Erbium-Hydrogen System: Kinetics & Thermodynamics

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Cajun Queen, June 2003

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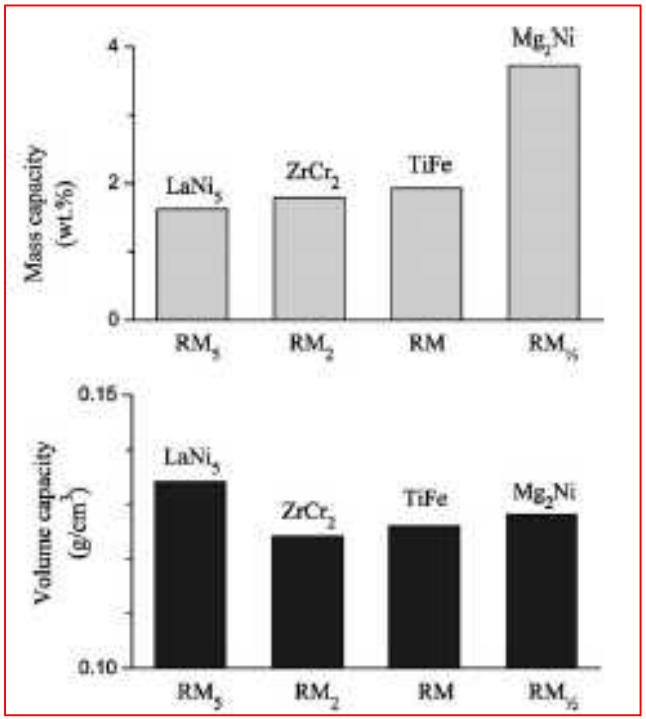
Metal Hydrides

Application: Energy Storage

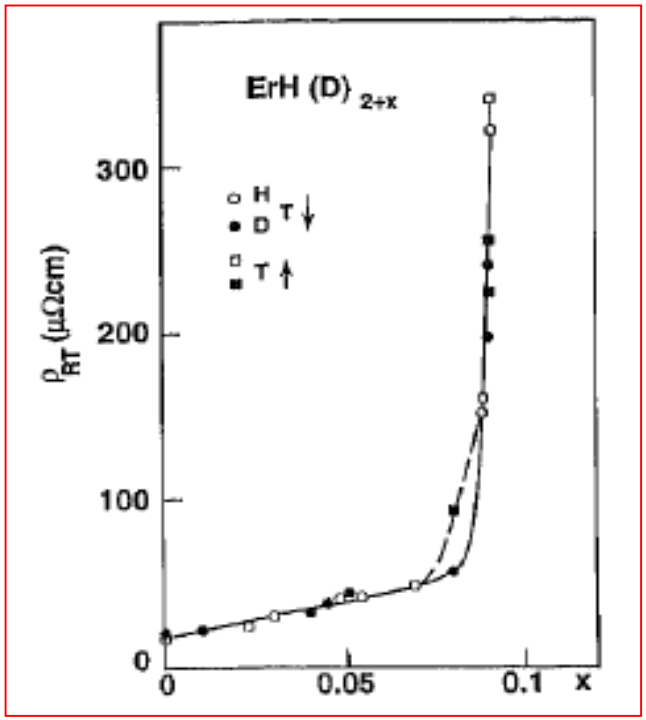
M. Latroche, Journal of Physics and Chemistry of Solids 65 (2004) 517-522



Hydrogen storage capacity of select RM_n-type metal hydrides

Application: Switchable Mirror

P. Vajda, Handbook of the Physics and Chemistry of Rare Earths Vol. 20 (1995) 207-292



Resistivity of rare earth hydrides change with composition

- **Properties (optical, mechanical, electrical, etc) change w/ composition**
- **Often, change in composition IS the property of interest**

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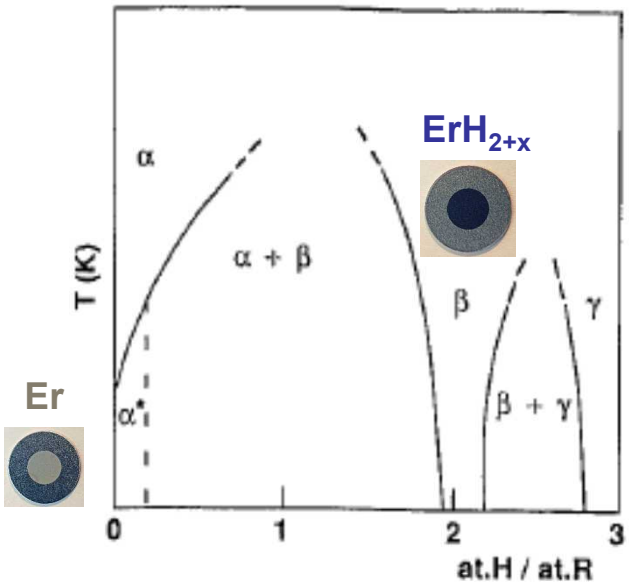
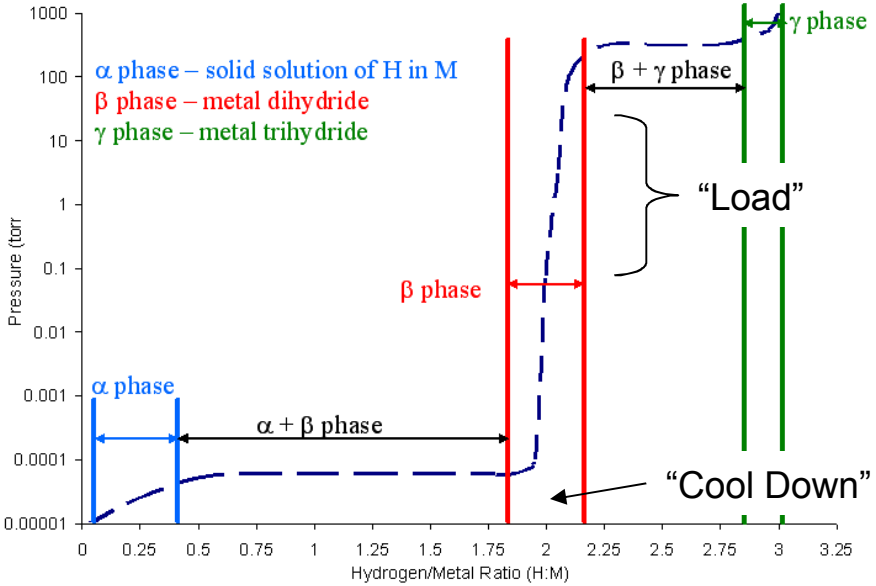
Erbium Dihydride

