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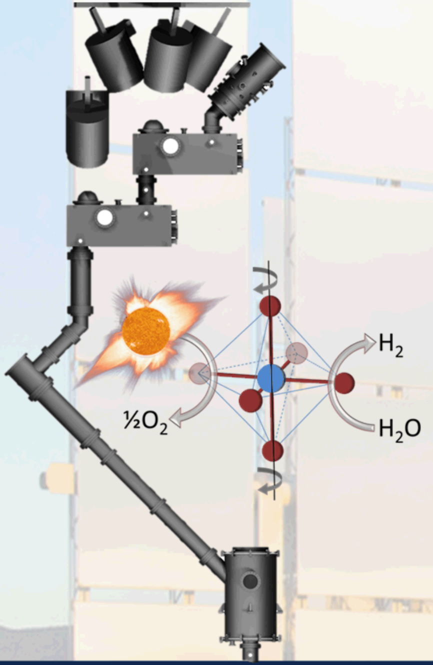

Model-free Thermodynamic Relationships for Non-stoichiometric Metal Oxides from Experimental Measurements

Anthony H. McDaniel, presenting
Sandia National Labs

Exceptional service in the national interest

Acknowledgments to the team

- Sandia Labs
  - Jim Miller
  - Andrea Ambrosini
  - Sean Babiniec
  - Eric Coker

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U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

- DOE/Fuel Cell Technologies Office
- DOE/SunShot Initiative

Outline

- Challenges for material characterization and evaluation.
  - Standard protocols for measuring data need development
    - Temperature and O_2 partial pressure ranges too narrow
    - Sample purity and experimental methods always in question
  - Benchmarked protocols for extracting properties need development
    - Thermodynamic and kinetic properties
- Extracting thermodynamic properties from (T, p_{O_2}, δ) data.
  - van’t Hoff approximation with or without invoking defect models
    - Apply arbitrary or “informed” δ-dependence
  - CALPHAD (very rigorous!)
- Model-free approach to analyzing (T, p_{O_2}, δ) data.
  - ΔH(δ, T) and ΔS(δ, T) derived from equilibrium response surface
- US Government investments in solar H_2 production.
  - HydroGen Consortium and H2@Scale

Solar powered two-step thermochemical water-splitting cycle to produce H_2 (STCH)

$$MO_x \rightarrow MO_{x-\delta} + \frac{\delta}{2} O_2 \qquad \text{(1) Reduction}$$

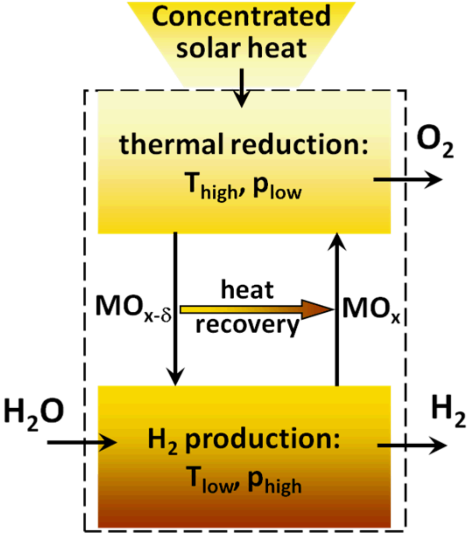
$$MO_{x-\delta} + \delta \cdot H_2O \rightarrow MO_x + \delta \cdot H_2 \qquad \text{(2) Oxidation}$$

$$\delta \cdot H_2O \rightarrow \frac{\delta}{2} O_2 + \delta \cdot H_2 \qquad \text{(3) Thermolysis}$$

MW scale concentrating solar power facilities provide heat before making electricity

Cycle conditions and system metrics:

Reduction Temperature (T_{high})	<2000ºC
"O" activity in reduction (p_{low})	$\mu_{gas} < \mu_{solid}$
Oxidation Temperature (T_{low})	debated
"O" activity in oxidation (p_{high})	$\mu_{gas} > \mu_{solid}$
H_2 production rate	50-100mt/day
Solar-to-H_2 conversion efficiency	>25%
H_2 production cost (US DOE)	$3/gge at plant gate



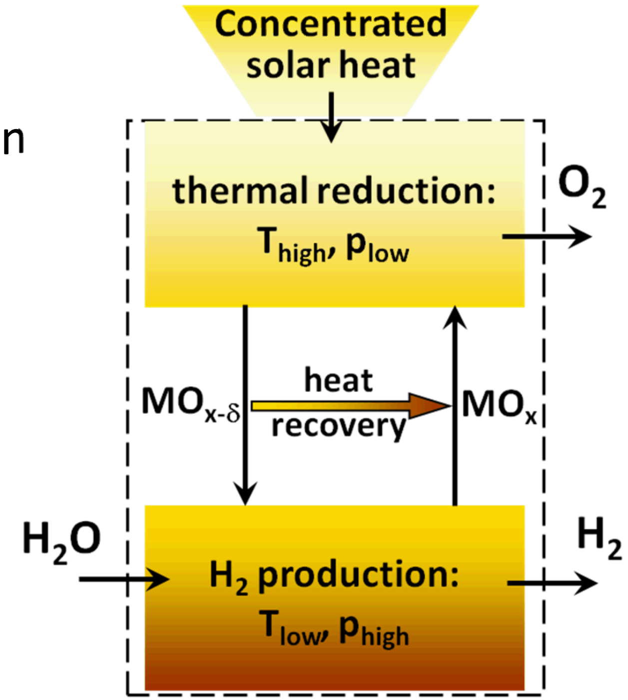
Two-step metal oxide cycle

- The challenge is to develop efficient and scalable solar-powered reduction receivers and water-splitting reactors.

Technological challenges for materials

Miller et. al, *Advanced Energy Materials* **2013**, DOI:10.1002/aenm.201300469

- Redox thermodynamics and kinetics.
  - Critical to reactor design and efficient operation
  - Large, reversible oxygen deficiency (reduction extent)
  - Fast redox rates and matched to solar flux
- Stability and long-term durability of redox active ceramic structures.
  - Cycle life ~ 300,000 cycles (10 year life)
    - heating rates (1000°C/min)
  - Compatibility with materials of construction
- Earth abundant and easy to manufacture.



Two-step metal oxide cycle

$\Delta H(\delta;T)$ to model reactor efficiency

requires high-quality experimental data over sufficient P_{O2}-T-δ range.

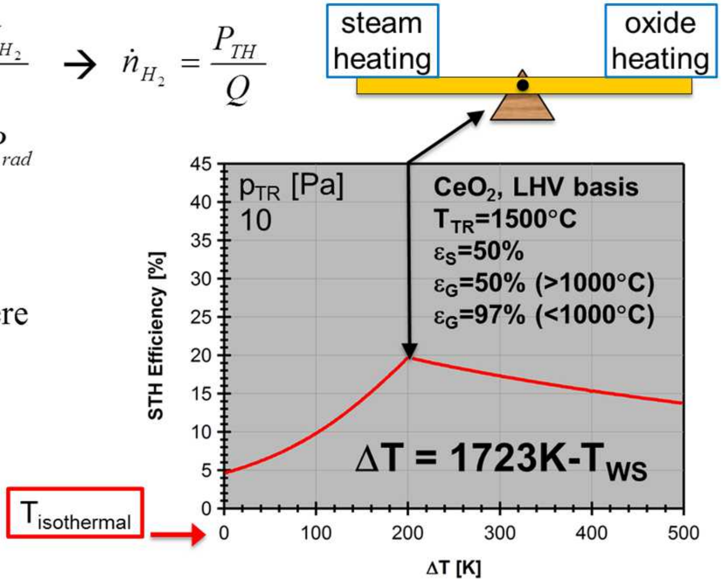
All inclusive efficiency metric

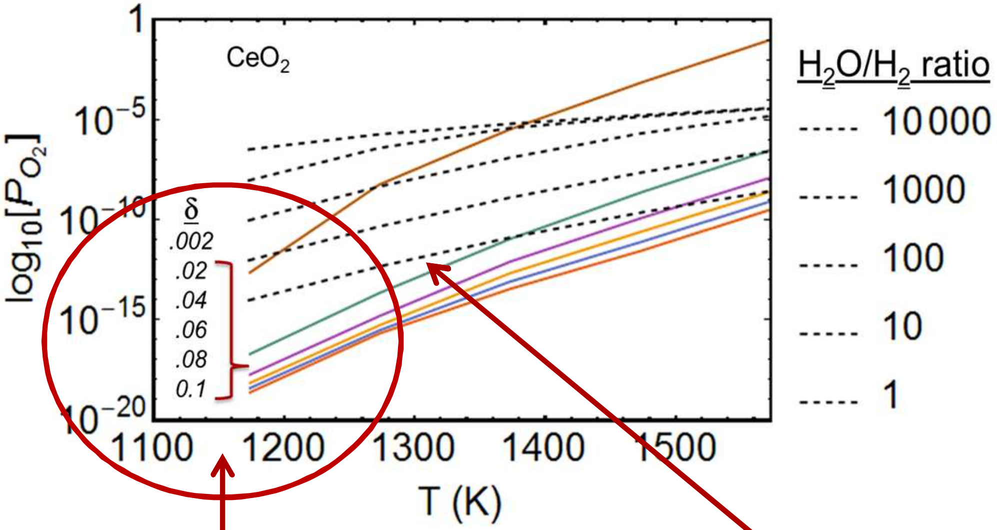
$$\eta = \left(\frac{P_{TH}}{P_S}\right)\left(\frac{LHV_{H_2}}{Q}\right) = \frac{\dot{n}_{H_2} LHV_{H_2}}{P_S} \rightarrow \dot{n}_{H_2} = \frac{P_{TH}}{Q}$$

$$P_{TH} = r_{12} * r_d * t_W * A * P_S - P_{rad}$$

$$Q = Q_{TR} + Q_{SH} + Q_{AUX}$$

$\Delta H(\delta;T)$ embedded here





- No *a priori* assumptions about material defect behavior required to model reactor efficiency.

