The Effect of IGFC Warm Gas Cleanup System Conditions on the Gas-Solid Partitioning and Form of Trace Species in Coal Syngas and Their Interactions with SOFC Anodes

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Fuel Cell Research Group

Introduction

- **Today's Power Generation Market**
  - Coal fired power generation under increased scrutiny
    - More efficient processes with less environmental impact
  - Coal is the U.S.' most abundant and pollutant laden fuel
  - Economics dictates it will be used for years to come
  - New technologies show great promise
    - Gasification – Convert coal into coal syngas (CSG)
    - Cleanup – Remove contaminants from CSG
    - Fuel Cells – Directly convert chemical energy to electricity
  - U.S. DOE investing in development of all technologies

Introduction

- **Coal Gasification**
  - Coal is transformed into a syngas by the addition of O_2 and H_2O.
  - Reactors operate at temperatures up to 1700°C and 70atm.
  - The syngas contains a mixture of H_2, CO, CO_2, H_2O, CH_4, N_2, and many trace species.
  - O_2 blown entrained flow gasification is used in today's IGCC power plants and anticipated to be used in the future [1].

Introduction

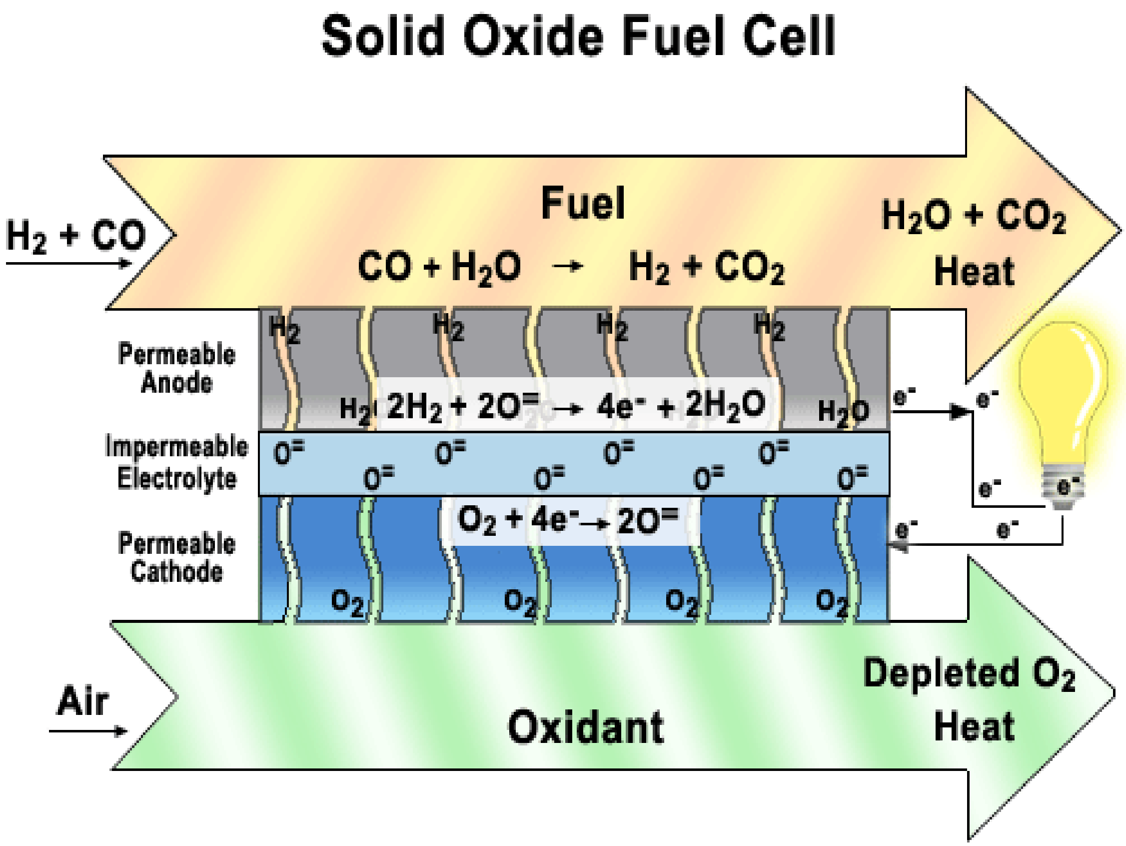

Figure 1. Solid Oxide Fuel Cell Operation [2].

