NASA/CR-97-113013

/ 124772

MCR-96-1303, Issue 04

Contract Number: NAS8-40633

Membrane Transport Phenomena (MTP)

Semi-Annual Technical Progress Report

June 1997 - October 1997

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MTP PROJECT ACTIVITIES

The activities during the fourth semi-annual period of the MTP project have involved the completion of the Science Concept Review (SCR) presentation and peer review, continuation of analyses for the mass transfer coefficients measured from MTA experiment data, and development of the second generation (MTP-II) instrument. These activities are detailed in following sections.

MTP SCIENCE CONCEPT REVIEW

The MTP SCR was held on 13 June 1997 at Lockheed Martin Astronautics in Denver, CO. The SCR panel members were intrigued by the experiment, but did not recommend support for the current proposal to fly the MTP experiment in a microgravity environment. The panel generated several recommendations for the MTP project. The primary recommendations are summarized in Table 1.

Table 1 Summary of Primary SCR Panel Recommendations

(1) Continue and refine development of mass transfer coefficient analyses
(2) Refine and upgrade analytical modeling associated with the MTP experiment.
(3) Increase resolution of measurements in proximity of the membrane interface.
(4) Shift emphasis to measurement of coupled transport effects (*i.e.*, development of MTP phase II experiment concept).

The first recommendation involves analysis of data acquired during the MTP experiments, relating the measurements of osmosis kinetics and refractive index profiles to mass transfer coefficients and fluid dynamic properties. Progress has been made in this analysis, as described later in this report.

The second recommendation is directed towards the development of a complete Computational Fluid Dynamics (CFD) model of the MTA system, activity that will require the addition of a Co-Investigator to the project. The current MTP funding level does not support this additional effort, and a result, the modeling activity has been postponed until such time when support is available.

The third recommendation is related to the resolution of optical measurements in the proximity of the membrane, a measurement that is limited by the Membrane Seal Assembly. The thickness of the seal extends to about 2 mm on each side of the membrane in the current prototype instrument. The Viton material used to create the seal obscures the refractometer laser beam, and interferes with measurement of the refractive index in this region. Prior to the SCR, the Membrane Seal Assembly was only developed to the point where a leak free fluid cell configuration was attained. No further attempt was made to optimize the seal geometry or dimension. An improved design for the MTA fluid cell geometry and Membrane Seal Assembly has been developed, and is described later in this report.

The forth recommendation involves investigation of coupled transport effects, and development of instrumentation for measurement of these effects in the MTA. This activity was included in the original plan as Phase II of the MTP instrument development. Progress is reported here for the design and fabrication of the second generation MTA instrument (MTA-II). The MTA-II includes capabilities to allow application of trans-membrane chemical, thermal, and electrical driving potentials. These driving potentials may be applied singly or in combination to produce and create various osmotic and coupled transport phenomena. The instrumentation for imposition of these additional driving potentials has been completed, and is detailed later in this report.

MASS TRANSFER COEFFICIENT ANALYSIS

The analysis protocol for the mass transfer coefficient from the MTA experiment data and image processing analysis procedure has progressed. The mass transfer coefficient values generated in this analysis compare favorably with published values in the literature, but show a great deal of scatter. Methods for improving the analysis are in progress, including the use of a polynomial regression algorithm to interpolate the data relative to surrounding values, and smooth out the contours. This eliminates spurious fluctuations in apparent solution composition, and decreases the scatter of the contour lines. The analysis is not yet complete, but should show significantly improved capabilities for determination of the mass transfer coefficient in the fluid boundary layer.

The structure of the boundary layer that forms in an MTP osmosis experiment is determined by the relative interaction of the solvent and solution molecules in the fluid region next to the membrane. In the (-1g) gravity orientation, osmosis acts to continually introduce fresh solvent molecules into the fluid boundary layer that forms in this region, lowering the solute molecule concentration adjacent to the membrane. Diffusion acts in the opposite direction to increase the solute concentration next to the membrane, and continue to drive the osmotic process. These two driving forces are thus coupled, and act in opposite directions. The structure of the boundary layer that forms is a direct result of the interaction between these two transport phenomena.

The refractive index profile image data acquired during MTP experiments is processed to show lines of constant fluid composition within the time-distance parameter space defined by the experiment. In the data, lines of constant solution composition are shown as contours, with the slope of a contour at every point representative of the sum of the interaction between the diffusion and osmotic fluxes. The slope of a contour line has units of velocity (dx/dt = distance/time), and represents the net velocity vector that results from vector addition of the bulk (osmotic) flux velocity vector, and the opposed diffusion velocity vector. The analysis also includes partial molar volume effects, the change in solution specific volume that occurs upon mixing for solute and solvent. The magnitude of the partial molar volume effects are determined in separate experiments that measure the partial molar volumes of the solute and solvent. The rate of change of the solution molar volume with concentration is then linked to the diffusion velocity, as these effects are dependent on diffusive mixing kinetics. Table 2 summarizes the velocity vectors required in the Mass Transfer Coefficient analysis, the measured parameter, and the origin of data used to determine each vector.

