Conceptual Design and Projected Performance for a Hybrid Sulfur Process (348c)




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Outline

- Background
- SRNL HyS Process Conceptual Design
- HyS Process Economics
- Physical Properties Issues
- Conclusions / Future Work

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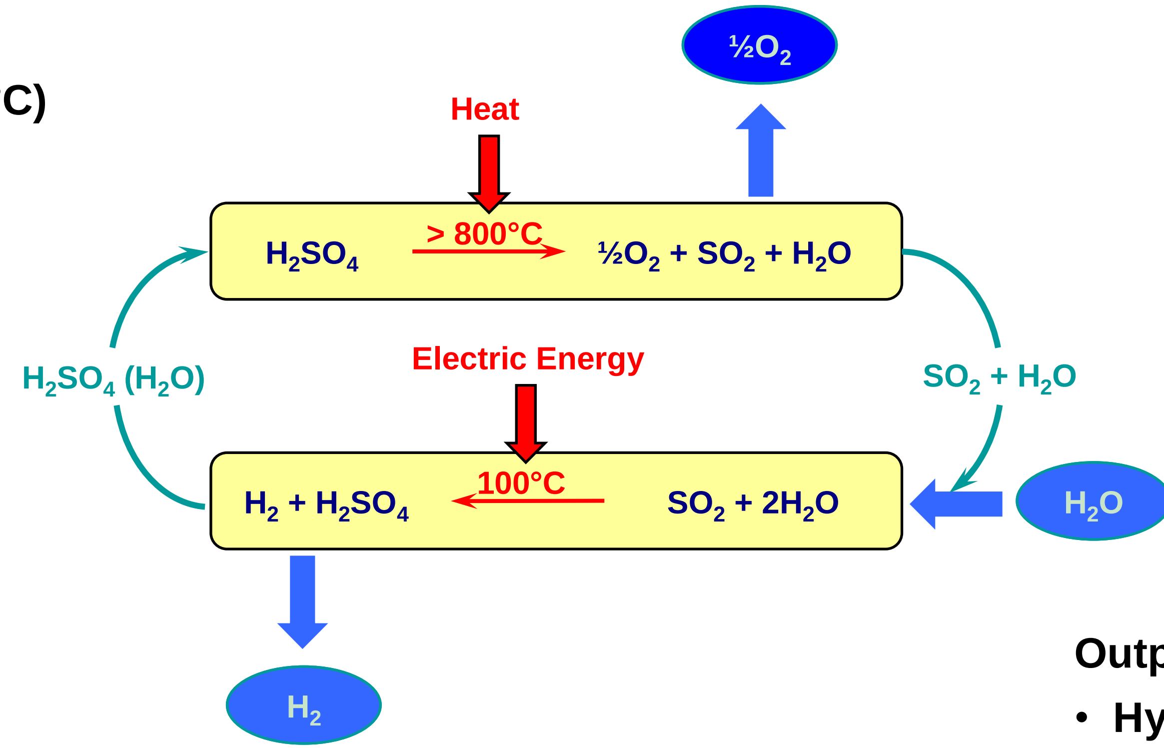
Hybrid Sulfur (HyS) Hybrid Cycle for Production of H_2

Inputs:

- **Water**
- **Heat (>800°C)**
- **Electricity**



Outputs:

- **Hydrogen**
- **Oxygen**
- **Waste heat**

At least 115 different thermochemical cycles have been proposed

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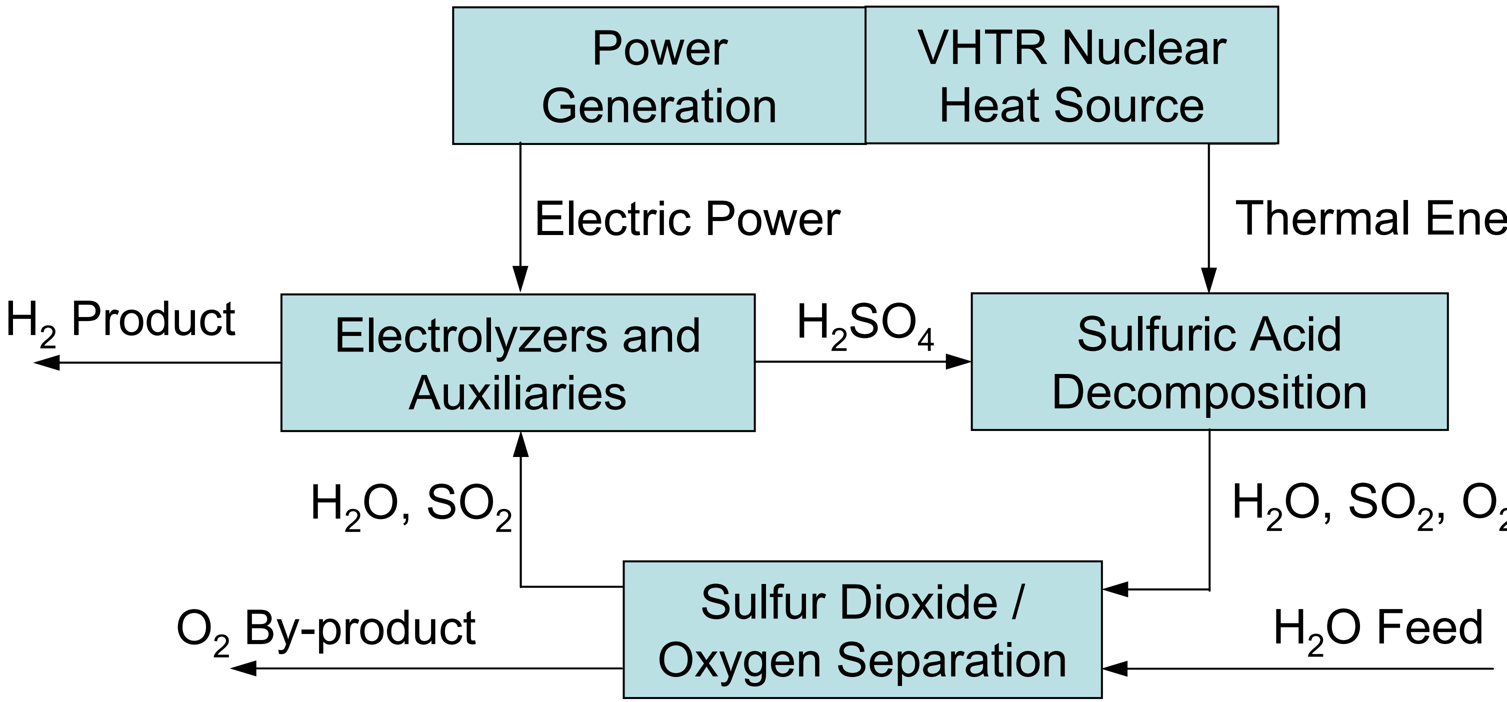
HyS Cycle Simplified Flowsheet



HyS Current Status

- Proof of concept established by Westinghouse Electric Corporation in late 1970s
- Development suspended in 1983
- Renewed interest in hydrogen economy and nuclear power revived interest in process
- DOE-funded Conceptual Design completed by SRNL in 2004
- Technical issues defined and development plan established
- Improved Conceptual Design developed by SRNL in 2005
- Bench-scale atmospheric pressure PEM electrolyzer demonstration experiments successfully completed in 2005
- Electrolyzer development and flowsheet optimization continuing under DOE funding at SRNL

Contents of Conceptual Design Report

- Conceptual design: Aspen Plus™ flowsheet, material and energy balances, performance estimates, heat source integration, plant cost considerations including capital cost estimate, and hydrogen production cost
- Key technology issues for electrolyzer, SO_2/O_2 handling, and other process sections identified
- Electrolyzer cell development plan
- Approach for lab-scale experiment identified, equipment described, and development plan outlined
- Multi-MW pilot plant considerations
- Development plan schedule and budget