challenged to measure P_{O2}-T-δ @ low T, low P_{O2}

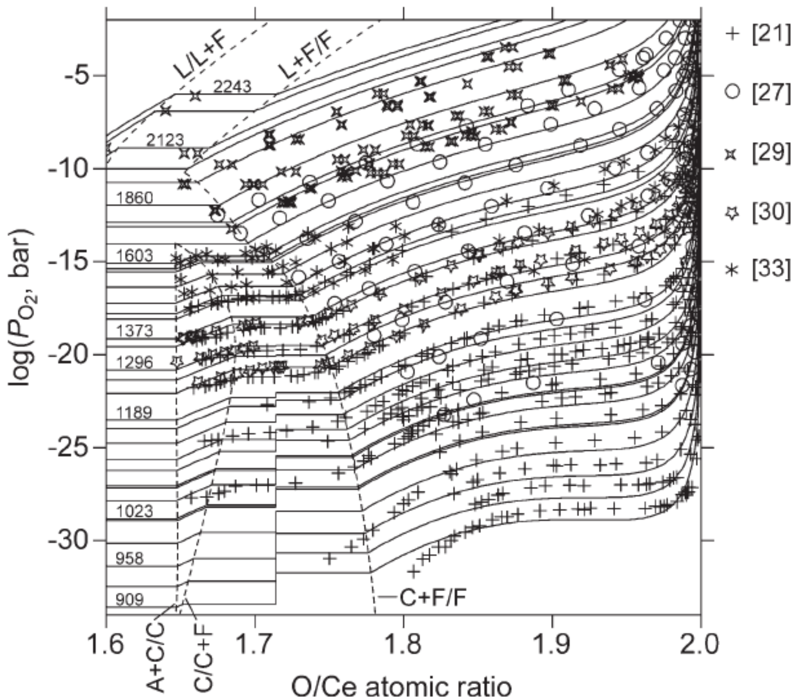
"O" activity in reduction (p_{low})	$\mu_{gas} < \mu_{solid}$
"O" activity in oxidation (p_{high})	$\mu_{gas} > \mu_{solid}$

Mapping the P_{O2}-T-δ space

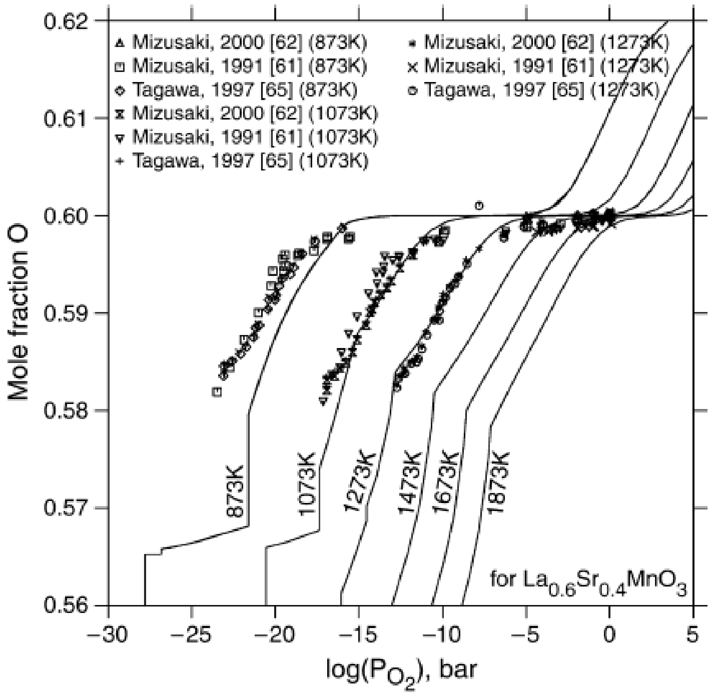
M. Zinkevich et al., *Solid State Ionics*. **177**, 989–1001 (2006).

A. N. Grundy et al., *Calphad*. **28**, 191–201 (2004).

CeO_2



$La_{0.6}Sr_{0.4}MnO_3$ (LSM40)

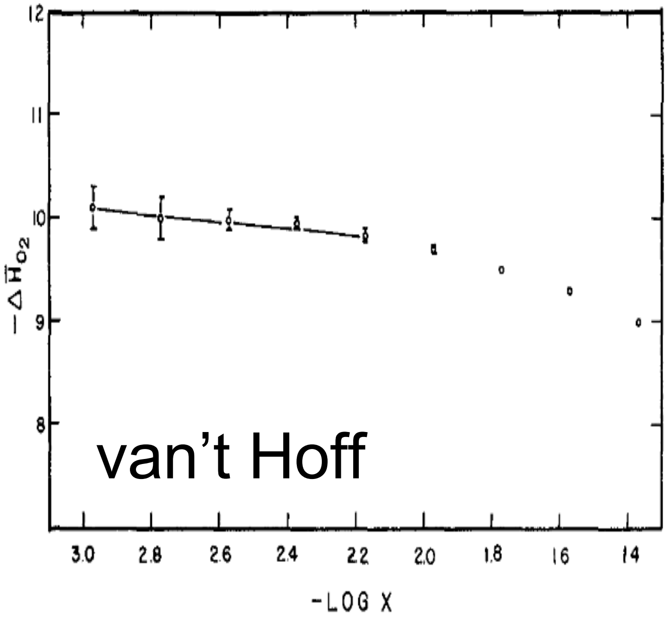


- Measure oxygen defect concentration (δ) in non-stoichiometric oxides as a function of P_{O2} and Temperature.
  - Thermogravimetry (TGA), coulometric titration, other methods?

ΔH(δ): from van’t Hoff to CALPHAD

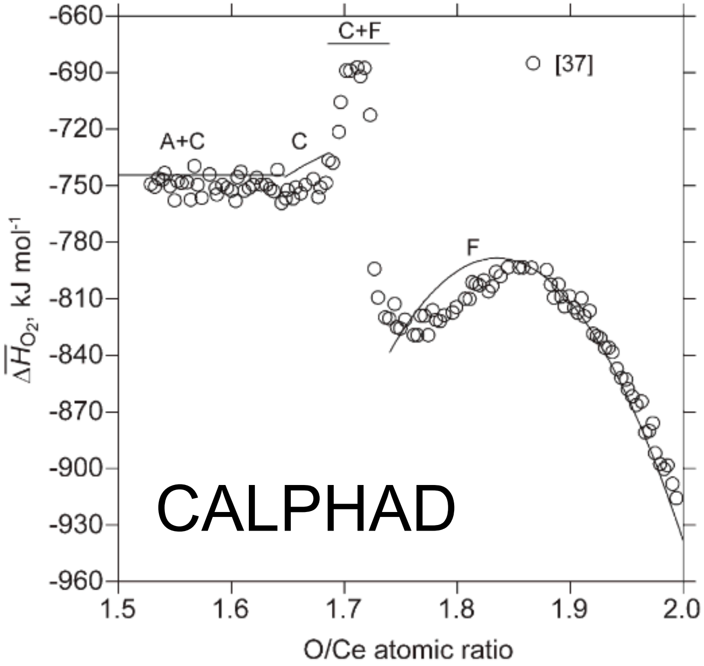
CERIA

R. J. Panlener et al., *Journal of Physics and Chemistry of Solids*. **36**, 1213–1222 (1975).



- Invoke assumptions about defect behavior.
  - Species [], reactions, K_{eq}’s, etc.
- Linearize system then use slopes and/or intercepts.