Introduction

- **SOFCs and Coal Syngas (CSG)**
  - Recent studies have shown feasibility of operating solid oxide fuel cell (SOFC) systems with coal syngas [4-5].
  - Current CSG cleanup systems work very well for the removal of S and Cl species, however operating temperature is too low (ambient).
  - Future warm/hot gas cleanup systems will operate at much higher temperatures (250-500°C).
  - The effect of trace species that may pass through warm gas cleanup conditions is not known.

Introduction

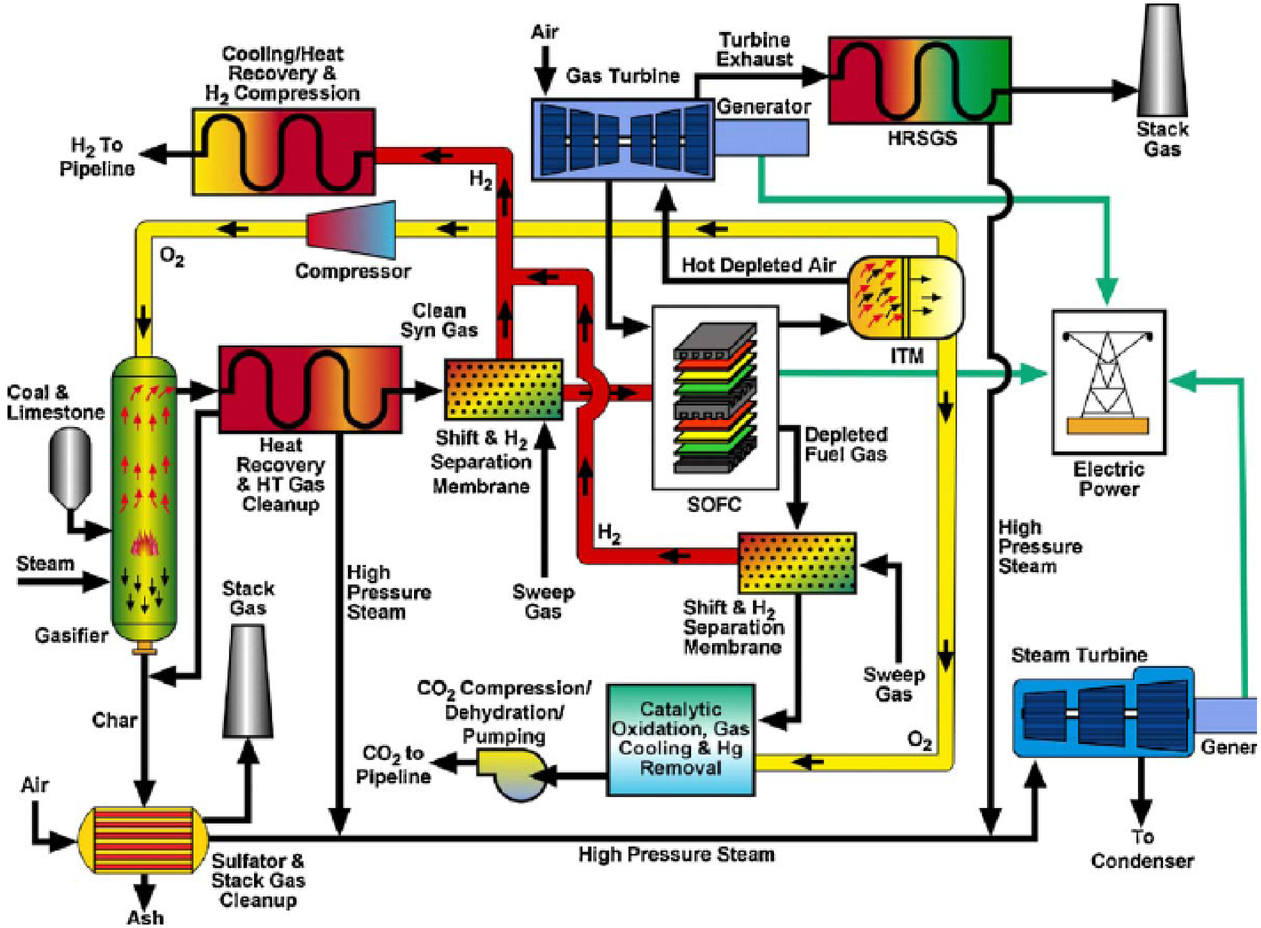

Figure 2. U.S. DOE FutureGen [3].