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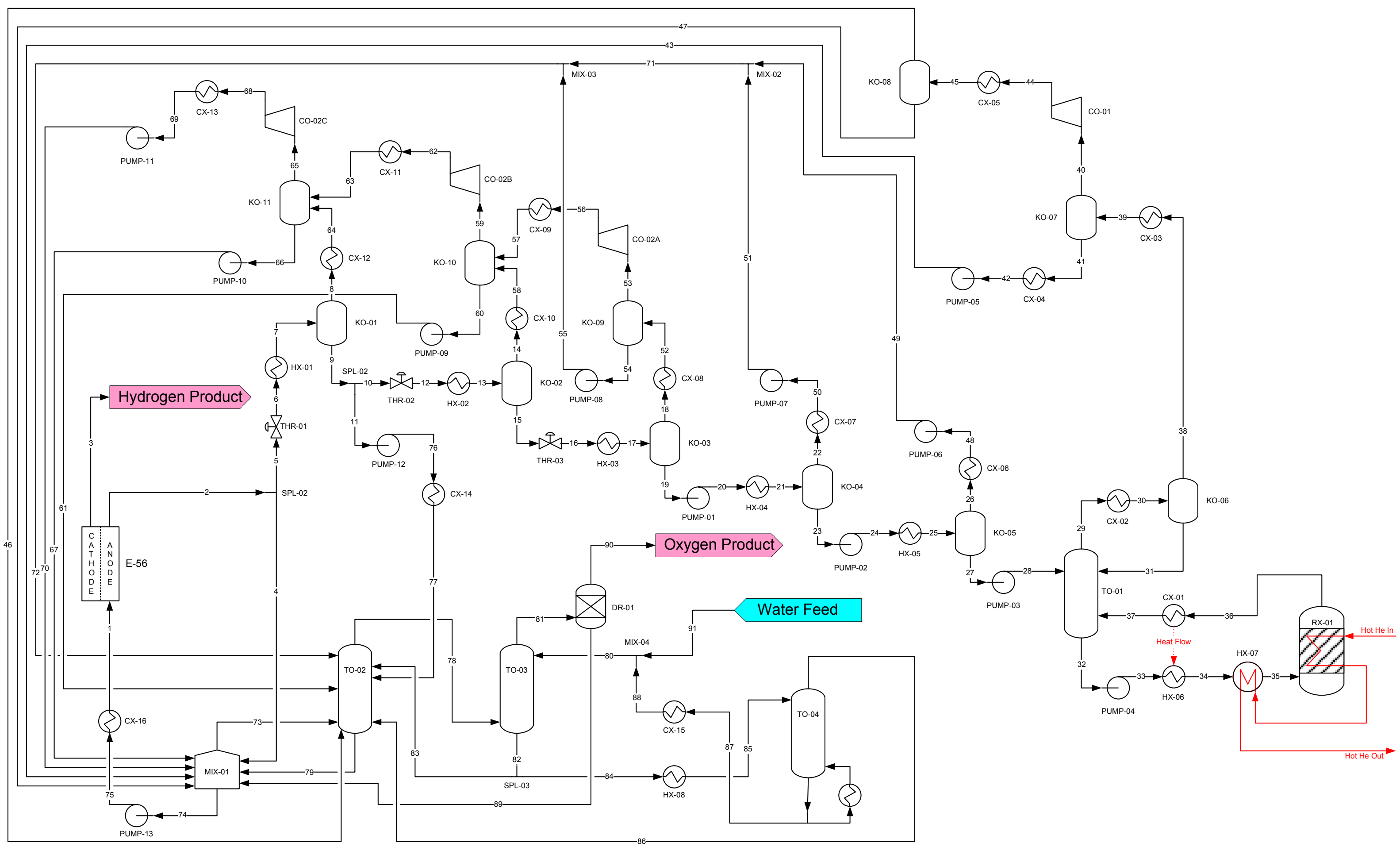
Design Report Results and Conclusions

- HyS Process is a viable option for thermochemical hydrogen production
  - All major process steps and unit operations defined
  - Material and energy balances established
  - Simplest known cycle with least equipment requirements
  - Plant thermal efficiency equals or exceeds other cycles
  - Hydrogen production costs are attractive
- Major technical issues identified and development plan established
  - Key component is SO_2 anode-depolarized electrolyzer
  - High-temperature sulfuric acid decomposition is common issue with other thermochemical sulfur cycles, e.g. Sulfur-Iodine (SI)

HyS Process Flowsheet



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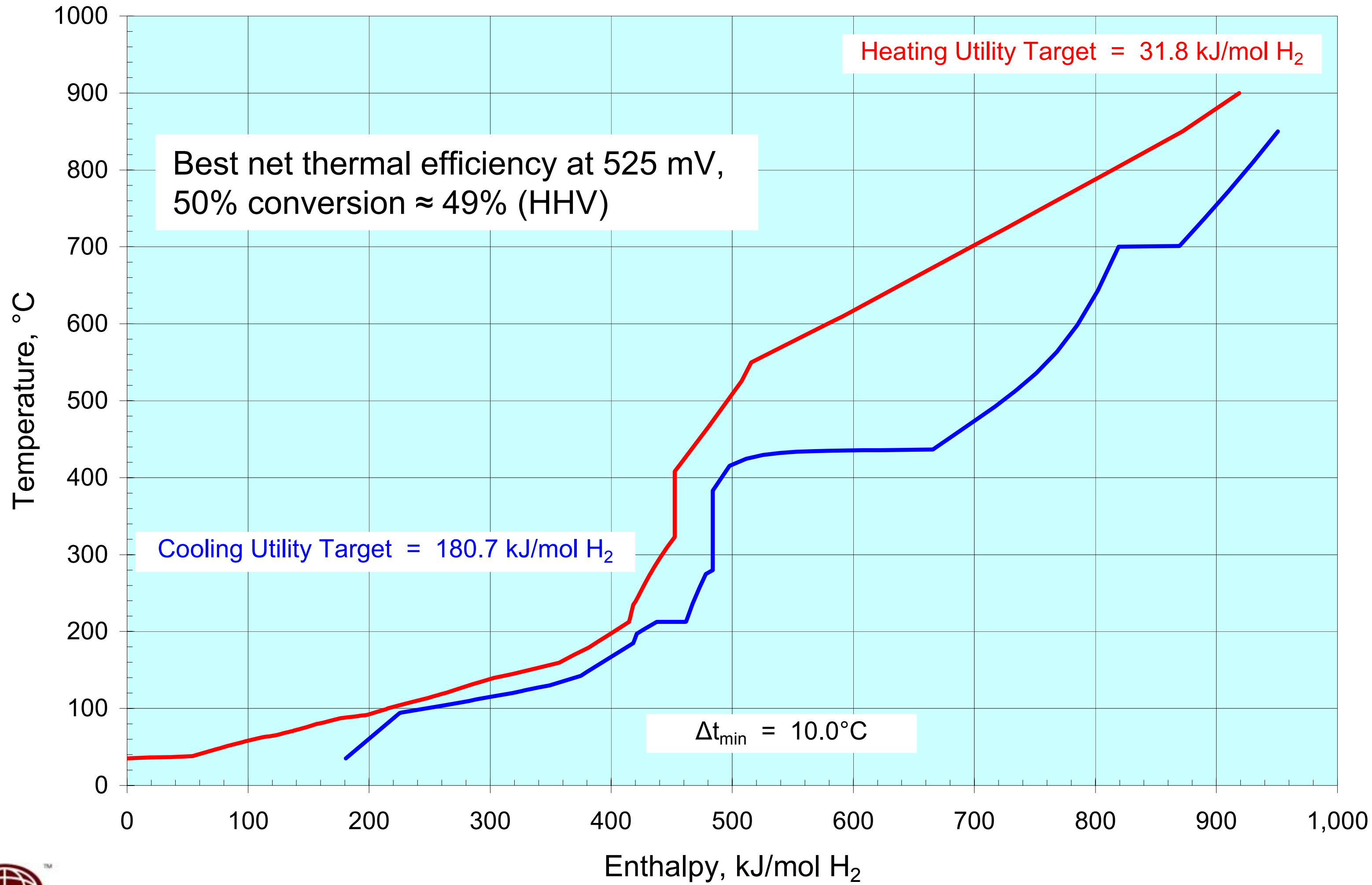
Electrolyzer Design Basis

Parameter	Westinghouse flowsheets 1976	Westinghouse flowsheets 1983	Current flowsheet
Operating pressure, bar	25.86	20	21
Operating temperature, °C	90	100.5	80
H_2SO_4 concentration, wt%	66.3	63	65
SO_2 concentration, wt%	7.7	10.8	8.95
Conversion per pass, %	47.2	2.2*	50
Current efficiency, %	>99	100	99
Current density, mA/cm^2	200	200-400	500
Cell Voltage, mV	450	607	525

* Test unit, not commercial cell design. Conventional chlor-alkali cells operate at 75% or higher.