M. Zinkevich et al., *Solid State Ionics*. **177**, 989–1001 (2006).



- Combine all reported phase behavior.
  - Various approximations for phase-dependent ΔG’s
  - ΔG’s are additive

CALPHAD rigor is a lost art

M. Zinkevich et al., *Solid State Ionics*. **177**, 989–1001 (2006).

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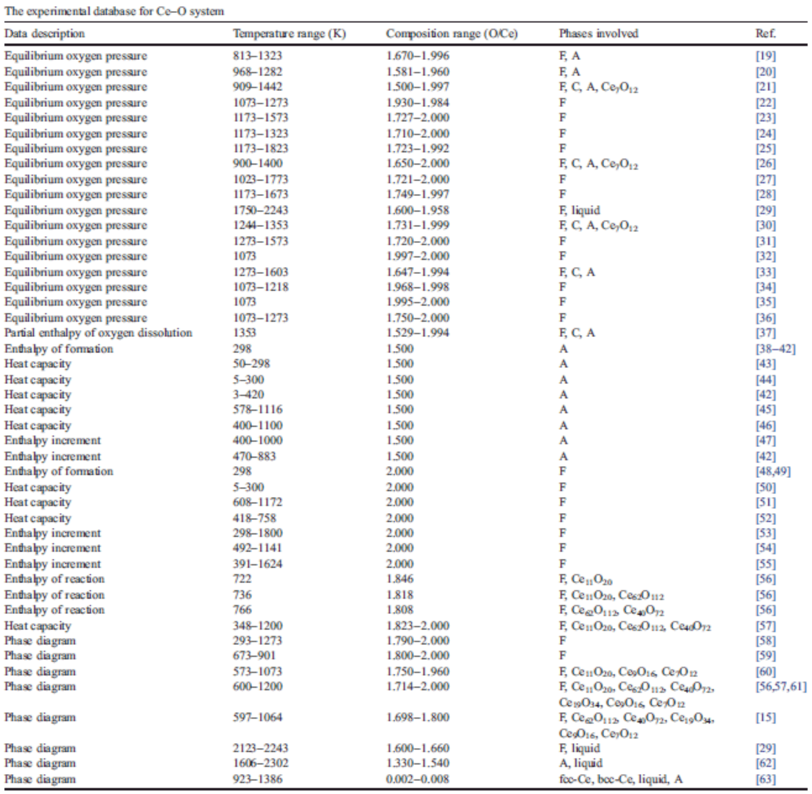
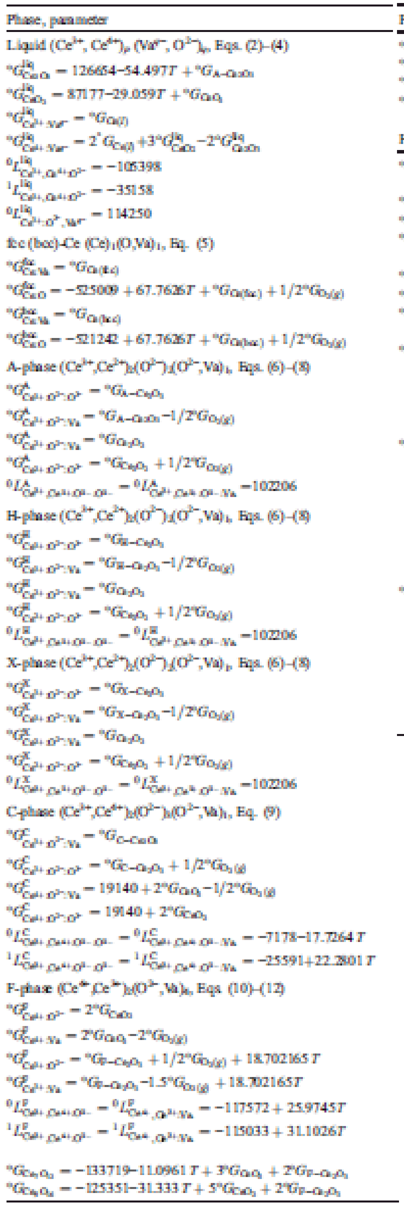


The experimental database for Ce–O system

Data description	Temperature range (K)	Composition range (O/Ce)	Phases involved	Ref.
Equilibrium oxygen pressure	813–1323	1.670–1.996	F, A	[19]
Equilibrium oxygen pressure	968–1282	1.581–1.960	F, A	[20]
Equilibrium oxygen pressure	909–1442	1.500–1.997	F, C, A, Ce_7O_{12}	[21]
Equilibrium oxygen pressure	1073–1273	1.930–1.984	F	[22]
Equilibrium oxygen pressure	1173–1573	1.727–2.000	F	[23]
Equilibrium oxygen pressure	1173–1323	1.710–2.000	F	[24]
Equilibrium oxygen pressure	1173–1823	1.723–1.992	F	[25]
Equilibrium oxygen pressure	900–1400	1.650–2.000	F, C, A, Ce_7O_{12}	[26]
Equilibrium oxygen pressure	1023–1773	1.721–2.000	F	[27]
Equilibrium oxygen pressure	1173–1673	1.749–1.997	F	[28]
Equilibrium oxygen pressure	1750–2243	1.600–1.958	F, liquid	[29]
Equilibrium oxygen pressure	1244–1353	1.731–1.999	F, C, A, Ce_7O_{12}	[30]
Equilibrium oxygen pressure	1273–1573	1.720–2.000	F	[31]
Equilibrium oxygen pressure	1073	1.997–2.000	F	[32]
Equilibrium oxygen pressure	1273–1603	1.647–1.994	F, C, A	[33]
Equilibrium oxygen pressure	1073–1218	1.968–1.998	F	[34]
Equilibrium oxygen pressure	1073	1.995–2.000	F	[35]
Equilibrium oxygen pressure	1073–1273	1.750–2.000	F	[36]
Partial enthalpy of oxygen dissolution	1353	1.529–1.994	F, C, A	[37]
Enthalpy of formation	298	1.500	A	[38–42]
Heat capacity	50–298	1.500	A	[43]
Heat capacity	5–300	1.500	A	[44]
Heat capacity	3–420	1.500	A	[42]
Heat capacity	578–1116	1.500	A	[45]
Heat capacity	400–1100	1.500	A	[46]
Enthalpy increment	400–1000	1.500	A	[47]
Enthalpy increment	470–883	1.500	A	[42]
Enthalpy of formation	298	2.000	F	[48,49]
Heat capacity	5–300	2.000	F	[50]
Heat capacity	608–1172	2.000	F	[51]
Heat capacity	418–758	2.000	F	[52]
Enthalpy increment	298–1800	2.000	F	[53]
Enthalpy increment	492–1141	2.000	F	[54]
Enthalpy increment	391–1624	2.000	F	[55]
Enthalpy of reaction	722	1.846	F, $Ce_{11}O_{20}$	[56]
Enthalpy of reaction	736	1.818	F, $Ce_{11}O_{20}$, $Ce_{62}O_{112}$	[56]
Enthalpy of reaction	766	1.808	F, $Ce_{62}O_{112}$, $Ce_{40}O_{72}$	[56]
Heat capacity	348–1200	1.823–2.000	F, $Ce_{11}O_{20}$, $Ce_{62}O_{112}$, $Ce_{40}O_{72}$	[57]
Phase diagram	293–1273	1.790–2.000	F	[58]
Phase diagram	673–901	1.800–2.000	F	[59]
Phase diagram	573–1073	1.750–1.960	F, $Ce_{11}O_{20}$, Ce_9O_{16}, Ce_7O_{12}	[60]
Phase diagram	600–1200	1.714–2.000	F, $Ce_{11}O_{20}$, $Ce_{62}O_{112}$, $Ce_{40}O_{72}$, $Ce_{19}O_{34}$, Ce_9O_{16}, Ce_7O_{12}	[56,57,61]
Phase diagram	597–1064	1.698–1.800	F, $Ce_{62}O_{112}$, $Ce_{40}O_{72}$, $Ce_{19}O_{34}$, Ce_9O_{16}, Ce_7O_{12}	[15]
Phase diagram	2123–2243	1.600–1.660	F, liquid	[29]
Phase diagram	1606–2302	1.330–1.540	A, liquid	[62]
Phase diagram	923–1386	0.002–0.008	fcc-Ce, bcc-Ce, liquid, A	[63]



Phase, parameter

Liquid $(\mathrm{Ce^{3+},Ce^{4+}})_p(\mathrm{Va^{q-},O^{2-}})_q$, Eqs. (2)–(4)

$^{\circ}G^{\mathrm{liq}}_{\mathrm{Ce_2O_3}} = 126654-54.497T + {}^{\circ}G_{\mathrm{A-Ce_2O_3}}$

$^{\circ}G^{\mathrm{liq}}_{\mathrm{CeO_2}} = 87177-29.059T + {}^{\circ}G_{\mathrm{CeO_2}}$

$^{\circ}G^{\mathrm{liq}}_{\mathrm{Ce^{3+}:Va^{q-}}} = {}^{\circ}G_{\mathrm{Ce(l)}}$

$^{\circ}G^{\mathrm{liq}}_{\mathrm{Ce^{4+}:Va^{q-}}} = 2\,{}^{\circ}G_{\mathrm{Ce(l)}} + 3\,{}^{\circ}G^{\mathrm{liq}}_{\mathrm{CeO_2}} - 2\,{}^{\circ}G^{\mathrm{liq}}_{\mathrm{Ce_2O_3}}$

