

# TITANIUM DIOXIDE VOLATILITY IN HIGH TEMPERATURE WATER VAPOR

## ABSTRACT

Titanium (Ti) containing materials are of high interest to the aerospace industry due to its high temperature capability, strength, and light weight. As with most metals an exterior oxide layer naturally exists in environments that contain oxygen (i.e. air). At high temperatures, water vapor plays a key role in the volatility of materials including oxide surfaces. This study will evaluate cold pressed titanium dioxide (TiO<sub>2</sub>) powder pellets at a temperature range of 1400°C - 1200°C in water containing environments to determine the volatile hydroxyl species using the transpiration method. The water content ranged from 0-76 mole % and the oxygen content range was 0-100 mole % during the 20-250 hour exposure times. Preliminary results indicate that oxygen is not a key contributor at these temperatures and the following reaction is the primary volatile equation for all three temperatures:  $\text{TiO}_2 (\text{s}) + \text{H}_2\text{O} (\text{g}) = \text{TiO}(\text{OH})_2 (\text{g})$ .



# *Titanium Dioxide Volatility in High Temperature Water Vapor*

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# Literature Review

- New development in gas turbine engines require increased efficiency (reduced fuel consumption), higher temperature capability and lighter materials
- One proposed ceramic is titanium carbide (TiC) and its oxide, TiO<sub>2</sub>
- Shimada<sup>1</sup> published “Oxidation of HIPed TiC Ceramics in Dry O<sub>2</sub>, Wet O<sub>2</sub> and H<sub>2</sub>O Atmospheres,” in the J. Am. Ceram. Soc. in early 2006 indicating that there is a reaction between TiC and H<sub>2</sub>O
- Opila<sup>1</sup>, Jacobson<sup>3-5</sup>, et. al published a series of thermodynamic papers on the volatility of Cr<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> in water vapor using the transpiration method to identify these gas species

<sup>1</sup>“Oxidation of HIPed TiC Ceramics in Dry O<sub>2</sub>, Wet O<sub>2</sub>, and H<sub>2</sub>O Atmospheres,” J.A.Cer, **89** [4] 1218-1225 (2006)

<sup>2</sup>“Theoretical and Experimental Investigation of the Thermochemistry of CrO<sub>2</sub>(OH)<sub>2</sub>(g),” J.Chem A, **111**, 1971-1980 (2007)

<sup>3</sup>“Interactions of Water Vapor with Oxides at Elevated Temperatures,” J.Physics & Chem of Solids, **66** 471-478 (2005)

<sup>4</sup>“Thermodynamics of Gas Phase Species in the Si-O-OH System,” J. Chem Thermodynamics, 37 1130-1137 (2005)

<sup>5</sup> Margrave, J.L. ed., The Characterization of High-Temperature Vapors, Library of Congress Catalog Card Number 66-22842 (1967)



# H<sub>2</sub>O Transpiration Experiment Theory and Techniques

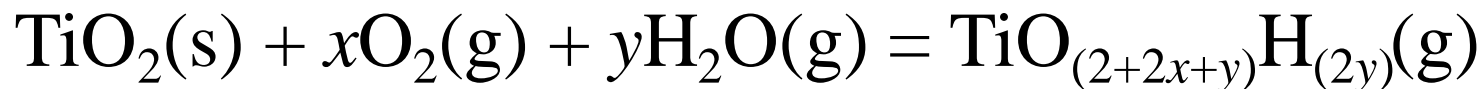
- “Transpiration method (also called transportation or entrainment method) – one of the oldest and most versatile ways of studying heterogeneous equilibria involving gases.”<sup>5</sup>
- Primarily used for measuring vapor and dissociation pressures at 1 atm
- General Principles:
  - Gas is passed over a sample at a rate sufficiently low enough for equilibrium conditions to be established
  - This gas is condensed downstream from the sample and is analyzed to determine the vapor or dissociation pressures of components in the sample
  - This method is very useful for systems in which vapor pressures and dissociation pressures cannot be measured by more direct means

<sup>5</sup> Margrave, J.L. ed., [The Characterization of High-Temperature Vapors](#), Library of Congress Catalog Card Number 66-22842 (1967)

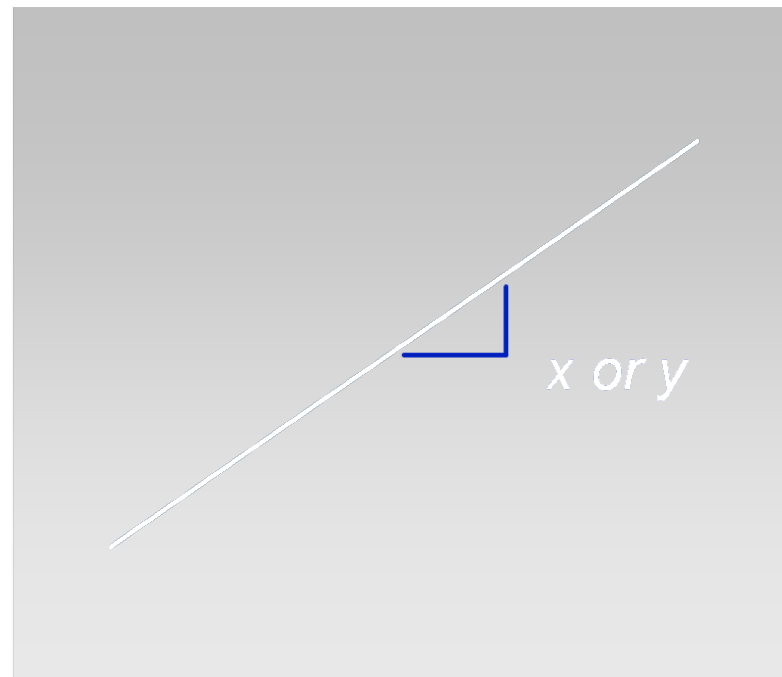


# H<sub>2</sub>O Transpiration Experimental Techniques

- The proposed reaction for TiO<sub>2</sub>:

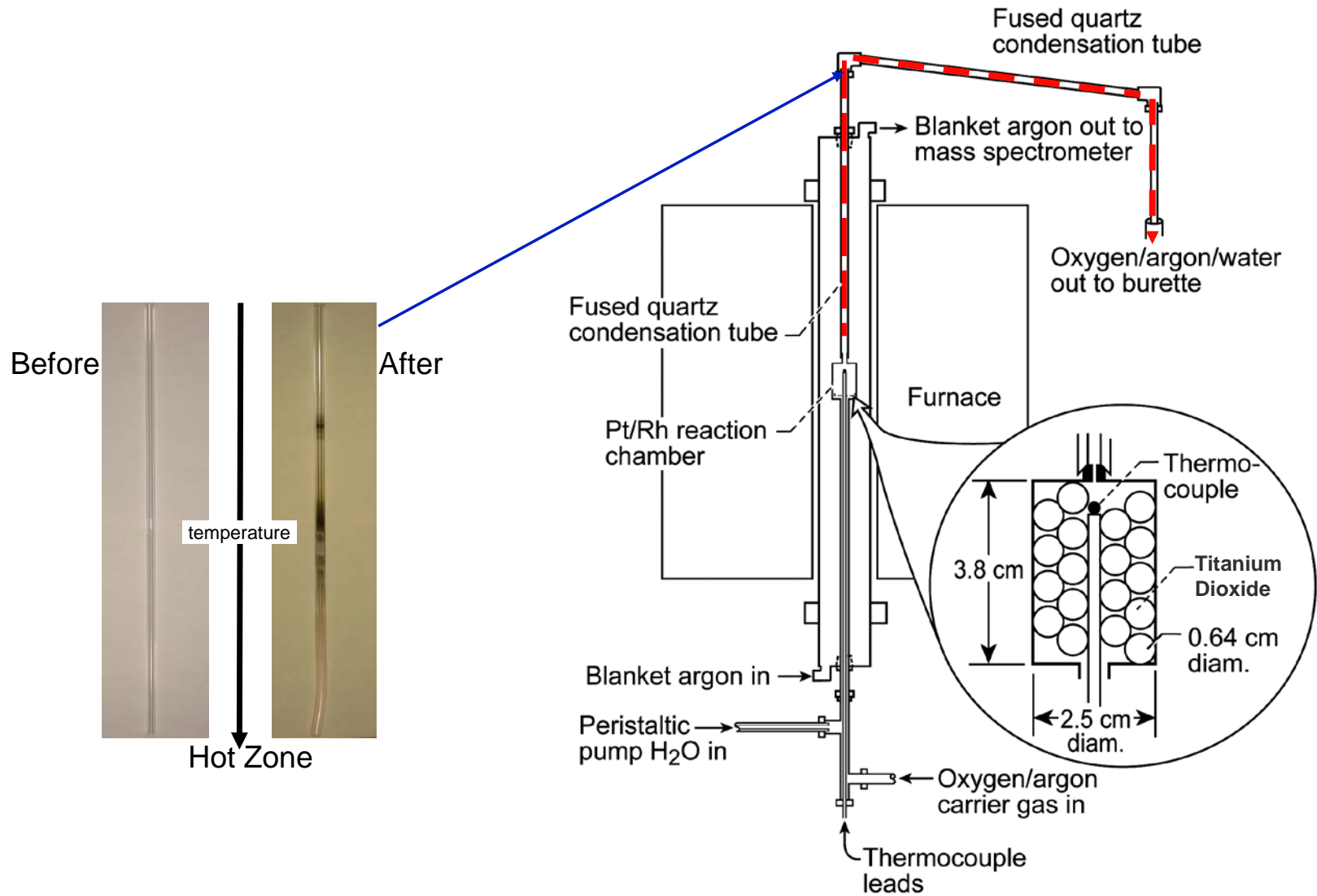


- O<sub>2</sub>(g) and H<sub>2</sub>O(g) coefficient can be determined by independently varying the pressure and gases
- Temperature dependence under different conditions allow for the enthalpy of reaction measurement