Rare-Earth/Hydrogen Phase Diagram



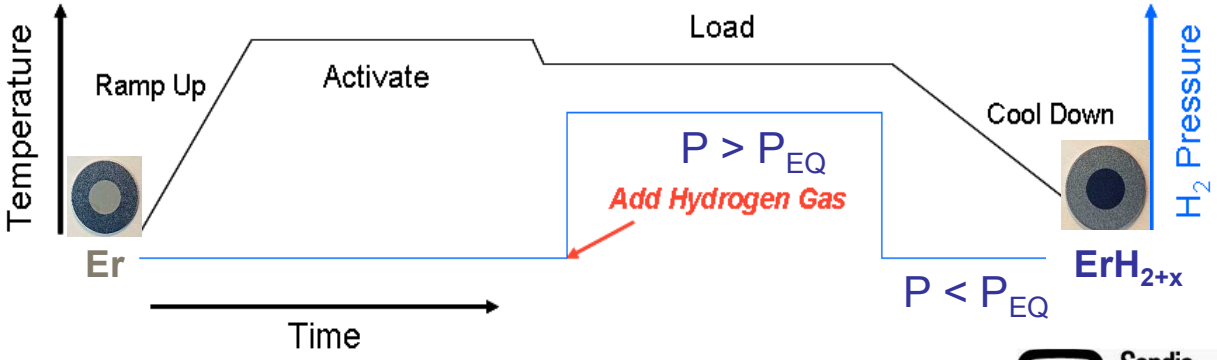
Isothermal Phase Diagram



Why ErH_2 as "base case"?

- **Interesting optical properties**
- Well-known system (PCT properties, crystal structure, etc.)
- **Verify technique --- then extend to film samples, novel materials**

Loading Process: Rare-Earth Hydride Film



Goal: control composition thru understanding of isotherms & kinetics

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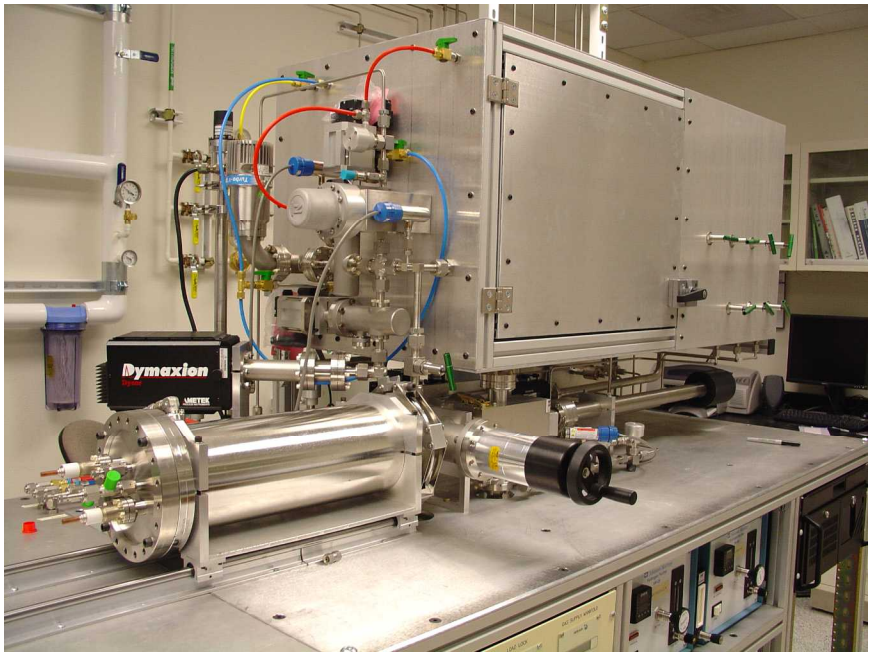
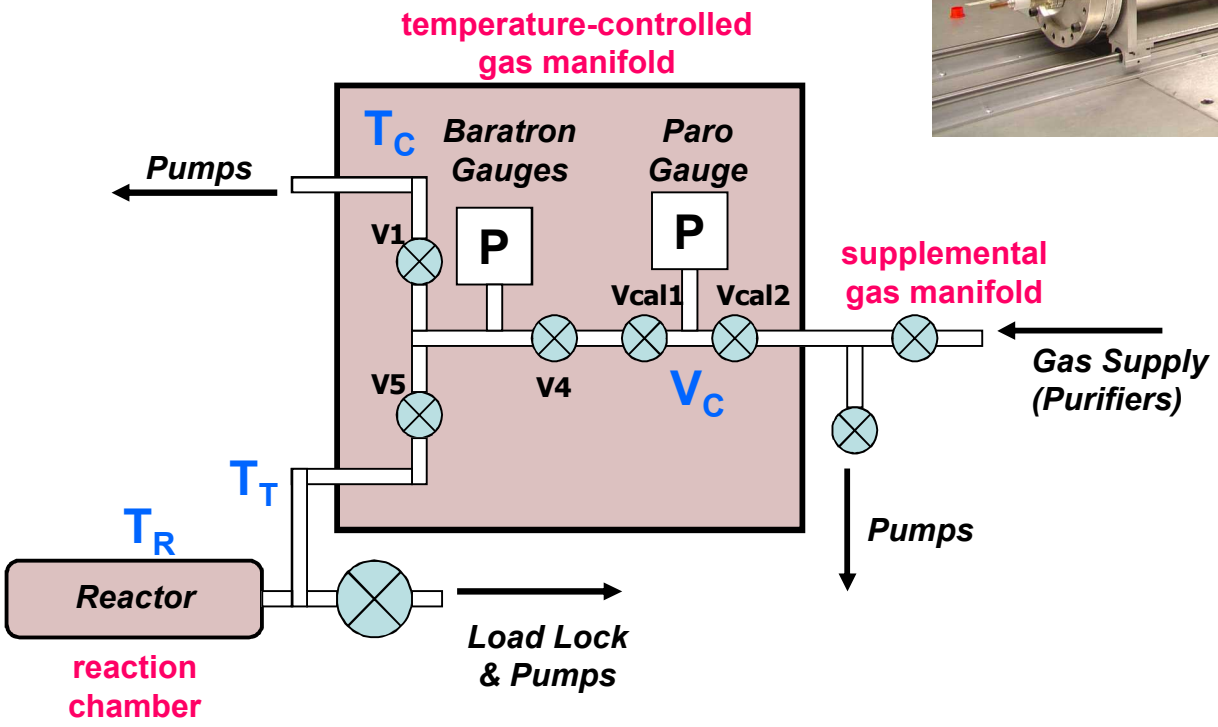
PCT Apparatus (Isotherms)

