Liquid-Liquid and Vapor-Liquid Equilibrium Measurements for the Sulfur-Iodine Cycle: Design and Construction of a Continuous-Flow Apparatus

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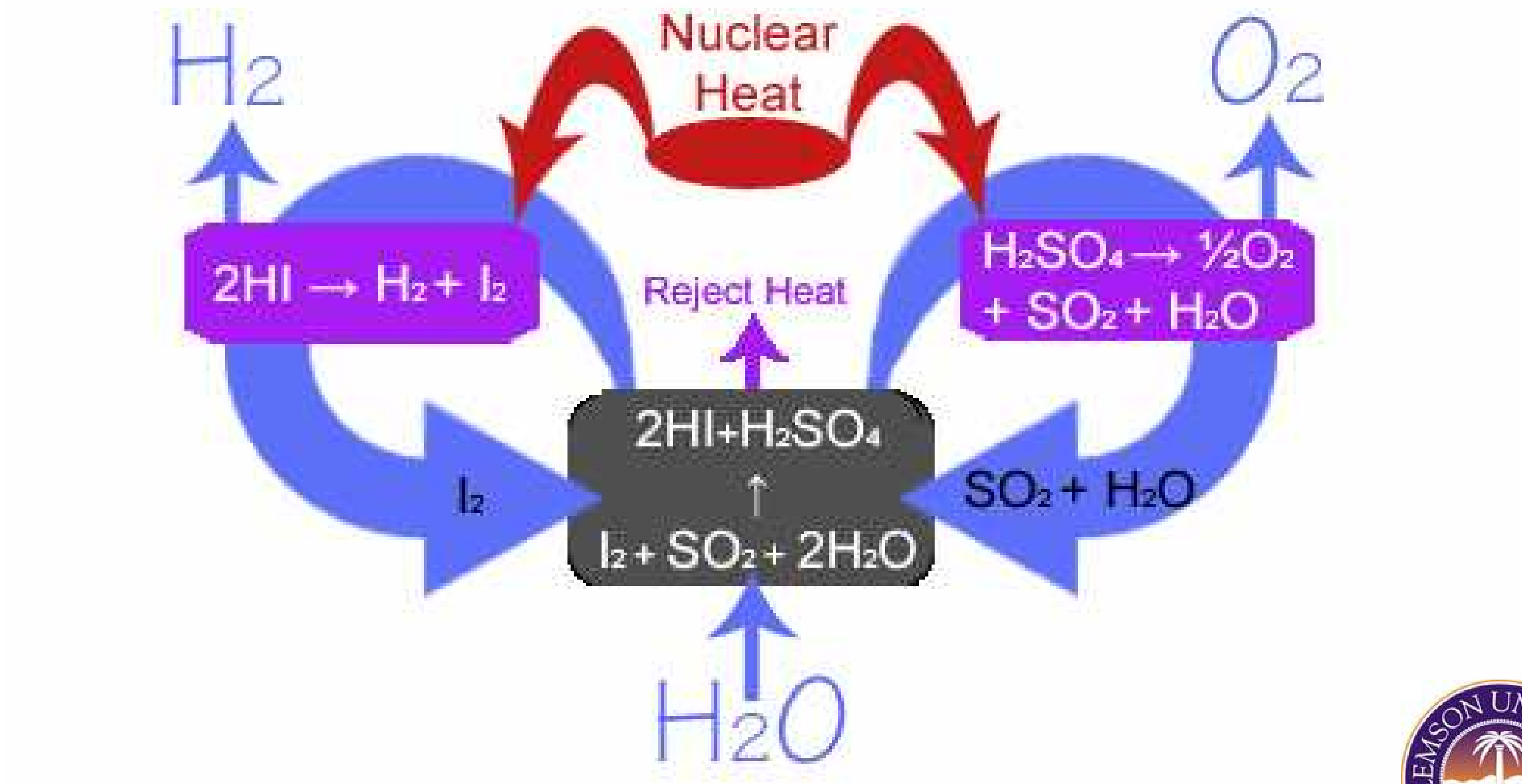
Overview

- Background
- Project Objective
- Proposed Phase-Equilibrium Measurements
- Challenges
  - Materials of construction
  - Design and construction of continuous-flow apparatus
  - Interface detection
  - Analytical methods
- Conclusions

Background

- Of 100+ thermochemical hydrogen cycles, the Sulfur-Iodine (S-I) cycle is a primary target