Composite Heating and Cooling Curves for 2005 SRNL HyS Process Flowsheet



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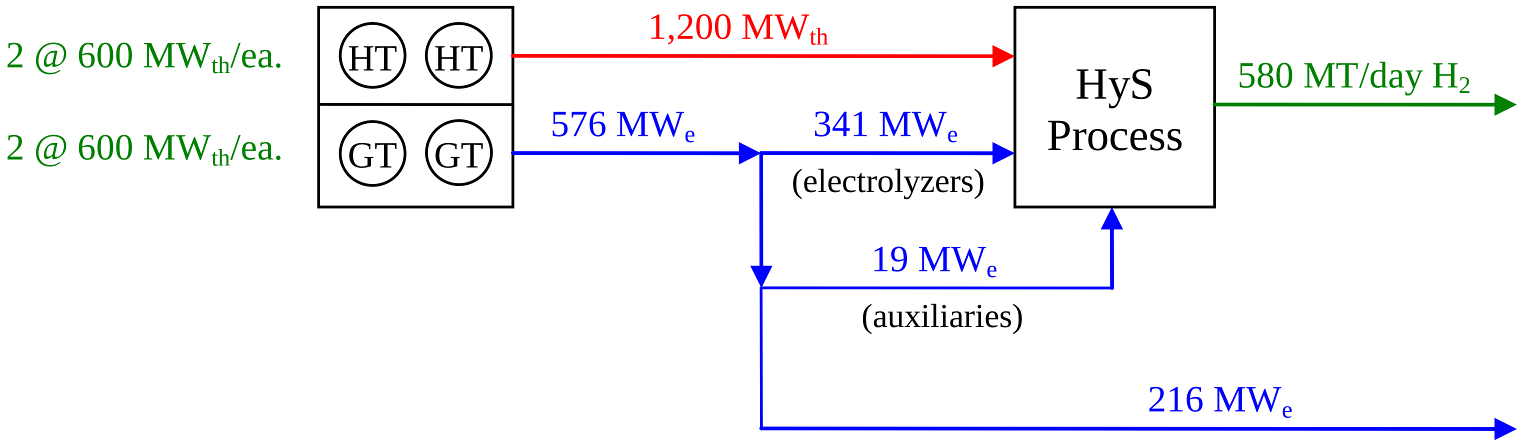
Commercial Plant Energy Balance



HyS Energy Requirement:

- 62% thermal energy
- 38% heat value of electricity (48% efficiency)

Higher efficiency projected with optimized flowsheets

HyS Hydrogen Production Costs Comparable to SI Process

	Sulfur-Iodine*	Hybrid Sulfur
GT-MHR Reactors	0	2
H2-MHR Reactors	4	2
Reactor System Cost	$1,150M	$1,198M
Hydrogen Output	760 MT/day	580 MT/day
Electrolyzer Basis		$2,000/m^2
H2 Plant Cost	$819M	$516M
Total Annual Cost	$413M	$357M
Electricity Credit		($51.1M)
Hydrogen Cost, $/kg	$1.65	$1.60
Range, $/kg		$1.42-$1.88

* W.A. Summers et al., “Centralized Hydrogen Production from Nuclear Power: Infrastructure Analysis and Test-Case Design Study, Interim Project Report, Phase A Infrastructure Analysis”, US DOE NERI Topical Report, Project No. 02-160, 07/31/2004

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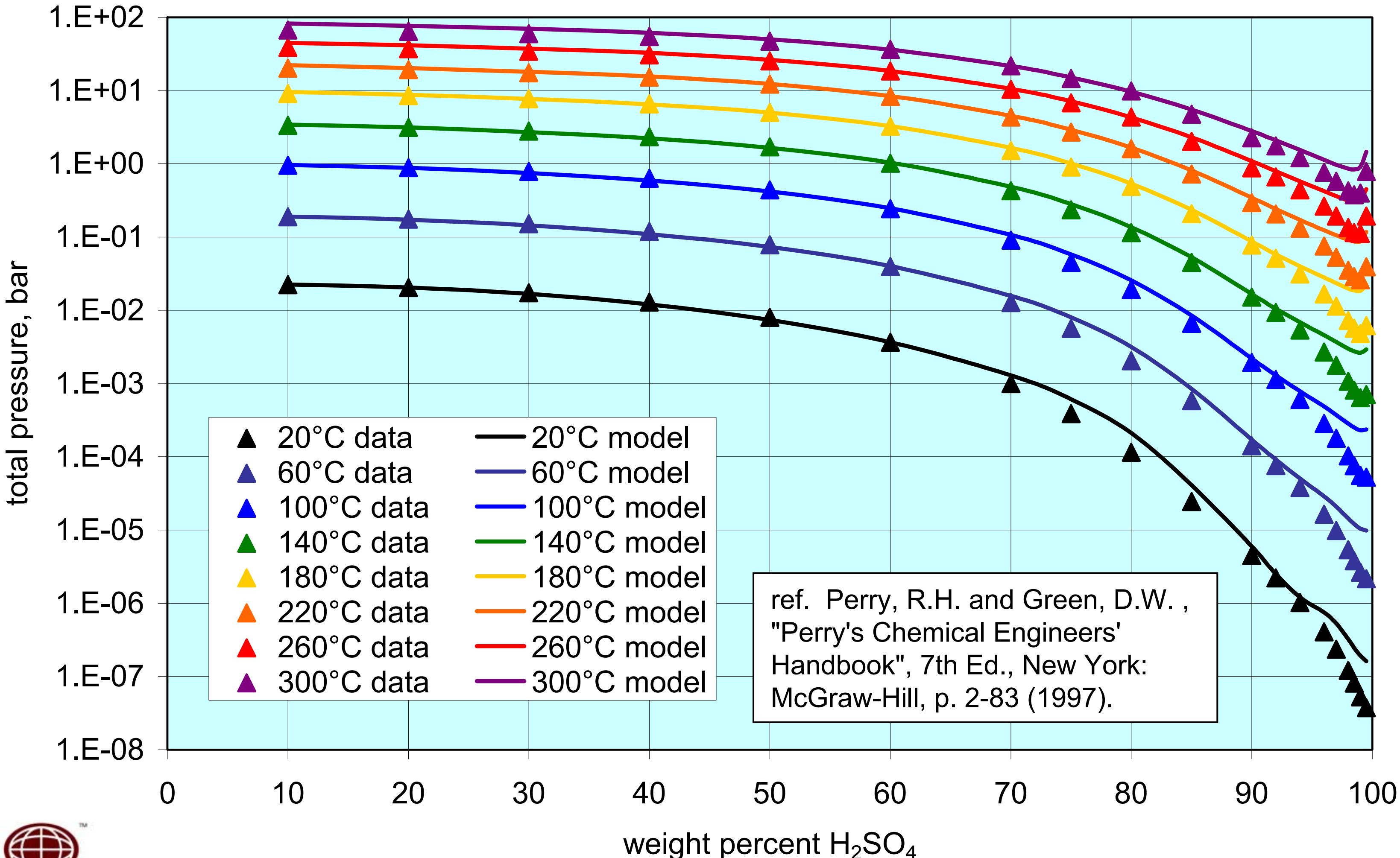
Physical Properties Issues

- Different physical properties methods used
  - Asymmetric (Henry's Law) convention for SO_2 in some sections, treated as solvent species in others
  - ELECNRTL used in some sections, NRTL-RK in others
  - Low temperature vs. high temperature H_2SO_4-H_2O model
  - Result: temperature / enthalpy discontinuities between consecutive operations using different properties methods
- Need to eliminate discontinuities for heat integration
- Attempts to treat SO_2 as liquid species dissolved in sulfuric acid using ELECNRTL unsuccessful so far