Introduction

- **Trace Species in CSG**
  - Trace elements contained in coal are classified into three groups base upon their volatility [1].
    - *Class I*: Least volatile, will remain in the ash.
    - *Class II*: More volatile, partition between condensed and gas phases.
    - *Class III*: Volatile, show little to no tendency to condense.
  - Previous reports have shown the presence of As, P, Sb, Cd, Be, Cr, Hg, K, Se, Na, V, Pb, Zn.

Thermodynamic Evaluation

- **Thermodynamics are used to determine the condensation behavior of trace species contained in CSG.**
  - Gaseous species are assumed to travel to SOFC module.
  - Solid species are assumed to have a 100% removal efficiency.
  - System temperatures and pressures were varied from 200-500°C and 1-15atm.
- **Thermodynamic analyses of the anode was also completed based upon warm gas cleanup results.**
  - Study evaluated anode composition (Ni, ZrO_2, and Y_2O_3).
  - Study completed over SOFC operational temperatures 700-900°C and anticipated pressures 1-15atm.

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Thermodynamic Evaluation

Table 1. Coal Syngas Composition [6].

Component	Composition (vol%)
H_2	29.3
CO	28.7
CO_2	11.8
N_2	3.0
H_2O	27.2

Thermodynamic Evaluation

Table 2. Trace Species Contained in Coal Syngas [1,7-9].

Component	Concentration (ppmv)	Volatility Class
AsH_3	0.6	II
HCl	1	III
PH_3	1.91	II
Sb	0.07	II
Cd	0.011	II
Be	0.025	II
Cr	6	II
Hg	0.025	II
K	512	I
Se	0.15	II
Na	320	I
V	0.025	II
Pb	0.26	II
Zn	9	II

Results

Table 3. Trace Species Behavior.

Component	Behavior
As	**Gas/Solid**
P	**Gas/Solid**
Sb	**Gas**
Cd	**Gas/Solid**
Be	Solid
Cr	Solid
Hg	**Gas**
K	Solid
Se	**Gas/Solid**
Na	Solid
V	Solid
Pb	**Gas/Solid**
Zn	Solid

Thermodynamic Evaluation

Table 4. Trace Species in Anode Fuel.

Component	Concentration (ppmv)
Sb	0.07
As	0.6
Cd	0.011
Pb	0.26
Hg	0.025
P	1.91
Se	0.15

Thermodynamic Evaluation

Table 5. Outlet Edge Fuel Composition.

Component	Composition (vol%)
H_2	4.6
CO	4.0
CO_2	36.5
N_2	3.0
H_2O	51.9

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Anode Evaluation Results

- **Study Results**
  - Sb, As, and P trace species were found to form secondary Ni phases.
  - Cd, Pb, Hg, and Se were not found to form secondary phases in the anode.