Mole Balance: $n_U = \Sigma n_{Ai} - n_G$

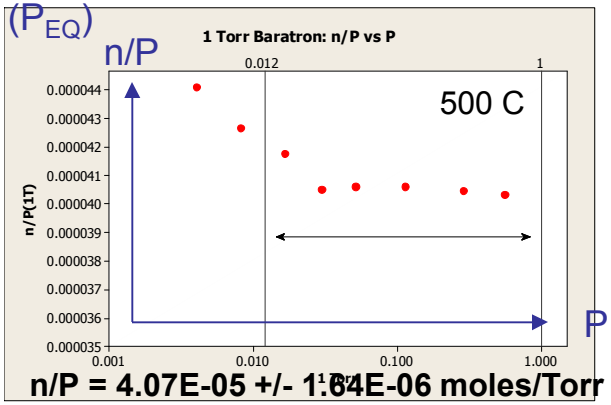
n_U = total molar uptake (H_2)
n_A = aliquot addition (H_2)
n_G = gas phase moles (H_2)

- Fill calibrated volume: $n_A \equiv P_{PARO} V_C / RT_C$)
- Expand H_2 gas to reactor
- Wait for equilibrium: $n_G \equiv f(P_{EQ})$
- Repeat





'mole meter' calibration : $n_G = f(P_{EQ})$



n/P = 4.07E-05 +/- 1.64E-06 moles/Torr

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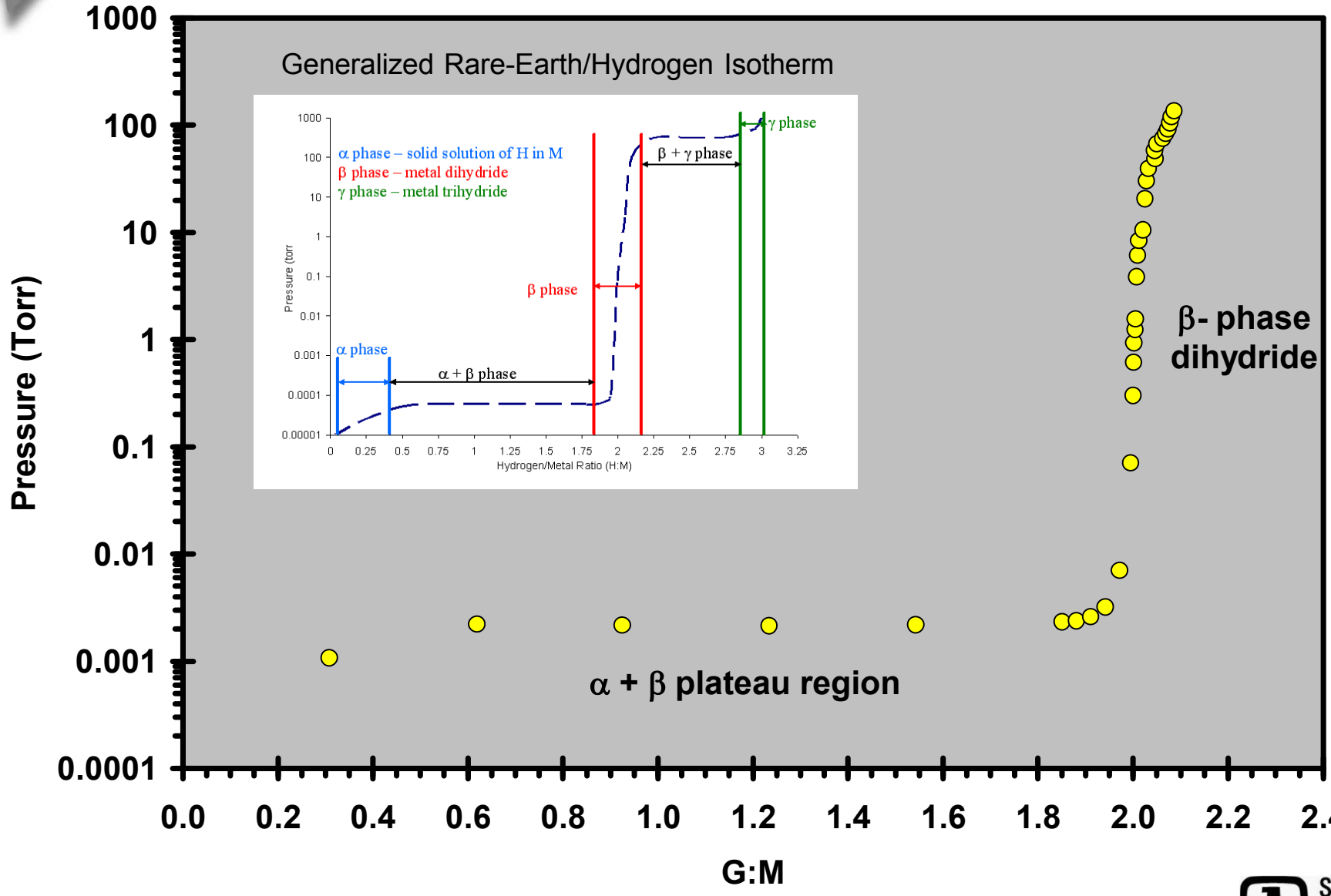
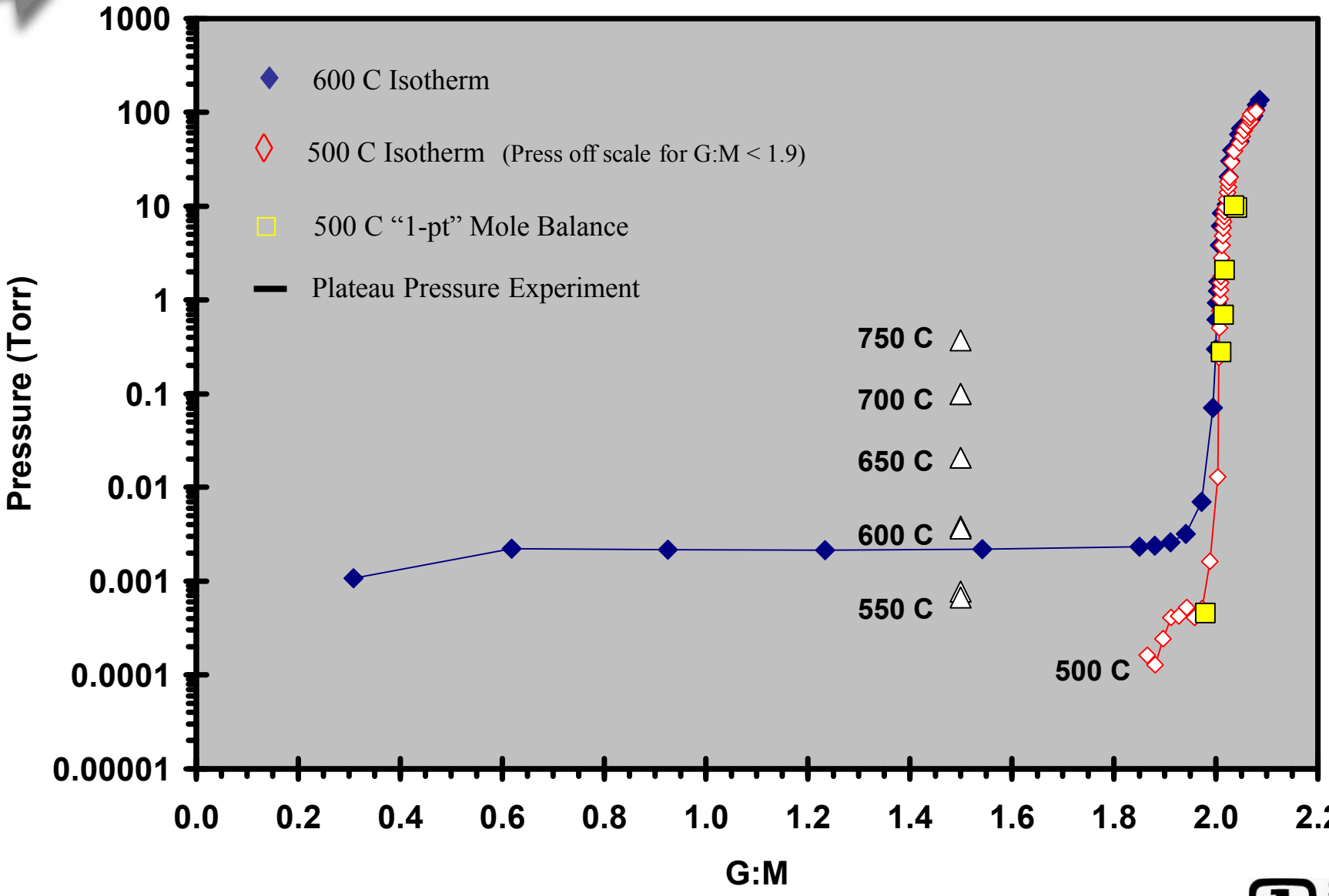
600 C Bulk Er-D Isotherm