Total Pressures of 10 to 99.5% Sulfuric Acid Solutions at Temperatures Between 20 and 300°C



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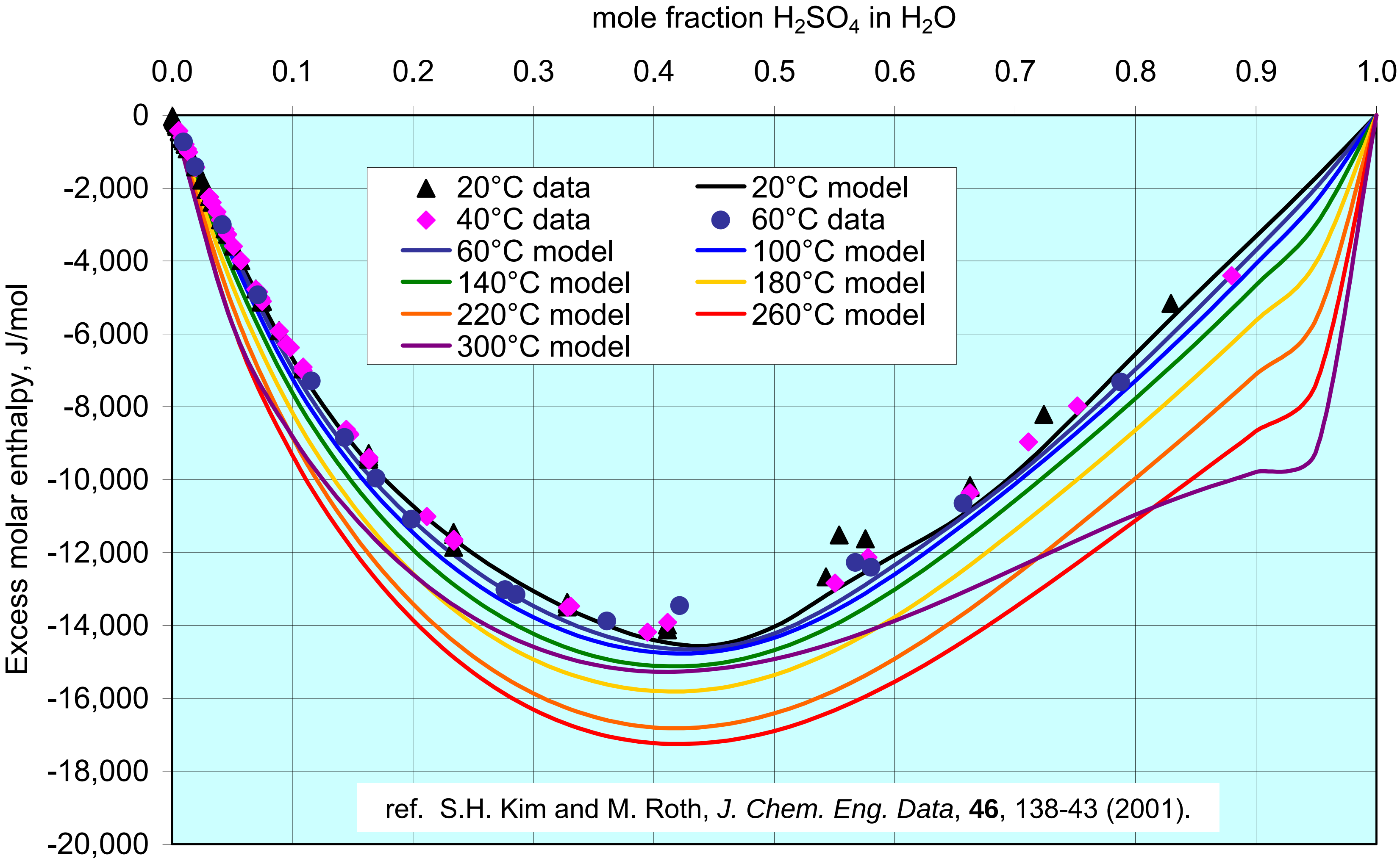
Excess Molar Enthalpies of 0-100% Sulfuric Acid Solutions at Temperatures Between 20 and 300°C



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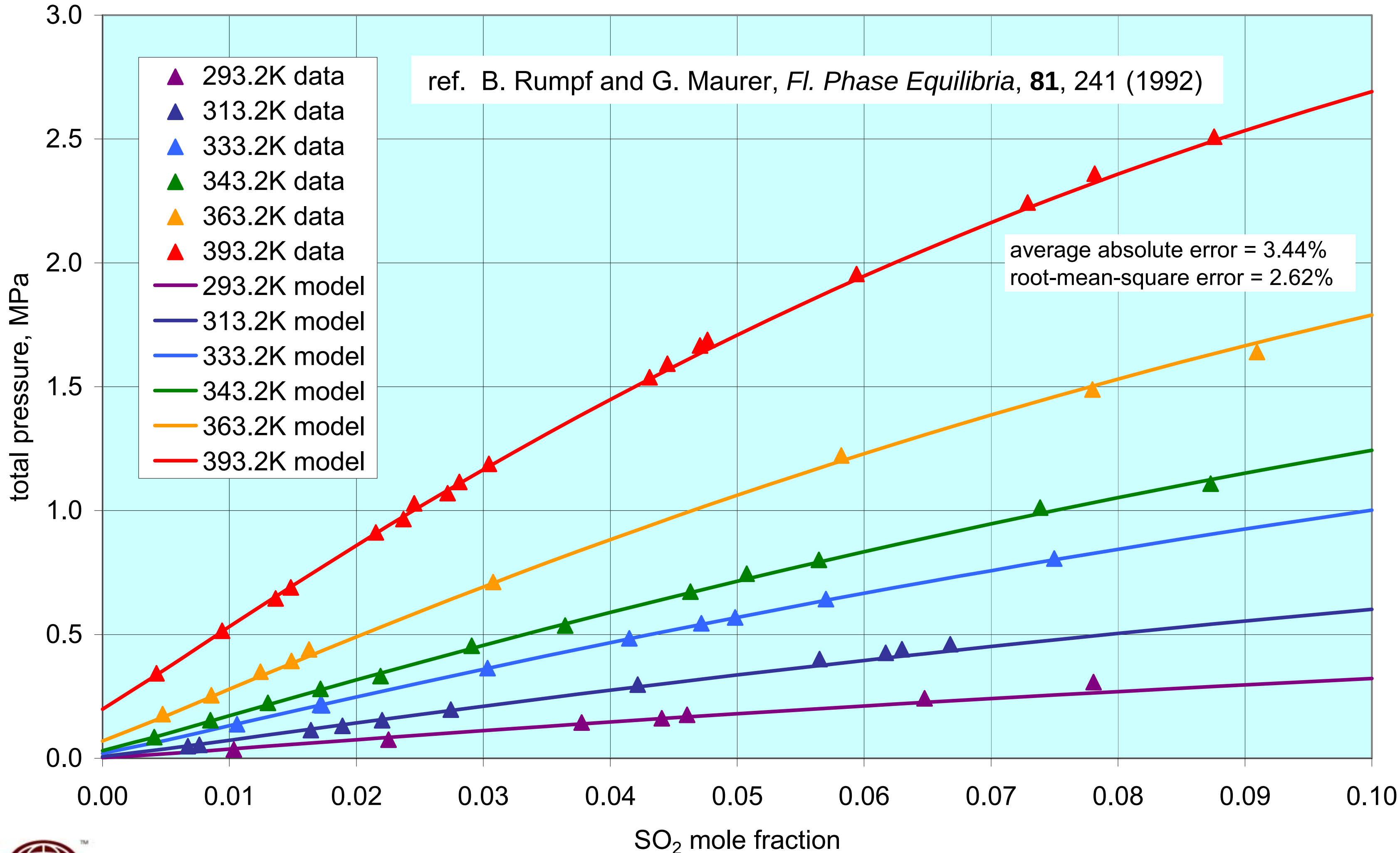
Solubility of SO_2 in Water at Total Pressures up to 2.5 MPa