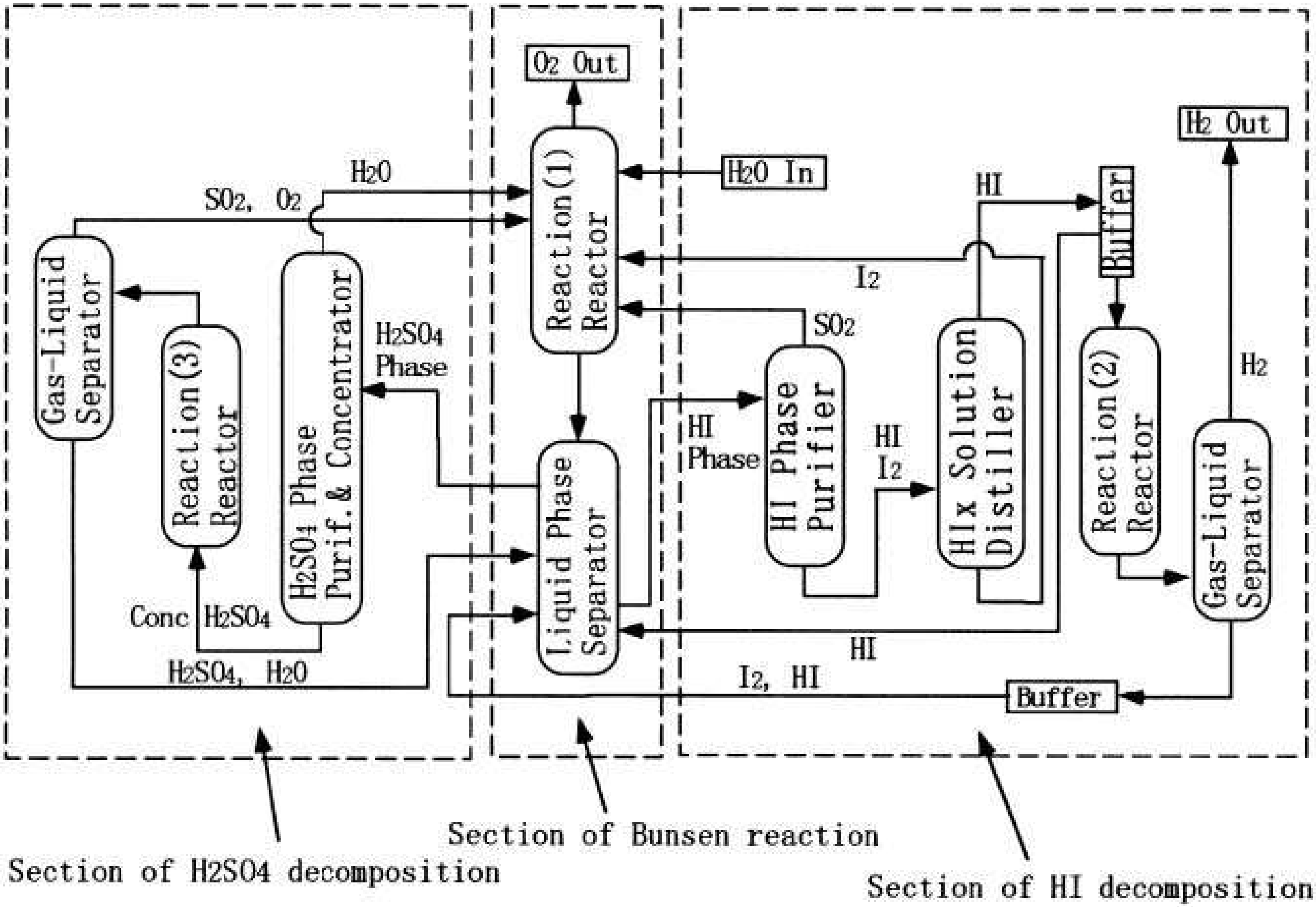


Background

- S-I cycle involves complex, highly non-ideal phase behavior
  - Poorly understood
- Performance projections based on uncertain or incomplete data
- Thermodynamic measurements and property models have been identified as a basic research need
- With carefully constructed property and process models that correctly describe the process, the true potential of the S-I process can be assessed