Sb/Anode Interactions

$$As_3Sb(g) + Ni(s) \rightarrow NiSb(s) + 0.75As_4(g) \qquad Eq.1$$

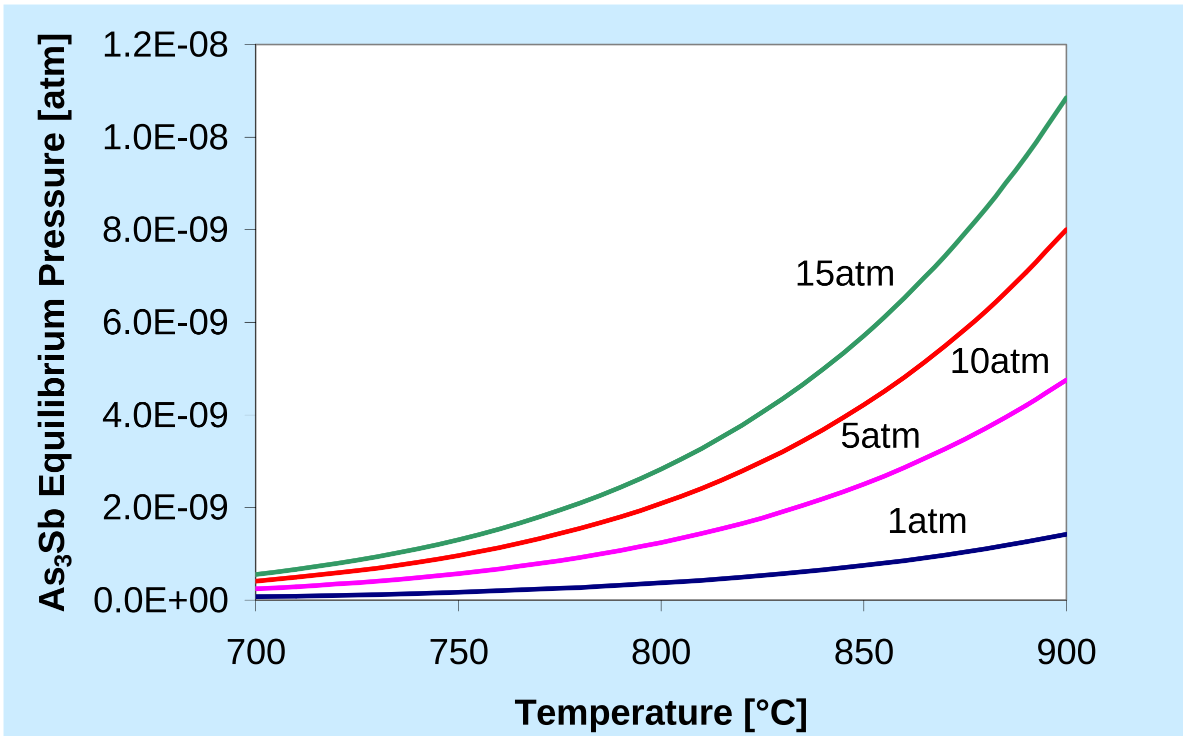

Figure 3. Equilibrium Pressures of As_3Sb Associated with Equation 1 Over SOFC Operation Conditions.