Bulk Er-D Isotherms



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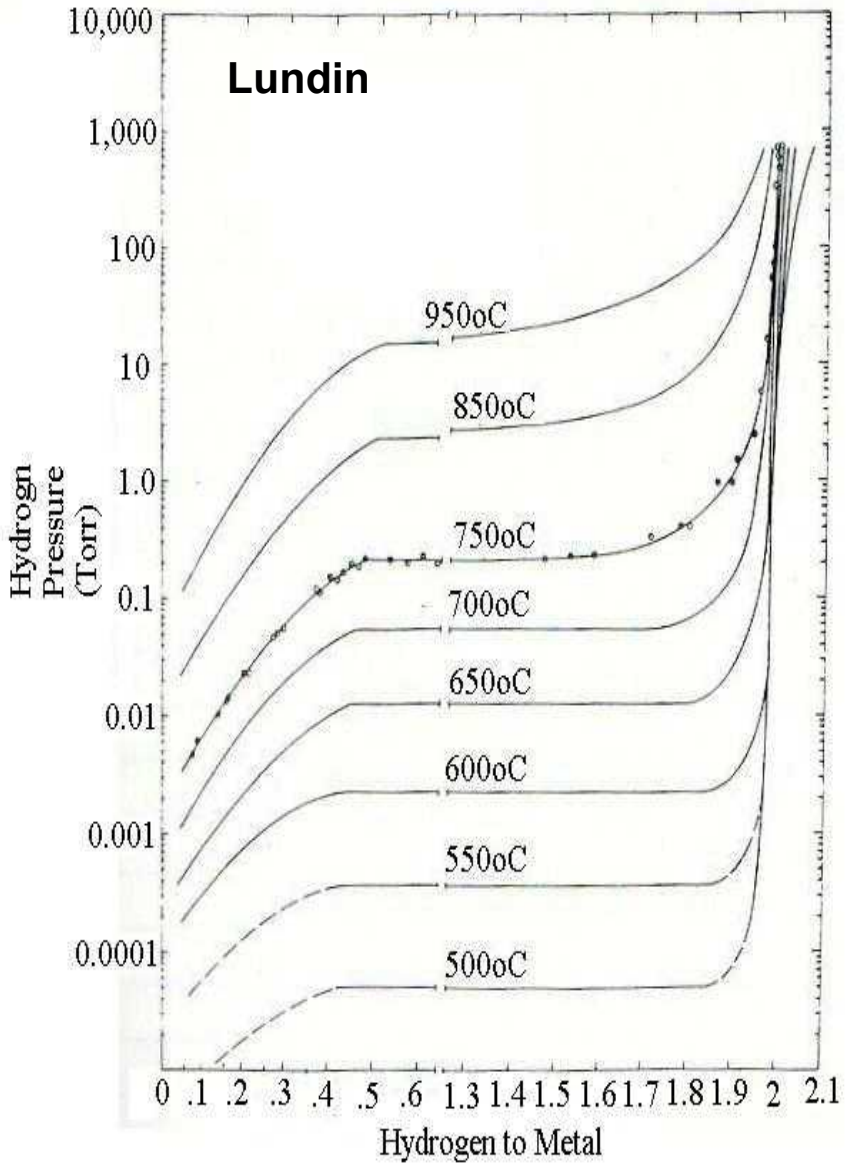
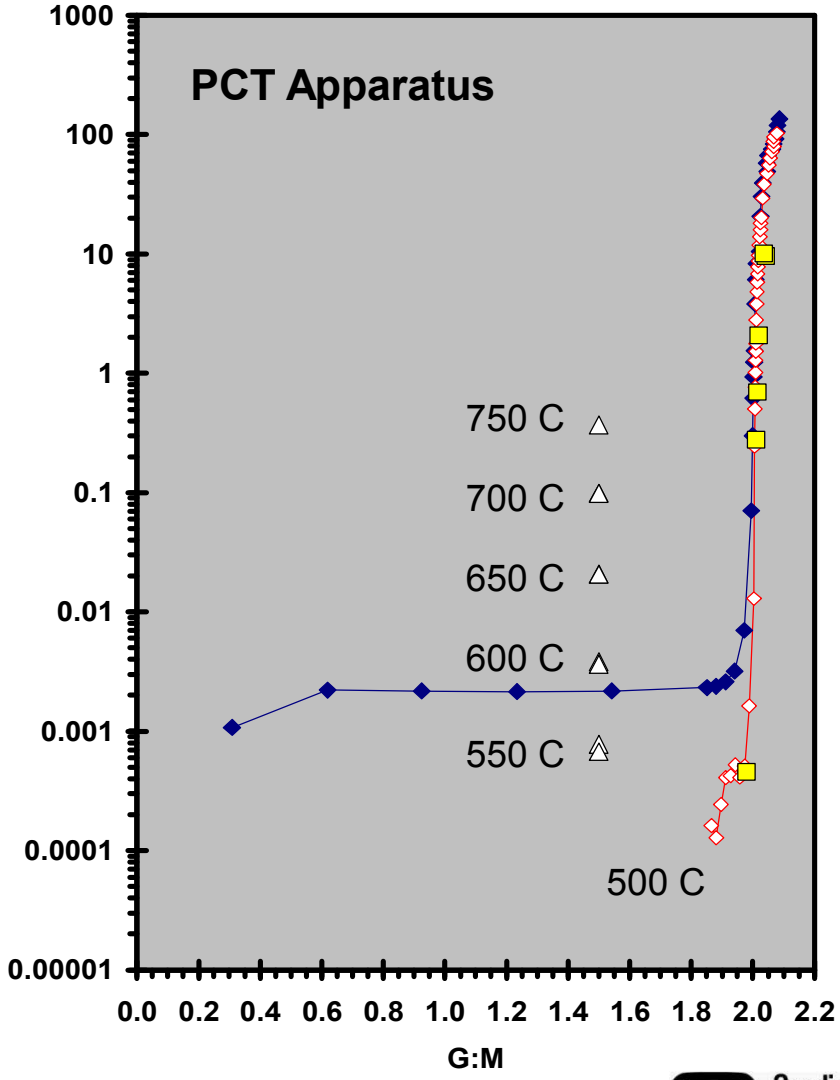
Er-D Isotherms (Comparison w/ Literature)