Sulfur-Iodine Cycle

Sakurai et al., IJHE, 1999

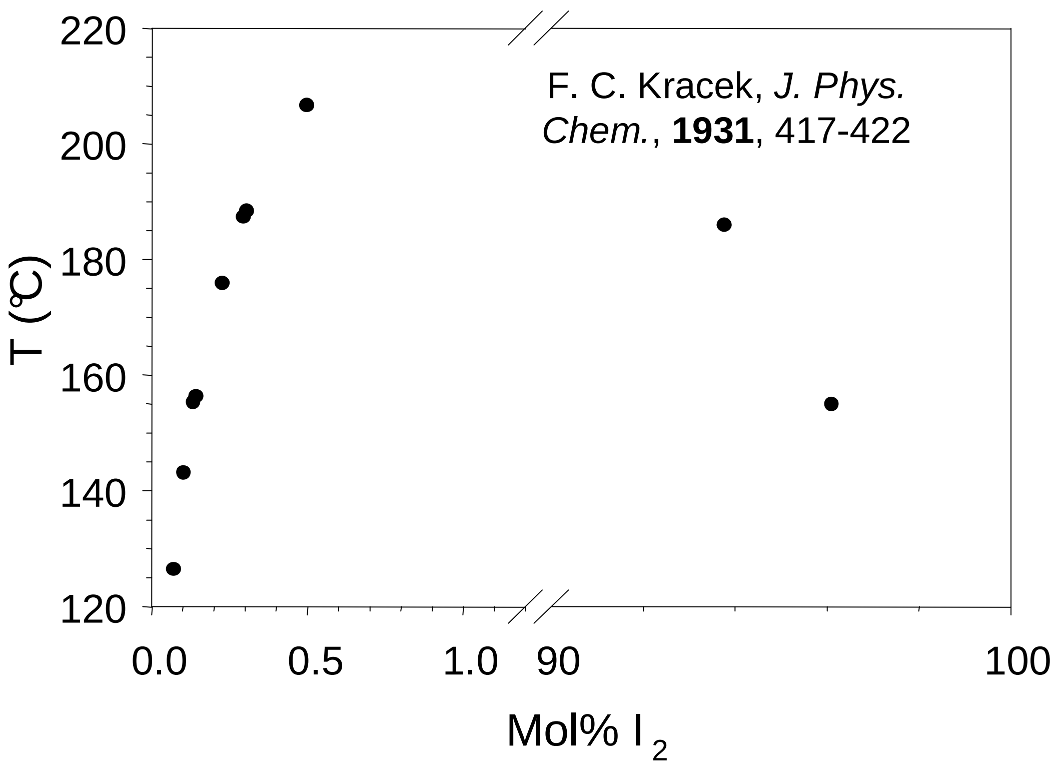


Objectives

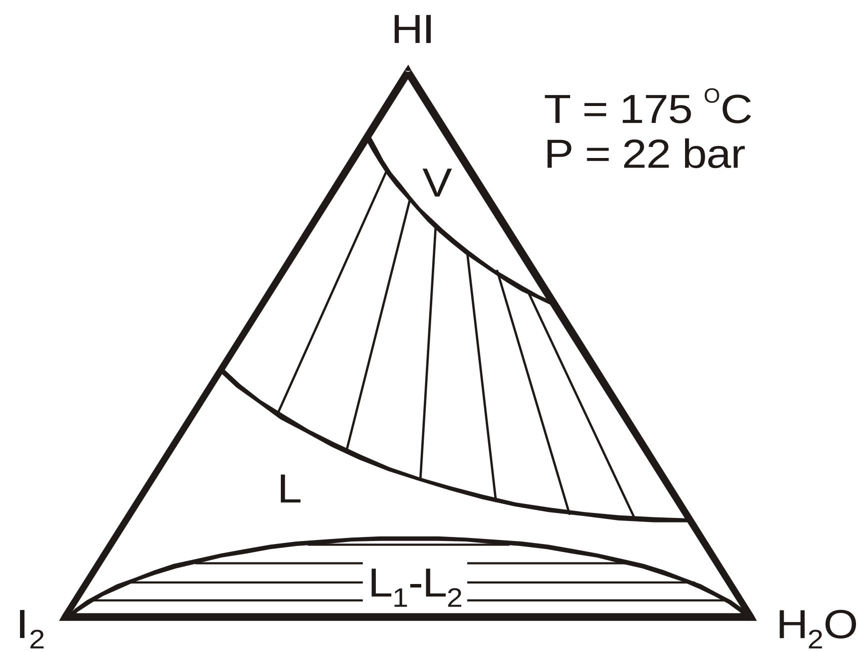
- Measure phase-equilibrium data for the HI dissociation section of the S-I cycle
  - Little to no data are available for the systems involved
    - I_2 –water binary
    - HI–water binary
    - I_2 –HI–water ternary
- Initially, properties and process modeling used as a guide for the selection of conditions for experimental measurement
- Experimental results will help to refine property models
- Improved property models are then used to identify additional experiments for minimizing any remaining process uncertainties

Liquid-Liquid Equilibrium for the I_2-HI-Water System

I_2-Water binary system



I_2-HI-Water ternary system



- Initial process modeling has identified the I_2-water binary as a high priority system for measurement

Challenges

- Material of construction must be compatible with iodine, hydriodic acid, and water at elevated T and P
- Continuous-flow apparatus concept must be redesigned with corrosion-resistant materials for all wetted surfaces
- Detection of liquid-liquid interface for iodine-rich and water-rich liquid phases
- Analytical methods need to be developed for individual species (including speciation into other compounds, such as I_3^-)