# H<sub>2</sub>O Transpiration Experiment Furnace Schematic





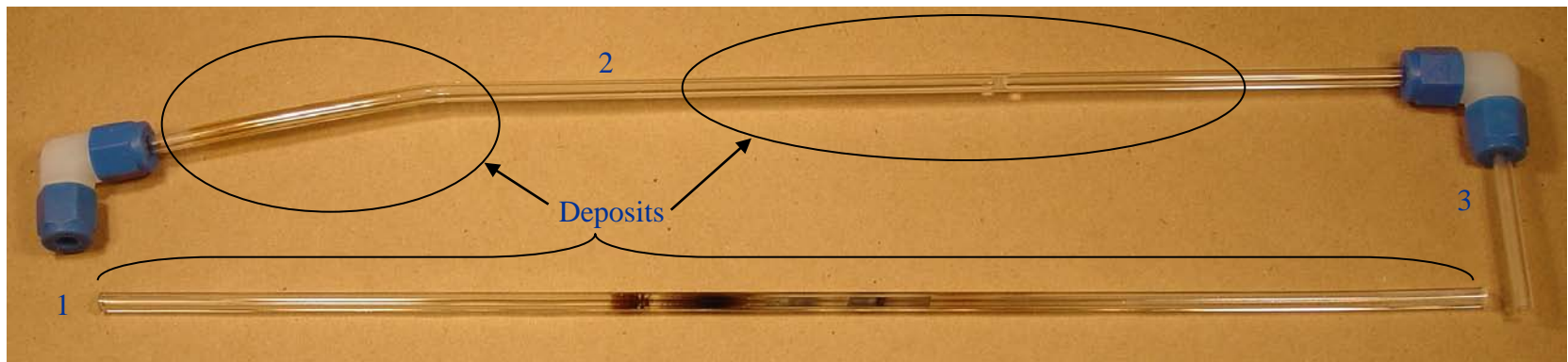
# H<sub>2</sub>O Transpiration Experiment Conditions

## Experimental Set-up/Design:

- Water vapor range 0-76% (by moles)
- Oxygen gas range 0-100% (by moles)
- Test length 20-250 hours
- Test temperatures: 1400°, 1300° and 1200°C
- Ambient pressure
- 99.999% pure titanium (IV) oxide, predominately rutile, with a molecular weight of 79.9 g/mole was purchased from Fisher Scientific (Acros Organics)

# H<sub>2</sub>O Transpiration Experiment

Typical post-run  
Transpiration quartz collection tubes and polyfluoroethylene fittings







# H<sub>2</sub>O Transpiration Experiment

The transpiration method is extremely dependent on the analytical measurement of the Ti precipitation

- Ti (μg) was measured using inductively coupled plasma atomic emission spectroscopy (ICP-AES)
  - All three collection tubes, fittings and exhaust H<sub>2</sub>O were analyzed
  - Exhaust H<sub>2</sub>O and fittings were soaked in a 5% (by volume) hydrochloric acid (HCl) + 2% hydrofluoric (HF) solution for 2-3 hours
  - Quartz tubes were soaked in an aqua regia solution (3 part HCl + 1 part nitric acid (HNO<sub>3</sub>)) for two hours followed by a rinse with concentrated HF
- Runs that contained oxygen went through a second series of analysis in which an acidic flux (fusion)
  - Filtered and dried deposit; followed by an acidic flux step through the use of potassium hydrogen sulfate (pyrosulfate). This mixture is heated over a Bunsen burner until it liquefies, thus converting any remaining TiO<sub>2</sub> (s) into a soluble solution



## H<sub>2</sub>O Transpiration Experiment Techniques

The partial pressure of the volatile species, Ti-O-H can be calculated using the ideal gas law:

$$P_{Ti-O-H} V_{gas} = n_{Ti} \cdot RT$$

where P = the partial pressure of Ti-O-H (atm)

V = total flow rate in the transpiration cell (mole/mL)

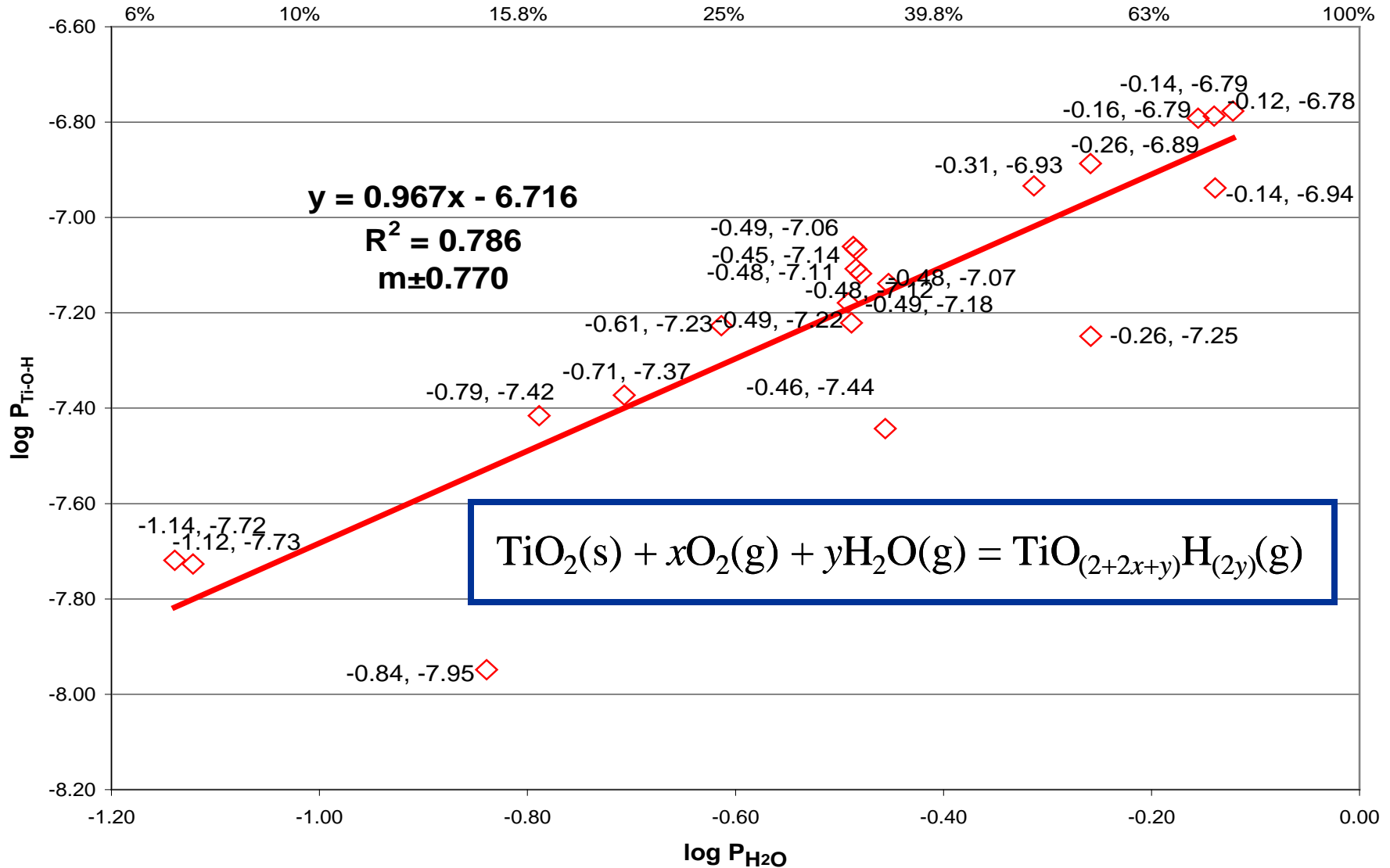
n = the rate of moles of Ti transported (μg)