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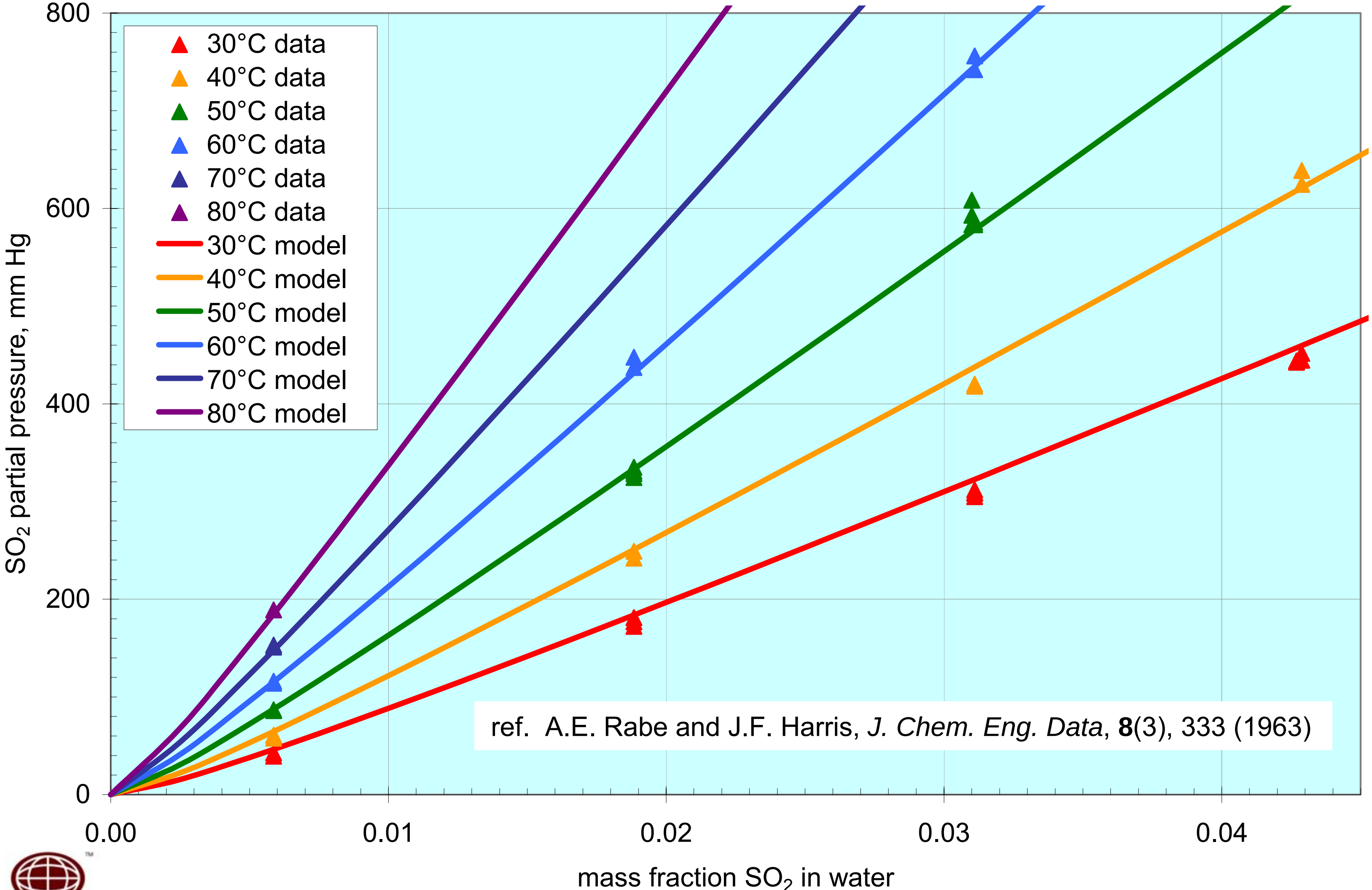
Solubility of SO_2 in Water at Partial Pressures up to 760 mm Hg



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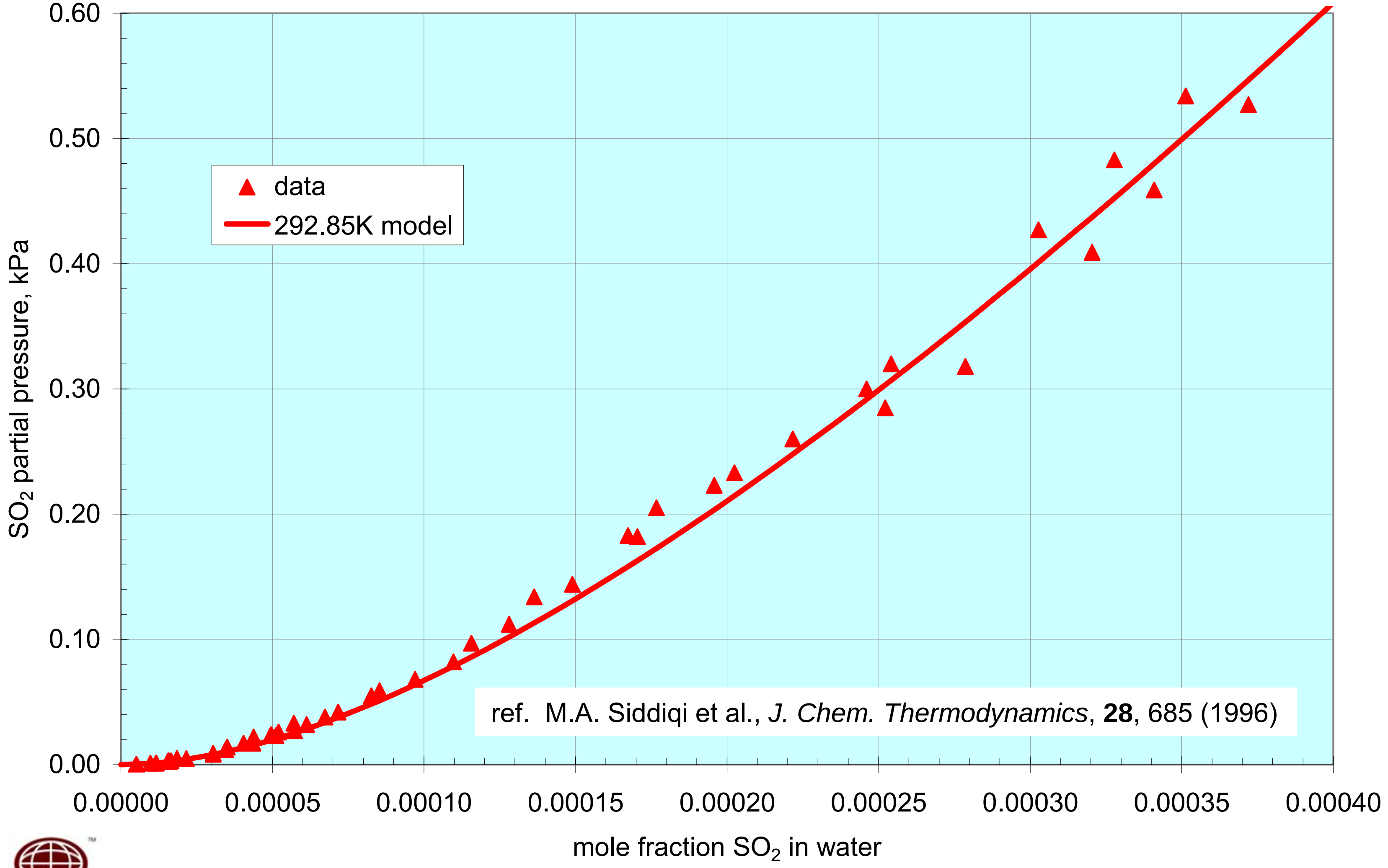
Solubility of SO_2 in Water at Temperatures Between 290.15K and 294.65K and Partial Pressures Below 0.6kPa