Choosing a Material of Construction

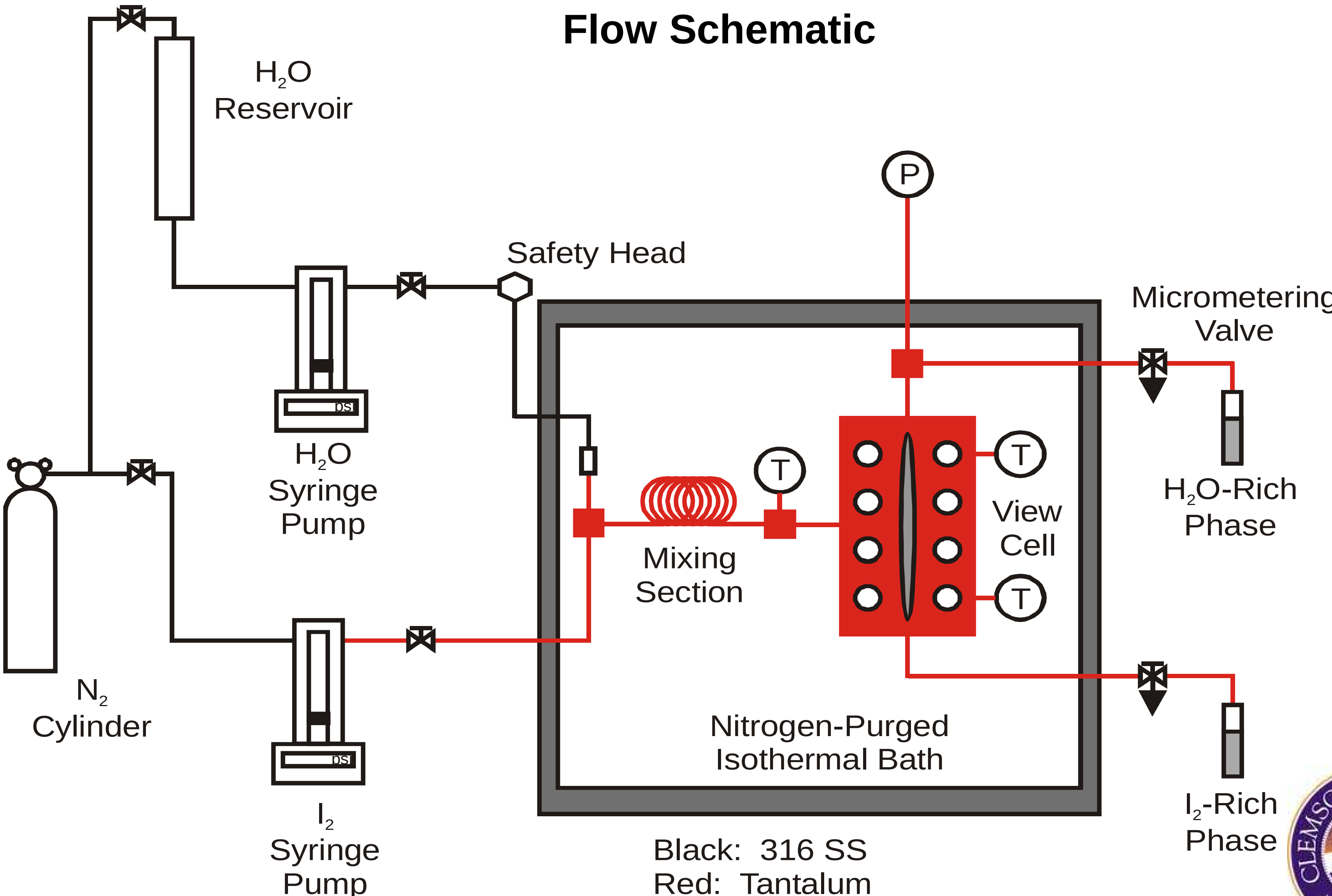
- Corrosion study of HI–I_2–water mixtures obtained from General Atomics
  - Excellent resistance obtained for Ta and Ta alloys (Ta-2.5W, Ta-10W) and Niobium
  - Poor resistance with 316 SS and Titanium
  - Hastelloy C acceptable only for pure molten iodine
- Ta-2.5W was chosen b/c has significantly higher mechanical strength than pure Ta

Difficulties in working with Tantalum

- Only a small number of vendors are available (none for 1/16" fittings and only a couple for Ta block and rod
- Difficult to machine
  - More care in drilling and threading; specialized tools required
  - Significantly longer machining times req'd compared to SS
- Long delivery times (5-12 weeks)
- Cost (~$300-400 per lb)
- Oxidation issues at temperatures above 350-400 ℃
- Niobium alternative is even more difficult to work with than Ta
- Clemson CoES Machining and Technical Services (MTS) was selected for Ta fabrication