$^{0}L^{\mathrm{liq}}_{\mathrm{Ce^{3+},Ce^{4+}:O^{2-}}} = -105398$

$^{1}L^{\mathrm{liq}}_{\mathrm{Ce^{3+},Ce^{4+}:O^{2-}}} = -35158$

$^{0}L^{\mathrm{liq}}_{\mathrm{Ce^{3+}:O^{2-},Va^{q-}}} = 114250$

fcc (bcc)-Ce $(\mathrm{Ce})_1(\mathrm{O,Va})_1$, Eq. (5)

$^{\circ}G^{\mathrm{fcc}}_{\mathrm{Ce:Va}} = {}^{\circ}G_{\mathrm{Ce(fcc)}}$

$^{\circ}G^{\mathrm{fcc}}_{\mathrm{Ce:O}} = -525009 + 67.7626T + {}^{\circ}G_{\mathrm{Ce(fcc)}} + 1/2\,{}^{\circ}G_{\mathrm{O_2(g)}}$

$^{\circ}G^{\mathrm{bcc}}_{\mathrm{Ce:Va}} = {}^{\circ}G_{\mathrm{Ce(bcc)}}$

$^{\circ}G^{\mathrm{bcc}}_{\mathrm{Ce:O}} = -521242 + 67.7626T + {}^{\circ}G_{\mathrm{Ce(bcc)}} + 1/2\,{}^{\circ}G_{\mathrm{O_2(g)}}$

A-phase $(\mathrm{Ce^{3+},Ce^{4+}})_2(\mathrm{O^{2-}})_2(\mathrm{O^{2-},Va})_1$, Eqs. (6)–(8)

$^{\circ}G^{\mathrm{A}}_{\mathrm{Ce^{3+}:O^{2-}:O^{2-}}} = {}^{\circ}G_{\mathrm{A-Ce_2O_3}}$

$^{\circ}G^{\mathrm{A}}_{\mathrm{Ce^{3+}:O^{2-}:Va}} = {}^{\circ}G_{\mathrm{A-Ce_2O_3}} - 1/2\,{}^{\circ}G_{\mathrm{O_2(g)}}$

$^{\circ}G^{\mathrm{A}}_{\mathrm{Ce^{4+}:O^{2-}:Va}} = {}^{\circ}G_{\mathrm{Ce_2O_3}}$

$^{\circ}G^{\mathrm{A}}_{\mathrm{Ce^{4+}:O^{2-}:O^{2-}}} = {}^{\circ}G_{\mathrm{Ce_2O_3}} + 1/2\,{}^{\circ}G_{\mathrm{O_2(g)}}$

$^{0}L^{\mathrm{A}}_{\mathrm{Ce^{3+},Ce^{4+}:O^{2-}:O^{2-}}} = {}^{0}L^{\mathrm{A}}_{\mathrm{Ce^{3+},Ce^{4+}:O^{2-}:Va}} = -102206$

H-phase $(\mathrm{Ce^{3+},Ce^{4+}})_2(\mathrm{O^{2-}})_2(\mathrm{O^{2-},Va})_1$, Eqs. (6)–(8)

$^{\circ}G^{\mathrm{H}}_{\mathrm{Ce^{3+}:O^{2-}:O^{2-}}} = {}^{\circ}G_{\mathrm{H-Ce_2O_3}}$

$^{\circ}G^{\mathrm{H}}_{\mathrm{Ce^{3+}:O^{2-}:Va}} = {}^{\circ}G_{\mathrm{H-Ce_2O_3}} - 1/2\,{}^{\circ}G_{\mathrm{O_2(g)}}$

$^{\circ}G^{\mathrm{H}}_{\mathrm{Ce^{4+}:O^{2-}:Va}} = {}^{\circ}G_{\mathrm{Ce_2O_3}}$

$^{\circ}G^{\mathrm{H}}_{\mathrm{Ce^{4+}:O^{2-}:O^{2-}}} = {}^{\circ}G_{\mathrm{Ce_2O_3}} + 1/2\,{}^{\circ}G_{\mathrm{O_2(g)}}$

$^{0}L^{\mathrm{H}}_{\mathrm{Ce^{3+},Ce^{4+}:O^{2-}:O^{2-}}} = {}^{0}L^{\mathrm{H}}_{\mathrm{Ce^{3+},Ce^{4+}:O^{2-}:Va}} = -102206$

X-phase $(\mathrm{Ce^{3+},Ce^{4+}})_2(\mathrm{O^{2-}})_2(\mathrm{O^{2-},Va})_1$, Eqs. (6)–(8)

$^{\circ}G^{\mathrm{X}}_{\mathrm{Ce^{3+}:O^{2-}:O^{2-}}} = {}^{\circ}G_{\mathrm{X-Ce_2O_3}}$

$^{\circ}G^{\mathrm{X}}_{\mathrm{Ce^{3+}:O^{2-}:Va}} = {}^{\circ}G_{\mathrm{X-Ce_2O_3}} - 1/2\,{}^{\circ}G_{\mathrm{O_2(g)}}$

$^{\circ}G^{\mathrm{X}}_{\mathrm{Ce^{4+}:O^{2-}:Va}} = {}^{\circ}G_{\mathrm{Ce_2O_3}}$

$^{\circ}G^{\mathrm{X}}_{\mathrm{Ce^{4+}:O^{2-}:O^{2-}}} = {}^{\circ}G_{\mathrm{Ce_2O_3}} + 1/2\,{}^{\circ}G_{\mathrm{O_2(g)}}$

$^{0}L^{\mathrm{X}}_{\mathrm{Ce^{3+},Ce^{4+}:O^{2-}:O^{2-}}} = {}^{0}L^{\mathrm{X}}_{\mathrm{Ce^{3+},Ce^{4+}:O^{2-}:Va}} = -102206$

C-phase $(\mathrm{Ce^{3+},Ce^{4+}})_2(\mathrm{O^{2-}})_3(\mathrm{O^{2-},Va})_1$, Eq. (9)

$^{\circ}G^{\mathrm{C}}_{\mathrm{Ce^{3+}:O^{2-}:Va}} = {}^{\circ}G_{\mathrm{C-Ce_2O_3}}$

$^{\circ}G^{\mathrm{C}}_{\mathrm{Ce^{3+}:O^{2-}:O^{2-}}} = {}^{\circ}G_{\mathrm{C-Ce_2O_3}} + 1/2\,{}^{\circ}G_{\mathrm{O_2(g)}}$

$^{\circ}G^{\mathrm{C}}_{\mathrm{Ce^{4+}:O^{2-}:Va}} = 19140 + 2\,{}^{\circ}G_{\mathrm{CeO_2}} - 1/2\,{}^{\circ}G_{\mathrm{O_2(g)}}$

$^{\circ}G^{\mathrm{C}}_{\mathrm{Ce^{4+}:O^{2-}:O^{2-}}} = 19140 + 2\,{}^{\circ}G_{\mathrm{CeO_2}}$

$^{0}L^{\mathrm{C}}_{\mathrm{Ce^{3+},Ce^{4+}:O^{2-}:O^{2-}}} = {}^{0}L^{\mathrm{C}}_{\mathrm{Ce^{3+},Ce^{4+}:O^{2-}:Va}} = -7178-17.7264T$

$^{1}L^{\mathrm{C}}_{\mathrm{Ce^{3+},Ce^{4+}:O^{2-}:O^{2-}}} = {}^{1}L^{\mathrm{C}}_{\mathrm{Ce^{3+},Ce^{4+}:O^{2-}:Va}} = -25591+22.2801T$

F-phase $(\mathrm{Ce^{4+},Ce^{3+}})_2(\mathrm{O^{2-},Va})_4$, Eqs. (10)–(12)

$^{\circ}G^{\mathrm{F}}_{\mathrm{Ce^{4+}:O^{2-}}} = 2\,{}^{\circ}G_{\mathrm{CeO_2}}$

$^{\circ}G^{\mathrm{F}}_{\mathrm{Ce^{4+}:Va}} = 2\,{}^{\circ}G_{\mathrm{CeO_2}} - 2\,{}^{\circ}G_{\mathrm{O_2(g)}}$

$^{\circ}G^{\mathrm{F}}_{\mathrm{Ce^{3+}:O^{2-}}} = {}^{\circ}G_{\mathrm{F-Ce_2O_3}} + 1/2\,{}^{\circ}G_{\mathrm{O_2(g)}} + 18.702165T$