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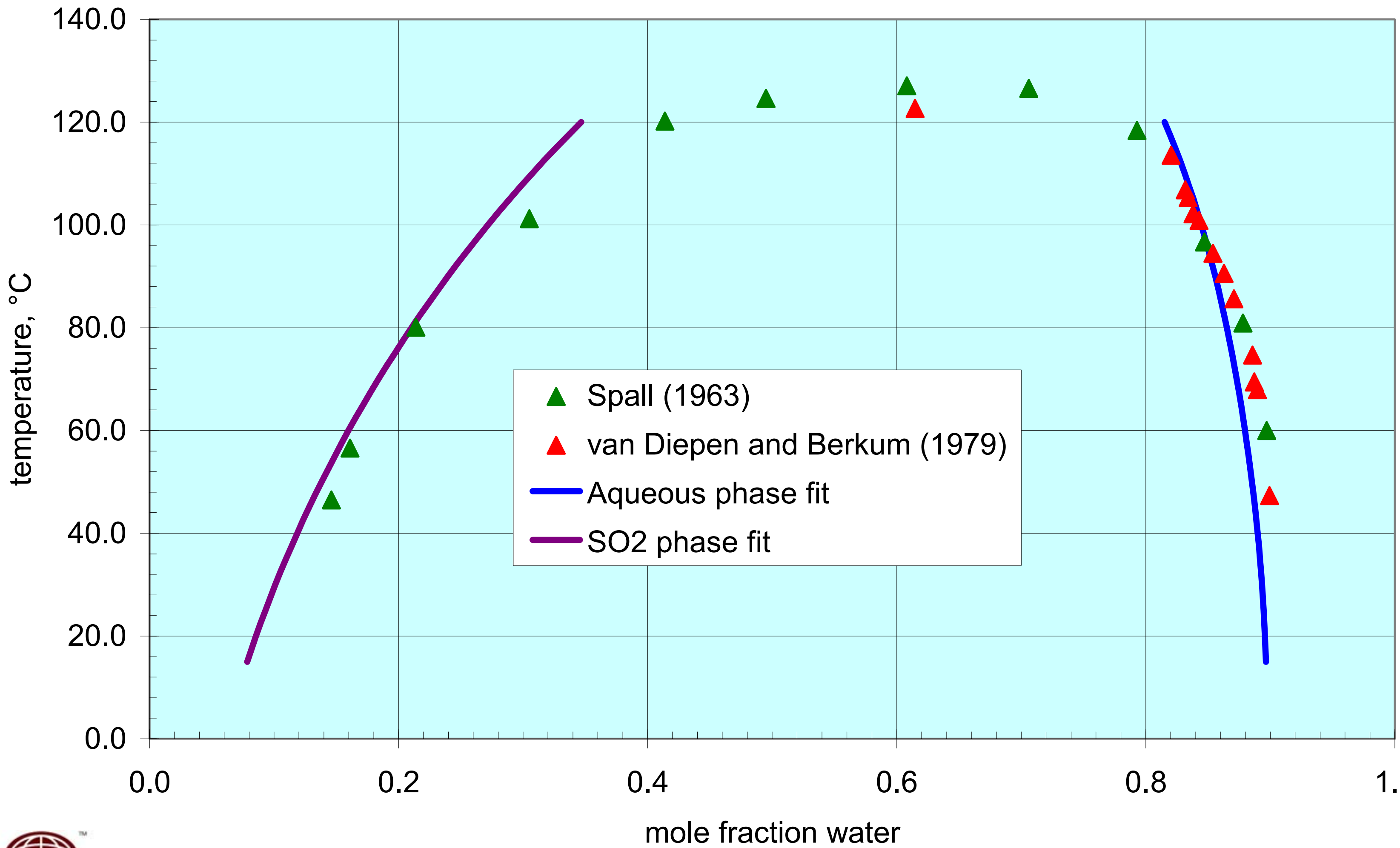
Liquid-liquid Phase Equilibrium in the SO_2-H_2O System



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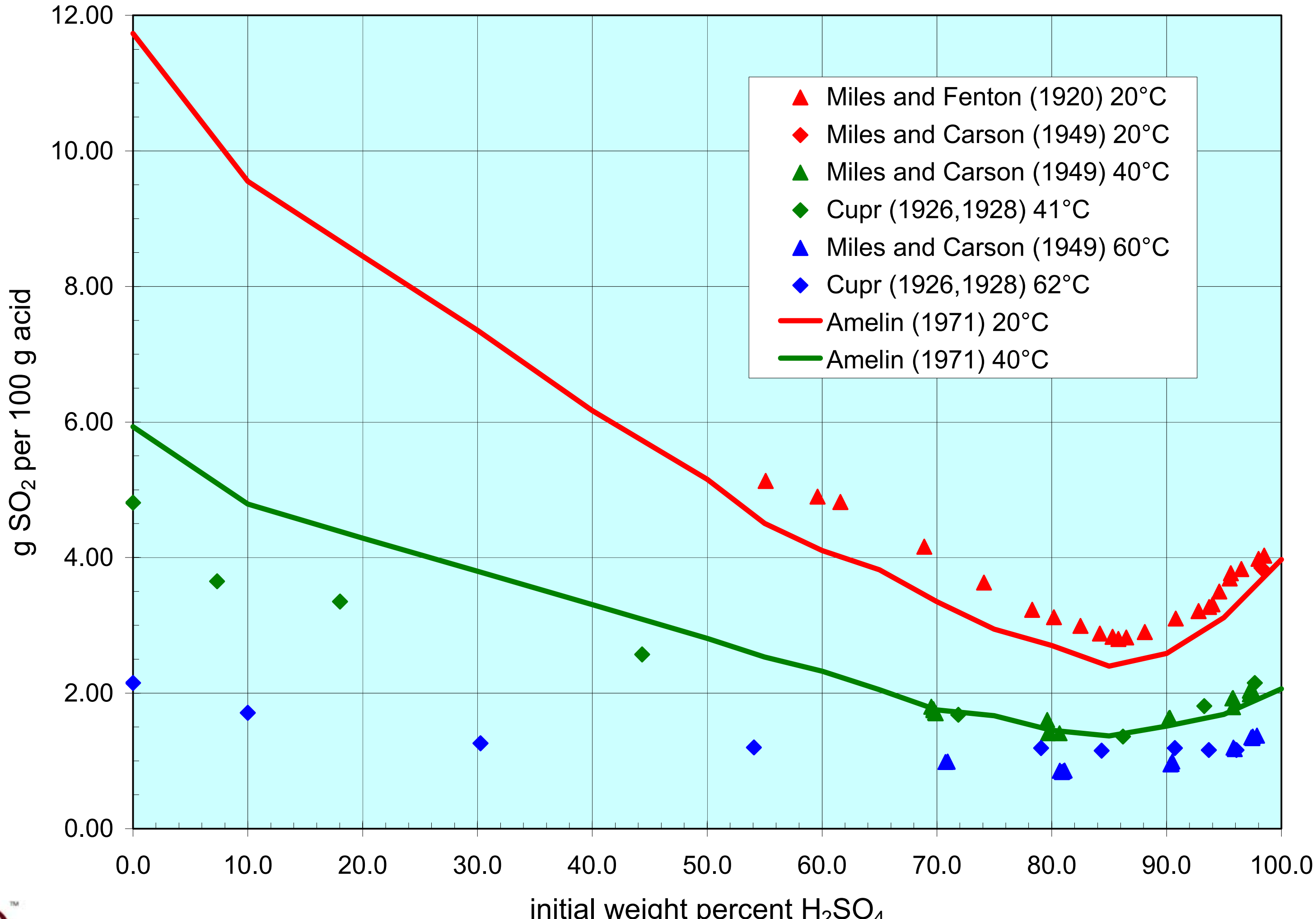
Solubility of SO_2 in Sulfuric Acid Solutions at 760 mm Hg Partial Pressure as Reported by Several Different Sources