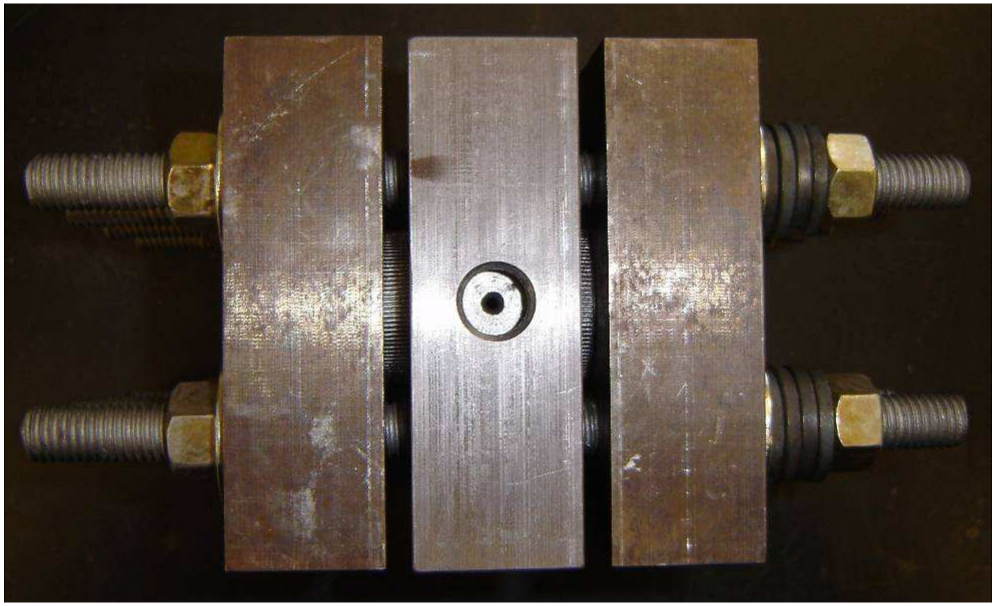
Continuous-Flow Apparatus (CFA)

Flow Schematic



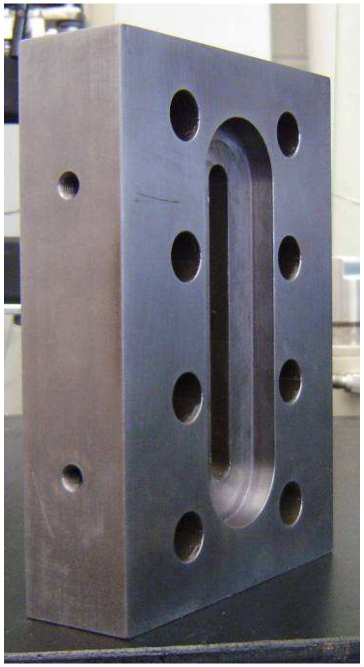
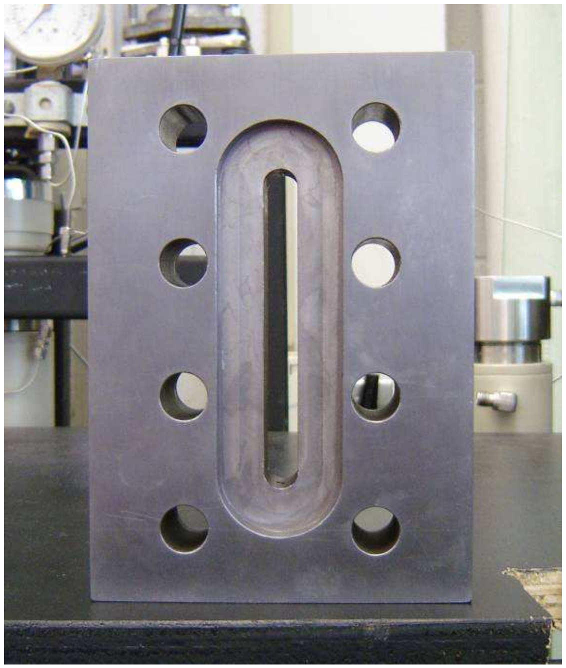
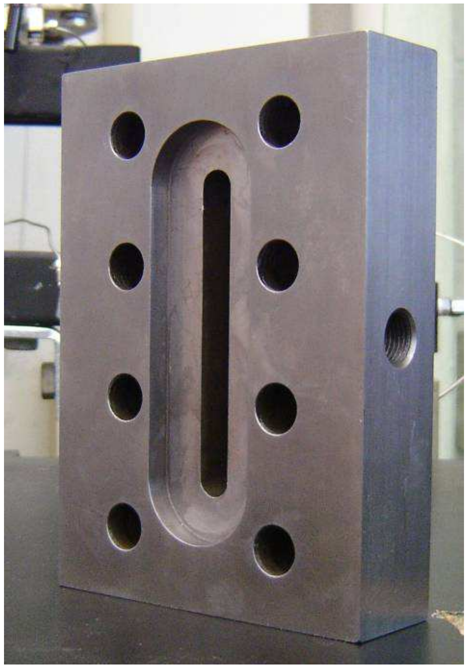
Redesign of CFA: View Cell

