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Retrofit of a Rubotherm ISOSORP® 2000 for PVT-x and Sorption Measurements at Cryogenic Temperatures

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Abstract. Type V composite storage tanks have significantly increased the working pressures of cryogenic systems for aerospace applications. However, the current operating pressures often exceed the range of available mixture property models and measurements. The majority of cryogenic mixture property measurements are historical, having not been reviewed in over 40 years, which represents a growing problem. This paper describes the retrofit of an established Rubotherm ISOSORP® 2000 dual-sinker densimeter for cryogenic service. Design of a cryostat with vibration-isolation bellows to minimize vibration from the pulse-tube cryocooler is presented. Parasitic heat load calculations are provided to estimate the minimum operating temperature. The system is capable of achieving pressure up to 30 MPa. The design and anticipated capabilities of the experimental system are described.

Keywords: Sorption, Density, Mixture, PVT-x, Rubotherm, Magnetic suspension balance
PACS: 06.30.Dr, 68.43.-h

INTRODUCTION

The current renaissance in aerospace is fueled, at least in part, by the new classes (Type IV and V) of cryogenic compatible composite fuel tanks. Liner-less (Type V) tanks are currently in use with liquid oxygen and liquid nitrogen at pressures up to 41.3 MPa and plans exist to extend use to lower temperature cryogenic mixtures [1]. However, the high operating pressures present new challenges for measurement of sorption into the composite materials and for precision Pressure-Volume-Temperature-Composition (PVT-x) measurements of the fluid mixtures. Sorption and PVT-x measurements are necessary for modeling tank degradation, heat transfer at the fluid-tank interface, pressurization, and development of reference quality mixture equations of state [2]. The latter need is the most pressing; the majority of cryogenic mixture property measurements are historical, having not been reviewed in over 40 years [3]. When correlated with a reference quality mixture equation of state, these measurements form the basis for all subsequent system design and modeling.

We have begun the retrofit of an established Rubotherm ISOSORP® 2000 magnetic suspension balance with a vibration isolated Cryomech PT405 cryocooler to address the need for accurate sorption and PVT-x measurements at cryogenic temperatures and elevated pressures. The Rubotherm ISOSORP® instruments utilize a positional magnetic suspension coupling for higher accuracy comparative measurements while maintaining thermal-fluid isolation of the precision micro-balance. The most substantive measurements accomplished by this specific instrument at Washington State University (WSU) were PVT-x data measured simultaneously with dielectric constants and molar polarizabilities of Methane+Propane+Hexane mixtures over the temperature range from 297–313 K and pressures up to 12 MPa, *with uncertainties in densities less than ±0.06 %* [4,5]. The system has also measured sorption properties for natural polymer production [6].

This paper introduces this new experimental capability to the field. We first review the operational premise of the instrument and subsequently discuss the modifications necessary to retrofit the Rubotherm ISOSORP® 2000 for cryogenic service. Thermal and mechanical design calculations are presented for the modified test cell incorporating a high vacuum cryostat for interface with the vibration isolated cryocooler. The anticipated measurement procedure and capabilities are also provided.

MODUS OPERANDI

The Rubotherm ISOSORP® 2000 is a gravimetric densimeter utilizing Archimedes' principle to determine the density of a fluid. A sinker of known mass and volume is immersed in the fluid and the small change in weight is used to estimate fluid density or isothermal sorption into a sample. The operating principles for this type of system

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are well established and similar models are currently in use for designation of primary standards [7,8]. A conceptual schematic of the magnetic suspension balance is shown in Figure 1. Custom sinkers of known mass and volume are suspended in a fluid maintained at a fixed temperature and pressure. This sinker is mechanically coupled to a permanent magnet that has freedom to move vertically. The sinker and permanent magnet are sealed within the magnetic suspension housing which is subject to the conditions of the fluid being tested. The position of the permanent magnet, and thus the sinker, is controlled using an electromagnet which is suspended just above the housing. The electromagnet is then connected to the micro-balance. The load applied to the balance has thus been decoupled from the testing conditions due to the separation between the permanent magnet and the electromagnet.