Lundin, C. E. (1968). "The erbium-hydrogen system." Transactions of the Metallurgical Society of AIME 242: 903-907

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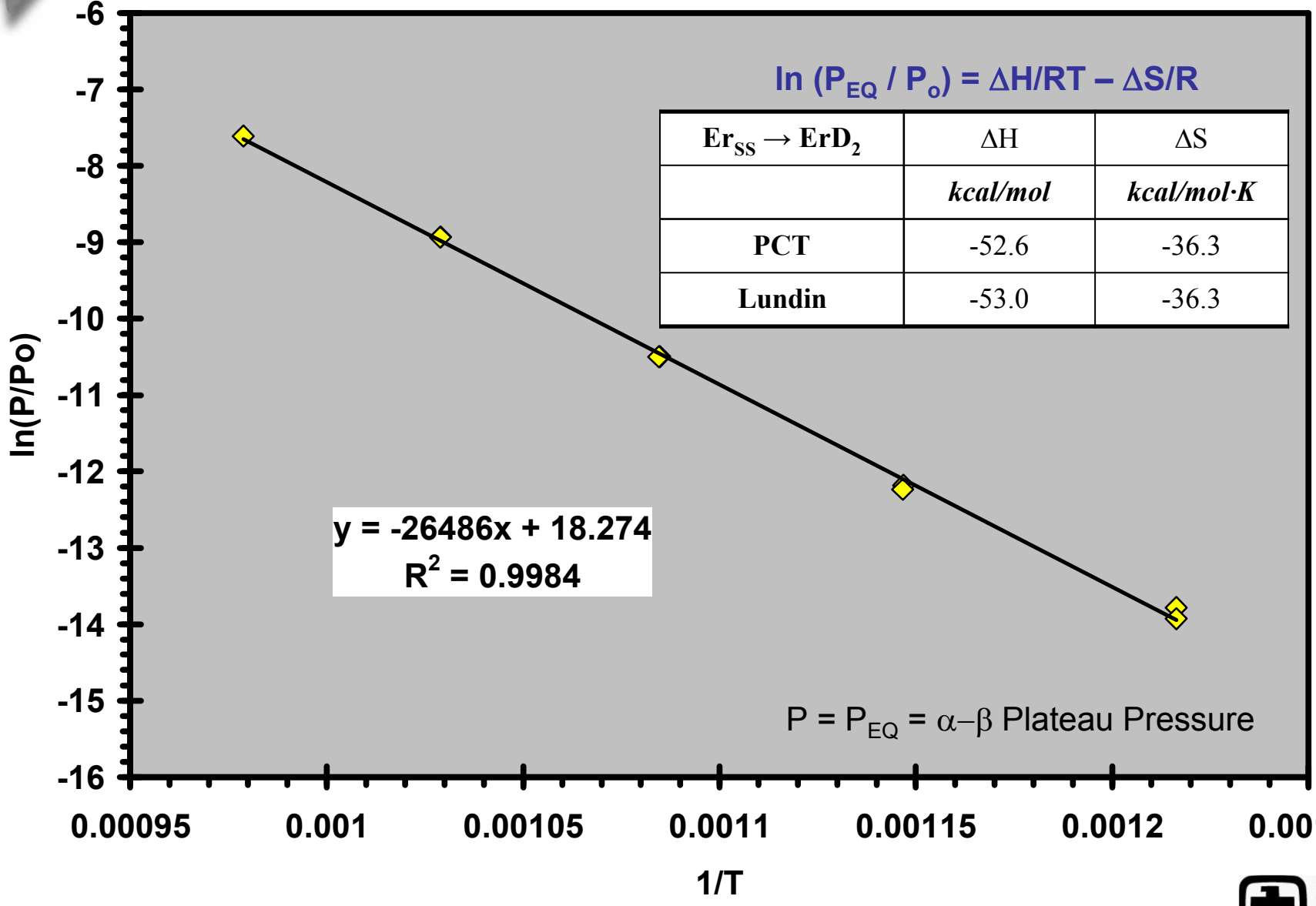
Van't Hoff Analysis