R = ideal gas constant (atm·mL/mole·K)

T = temperature (K)

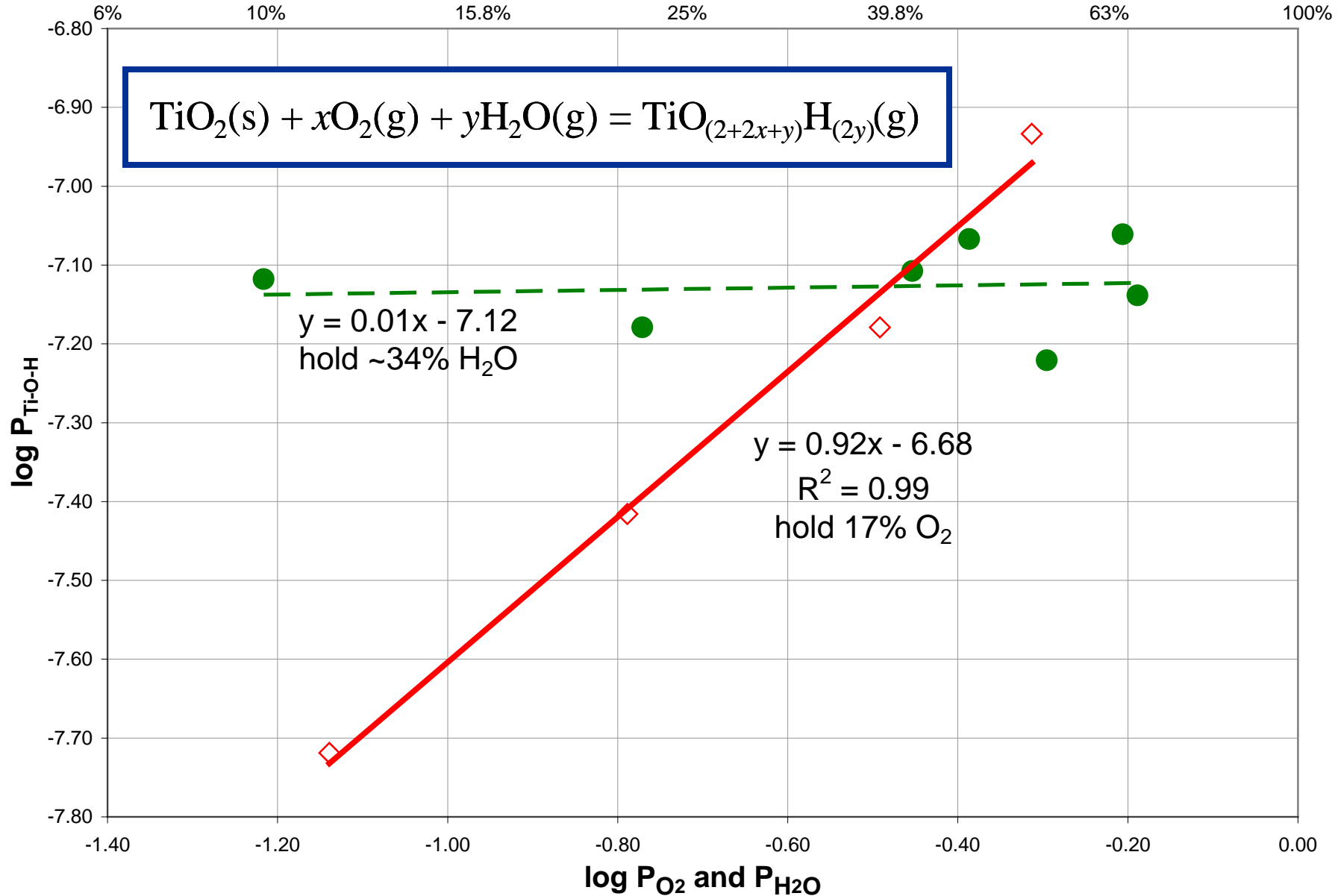


# H<sub>2</sub>O Transpiration Results for 1400°C



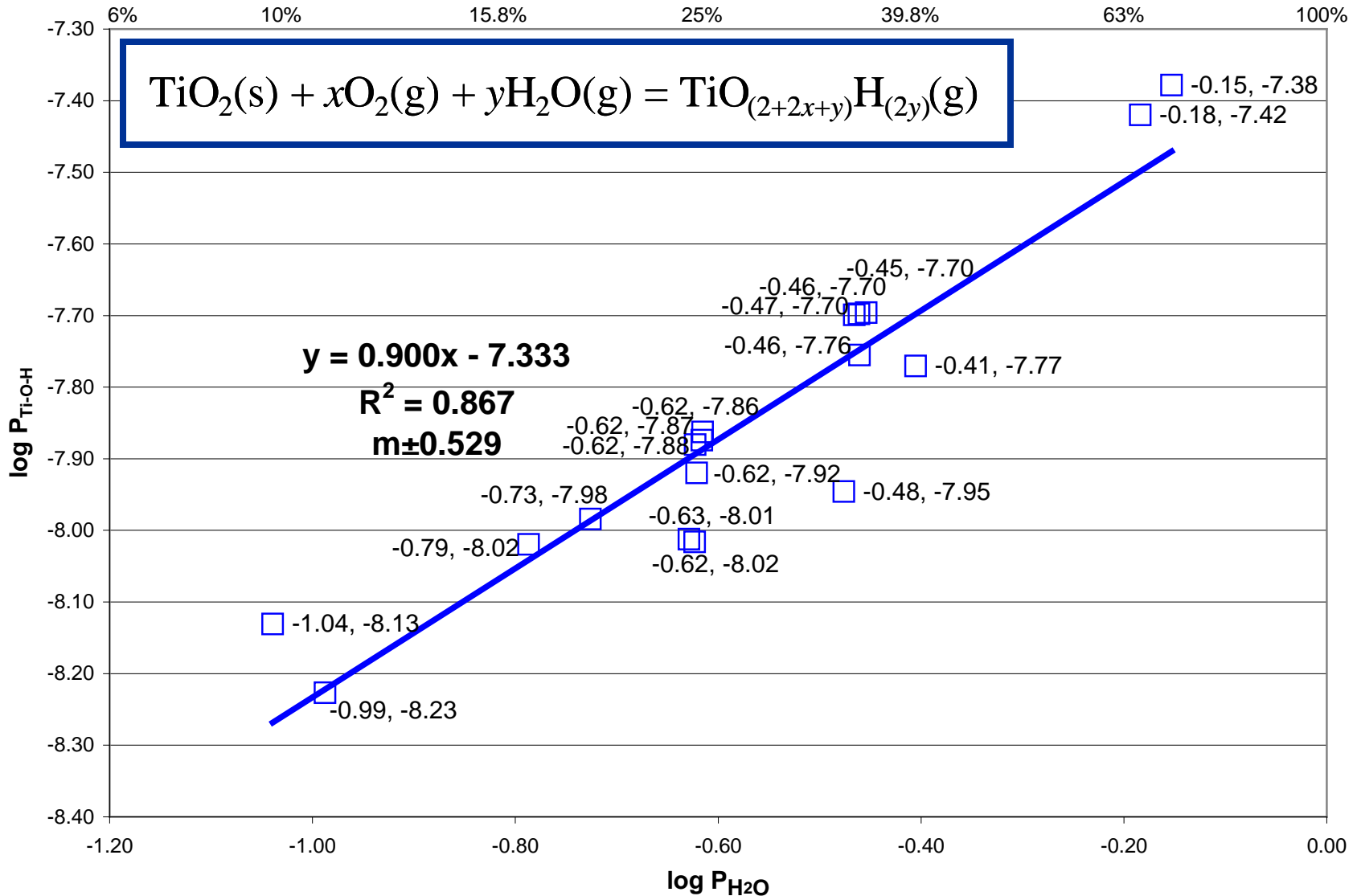