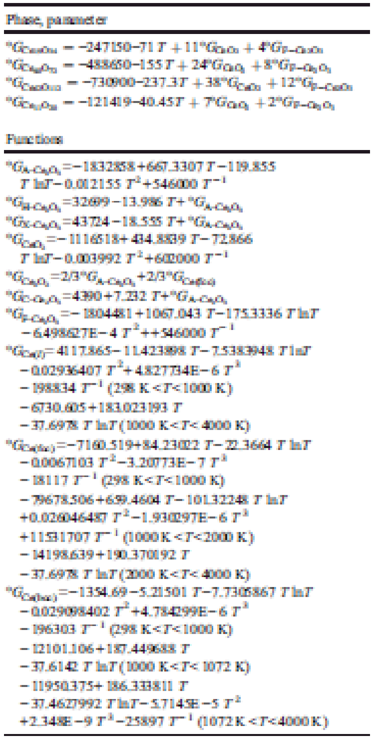
$^{\circ}G^{\mathrm{F}}_{\mathrm{Ce^{3+}:Va}} = {}^{\circ}G_{\mathrm{F-Ce_2O_3}} - 1.5\,{}^{\circ}G_{\mathrm{O_2(g)}} + 18.702165T$

$^{0}L^{\mathrm{F}}_{\mathrm{Ce^{3+},Ce^{4+}:O^{2-}}} = {}^{0}L^{\mathrm{F}}_{\mathrm{Ce^{4+},Ce^{3+}:Va}} = -117572 + 25.9745T$

$^{1}L^{\mathrm{F}}_{\mathrm{Ce^{3+},Ce^{4+}:O^{2-}}} = {}^{1}L^{\mathrm{F}}_{\mathrm{Ce^{4+},Ce^{3+}:Va}} = -115033 + 31.1026T$

$^{\circ}G_{\mathrm{Ce_7O_{12}}} = -133719-11.0961\,T + 3\,{}^{\circ}G_{\mathrm{CeO_2}} + 2\,{}^{\circ}G_{\mathrm{F-Ce_2O_3}}$

$^{\circ}G_{\mathrm{Ce_9O_{16}}} = -125351-31.333\,T + 5\,{}^{\circ}G_{\mathrm{CeO_2}} + 2\,{}^{\circ}G_{\mathrm{F-Ce_2O_3}}$



Phase, parameter

$^{\circ}G_{\mathrm{Ce_{19}O_{34}}} = -247150-71\,T + 11\,{}^{\circ}G_{\mathrm{CeO_2}} + 4\,{}^{\circ}G_{\mathrm{F-Ce_2O_3}}$

$^{\circ}G_{\mathrm{Ce_{40}O_{72}}} = -488650-155\,T + 24\,{}^{\circ}G_{\mathrm{CeO_2}} + 8\,{}^{\circ}G_{\mathrm{F-Ce_2O_3}}$

$^{\circ}G_{\mathrm{Ce_{62}O_{112}}} = -730900-237.3T + 38\,{}^{\circ}G_{\mathrm{CeO_2}} + 12\,{}^{\circ}G_{\mathrm{F-Ce_2O_3}}$

$^{\circ}G_{\mathrm{Ce_{11}O_{20}}} = -121419-40.45T + 7\,{}^{\circ}G_{\mathrm{CeO_2}} + 2\,{}^{\circ}G_{\mathrm{F-Ce_2O_3}}$

Functions

$^{\circ}G_{\mathrm{A-Ce_2O_3}} = -1832858+667.3307\,T-119.855$
$T\ln T - 0.012155\,T^2 + 546000\,T^{-1}$

$^{\circ}G_{\mathrm{H-Ce_2O_3}} = 32699-13.986\,T + {}^{\circ}G_{\mathrm{A-Ce_2O_3}}$

$^{\circ}G_{\mathrm{X-Ce_2O_3}} = 43724-18.555\,T + {}^{\circ}G_{\mathrm{A-Ce_2O_3}}$

$^{\circ}G_{\mathrm{CeO_2}} = -1116518+434.8839\,T-72.866$
$T\ln T - 0.003992\,T^2 + 602000\,T^{-1}$

$^{\circ}G_{\mathrm{Ce_2O_3}} = 2/3\,{}^{\circ}G_{\mathrm{A-Ce_2O_3}} + 2/3\,{}^{\circ}G_{\mathrm{Ce(fcc)}}$

$^{\circ}G_{\mathrm{C-Ce_2O_3}} = 4390+7.232\,T + {}^{\circ}G_{\mathrm{A-Ce_2O_3}}$

$^{\circ}G_{\mathrm{F-Ce_2O_3}} = -1804481+1067.043\,T-175.3336\,T\ln T$
$-6.498627\mathrm{E}-4\,T^2 + +546000\,T^{-1}$

$^{\circ}G_{\mathrm{Ce(l)}} = 4117.865-11.423898\,T-7.5383948\,T\ln T$
$-0.02936407\,T^2 + 4.827734\mathrm{E}-6\,T^3$
$-198834\,T^{-1}$ (298 K $< T <$ 1000 K)
$-6730.605+183.023193\,T$
$-37.6978\,T\ln T$ (1000 K $< T <$ 4000 K)

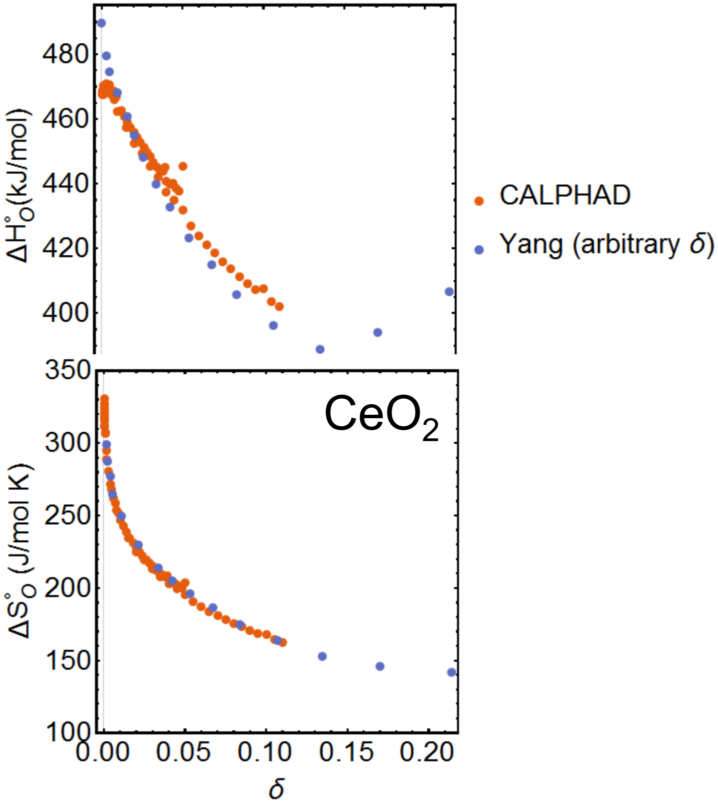
$^{\circ}G_{\mathrm{Ce(fcc)}} = -7160.519+84.23022\,T-22.3664\,T\ln T$
$-0.0067103\,T^2 - 3.20773\mathrm{E}-7\,T^3$
$-18117\,T^{-1}$ (298 K $< T <$ 1000 K)
$-79678.506+659.4604\,T-101.32248\,T\ln T$
$+0.026046487\,T^2 - 1.930297\mathrm{E}-6\,T^3$
$+11531707\,T^{-1}$ (1000 K $< T <$ 2000 K)
$-14198.639+190.370192\,T$
$-37.6978\,T\ln T$ (2000 K $< T <$ 4000 K)

$^{\circ}G_{\mathrm{Ce(bcc)}} = -1354.69-5.21501\,T-7.7305867\,T\ln T$
$-0.029098402\,T^2 + 4.784299\mathrm{E}-6\,T^3$
$-196303\,T^{-1}$ (298 K $< T <$ 1000 K)
$-12101.106+187.449688\,T$
$-37.6142\,T\ln T$ (1000 K $< T <$ 1072 K)
$-11950.375+186.333811\,T$
$-37.4627992\,T\ln T - 5.7145\mathrm{E}-5\,T^2$
$+2.348\mathrm{E}-9\,T^3 - 25897\,T^{-1}$ (1072 K $< T <$ 4000 K)

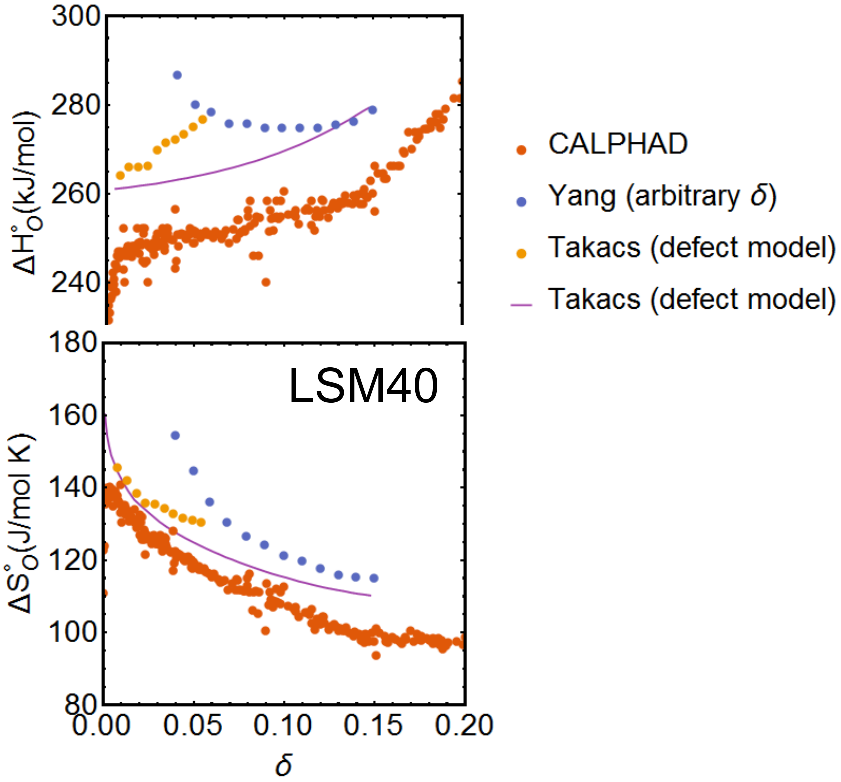
~ 50 independent observations!

species, phases, and governing equations

Comparing analysis methods using CALPHAD as ground truth



- Good agreement for the “best-known” system.