$Er_{SS} \rightarrow ErD_2$	ΔH	ΔS
	kcal/mol	*kcal/mol·K*
PCT	-52.6	-36.3
Lundin	-53.0	-36.3

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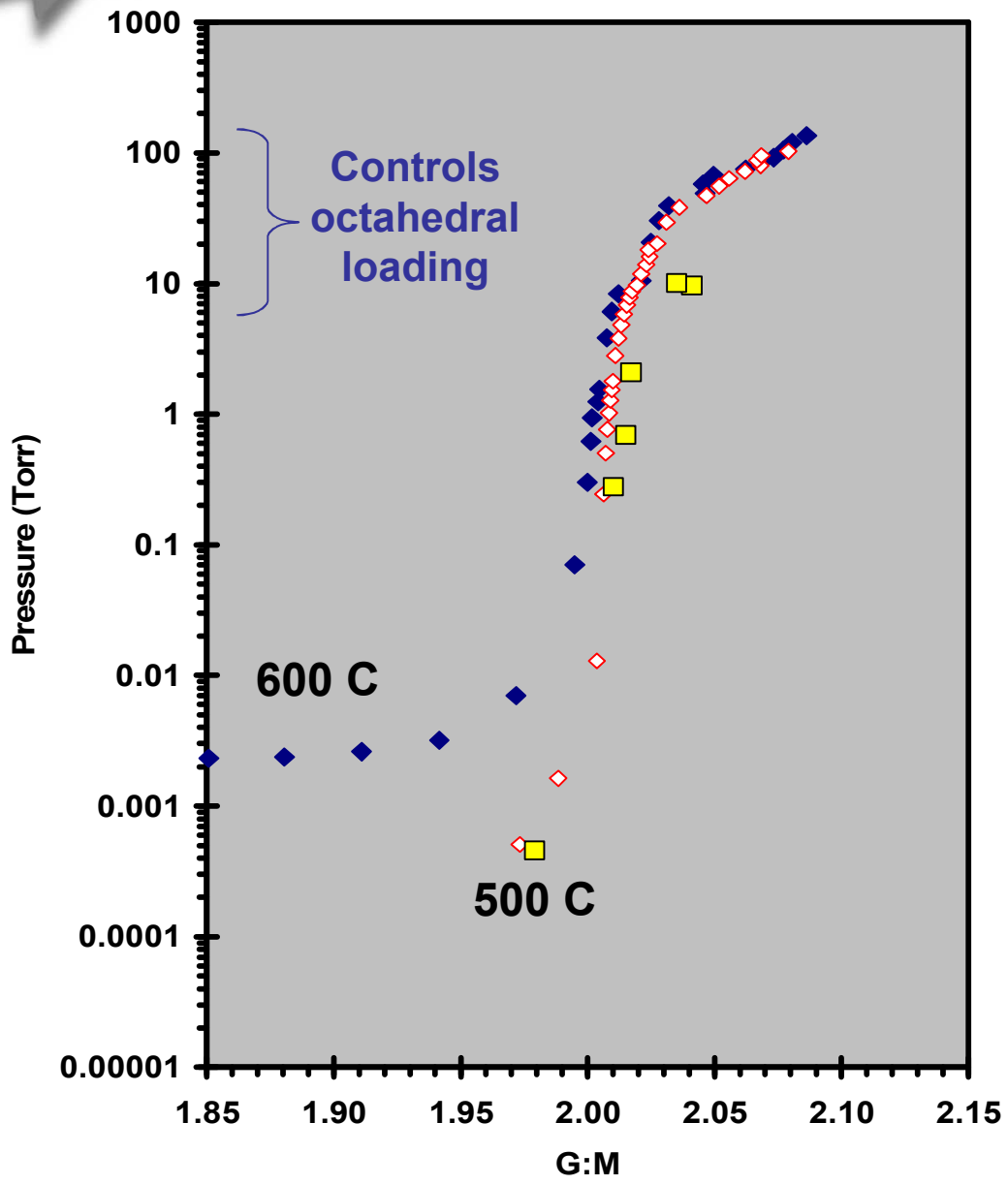
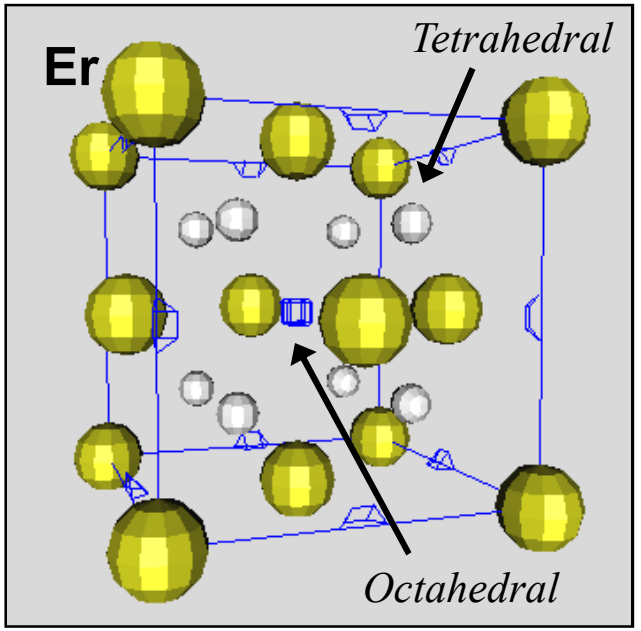
Er-D: β-phase



ErD_2: Crystal Structure



Face-Centered Cubic (CaF_2)

