equal to zero</td>
</tr>
<tr>
<td>Equilibrium Constant (K&lt;sub&gt;eq&lt;/sub&gt;)</td>
<td>A quantitative measure of reaction equilibrium based on product and reactant concentrations, partial pressures or chemical activity.</td>
</tr>
<tr>
<td>Reaction Quotient (Q)</td>
<td>A quantitative measure of current reaction state in reference to reaction equilibrium point. Q&gt;K - reaction proceeds to left; Q&lt;K – reaction proceeds to right.</td>
</tr>
<tr>
<td>Endothermic</td>
<td>Reaction is said to be endothermic when absorption of heat is required for completion (driving force)</td>
</tr>
<tr>
<td>Sensible Heat</td>
<td>Another term for Enthalpy or heat produced from a given reaction that is available for both reactants and products to absorb and raise the temperature.</td>
</tr>
</tbody>
</table>
**Procedure**

**Background** \[1\] [2] [3] [4]

Ultra-high temperature ceramics (UHTC’s) are a class of ceramics designed for service at temperatures greater than 1500°C. ZrB\(_2\) and HfB\(_2\) are primary candidates because of high melting points (~3000°C), thermal, electrical and mechanical properties and chemical stability at application temperatures. Primary applications for UHTC’s include hypersonic flight, atmospheric re-entry vehicles, refractory linings, electrodes, microelectronics and cutting tools. Most notably, the sharp leading edges of future hypersonic flight and atmospheric re-entry vehicle designs\[1\][2][3] require improved material performance under the ultra-high stagnation point temperatures, convective heating and extreme oxidation conditions. Composites of ZrB\(_2\) and HfB\(_2\) are often processed with SiC, typically in quantities of 10-30% by volume SiC or other carbide compounds.

Current materials are only refractory enough to withstand moderate stagnation temperatures. Typical radii are of centimeter scale which lowers the peak temperature considerably. However, maneuverability is drastically reduced at hypersonic velocities. Sharp wing leading edges (one order of magnitude smaller) provide the favorable aerodynamic design for optimum maneuverability at hypersonic speeds. However, temperature and stress demands increase significantly. Additionally, severe material degradation takes place due to oxidation at high temperatures. A combination of temperature, stress and chemical stability are required to maintain wing integrity.

\[2\][3] Temperature: To combat temperature, materials selected should have a high melting point. Hafnium and Zirconium Diboride ceramics satisfy this requirement. Operational temperatures are estimated to reach ~2200°C. The material must have a sufficiently high melting point to (a) keep from entering a liquid phase (complete degradation) and (b) retain strength at those temperatures. Another very important material property is thermal conductivity. Both aforementioned diboride materials have very high thermal conductivities when compared to other ceramics. This allows for heat to be transferred efficiently away from the wing leading edge to help reduce operating temperatures.

\[2\][3][4] Stress: Refractory materials typically have good strength retention at ultra-high temperatures due to the strong directional covalent bonding. This is important to resist excessive shape change due to friction forces at elevated temperatures. Essentially, strength retention ensures the material will withstand operational loading.

\[1\] Chemical Stability: Materials that are oxidation resistant are difficult to process which have the unique mechanical and thermal properties. Therefore understanding the influences of oxygen partial pressure on ceramic degradation and the kinetics is essential. Hafnium and Zirconium diboride ceramics have excellent oxidation resistance at specific temperature intervals. Both ceramics undergo a combination of active and passive oxidation. Active oxidation is a linear type kinetic problem where the material is continuously degraded. Passive oxidation involves a protective film formation (oxidation product) that protects the remaining underlying material from further oxidation. Meaning, oxidation kinetics decreases with increasing oxygen exposure time. Furthermore, to improve oxidation resistance, different carbides and slicides are added to scavenge oxygen in effect to form better passive films to protect the hafnium and zirconium diboride ceramics.

At this point the interested instructor is referred to select journal articles referenced within each paragraph and activity reference list. Most of the articles give an adequate description of the general topics discussed above.
Thermodynamics is incorporated to describe the oxidation problem and assess chemical stability using well tabulated thermodynamic data and thermodynamic relationships. Concepts of assessing Gibb’s free energy in reference to reaction feasibility are heavily used in engineering materials for oxidation resistance. Chemical equilibrium equations and reaction quotient knowledge assess minimum required pressures or concentration required for reactions to take place. A combination of the two thermo concepts yields phase road maps that show solid and solid/liquid phase field equilibrium with volatile gaseous species. These road maps help predict reaction products and vapor pressures to expect from experiments. Furthermore, this method helps reduce the number of costly experiments by focusing experimentation to top candidate material compounds.