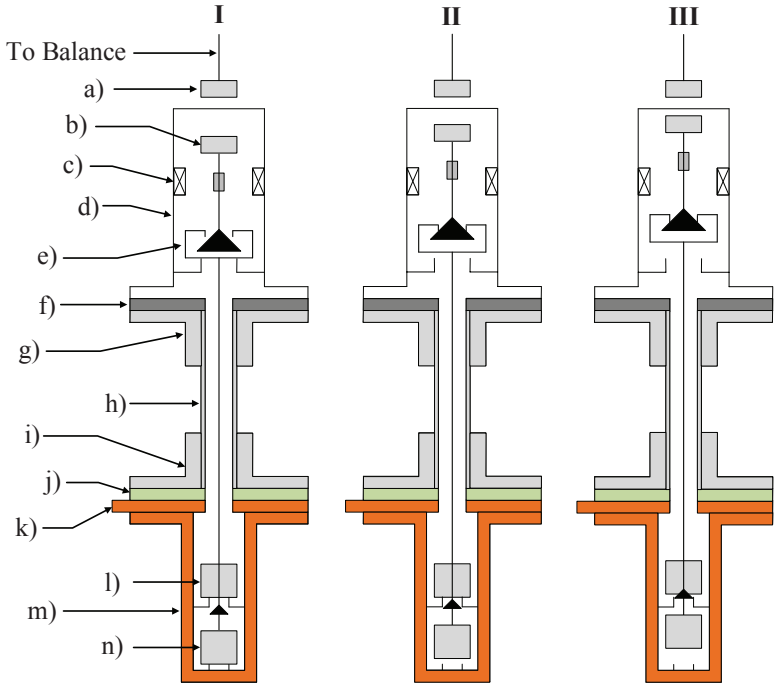

FIGURE 1. Sinker positions for the Zero Point position (I), Measurement Point 1 (II), and Measurement Point 2 (III) are shown for dual-sinker measurements using the Rubotherm ISOSORP® 2000. Components a through n are as follows: a) electromagnet, b) permanent magnet, c) sensor coil, d) magnetic suspension housing, e) magnetic suspension coupling, f) vacuum chamber wall, g) top stainless steel flange, h) stainless steel pipe, i) bottom stainless steel flange, j) G10 thermal barrier, k) copper bus bar to cryocooler, l) sinker 2, m) copper test cell, n) sinker 1.

The position of the permanent magnet is determined by a sensor coil which is used to control the electromagnet. The system can be configured to use two sinkers by having two measuring point positions. This allows for dual-sinker comparative measurements. The Zero Point position shown in Figure 1 is a reference position when both sinkers are resting on a stand and are not in contact with the suspension system. The balance will be zeroed in this position. Measurement Point 1 is the test position when the bottom sinker is lifted from its support and is suspended in the fluid. This load will then be transmitted up to the balance through the magnetic coupling. Measurement Point 2 is when both sinkers are suspended in the fluid. The load measured by the balance will differ from the true weight of the sinkers depending on the density of the fluid they are suspended in. This data can then be used to determine the density of the fluid, or sorption isotherms of a sample in the fluid.

RETROFIT DESIGN CALCULATIONS

Figure 2 shows a conceptual diagram of the experimental system. All components enclosed in the vacuum chamber that are subject to the testing conditions were designed to withstand pressures of 34.5 MPa with a factor of safety of at least 3. In order to determine the minimum wall thickness of the internal components, the components were treated as thick-walled cylindrical pressure vessels [9]. The critical stress occurs in the circumferential direction which is given by the equation

$$\sigma = \frac{r_i^2 P_i - r_o^2 P_o + (P_i - P_o) r_i^2 r_o^2 / r^2}{r_o^2 - r_i^2}, \tag{1}$$

where σ is the hoop stress, r_i and r_o are the inner and outer radii, P_i and P_o are the internal and external pressure, and r is the radius at the point of interest. Since the maximum stress occurs when $r = r_o$ and the internal components are under vacuum, Equation 1 can be simplified to

$$\sigma = \frac{2 r_i^2 P_i}{r_o^2 - r_i^2}. \tag{2}$$

Equation 2 was used to determine minimum thicknesses of internal components using the yield stress of the materials and size limitations on the internal diameter. The minimum internal diameter was set to ½ in. to allow sufficient room for the magnetic coupling wire to move without contacting any component. The thermal standoff consists of a ½ inch schedule 40 pipe made of 316 stainless steel welded to two custom flanges made from a 3.5 in. diameter round bar of 316 stainless steel. The top flange is bolted to the top wall of the vacuum chamber and sealed with a fluorocarbon o-ring while the bottom flange is bolted to the thermal barrier and sealed using 1/16" indium wire. The thermal barrier is made from G10 with dimensions of 3.5 in. diameter and ½ in. thickness. The 316 stainless steel used in the thermal standoff has minimum yield strength of 415 MPa at room temperature [10]. The bus bar and copper test cell are made from C110 H04 copper, having a yield strength of 303.4 MPa [10].