- Poor agreement for a well-known system.

C.-K. Yang et al., *Journal of Materials Chemistry A* (2014).
M. Takacs *et al.*, *Acta Materialia*. **103**, 700–710 (2016).

Reactions measured at fixed T and p_{O_2}

- What we refer to as ΔH(δ;T) and ΔS(δ;T) is really:

$$\Delta \mathrm{H}(\delta;T) = \lim_{d\delta\to 0}\frac{H_{sol}(\delta+d\delta;T)-H_{sol}(\delta;T)}{d\delta}+\frac{1}{2}H_{O_2,g}(T)$$

$$\boldsymbol{\frac{\partial H_{sol}(\delta;T)}{\partial\delta}=\frac{RT_0\partial\, ln\left(p^0/p_{O_2}\right)}{2\,\partial\left(T_0/T\right)}-\frac{1}{2}H_{O_2,g}(T)}$$

$$\Delta \mathrm{S}(\delta;T) = \lim_{d\delta\to 0}\frac{S_{sol}(\delta+d\delta;T)-S_{sol}(\delta;T)}{d\delta}+\frac{1}{2}S_{O_2,g}\left(T;p_{O_2}(\delta;T)\right)$$

$$\boldsymbol{\frac{\partial S_{sol}(\delta;T)}{\partial\delta}=\frac{-R\,\partial\, ln\left(p^0/p_{O_2}\right)}{2\,\partial\,\ln\left(T/T_0\right)}-\frac{1}{2}S_{O_2,g}\left(T;p_{O_2}(\delta;T)\right)}$$

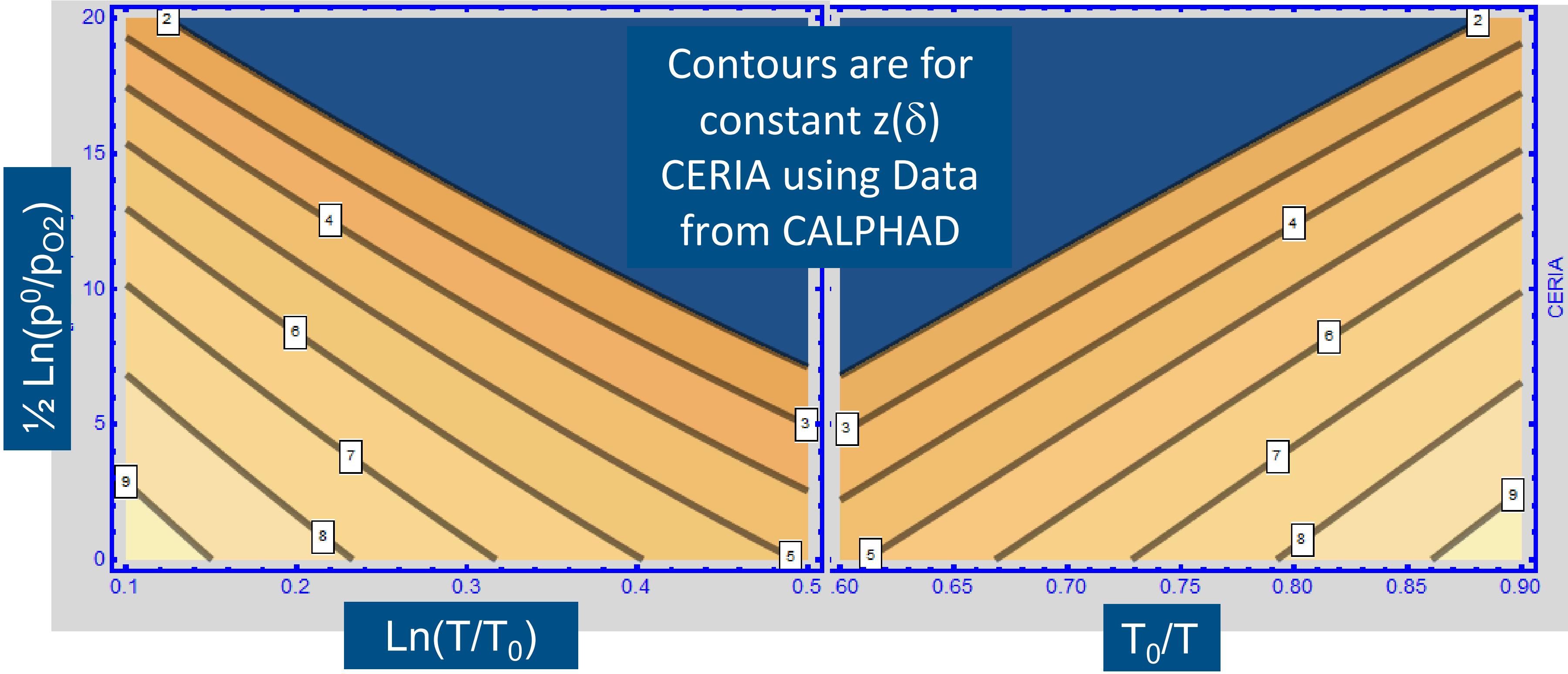
- Enthalpy and entropy of reaction (incremental change in δ) are local partial derivatives of the same function.

Knowing O_2 gas properties and equilibrium δ

- Fit a two dimensional response surface given measured triplets {T, p_{O_2}, δ} so that:
  - $z(\delta) \equiv f\left(\ln\frac{T}{T_0}, \frac{1}{2}\ln\frac{p^0}{p_{O_2}}\right)$ and
  - $\frac{1}{2}\ln\frac{p^0}{p_{O_2}} \equiv g\left(\ln\frac{T}{T_0}, z(\delta)\right)$ - convenient if easily invertible

- Take temperature derivatives of "g" from response surface to yield <u>incremental changes</u> with δ in the reaction enthalpy and entropy.
- Need reliable and reproducible (T, p_{O_2}, δ) data over a relevant range of expected conditions.
  - Low T, low P_{O2} for gas splitting
  - Avoid extrapolating outside data envelope