Presentation/Activity

- Instructor is to deliver presentation with any modifications desired by instructor to suit his/her classroom teaching format.
- During presentation there are questions plotted to engage students. Instructor should be actively seeking out participation from class for motivation.
- Upon completion of presentation, instructor is to request students to get into groups of 2-3 students.
- Using the Jeopardy presentation, instructor is to introduce the categories and point format. NOTE: Instructor is to let students know of the daily double and final jeopardy questions.
- Select a group, by any method, for choosing the category first and a point value. Assign group numbers to each for point tracking.
- Scroll and select designated question and proceed by reading the answer.
- First group to answer should present their result.
- Instructor then signals correct or incorrect.
  - If correct, point value is awarded to group and recorded and they select next category and point value
  - If incorrect, remaining groups may answer.
  - Select next group and determine correctness
  - If second group does not answer correctly present answer to entire class.
  - If instructor desires, it may be useful to explain result to entire class for instructional purposes
- Continue questioning and answer process while recording each groups accumulated points.
- If time constraints do not allow for entire grid to be completed proceed to final jeopardy question. Allow 10-15 minutes for final jeopardy question.
- Have students wager any point value not exceeding their total point value entering final jeopardy round.
- Have students present the answer and award or take-away points. Team with the most points after final jeopardy wins.

Attachments

- UHTCOxidationPresentation (ppt.)
- UHTCOxidationJeopardy (ppt.)
- FreeEnergyDiagram (doc)

Safety Issues

Troubleshooting Tips

Investigating Questions

None
Assessment
Activity Embedded Assessment
Instructor is to monitor participation throughout the presentation and thermo lesson. Additional handouts can be given to students to test their knowledge but is not required by the activity description. This activity is to link a very prevalent branch of chemistry with high-end practical science and engineering problems in aerospace.

Activity Extensions
Activity Scaling
None

Additional Multimedia Support
None

References

Other
None

Redirect URL
None

Contributors
Marc Bird

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None

Supporting Program
1. NSF GK12 program, Grant #0840889, University of Houston
2. AFOSR Grant FA9550-09-1-0200, University of Houston

Version: September 2010
Thermo-Jeopardy

Thermodynamics of Ultra High Temperature Ceramics Oxidation for Atmospheric Reentry Vehicles and Hypersonic Aircraft.

Marc W. Bird
University of Houston
GK12 Fellowship Program
<table>
<thead>
<tr>
<th>ZrB$_2$ Oxidation</th>
<th>SiC Oxidation</th>
<th>Vapor Pressure</th>
<th>Temperature Effects</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>200</td>
<td>200</td>
<td>200</td>
<td>200</td>
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<td>300</td>
<td>300</td>
<td>300</td>
<td>300</td>
</tr>
<tr>
<td>400</td>
<td>400</td>
<td>400</td>
<td>400</td>
</tr>
</tbody>
</table>
100-ZrB$_2$ Oxidation

Qualitatively this reaction has the lowest entropy.

\[
\begin{align*}
\text{ZrB}_2(s) + \frac{5}{2}\text{O}_2(g) &= \text{ZrO}_2(g) + \text{B}_2\text{O}_3(l) \\
\text{ZrB}_2(s) + \frac{3}{2}\text{O}_2(g) &= \text{Zr}(g) + \text{B}_2\text{O}_3(l) \\
\text{ZrB}_2(s) + \frac{5}{2}\text{O}_2(g) &= \text{ZrO}_2(s) + \text{B}_2\text{O}_3(g)
\end{align*}
\]

What is ZrB$_2$(s) + $5/2$O$_2$(g) = ZrO$_2$(s) + B$_2$O$_3$ (g)
200-ZrB$_2$ Oxidation

Of these reactions a $\Delta G = -1469$ KJ at 1400 K

ZrB$_2$(s) + 5/2O$_2$(g) = ZrO$_2$(s) + B$_2$O$_3$ (l)

ZrB$_2$(s) + 3/2O$_2$(g) = Zr(g) + B$_2$O$_3$ (l)

ZrB$_2$(s) + 5/2O$_2$(g) = ZrO$_2$(s) + B$_2$O$_3$ (g)

What is ZrB$_2$(s) + 5/2O$_2$(g) = ZrO$_2$(s) + B$_2$O$_3$ (l)
300-\(\text{ZrB}_2\) Oxidation

The total Gibb’s Free energy of \(-1259\) KJ for this overall reaction at 1700 K is equal to the sum of these two individual reactions.