As/Anode Interactions

$$0.25As_4(g) + Ni(s) \rightarrow NiAs(s) \qquad Eq.2$$

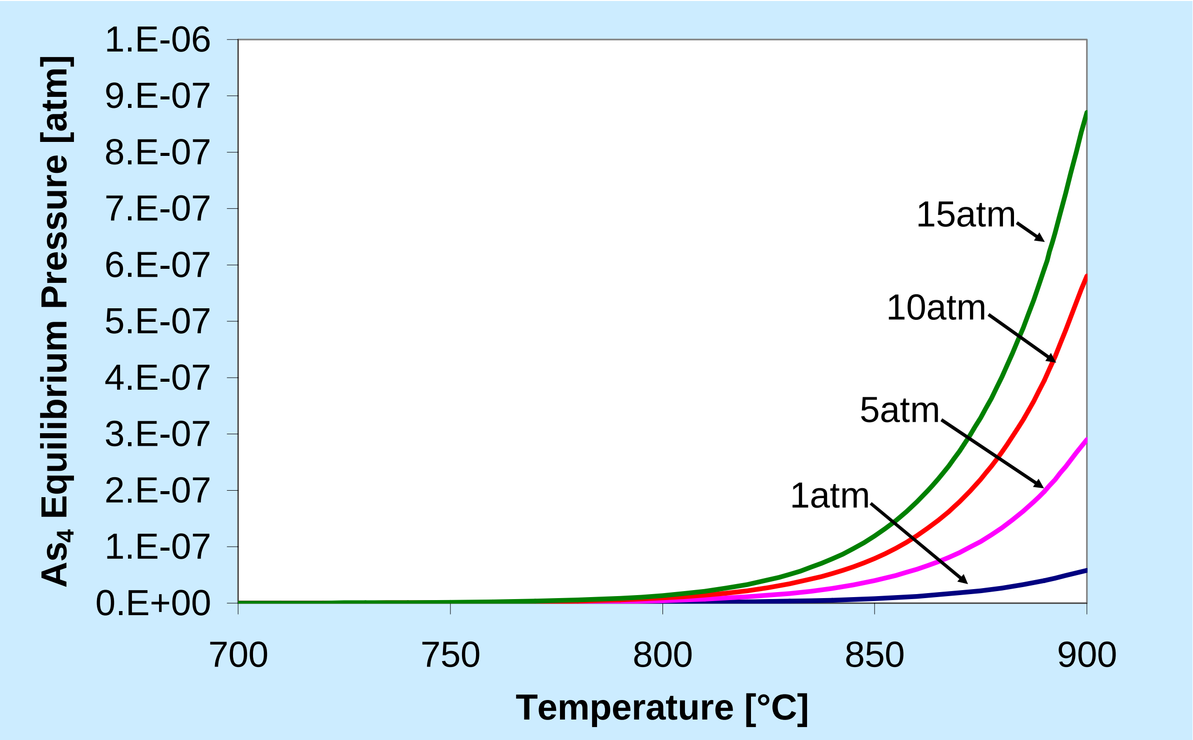

Figure 4. Equilibrium Pressures of As_4 Associated with Equation 1 Over SOFC Operation Conditions.

As/Anode Interactions

$$AsH_3(g) + Ni(s) \rightarrow NiAs(s) + 1.5H_2(g) \qquad Eq.3$$

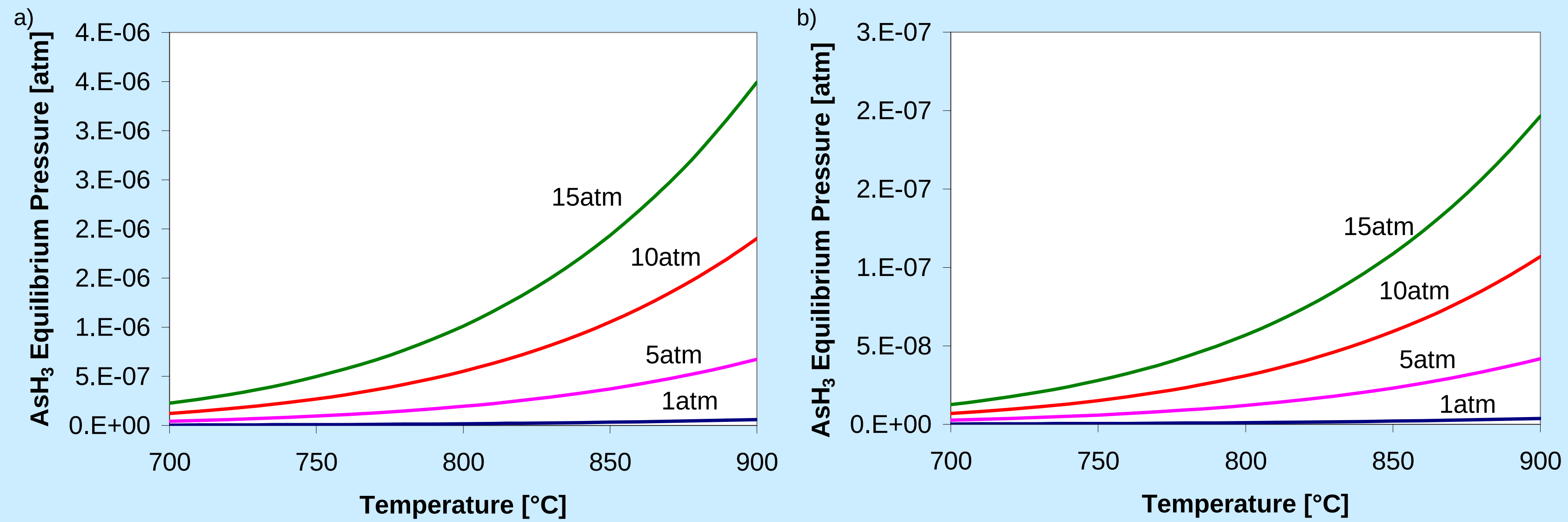

Figure 5. Equilibrium Pressures of AsH_3 Associated with Equation 3 Over SOFC Operation Conditions at the Inlet (a) and Outlet (b).