- "See-through" view cell design from Thies group (Roebers and Thies, 1990)
  - Aluminosilicate windows with Mica shields to be used initially; sapphire and quartz are also options
  - Graphite gaskets for sealing the dual windows
  - Belleville washer design prevents window leakage upon thermal expansion



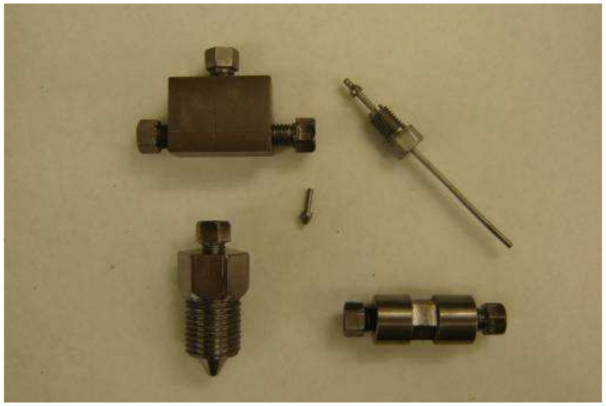
Redesign of CFA: New Inner Chamber of Ta

- Inner chamber and windows are wetted surfaces of the view cell
- New inner chamber was fabricated from Ta-2.5W block by MTS
- Design calculations to account for decreased strength, different thermal expansion properties of Ta were performed

Fabrication of Ta Fittings

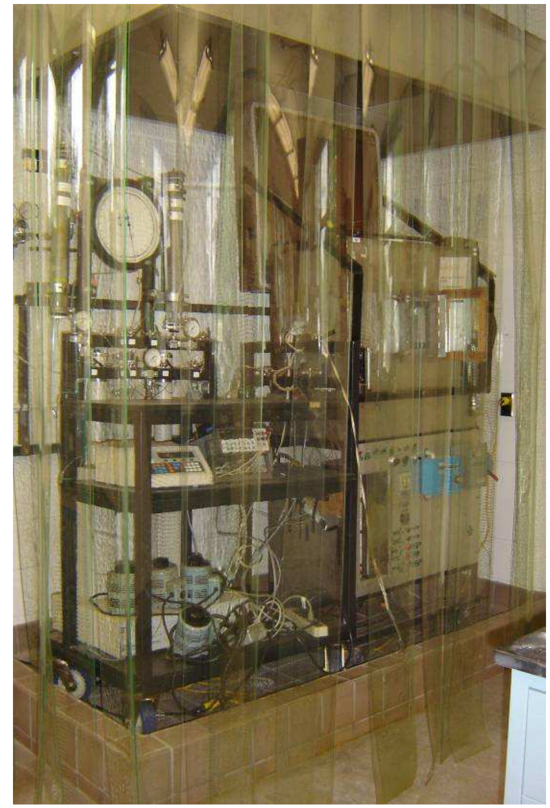
- 1/16” HIP-type fittings fabricated from Ta rod by Clemson MTS
- Initial tests were conducted to evaluate quality of fittings
  - Test fittings appeared similar to steel counterparts based on threading, holes and smoothed edges, so “mass production” was carried out
  - About 120 fittings fabricated, including 1/16” taper-seal glands, sleeves, plugs, couplings, and tees. Adapters to connect tubing to view cell were also fabricated
- Average cost of a fitting is ~$60 compared to ~$6 for its commercially available, stainless steel counterpart



High-Temperature Nitrogen Bath

- Low-oxygen atmosphere provided by nitrogen purge
  - ~0.3mol % oxygen in bath
  - Necessary to reduce/eliminate any oxidation of tantalum at elevated temperatures