What are:
\(\text{ZrB}_2(s) + \frac{5}{2}\text{O}_2(g) = \text{ZrO}_2(s) + \text{B}_2\text{O}_3(g)\) – overall reaction

\(\text{ZrB}_2(s) + \frac{5}{2}\text{O}_2(g) = \text{ZrO}_2(s) + \text{B}_2\text{O}_3(l)\) – First reaction

\(\text{B}_2\text{O}_3(l) = \text{B}_2\text{O}_3(g)\) – Second reaction
400-ZrB$_2$ Oxidation

This reaction from those listed below has an equilibrium constant of $1.11$ at 1600 K

\[
\text{ZrB}_2(s) + \frac{5}{2}\text{O}_2(g) = \text{ZrO}_2(s) + \text{B}_2\text{O}_3 \text{ (g)}
\]

\[
\text{ZrB}_2(s) + \frac{5}{2}\text{O}_2(g) = \text{ZrO}_2(s) + \text{B}_2\text{O}_3 \text{ (l)}
\]

\[
\text{ZrB}_2(s) + \frac{5}{2}\text{O}_2(g) = \text{ZrO}_2(g) + \text{B}_2\text{O}_3 \text{ (l)}
\]

What is: \[\text{ZrB}_2(s) + \frac{5}{2}\text{O}_2(g) = \text{ZrO}_2(s) + \text{B}_2\text{O}_3 \text{ (l)}\]
100-SiC Oxidation

This component of free energy is likely increasing based on free energy-temperature data for the following reaction:

\[
\text{SiC}(s) + \text{O}_2(g) = \text{SiO}(g) + \text{CO}(g)
\]

What is: Entropy
200-SiC Oxidation

Qualitatively, this reaction likely exhibits a larger decrease in entropy.

SiC(s) + \(\frac{3}{2}O_2(g)\) = SiO\(_2\)(l) + CO(g)

SiC(s) + O\(_2\)(g) = SiO(g) + CO(g)

SiC(s) + 3/2O\(_2\)(g) = SiO\(_2\)(s) + CO(g)

SiC(s) + 3/2O\(_2\)(g) = SiO\(_2\)(g) + CO(g)

What is: SiC(s) + 3/2O\(_2\)(g) = SiO\(_2\)(s) + CO(g)
300-SiC Oxidation

This reaction has a gibb’s free energy of -918 KJ at room temperature and likely shows a decrease in entropy

\[
\text{SiC}(s) + O_2(g) = \text{SiO}(g) + \text{CO}(g)
\]
\[
\text{SiC}(s) + \frac{3}{2}O_2(g) = \text{SiO}_2(l) + \text{CO}(g)
\]
\[
\text{SiC}(s) + \frac{3}{2}O_2(g) = \text{SiO}_2(s) + \text{CO}(g)
\]

What is: \(\text{SiC}(s) + \frac{3}{2}O_2(g) = \text{SiO}_2(l) + \text{CO}(g)\)
An equilibrium constant of 1.03 at 2000 K corresponds to this SiC oxidation reaction.

What is: \( \text{SiC}(s) + \text{O}_2(g) = \text{SiO}(g) + \text{CO}(g) \)
GAS PRODUCT IS MORE VOLATILE (LEAST STABLE) AT $P_{O_2} = 1$ atm

<table>
<thead>
<tr>
<th>Gas</th>
<th>Pressure (atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B2(g)</td>
<td>6.73E-25</td>
</tr>
<tr>
<td>2BO(g)</td>
<td>5.28E-04</td>
</tr>
<tr>
<td>2B(g)</td>
<td>4.10E-13</td>
</tr>
<tr>
<td>B2O3 (g)</td>
<td>1.60</td>
</tr>
<tr>
<td>2BO2(g)</td>
<td>0.17</td>
</tr>
</tbody>
</table>