Initial response surface for Ceria

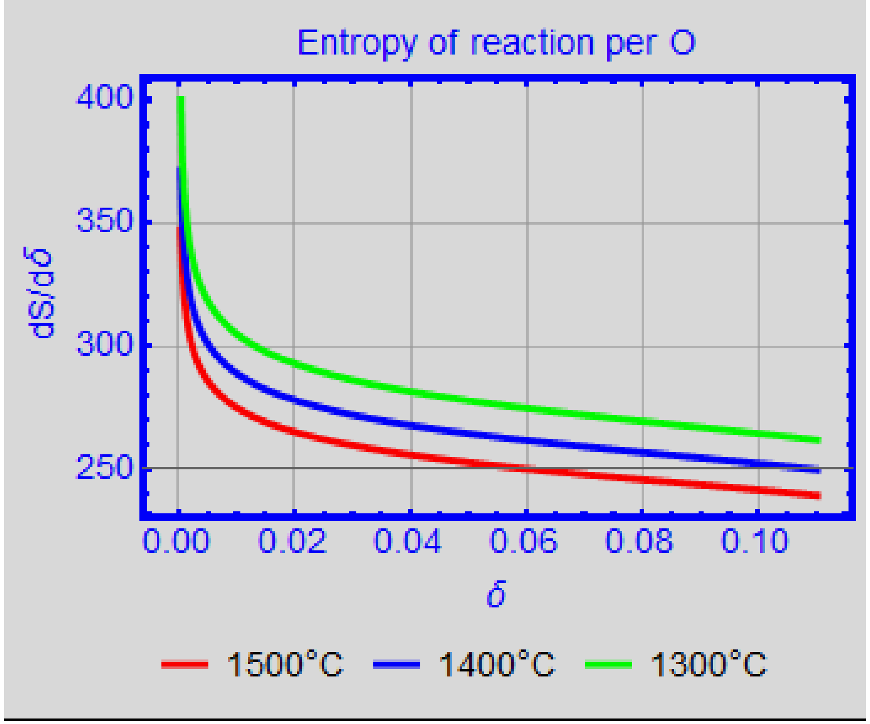


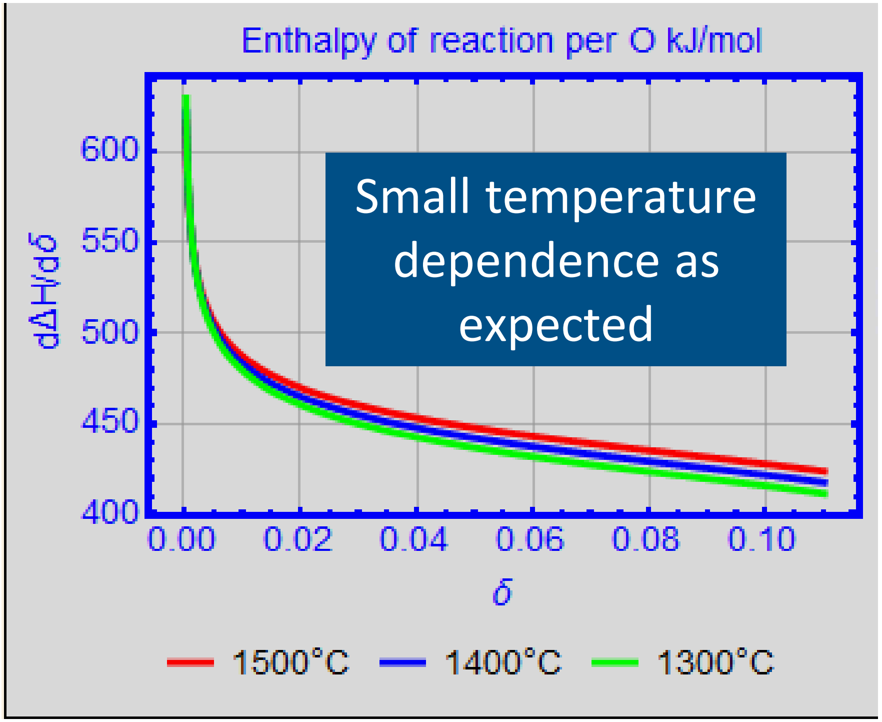
Contours are for constant z(δ) CERIA using Data from CALPHAD

Negative of the slope determines $\frac{\partial \Delta s(\delta;T)}{\partial \delta}$

Slope determines $\frac{\partial \Delta H(\delta;T)}{\partial \delta}$

Derivatives determine enthalpy and entropy of incremental reaction for Ceria



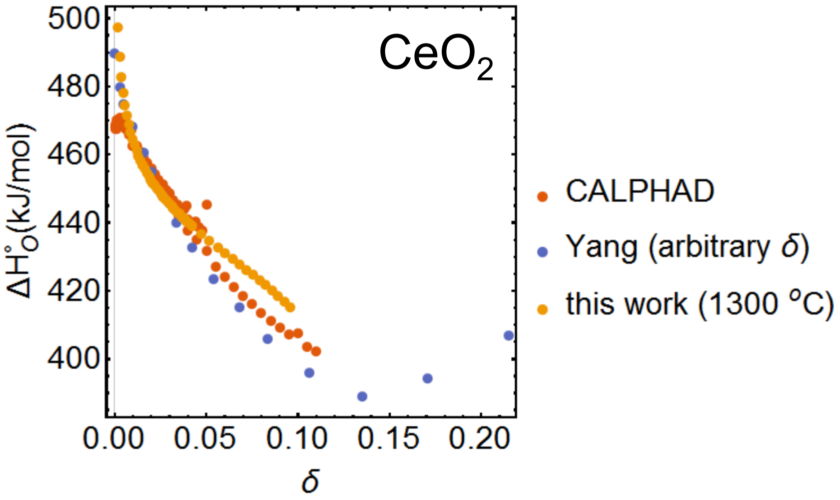


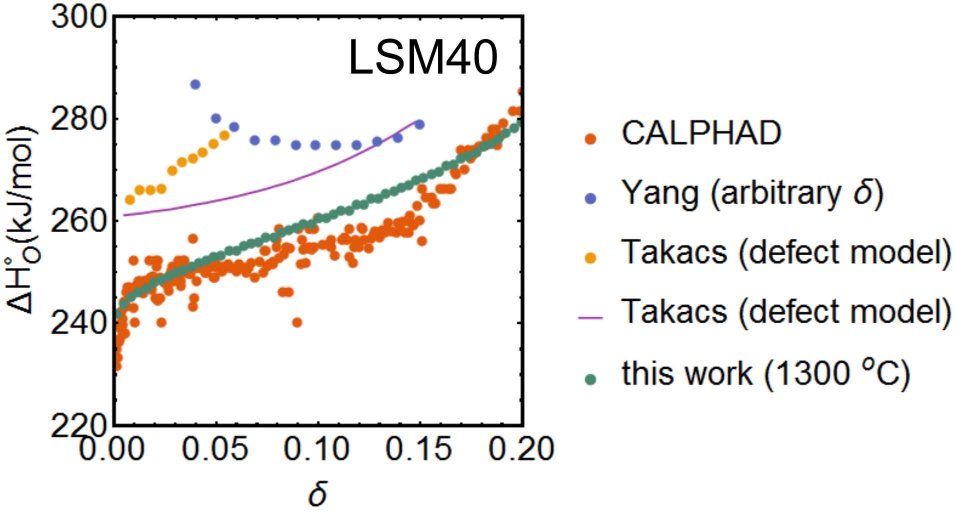
Small temperature dependence as expected

Negative of the slope and scaling R determined $\frac{\partial \Delta S(\delta;T)}{\partial \delta}$

Slope and scaling parameter RT_0 determined $\frac{\partial \Delta H(\delta;T)}{\partial \delta}$

Comparing analysis methods for ΔH(δ)





- Established a sound framework to analyze and explore material thermodynamic properties.
- Continue to refine fitting of the equilibrium response surface.

Summary and future direction

- Defect models are not needed to extract ΔH or ΔS.
- Apply advanced surface fitting strategies to further develop method (i.e., Basis Splines).
  - Caveat: ***extrapolate*** at your own peril
- Formulate new insights from manipulating thermodynamic equations.
  - Made possible by vetted response surface representative of equilibrium phase space
- Rigorously evaluate the impact of uncertainties.
  - Statistically-based UA/UQ enabled by this approach

- Leverage ideas to build consensus around standard practices.
  - Experimental protocols and benchmarked tools

Challenged by moving beyond these popular non-stoichiometric oxide material systems

Fe^{2+}/Fe^{3+} systems:

- Deep reduction at 1400 °C.
- High redox capacity ($\Delta\delta>0.1$).
- Slow H_2O oxidation kinetics.
- YSZ, ZrO_2, Al_2O_3 matrix required.

Ce^{3+}/Ce^{4+} systems:

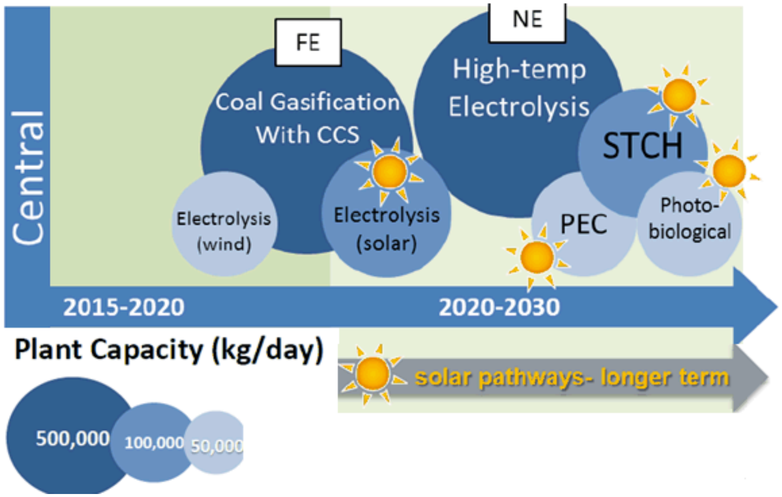
- Shallow reduction at 1500 °C.
- Low redox capacity ($\Delta\delta<0.08$).
- Fast H_2O oxidation kinetics.
- Durable.

$TM^{2+}/TM^{3+}/TM^{4+}$ perovskite systems:

- Deep reduction at 1400 °C.
- High redox capacity ($\Delta\delta>0.1$).
- Promising H_2O oxidation kinetics.
- Vast material space!