Inside view



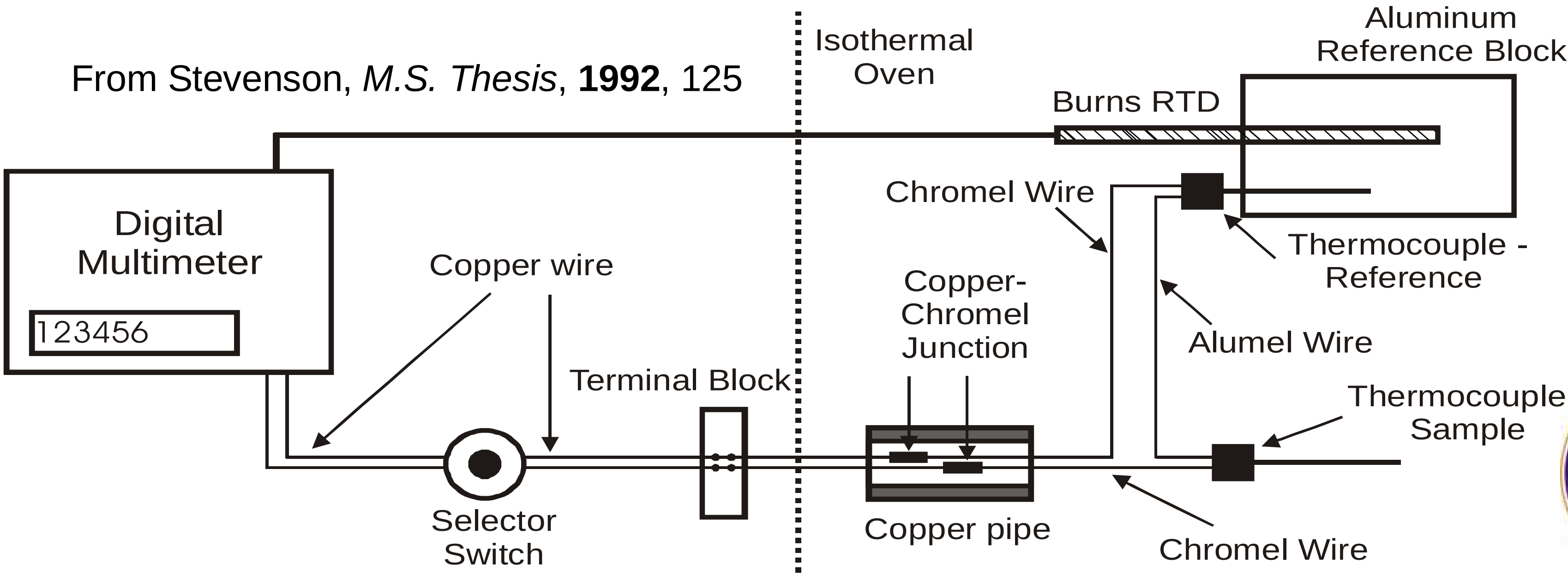
Side view

- Entire CFA located in a dike to prevent accidental spillage of chemicals
- Surrounded by safety curtains in case of accidental release of fumes to lab area
- Overhead exhaust ventilation

Precision Temperature Measurement

- Using differential thermocouples to determine system temperature
- Calibration of T/Cs not required b/c only small (~1 ℃) differences b/n cell and Al block are measured
- 0.032” Type K T/Cs inside 1/16” Ta or Hastelloy protection tubes
- Three sample locations: Feed into view cell, top and bottom phases in view cell