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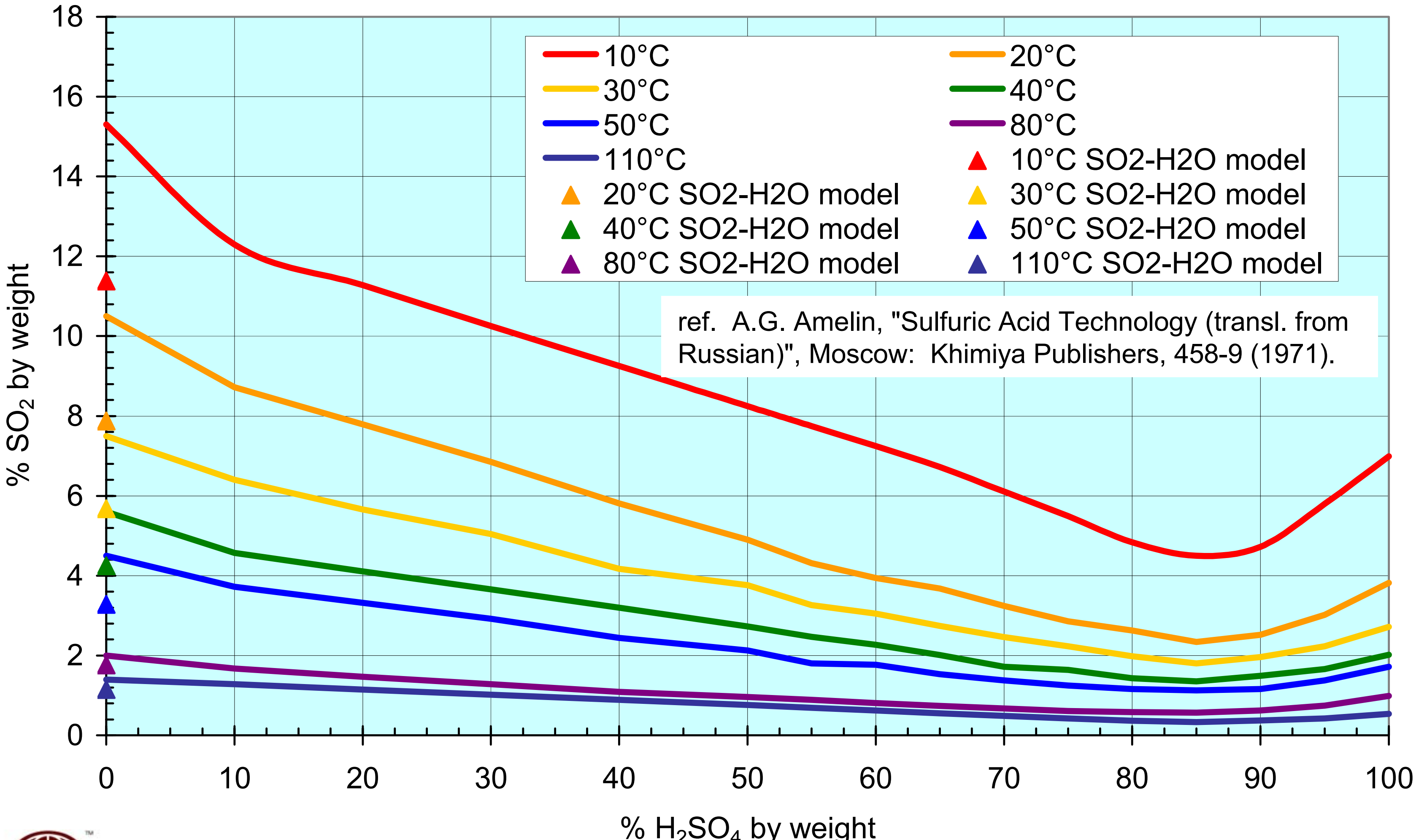
Solubility of SO_2 in Sulfuric Acid Solutions at 760 mm Hg Partial Pressure as Tabulated by Amelin (1971)



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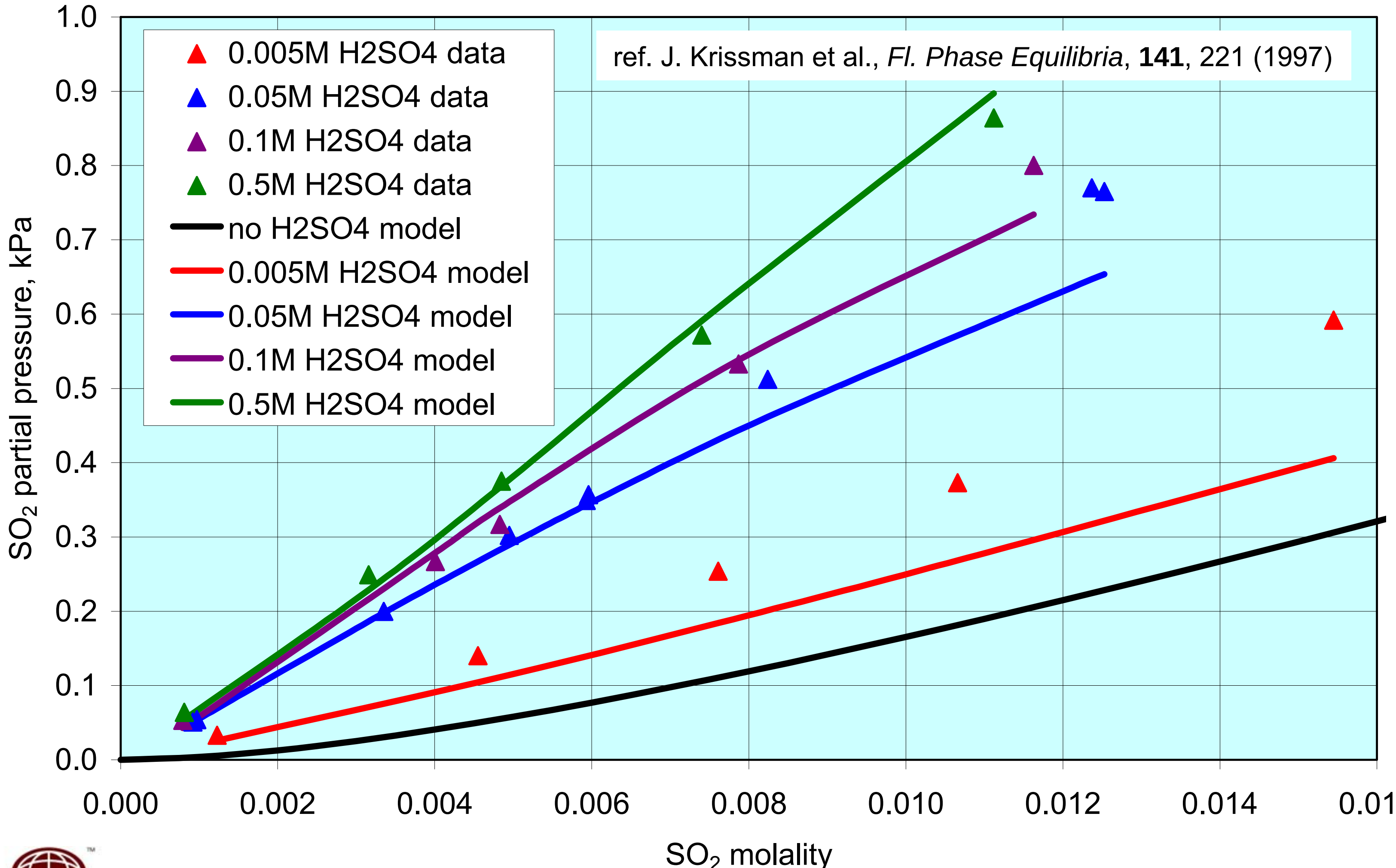
Solubility of SO_2 in 0 to 0.5M Sulfuric Acid at 298.15K and Partial Pressures Below 1 kPa