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P/Anode Interactions

$$2PH_3(g) + 5Ni(s) \rightarrow Ni_5P_2(s) + 3H_2(g) \qquad Eq.4$$

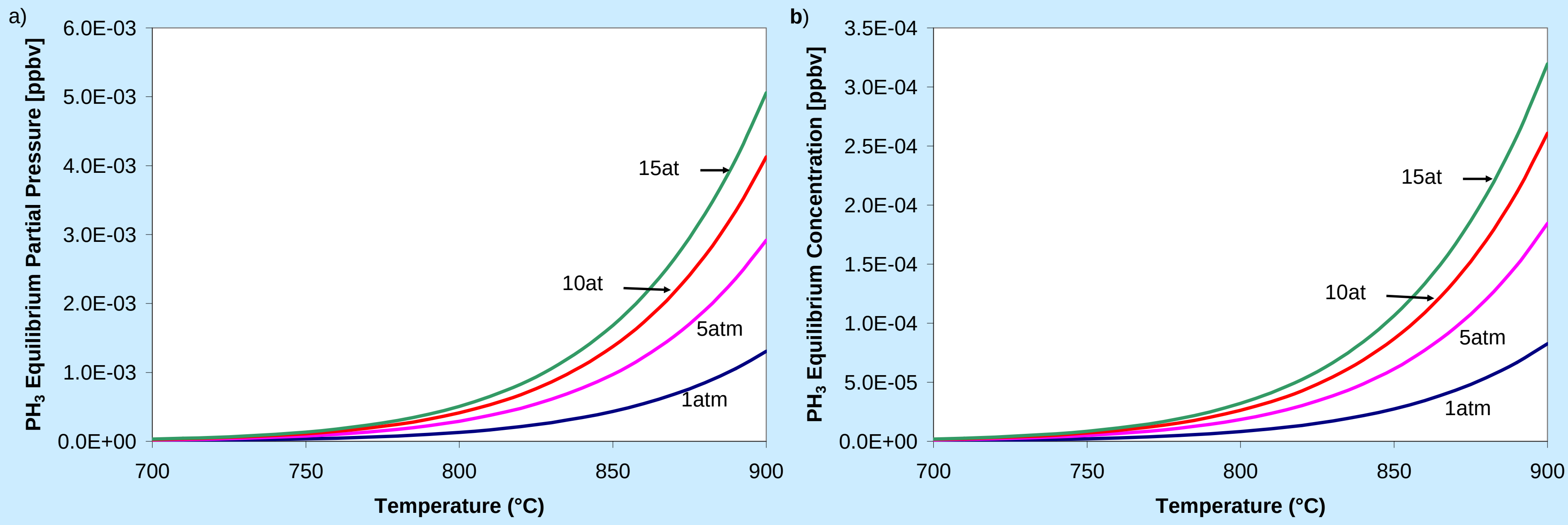

Figure 6. Equilibrium Pressures of PH_3 Associated with Equation 3 Over SOFC Operation Conditions at the Inlet (a) and Outlet (b).

Trace Metal Oxidation

$$Pb(g) + 0.5O_2(g) \rightarrow PbO(s) \qquad Eq.5$$

$$Cd(g) + 0.5O_2(g) \rightarrow CdO(s) \qquad Eq.6$$

$$Hg(g) + 0.5O_2(g) \rightarrow HgO(g) \qquad Eq.7$$

$$Ni(s) + 0.5O_2(g) \rightarrow NiO(g) \qquad Eq.8$$

Table 6. O2 Equilibrium Partial Pressures Associated with Equations 5-8.

T(ºC)	pO_2(syngas)	pO_2(Eq.5)	pO_2(Eq.6)	pO_2(Eq.7)	pO_2(Eq.8)
700	1.60E-17	9.80E-15	8.50E-07	7.50E+15	5.42E-17
800	6.40E-15	1.00E-10	3.50E-03	1.90E+17	1.20E-14
900	9.80E-13	2.20E-07	3.40E+00	2.70E+18	1.04E-12

Thermodynamic Evaluation Conclusions

1. Many trace species in coal syngas will form solid phases over warm gas cleanup conditions. In particular Be, Cr, K, Na, V, and Zn all formed condensed species.
2. Thermodynamic evaluations showed that Sb, As, Cd, Hg, P, and Se vapor species form in warm gas cleanup conditions.
3. No secondary phase formations between the vapor specie forms and oxide components were found.
4. No phase formations between Se vapor species and Ni were found.
5. Sb, As, and P vapor species were shown to have the potential to form secondary phases with Ni.
6. Oxidation of the fuel species was shown to have a large effect on the amount of secondary Ni phases formed in the anode.
7. The oxidation of the trace metal vapor species was shown not to be feasible.

Future Testing

- Experimentally determine the effects of trace syngas species
  - AsH_3 (Fall/Winter '06/'07)
  - PH_3, Hg, and Sb (Spring '07)
  - Cd, Pb, and Se (Summer '07)

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Acknowledgements

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Questions

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