PROPERTY	FERRITE ($MFeO_x/ZrO_2$) ($MFeO_x/Al_2O_3$)	CERIA (CeO_2) Current State of the Art	PEROVSKITE (ABO_3)	IDEAL
Redox Kinetics	SLOW	FAST	?	FAST
Capacity ($\Delta\delta$)	HIGH	LOW	HIGH	HIGH
T_{TR} @ Reduction	MED/HIGH	HIGH	LOW	LOW
H_2O/H_2 @ Oxidation	MED	LOW	?	LOW
Durability	MED/HIGH	HIGH	?	HIGH
Earth Abundance	HIGH	LOW/MED	HIGH	HIGH

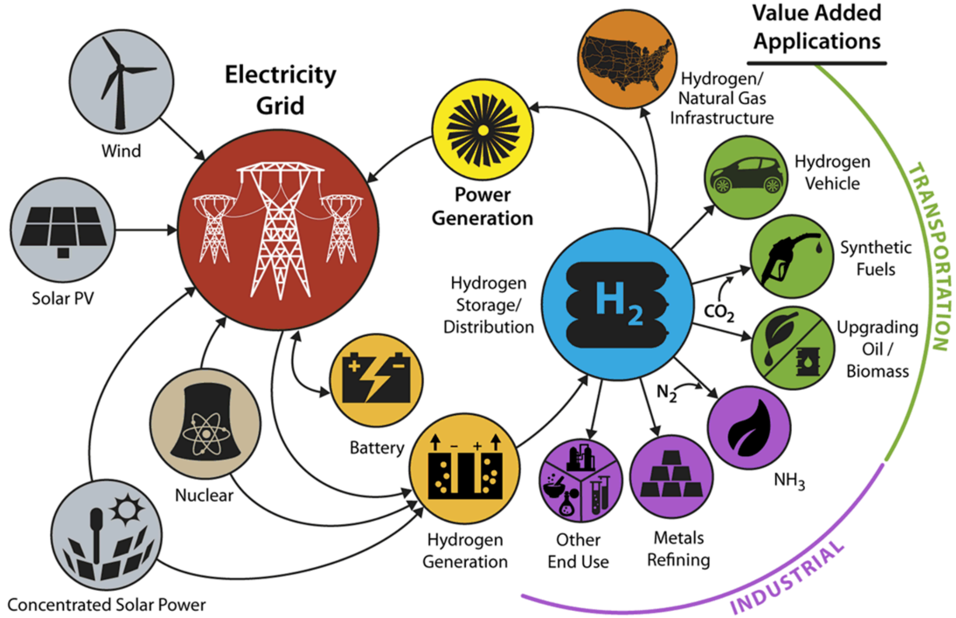
US DOE vision for H_2 production and utilization



- Multi-laboratory consortium and Energy Materials Network announced in 2016.

HydroGen
Advanced Water Splitting Materials

http://energy.gov/eere/energy-materials-network/energy-materials-network



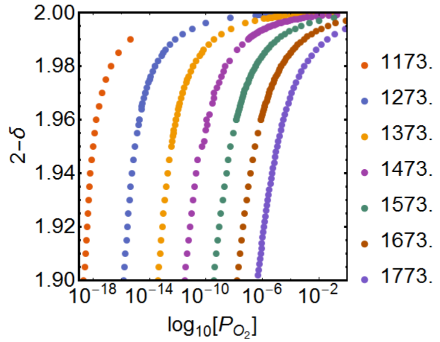
H_2 at Scale:

Deeply Decarbonizing our Energy System

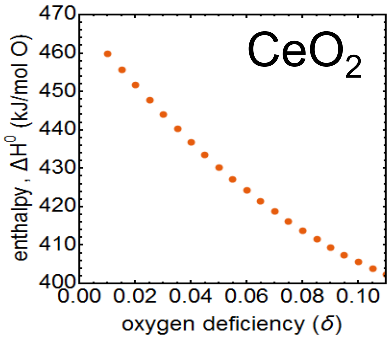
BIG IDEA

Opportunities to work with Sandia

determine P_{O2}-T-δ relation using TGA or other methods

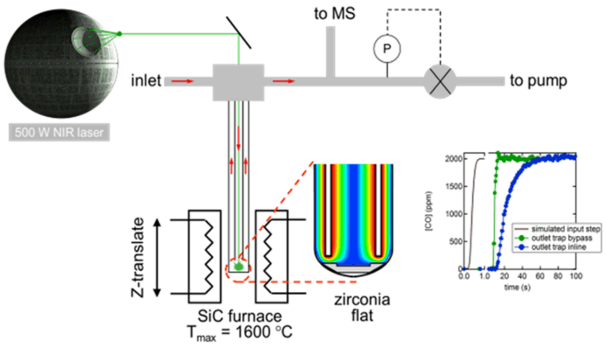


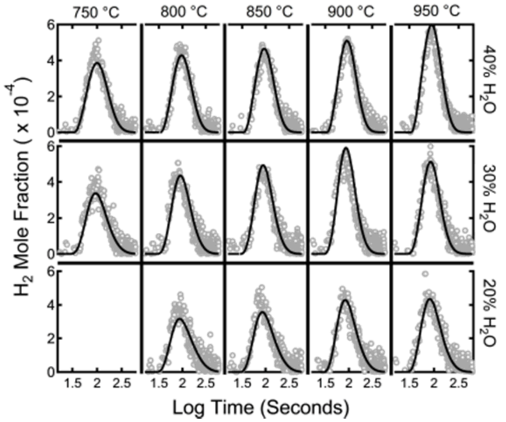
derive thermodynamic properties for material from P_{O2}-T-δ relation



- Requires high-quality experimental data over large P_{O2}-T-δ range.

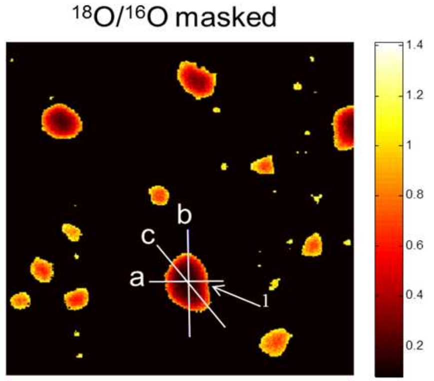
derive kinetic information at technology-specific conditions using idealized flow reactor

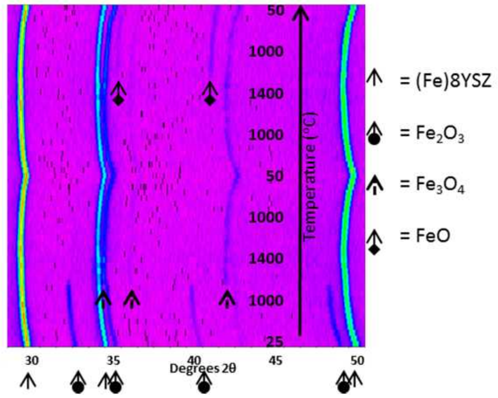




- Cycled under high radiative flux.
- Technology-specific operation.

derive structural and mechanistic information using advanced diagnostics (i.e., HTXRD, ToF-SIMS)





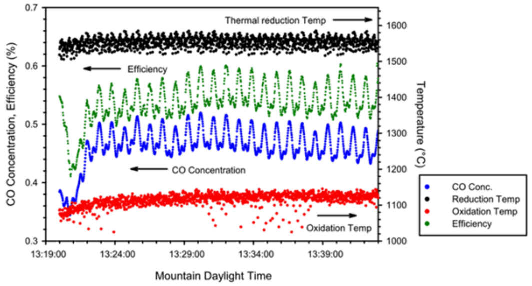
- Great potential for operando X-ray scattering.

Opportunities to work with Sandia

Sandia National Laboratories

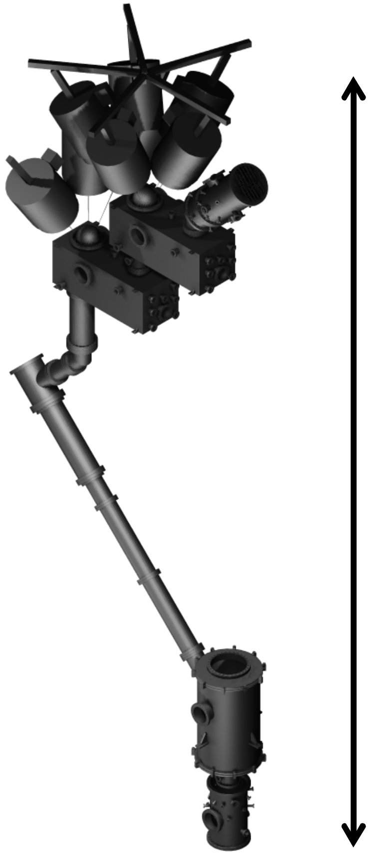
National Solar Thermal Test Facility

PATHWAY FOR ADVANCING TRL...



- 16kWth solar furnace.
- 6MW$_{th}$ power tower.
- Technology-specific operation at scale.

Cascading Pressure Receiver/Reactor (CPR2)



25 ft. tall

- ~5kW$_{th}$ system capable of producing 0.5slpm H_2.
- Derive engineering test data necessary for model validation and scale-up.

Thank you for your attention.

Questions?