# H<sub>2</sub>O Transpiration Results for 1400°C



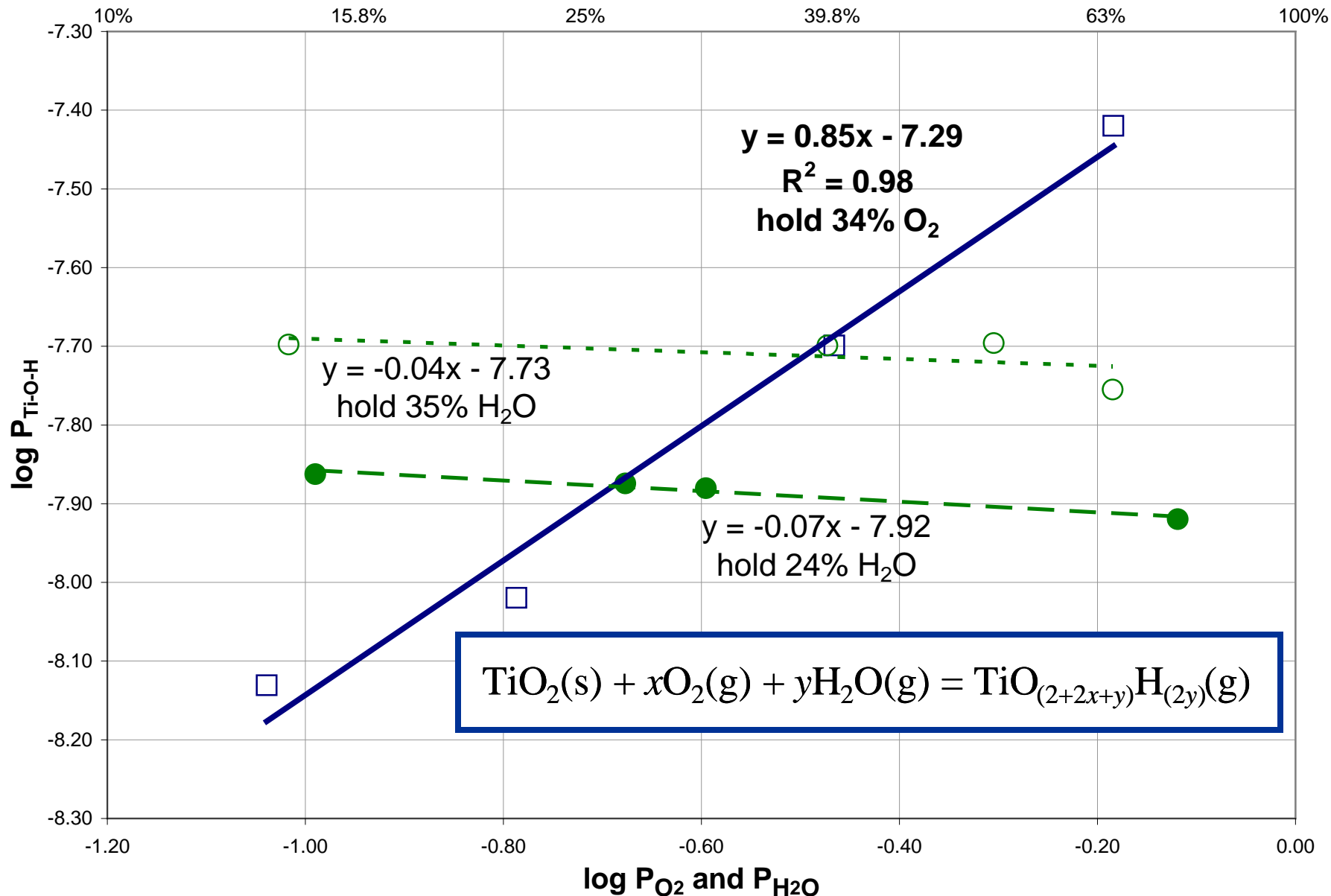


# H<sub>2</sub>O Transpiration Results for 1300°C



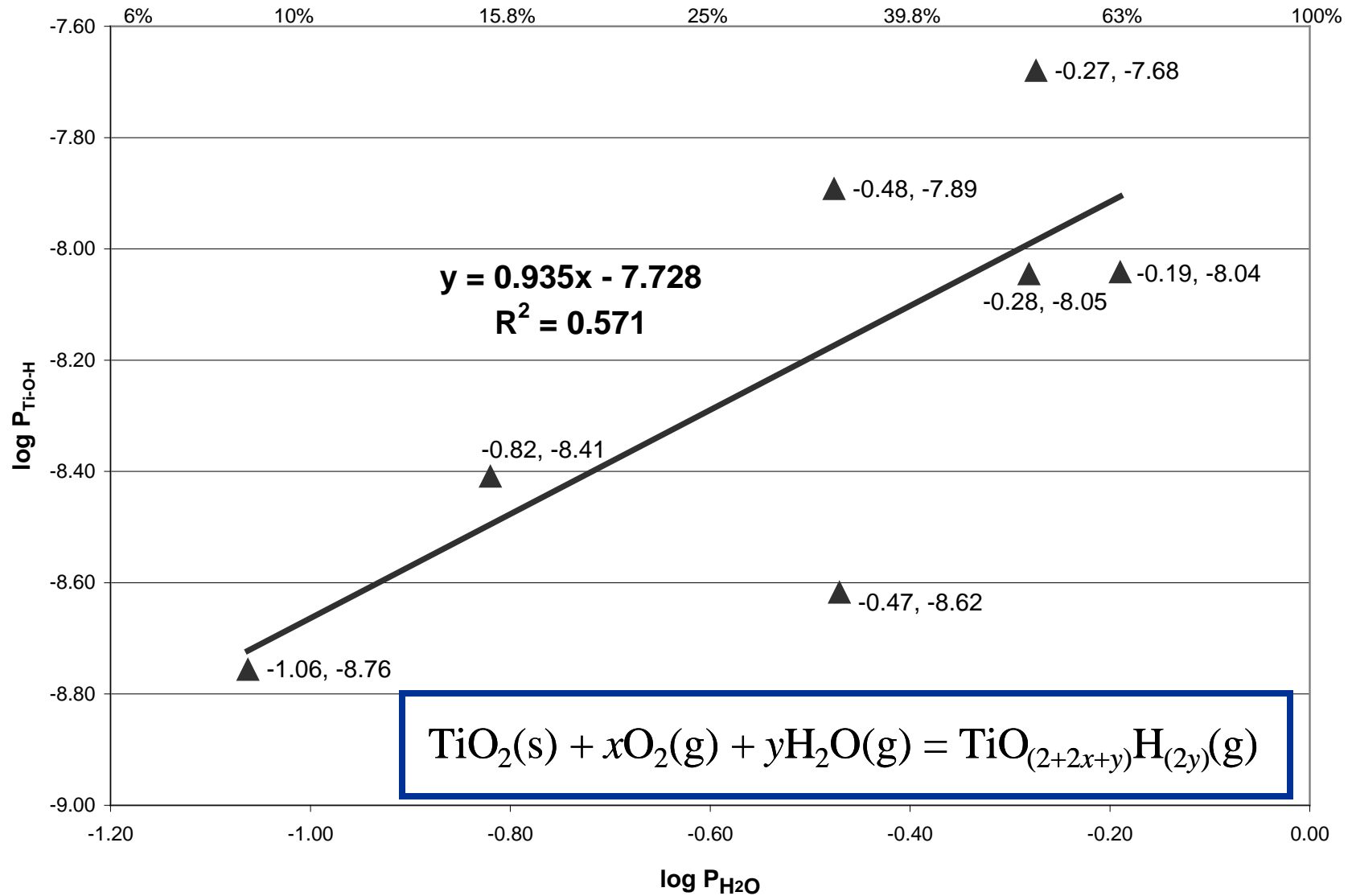


# H<sub>2</sub>O Transpiration Results for 1300°C