ErD_{2+x} → G:M ≡ 2+x

tetrahedral *octahedral*

Vajda "Rule of Thumb" → 0.01 x per Torr

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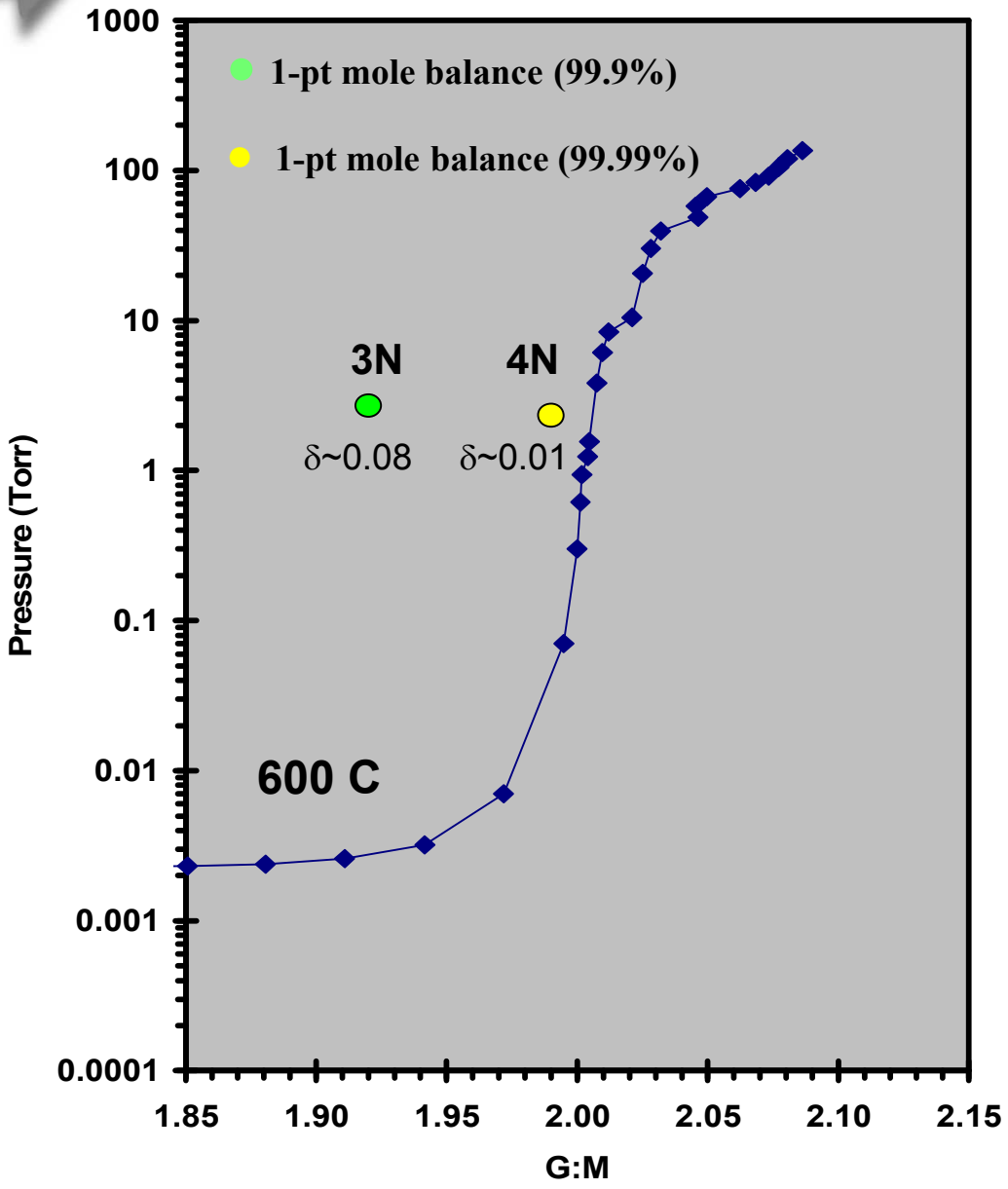
Er-D: β-phase boundary



$\delta \equiv$ *"stoichiometric deficit"*

$ErD_{2-\delta+x}$

$G:M = 2-\delta+x$

tetrahedral *octahedral*

Vajda reference

R	2 – δ
Y 3N	1.80
	1.90
Y 4N	1.97–1.99
Tb 3N	1.92–1.94
Tb 4N	1.96–2.00

PCT Data

R	2 – δ
Er 3N	~1.92
Er 4N	~1.99

Purity, grain size, defect structure, etc. controls stoichiometric deficit

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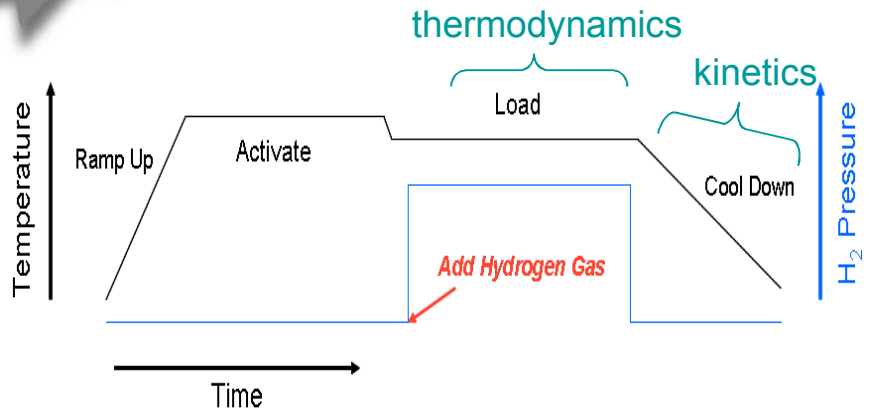
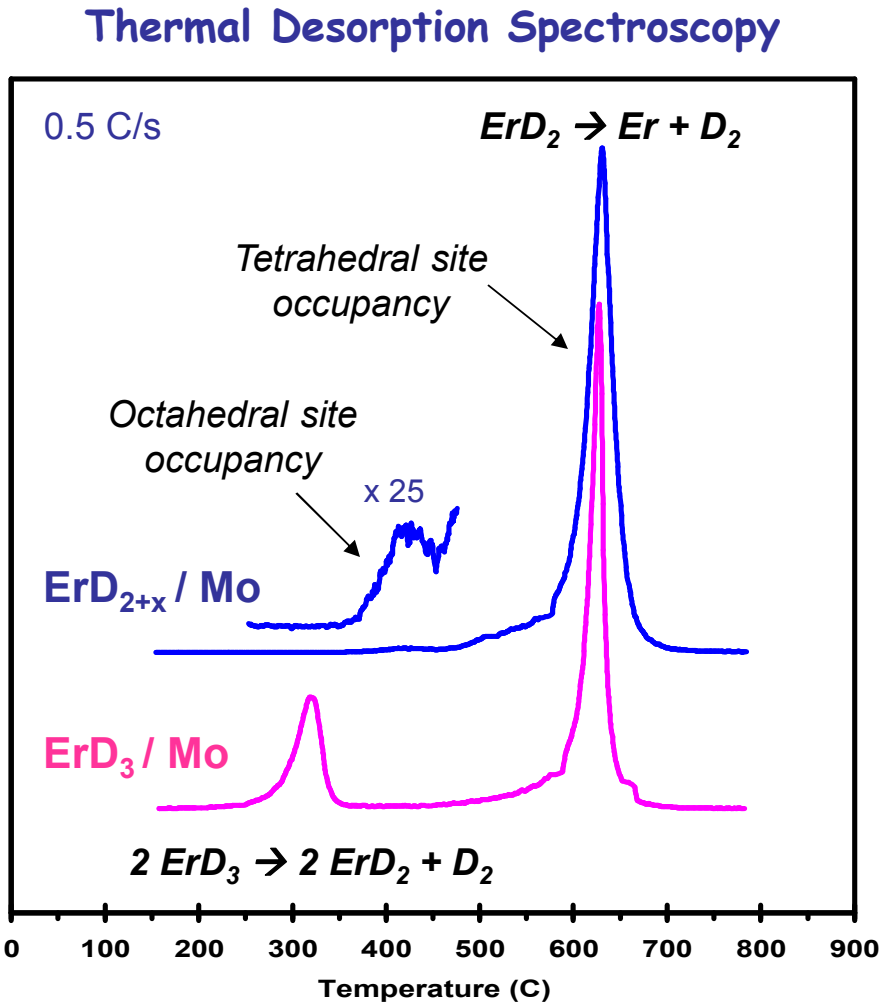
Desorption Kinetics