What is: $SiC(s) + O_2(g) = SiO(g) + CO(g)$
The partial pressure of Oxygen required for the oxidation reaction below does this when temperature is decreased from 2000 K to 1200 K.

$$\text{ZrB}_2(\text{s}) + \frac{5}{2}\text{O}_2(\text{g}) = \text{ZrO}_2(\text{s}) + \text{B}_2\text{O}_3(\text{l})$$
300 – Vapor Pressure

ZrB$_2$(s) + $\frac{5}{2}$O$_2$(g) = ZrO$_2$(s) + B$_2$O$_3$ (l) is in equilibrium with
SiC(s) + $\frac{3}{2}$O$_2$(g) = SiO$_2$(l) + CO(g) at 1600 K
yielding this product and reactant gas relationship.

What is: $\frac{1}{P_{O_2}} = P_{CO}$
An equilibrium constant of $1.09$ at $1$ atm $P_{O_2}$ and $1800$ K equates to this partial pressure for $B_2O_3$ product gas.
100-Temperature Effects

What component of free energy is likely to decrease with increase in temperature for the following reaction:

\[ \text{B}_2\text{O}_3(\text{l}) = \frac{1}{2}\text{O}_2(\text{g}) + \text{B}_2\text{O}_2(\text{g}) \]

What is: Enthalpy
He lives in a pineapple under the sea

Who is: Sponge Bob Square Pants
Considering the following oxidation reactions this UHTC component would preferentially oxidize rather than the other with increase in temperature.

(1) \[ \text{SiC(s)} + \text{O}_2(\text{g}) = \text{SiO(g)} + \text{CO(g)} \]

(2) \[ \text{ZrB}_2(\text{s}) + \frac{3}{2}\text{O}_2(\text{g}) = \text{Zr(g)} + \text{B}_2\text{O}_3 \text{(l)} \]

What is: SiC
400-Temperature Effects

With an increase in temperature the required Oxygen partial pressure for oxidation increases for both ZrB₂ and SiC. However, with an increase in temperature the reaction kinetics most likely ______________ the reaction rate.

What is: Increases
Final Jeopardy

(Graphing Calculator Needed)

Plot \( \log P_{O_2} \) and \( 1/T \) for \( ZrB_2(s) + \frac{5}{2}O_2(g) = ZrO_2(s) + B_2O_3 \text{ (l)} \) and \( SiC(s) + O_2(g) = SiO(g) + CO(g) \). This temperature marks a specific point where both \( ZrB_2 \) and \( SiC \) are in equilibrium with their oxidation products.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>( \log P_{O_2} )</th>
<th>( T \text{ (K)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( ZrB_2(s) + \frac{5}{2}O_2(g) = ZrO_2(s) + B_2O_3 \text{ (l)} )</td>
<td>-21.0</td>
<td>1430</td>
</tr>
<tr>
<td></td>
<td>-17.0</td>
<td>1667</td>
</tr>
<tr>
<td></td>
<td>-12.5</td>
<td>2000</td>
</tr>
<tr>
<td></td>
<td>-9</td>
<td>2500</td>
</tr>
<tr>
<td>( SiC(s) + O_2(g) = SiO(g) + CO(g) )</td>
<td>-25.5</td>
<td>1430</td>
</tr>
<tr>
<td></td>
<td>-20.0</td>
<td>1667</td>
</tr>
<tr>
<td></td>
<td>-11.5</td>
<td>2000</td>
</tr>
<tr>
<td></td>
<td>-3.0</td>
<td>2500</td>
</tr>
</tbody>
</table>
Aerospace Thermodynamics

A look at applying thermodynamics to space flight vehicle oxidation
CERAMIC MATERIAL AND WING DESIGN INTRODUCTION

Aerospace and hypersonic vehicle candidate materials
Ultra High Temperature Ceramic (UHTC) materials are Group IV transition metal borides (MeB\textsubscript{x}) with or without refractory type reinforcements (e.g. SiC).

Unique due to high melting points, high thermal conductivity, strength retention and oxidation properties.

THINK OF A HIGH STRENGTH CERAMIC DINING PLATE THAT CAN CONDUCT ELECTRICITY AND HEAT LIKE A METAL!!!
Where are UHTC materials used?

Structural materials for use in hypersonic aircraft – Next generation reentry vehicles

Why do you think the space shuttle is shaped the way it is?

To reduce the amount of heat generated upon reentry.