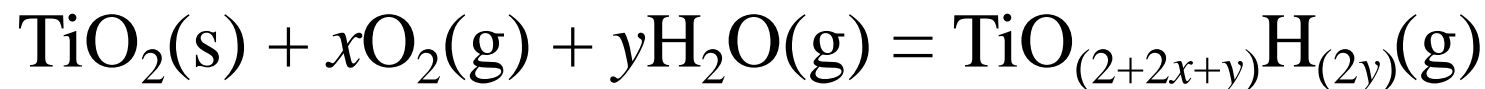


# H<sub>2</sub>O Transpiration Results for 1200°C

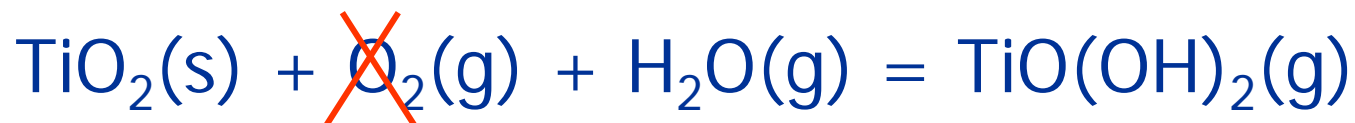




# H<sub>2</sub>O Transpiration Results



when  $x = 0$  and  $y = 1$ , then:

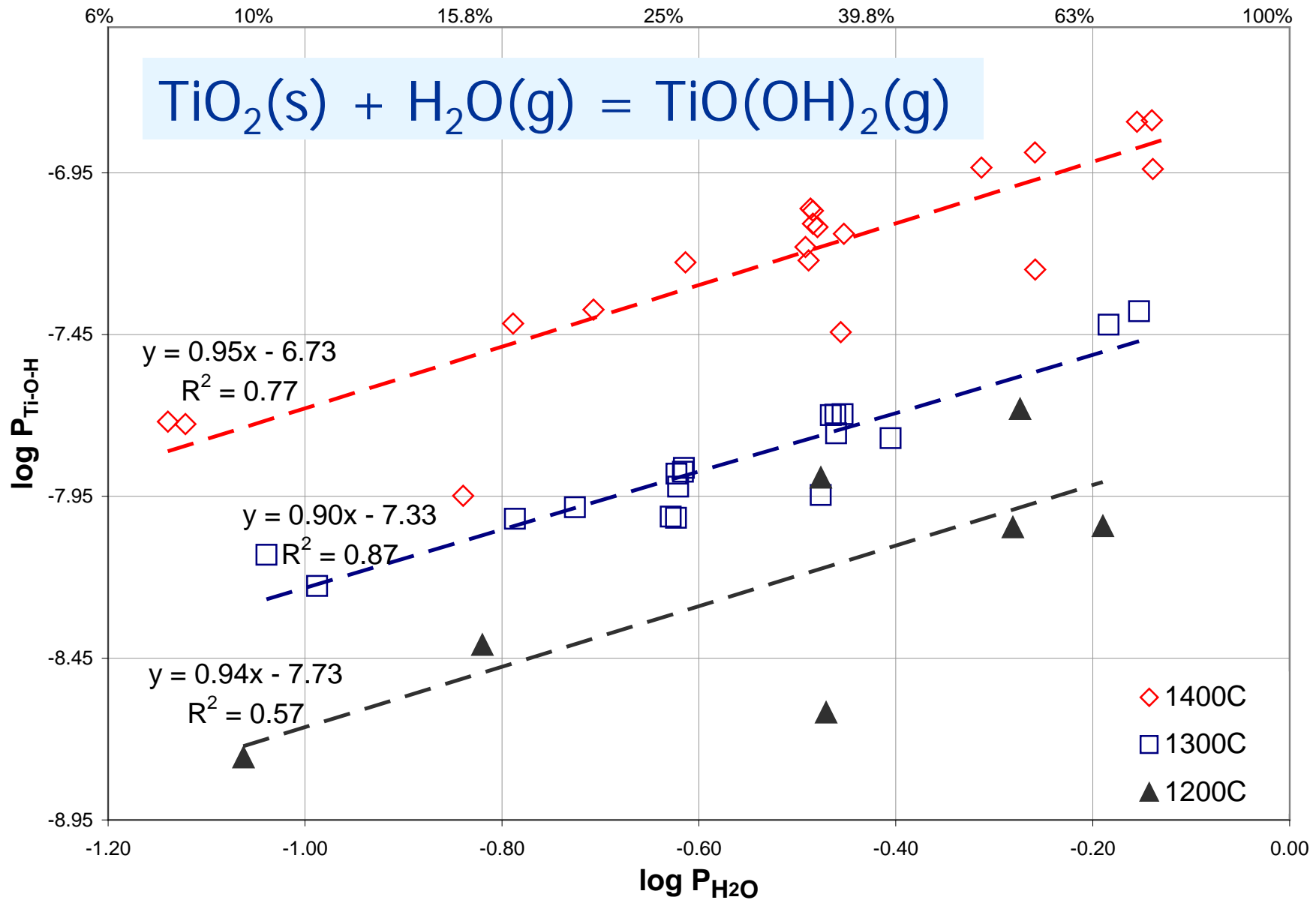


  
First identified



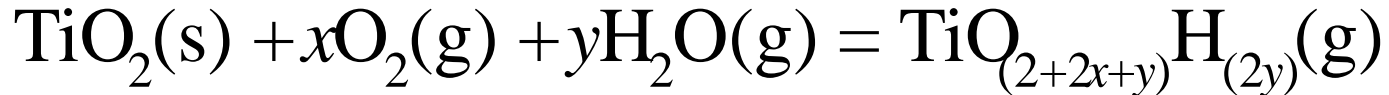


# All Three Temperatures





## Calculating the Equilibrium Constant ( $K_{eq}$ )



$$K_{eq} = \frac{P_{\text{TiO(OH)}_2}}{(a_{\text{TiO}_2})(X_{\text{O}_2}^x P_{tot})(X_{\text{H}_2\text{O}}^y P_{tot})}$$

Where

$P_{\text{TiO(OH)}_2}$  = is the partial pressure of volatile species (atm)

$a_{\text{Ti-O-H}}$  = activity of the  $\text{TiO}_2$ , which would equal one assuming that the  $\text{TiO}_2$  remains pure

$X$  = the mole fraction of the gases as can be seen in the following equation

$P_{tot}$  = the transpiration cell pressure as measured by the capacitance monitor (atm)

$$X_{\text{H}_2\text{O}} = \frac{\dot{n}_{\text{H}_2\text{O}}}{\dot{n}_{\text{O}_2} + \dot{n}_{\text{Ar}} + \dot{n}_{\text{H}_2\text{O}}}$$

where  $\dot{n}$  = gas flow rate (mole/sec)



# Van't Hoff Equation

$$\ln K_{eq} = -\frac{\Delta H_r^\circ}{R} \left( \frac{1}{T} \right) + \frac{\Delta S_r^\circ}{R}$$

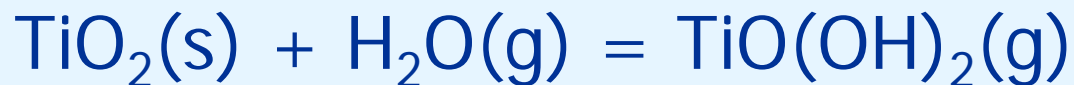
Where:

- $K_{eq}$  = the equilibrium constant (atm)
- $\Delta H_r^\circ$  = the of enthalpy of the reaction (J/mole)
- $R$  = ideal gas constant 8.3144 J/(K•mole)
- $\Delta S_r^\circ$  = the entropy (J/mole)
- $T$  = temperature (K)



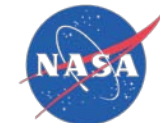


## Summary, Discussion and Conclusions



- The  $\Delta H_{r1573}^\circ$  for this study calculated at an average temperature of 1573K (1300°C) is 247 KJ/mole.
- These values can be compared to published values for a similar molecule,  $\text{SiO}(\text{OH})_2$  (g), which has a reported value of 314 KJ/mole<sup>7</sup>.