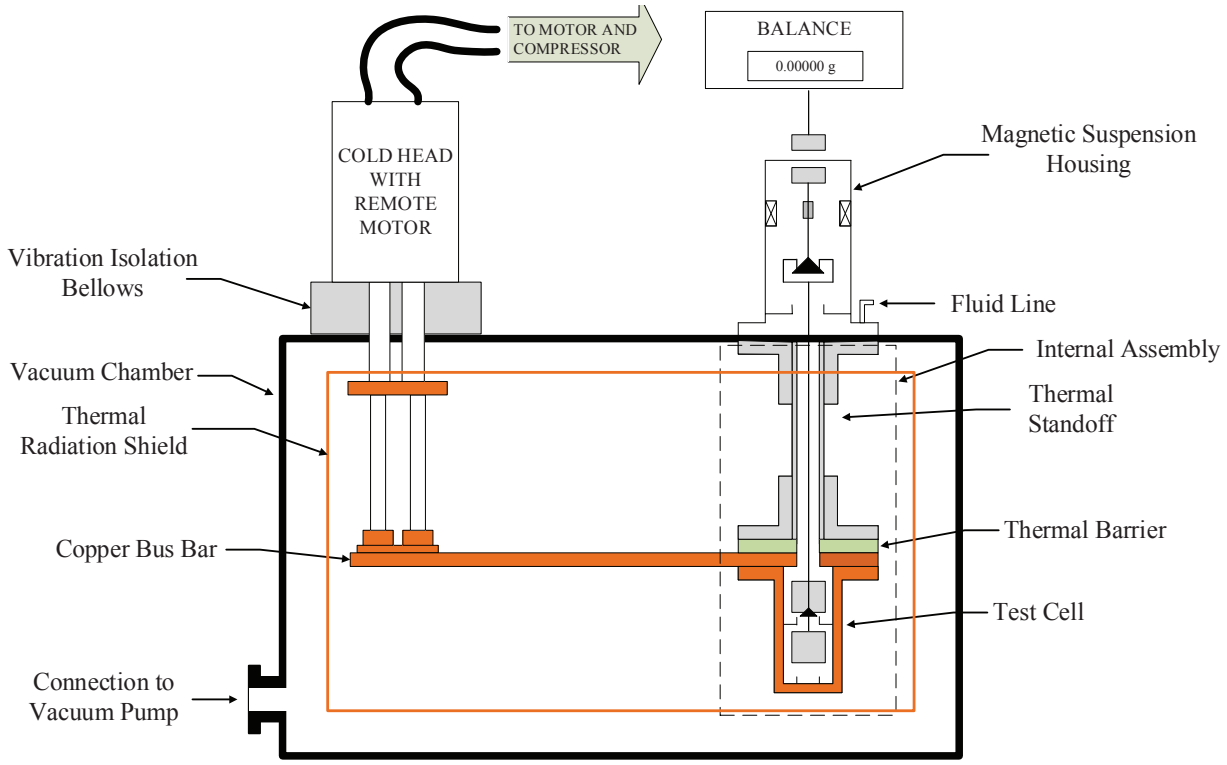

FIGURE 2. Conceptual diagram of retrofitted Rubotherm.

The internal assembly, pictured in Figure 3, was also designed to optimize the lowest achievable temperature. The internal assembly is enclosed in a 22.5 in. x 10.5 in. x 19.0 in. vacuum chamber made of 304 stainless steel that is capable of achieving a vacuum pressure of 10^{-7} torr so parasitic heat loads due to convection are assumed negligible. Heat transfer due to radiation will be mitigated by enclosing the internal assembly in a copper radiation shield that is covered by 30 layers of MLI. Thus, the only heat leak into the test cell considered is conduction through the internal assembly. The thermal standoff pipe was sized to minimize the cross sectional area in which conduction occurs while being able to withstand the pressure requirements and allow enough room for the magnetic suspension wire to pass through unhindered. The G10 thermal barrier separates the thermal standoff from the

copper bus bar. The test cell is located below the copper bus bar to create a thermal dead end for isothermal temperature measurements as recommended by Ekin [11].