UHTC materials can change the shape of next generation space planes because of unique combinations of properties.
WING DESIGN

Leading Edge Radius

Traditional Materials $\rightarrow R = \text{cm}$

UHTC $\rightarrow R = \text{mm}$

Temperature Distribution

$T_1$ Increases

$T_1 >> T_2$

Estimated $T_1$ Temperatures

$R=\text{mm}: T_1 > 2000^\circ \text{C} (3632^\circ \text{F})$

$R=\text{cm}: T_1 < 2000^\circ \text{C} (3632^\circ \text{F})$

$\sim$ Melting Point UHTC

$3245 – 3380^\circ \text{C} (\text{ZrB}_2, \text{HfB}_2)$

Environment description

- Atmospheric re-entry vehicles operate at extreme temperatures and oxygen rich environments (air).
- Pressure also changes as the vehicle approaches Earth’s surface.

**WHAT IS SO SPECIAL THEN?**

- What happens to steel or iron when exposed to air over time? It rusts or corrodes or oxidizes (take your pick). Does this decrease the part’s performance?
- Increase the temperature and oxygen attacks all non oxygen-bonded materials. Increase the temperature to operating temperatures discussed and this process happens very quickly.
- What happens when the material oxidizes? The advantages of using UHTC begin to disappear. Edge geometry retention decreases (strength and corrosion) and thermal conductivity decreases.

**WHAT DOES THIS EFFECT?** Maneuverability at high speeds; wing integrity

- **WHAT CAN MATERIAL SCIENTIST DO?** Engineer these UHTC materials to improve oxidation resistance.
Thermodynamics and UHTC’s

- Oxidation behavior of ZrB₂ based UHTC’s can be investigated using thermodynamic principles.

- Using Gibb’s free energy and knowledge of chemical equilibria one can map and determine critical oxygen concentrations and predict reaction products.

- These methodologies lend themselves to engineering ZrB₂ based UHTC’s to withstand oxygen containing environments at excessively high temperatures and forces.

- Let us see what types of information can be obtained.
**ZrB₂ Oxidation**

Volutility diagrams at 2000 K describe solid gas equilibrium- Black lines indicate equilibrium points between solid and gas.

![Graph of ZrB₂ Oxidation](image-url)
SiC Oxidation

Volutility diagrams at 2000 K describe solid gas equilibrium. Blue lines indicate equilibrium points between solid and gas.

$P_{CO} (Pa) = P_{SiO}$

### SiC Oxidation Resistance

<table>
<thead>
<tr>
<th>Reactions</th>
<th>Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 $SiC (cr) + 1.5 O_2 (g) = SiO_2 (l) + CO(g)$</td>
<td>$T&lt;1550^\circ C$ &amp; high $PO_2$</td>
</tr>
<tr>
<td>2 $SiC (cr) + O_2 (g) = SiO (l) + CO(g)$</td>
<td>Low $PO_2$</td>
</tr>
<tr>
<td>3 $SiC (cr) + 2SiO_2 (l) = 3SiO (g) + CO(g)$</td>
<td>$T&gt;1600^\circ C$ at interface</td>
</tr>
<tr>
<td>4 $2SiO_2 (l) = 2SiO (g) + O_2(g)$</td>
<td>$T&gt;1775^\circ C$</td>
</tr>
</tbody>
</table>

The $SiO_2$ liquid layer is non-protective in most projected hypersonic application conditions.
Thermodynamics and UHTC’s

• Material scientists construct volatility diagrams to locate gas/solid equilibrium vapor pressures at specific oxygen partial pressures.
  • If the gas partial pressure is greater than the external partial pressure boiling of a liquid phase occurs.
  • Likewise if gas partial pressure is lower than external pressure the liquid and solid phases are stable.
  • Predicting oxidation mechanisms can be tricky but is possible based on vapor pressure comparisons calculated from thermodynamic quantities.

EXAMPLE

Consider an $O_2$ partial pressure = 1 pa (corresponds to 4.76 Pa total pressure) for ZrB$_2$ diagram. Intersection with B$_2$O$_3$ (g) line indicates a B$_2$O$_3$ (g) partial pressure = $\sim$101325 Pa. This is much greater than the externally applied pressure. Therefore, B$_2$O$_3$ (l) from the ZrO2 (s)+B2O3 (l) phase field would be expected to boil.
Example of Oxidation Experiment

Material scientists use thermodynamics and chemical equilibria to engineer UHTC’s oxidation resistance.