Load @ 250 C
150 Torr

Load @ 450 C
10 Torr

Analysis (6 samples)	ErD_3 $ErD_3 \rightarrow ErD_2$	ErD_3 $ErD_2 \rightarrow Er$	ErD_2 $ErD_2 \rightarrow Er$
$T_{P,\,AVG}$ (C)	314.3	621.3	617.5
Confidence (95%)	19.2	13.2	7.3
E_A (kcal/mol)	39.1	60.2	60.0



- **For T > ~400 C, "pumping octahedrals" during thermal vacuum treatment can lower β-phase G:M**
- **Qualitatively confirmed by *in-situ* neutron diffraction & PCT desorption study**

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Conclusions

Composition can significantly impact hydride properties and performance

- composition = G:M (amount of hydrogen)

- or, composition = % octahedral

(either, or both, may be important)

PCT Apparatus: well-calibrated to generate adsorption isotherms

- Erbium-Deuterium data consistent with Lundin's results (ΔH, ΔS)

ErD_2 – control octahedral loading (assuming equilibrium conditions) by choosing appropriate load pressure (5 to 100 Torr regime)

ErD_2 – lower β-phase boundary dependent on sample (3N vs 4N)

ErD_2 desorption kinetics - removing sample from reactor (i.e. non-equilibrium conditions) can change the final composition

- pump octahedrals above ~ 400 C

- decompose hydride above ~ 600 C

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Acknowledgements

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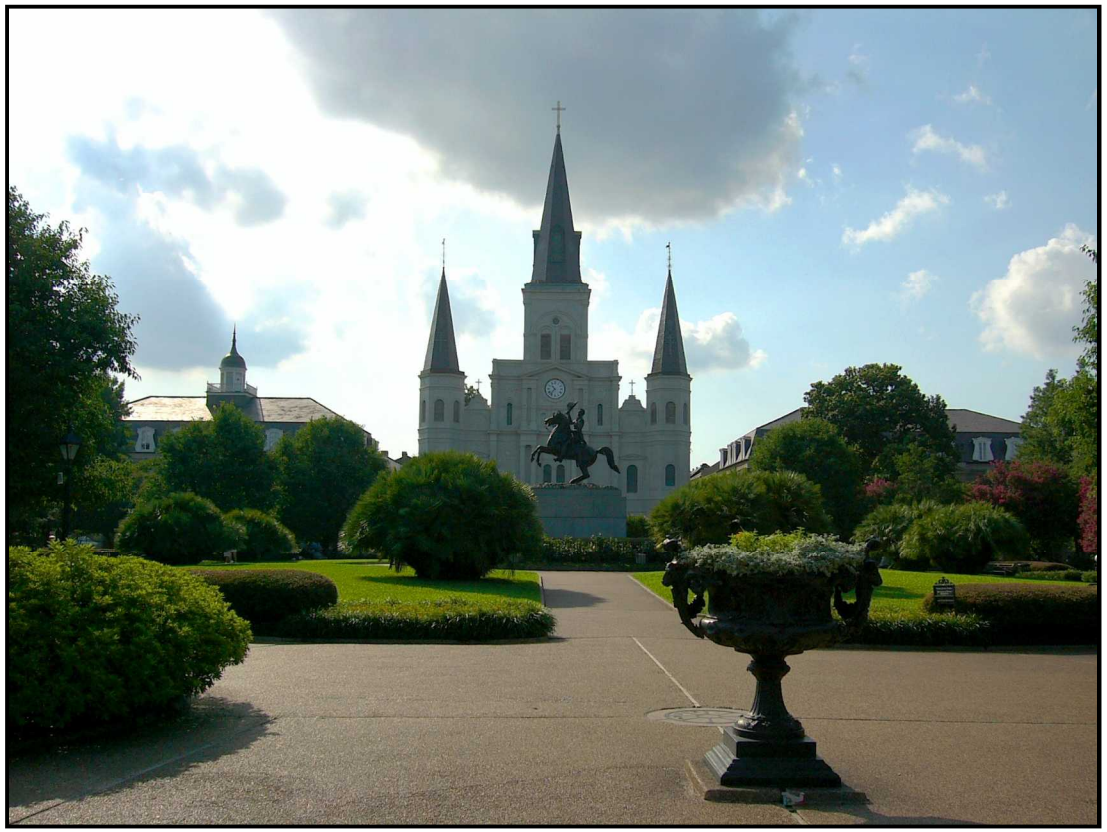

St. Louis Cathedral, June 2003

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