<sup>7</sup>Jacobson et al., "Thermodynamics of Gas Phase Species in the Si-O-H System," J Chemical Thermo, 37, 1130-1137 (2005)



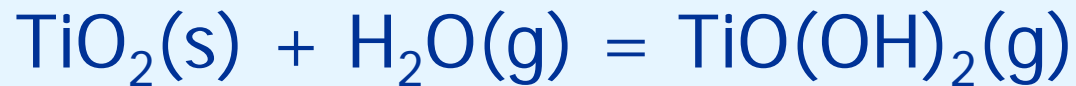
## cont. Summary, Discussion and Conclusions

- The calculated  $\Delta S_{r_{1573}}^{\circ}$  is 18.57 J/mole.
  - Entropy is dominated by the number of gas molecules at the start and end of a reaction; therefore, this particular molecule, a low  $\Delta S_r^{\circ}$  would be expected



## cont. Summary, Discussion and Conclusions

- This study addresses the water vapor attack on Ti-containing material that occurs at high temperatures in a combustion environment.
- The study resulted in identifying  $\text{TiO}(\text{OH})_2$  (g) as the primary volatile species at these temperatures. This molecule has not been reported in any published form.



- The recommended guidelines<sup>8,9</sup> for use in combustion environment for negligible recession is a partial  $P_{\text{volatile}} < 1 \times 10^{-6}$  atm in order to present no long-term problem with respect to the degradation of a structural material.

partial  $P_{\text{TiO}(\text{OH})_2} = 1 \times 10^{-8}$  atm at an average temperature of  $1300^\circ\text{C}$

- Based on the above guidelines,  $\text{TiO}_2$  (s) is a considerable material in a combustion environment for applications below  $1400^\circ\text{C}$ .

<sup>8</sup>Hillig, "Prospects for Ultra-High-Temperature Ceramic Composites," Tailoring Multiphase and Composite Ceramics, Plenum, (1986)

<sup>9</sup>Jacobson, "High-Temperature Durability Consideration for HSCT Combustor," NASA Technical Paper, 3162, January, (1992)



# Acknowledgements

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