From Stevenson, *M.S. Thesis*, **1992**, 125

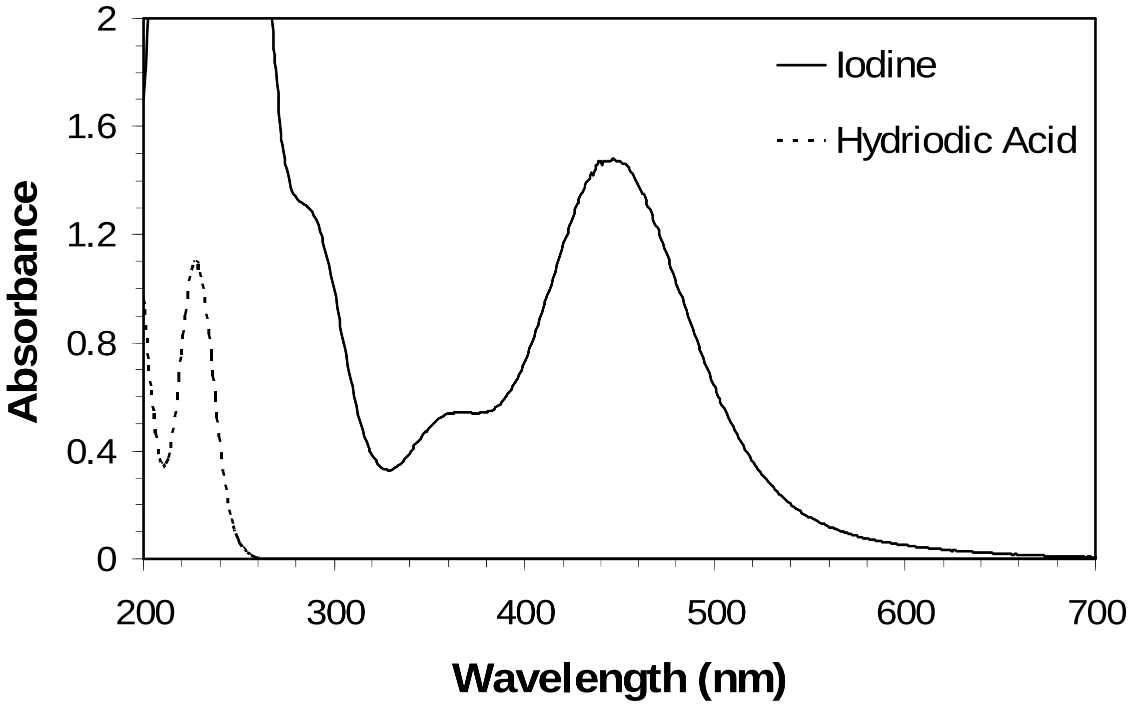


Interface Detection in View Cell for I_2 Mixtures

- Fluid interfaces in equilibrium cell should be observed to ensure that complete phase separation is obtained and to ascertain whether system is in equilibrium
- Concern due to opaque nature of molten iodine: will the interface between iodine-rich and water-rich layers be visible at operating temperatures (i.e., 150-350 ℃) ?
- Tests were conducted with hot I_2-water liquid-liquid mixtures in sealed Pyrex tubes to determine if interface could be seen
  - Conc. ranging from 14-40 mol% I_2 were investigated
  - Interface not visible under normal lighting above 140 ℃
  - But interface easily visible up to 160 ℃ using IR detector

Analytical Methods

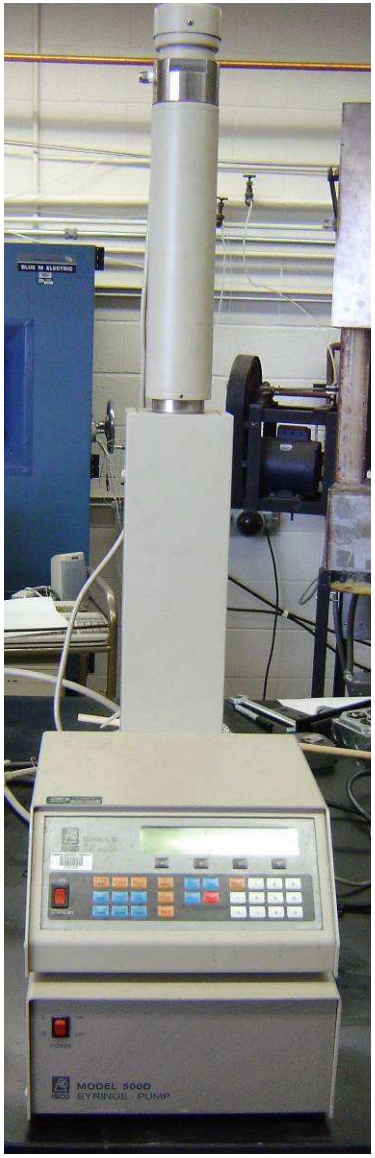
- For the iodine-rich phase, the water content will be determined by Karl-Fischer titration
- For the water-rich phase, iodine and HI content will be obtained via UV-Vis spectroscopy (I_2 @ 443 nm, HI @ 227 nm)
- A co-solvent (e.g., methanol) is necessary to homogenize the solid I_2–water samples for analysis at ambient conditions



Conclusions

- Continuous-flow apparatus with wetted surfaces of Ta has been designed and constructed for comprehensive VLE, LLE, and LLVE measurements
- Apparatus suitable for measurements with mixtures of HI, water, and iodine at elevated temperatures and pressures.
- Issues with materials of construction, interface detection, and analysis appear to have been essentially resolved
- T and P calibration, the pumping of molten iodine, and sample expansion/collection are final issues to resolve before I_2–water experiments can begin
- LLE composition measurements for I_2–water from ~150 ℃ up to the UCST should be completed by early summer

Pumping System



- I_2
  - Isco pump with Hastelloy C barrel
    - Heated in pump to ~130 ℃ using heating tape
    - Other connections outside of oven heated using heating tape
- HI (57 wt% in water)
  - Ion chromatograph pump (PEEK wetted parts)
- Water
  - Isco pump (standard)
- Flow rates of ~2 mL/min for each species

Precision Pressure Measurement

- Heise gauge calibrated with dead weight tester to ±1 psi used for pressure determination
- Line to pressure gauge from top of view cell
- Currently, can measure pressure up to 2,500 psi (can be extended to 5,000 psi)