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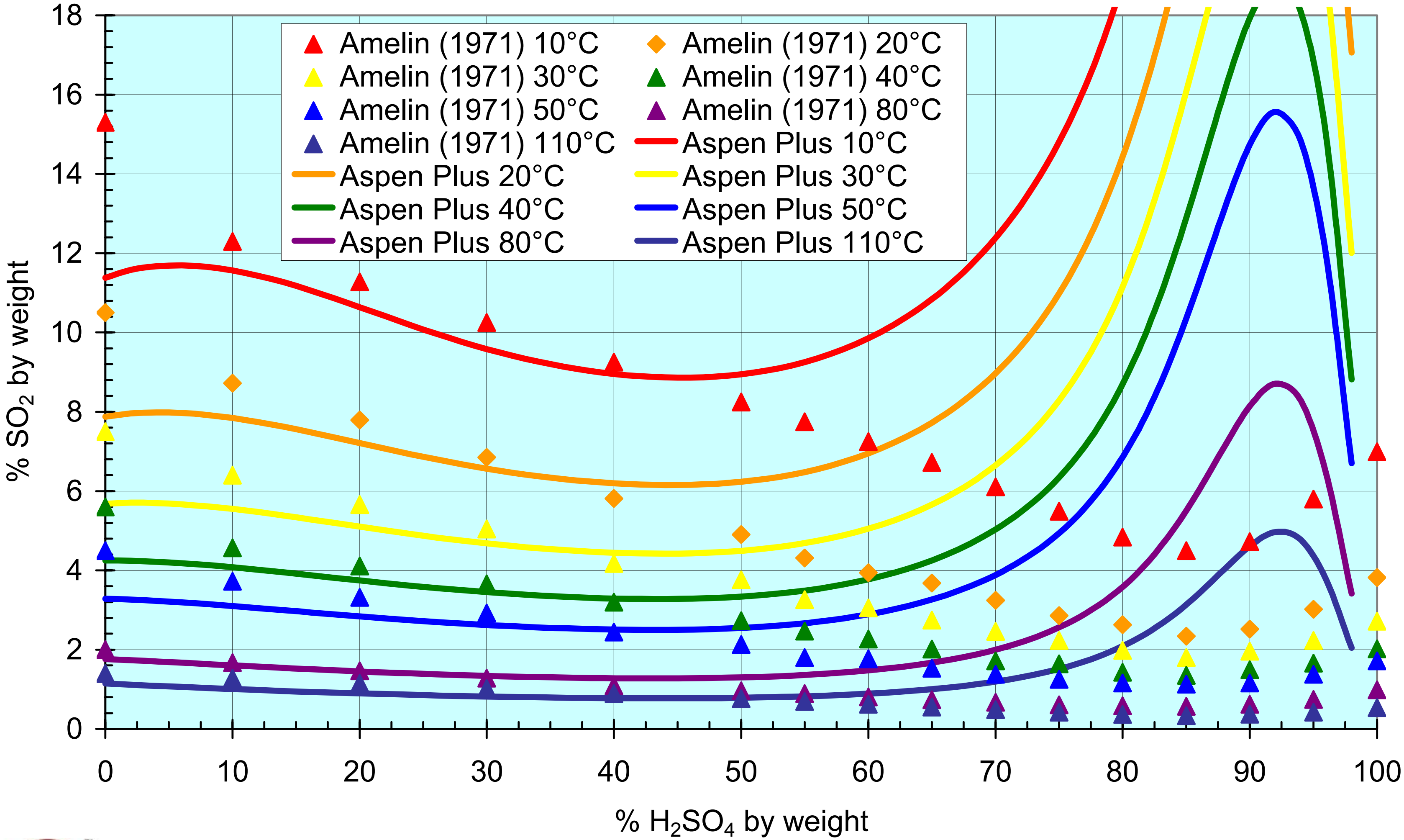
Solubility of SO_2 in H_2SO_4 Solutions; Comparison of Aspen Plus™ Model Without Fit to Amelin (1971) Data



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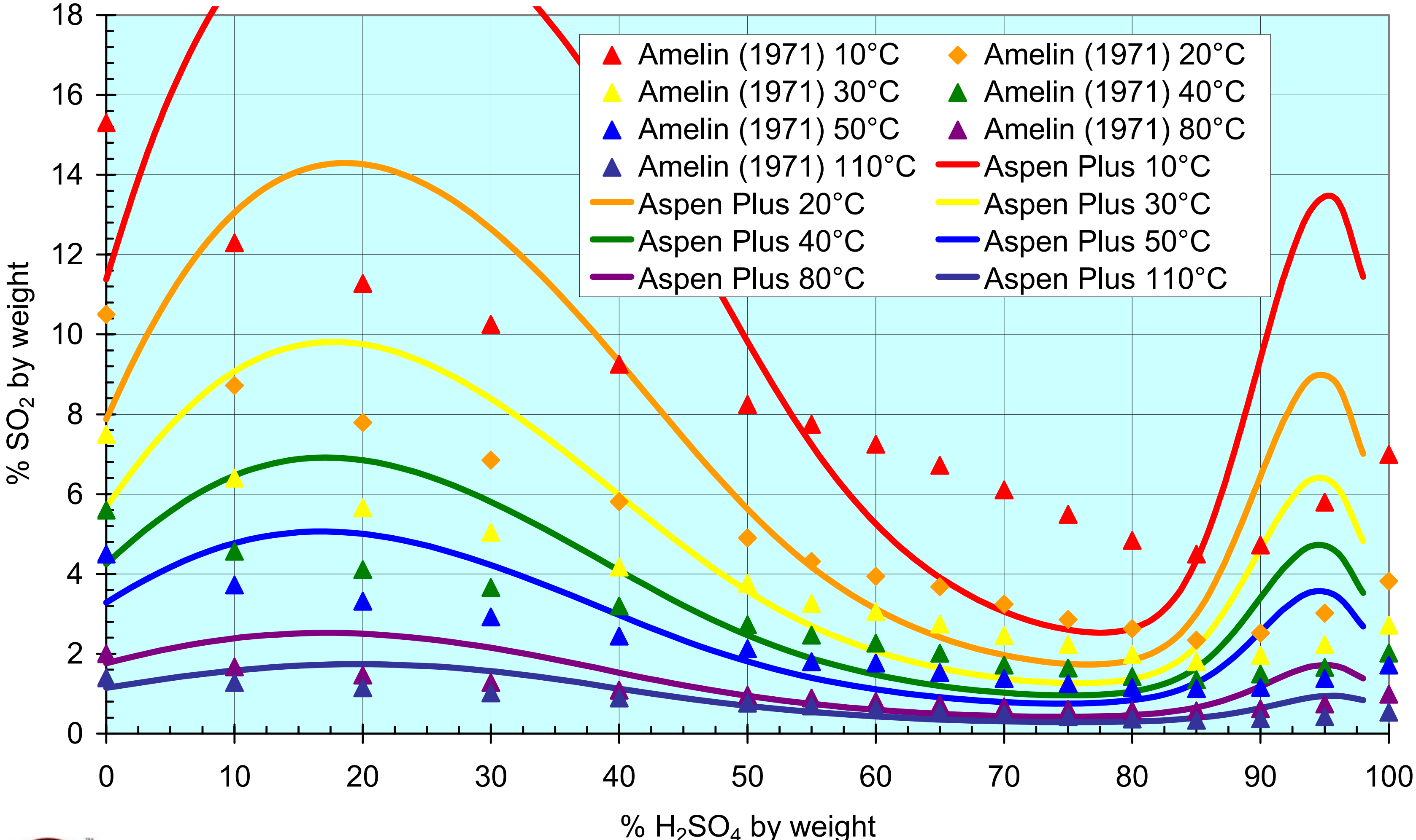
Solubility of SO_2 in H_2SO_4 Solutions; Comparison of Aspen Plus™ Model After Fit to Amelin (1971) Data



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Conclusions / Future Work

- A Hybrid Sulfur flowsheet has been developed that can achieve thermal efficiencies near 50% (HHV basis)
- Hybrid Sulfur production costs using this flowsheet are estimated at \$1.42-\$1.88/kg H_2
- Flowsheet optimization should improve Hybrid Sulfur process thermal efficiencies in excess of 50% (HHV basis)
- Discontinuities between physical property methods need to be resolved before further heat integration attempted
- ELECNRTL method gives anomalous results for SO_2 solubility in sulfuric acid
- Work ongoing to identify source of anomalous behavior for SO_2 solubility in sulfuric acid

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