With radiation and convection assumed negligible, the parasitic heat leak into the test cell was simplified to

$$\dot{q}_{parasitic} = \frac{T_{room} - T_{cell}}{R_{s\tan doff} + R_{barrier}}, \tag{3}$$

where T_{room} is the temperature of the room, T_{cell} is the test cell temperature, $R_{s\tan doff}$ is the thermal standoff resistance, and $R_{barrier}$ is the thermal barrier resistance. The resistances were calculated using

$$R = \frac{L}{kA_c}, \tag{4}$$

where L is the length of conduction, k is the integrated average thermal conductivity over the temperature differential, and A_c is the cross sectional area. The parasitic heat load was calculated to be 2.3 W at 20 K. The minimum temperature occurs when the cooling capacity of the cryocooler is equal to the heat leak due to conduction. A piecewise function of the cooling capacity of the Cryomech PT405 cryocooler was developed from the cooling capacity curve provided by the manufacturer [12]. The lowest achievable temperature was implicitly solved using Engineering Equation Solver (EES) [13]. The minimum temperature was calculated to be 10 K.

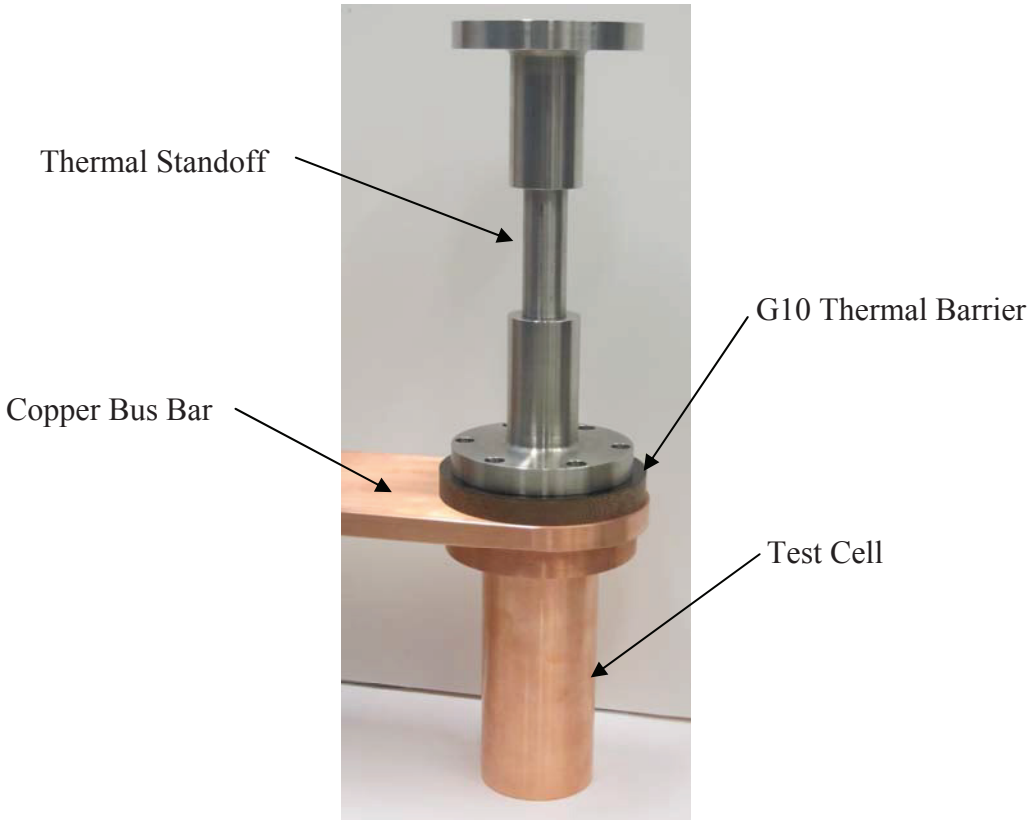

FIGURE 3. Picture of internal assembly components post machining.