Thermodynamics and UHTC’s

- Once material scientists understand oxidation mechanisms, developing materials to address issues is easier.
- Thermodynamics is a useful tool to predicting chemical reactions and equilibrium.
- Typically, a thermodynamic analysis is conducted to guide experiments and narrow the testing field.
-
It’s time for you to be the material scientist, put your knowledge of thermodynamics to the test and navigate through UHTC Oxidation Jeopardy!
THERMO-JEOPARDY STUDENT HANDOUT

### ZrB2 Oxidation reactions

- \[ \text{ZrB}_2(s) + \frac{5}{2}\text{O}_2(g) = \text{ZrO}_2(g) + \text{B}_2\text{O}_3(l) \]
- \[ \text{ZrB}_2(s) + \frac{3}{2}\text{O}_2(g) = \text{Zr}(g) + \text{B}_2\text{O}_3(l) \]
- \[ \text{ZrB}_2(s) + \frac{5}{2}\text{O}_2(g) = \text{ZrO}_2(s) + \text{B}_2\text{O}_3(g) \]
- \[ \text{ZrB}_2(s) + \frac{5}{2}\text{O}_2(g) = \text{ZrO}_2(s) + \text{B}_2\text{O}_3(l) \]
- \[ \text{B}_2\text{O}_3(l) = \frac{1}{2}\text{O}_2(g) + \text{B}_2\text{O}_2(g) \]
- \[ \text{B}_2\text{O}_3(l) = \text{O}_2(g) + \text{B}_2\text{O}(g) \]
- \[ \text{B}_2\text{O}_3(l) + \frac{1}{2}\text{O}_2(g) = 2\text{BO}_2(g) \]
- \[ \text{B}_2\text{O}_3(l) = \frac{1}{2}\text{O}_2(g) + 2\text{BO}(g) \]
- \[ \text{B}_2\text{O}_3(l) = 3\text{BO}_2(g) \]
- \[ \text{B}_2\text{O}_3(l) = \frac{1}{2}\text{O}_2(g) + 2\text{B}(g) \]
- \[ \text{B}_2\text{O}_3(l) = \frac{3}{2}\text{O}_2(g) + \text{B}_2(g) \]
- \[ \text{B}_2\text{O}_3(l) = \frac{3}{2}\text{O}_2(g) + \text{B}_2(g) \]
- \[ \text{B}_2\text{O}_3(l) = \text{B}_2\text{O}_3(g) \]

### SiC Oxidation reactions

- \[ \text{SiC}(s) + 3/2\text{O}_2(g) = \text{SiO}_2(s) + \text{CO}(g) \]
- \[ \text{SiC}(s) + 3/2\text{O}_2(g) = \text{SiO}_2(l) + \text{CO}(g) \]
- \[ \text{SiC}(s) + \text{O}_2(g) = \text{SiO}(g) + \text{CO}(g) \]
- \[ \text{SiC}(s) + 3/2\text{O}_2(g) = \text{SiO}_2(g) + \text{CO}(g) \]
- \[ \text{SiO}_2(l) = \text{SiO}(g) + \frac{1}{2}\text{O}_2(g) \]
- \[ \text{SiO}_2(l) = \text{SiO}_2(g) \]

### Constants/Conversions

- \[ R = 8.3147 \text{ J/mol-K} \]
- \[ T, \text{ K} = T, \text{ C} + 273.15 \]
- \[ P, \text{ stp} = 1 \text{ atm} \]

### Useful Equations:

#### Gibb’s Free Energy Relationships:

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

\[ \Delta G_{rxn} = \sum n\Delta G_{products} - \sum n\Delta G_{reactants} \]

\[ \Delta G_{rxn} = -RT\ln K_{eq} \]

#### Chemical Equilibria Relationships

\[ aA(g) + bB(g) = cC(g) + dD(g) \]

\[ K_{eq} = \frac{(P_C^c)(P_D^d)}{(P_A^a)(P_B^b)} \]

\[ aA(s) + bB(l) = cC(g) + dD(g) \]

\[ K_{eq} = \frac{(P_C^c)(P_D^d)}{(X_A^a)(X_B^b)} \]

\[ **X = \text{ mol fraction of solid or liquid. For pure components } X = 1** \]