INSTRUMENTATION AND ANTICIPATED MEASUREMENT ACCURACY

The system was plumbed to allow for measurement of pure fluids or fluid mixtures. Figure 4 shows the flow diagram of the system. All of the inlet plumbing components are rated to withstand pressures of at least 41 MPa. The system is outfitted with two inlet gas lines that converge prior to entering the Rubotherm assembly. A Paroscientific Digiquartz® pressure transducer with an accuracy of 0.01 % [14] is located upstream of the magnetic suspension housing. Once the fluid has filled the magnetic suspension housing, it enters the internal assembly which

is enclosed in a custom stainless steel vacuum chamber. The vacuum chamber is outfitted with a Varian DS 102 roughing pump and an Agilent Turbo-V 81-M turbomolecular pump capable of providing a minimum vacuum pressure of 10^{-7} torr.

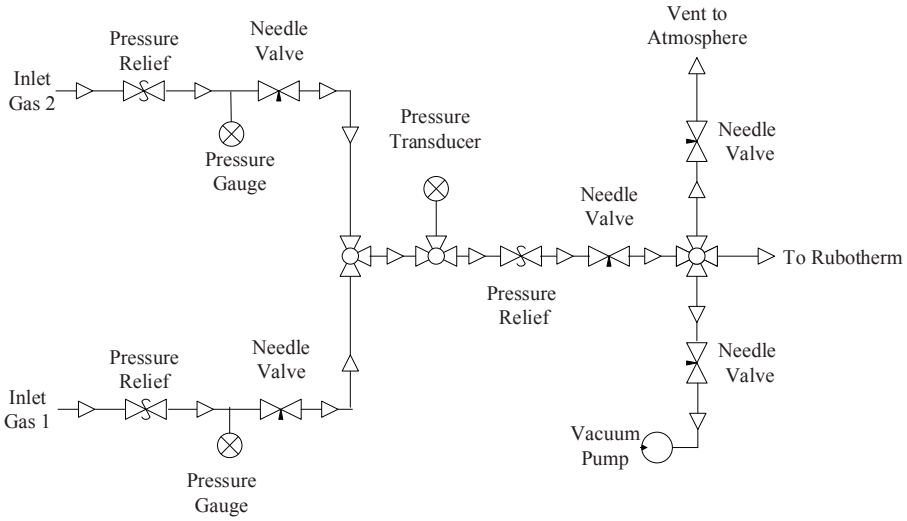

FIGURE 4. Plumbing diagram of the experimental system.

Once in the internal assembly, the fluid flows down the stainless steel thermal standoff, through the G10 thermal barrier, through the copper bus bar, and condenses in the copper test cell. The copper bus bar is connected to a Cryomech PT405 cryocooler which has a cooling capacity of 0.45 W at 4.2 K and 22 W at 65 K [12]. Temperature is measured using two Lake Shore GR-1400 secondary standard temperature sensors that are mounted to the copper test cell. These germanium RTDs have an accuracy of ± 4 mK at 4.2 K and will be controlled using a Lake Shore Model 336 temperature controller [15].

The primary sinkers that will be used in this apparatus are made from titanium and quartz. Volumetric changes of the sinkers due to thermal affects will be accounted for using thermal contraction data [16,17]. The sinkers are housed in the copper test cell which has a 2.30 in. (30 mm) diameter hole that is 3.937 in. (100 mm) deep. The sinkers are connected to the magnetic suspension coupling by a 0.04 in. diameter 316 stainless steel wire. The position of the sinkers is controlled using the Rubotherm ISOSORP® 2000 which determines the change in mass of the sinkers by using a Mettler Toledo AT261 DeltaRange® balance that is accurate to ±10 μg. These densimeters are known to consistently produce pρT data with a total uncertainty of 0.01 % to 0.02 % [7].

CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE RESEARCH

We have completed the design and are nearing completion of the retrofit of a Rubotherm ISOSORP® 2000 for cryogenic service. To our knowledge, this will be the first precision dual sinker density and sorption instrument capable of continuous operation below 60 K. Upon final assembly, calibration measurements will be conducted on well documented fluids to validate the accuracy of the system. This system will be used to measure binary mixtures including helium-hydrogen, and hydrogen-methane. We also plan to investigate wetting and sorption onto composite samples. Uncertainties arise in sorption measurements due to changes in the sample volume. These affects have been investigated for other Rubotherm devices and are discussed elsewhere [18]. Though sample volume changes are generally considered small, we may consider installing sapphire windows into the test cell to measure volume changes by direct observation.

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