Table 2 Measurement Parameters for Determination of Mass Transfer Coefficient

Vector Quantity	Measured Parameter	Data Origin
net velocity	slope of fluid contour	RI profile
diffusion velocity	solute mole fraction (activity) gradient	RI profile
bulk velocity	trans-membrane osmotic flux	VFS sensor
partial molar volume	change in specific volume on mixing	Solute char. exp.

The Volumetric Flow Sensor data used in this analysis is acquired from the pure solvent (water) side of the membrane. The volume effects of mixing propagate through the fluid on the opposite (solute) side of the membrane. The partial volume effect is small compared to the diffusion and osmotic velocities, but is cumulative over the entire boundary layer. Assuming the membrane does not move, the effect of the change in solution specific volume that occurs immediately adjacent to the membrane is also present throughout the entire solution side volume, and affects the structure of the entire boundary layer. This effect is included in the analysis when the partial molar volume velocity vector is integrated over the thickness of boundary layer, and combined with the osmotic and diffusion velocity vectors to calculate the effective mass transfer coefficient at every point within the experiment parametric space.

The use of the dimensionless solute mole fraction (Xa) has been adopted, as defined in the following equation:

$$Xa = C_a/(C_a + C_b)$$

where:
Xa is the solute mole fraction
C_a is solute (sucrose) concentration
C_b is the solvent (H_2O) concentration.

Xa is calculated from solute characterization experiment data performed prior to each osmosis experiment. The characterization experiments measure solution parameters such as solute weight percent, density, and refractive index. These data are then correlated over a range of solution concentrations, and used in the mass transfer coefficient analysis. Figure 1 shows the partial molar volume data obtained from a sucrose solution characterization experiment using a successive dilution technique. Polynomial regression analyses were used to relate the partial molar volumes of sucrose and water to the sucrose mole fraction, and shown as fits to the data.

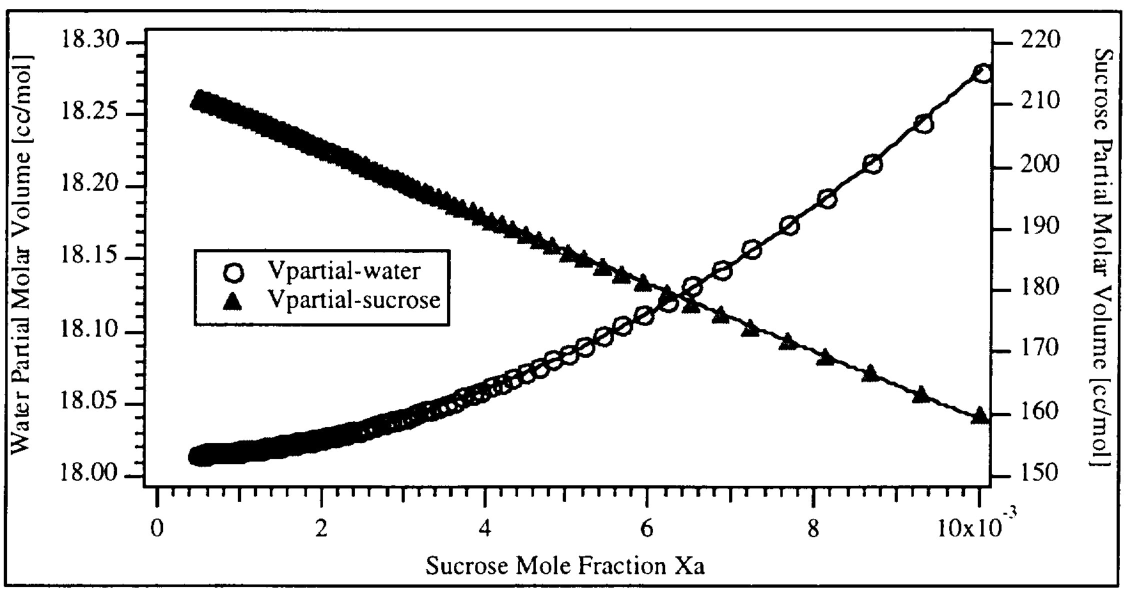

Figure 1 Partial Molar Volume of Sucrose and Water in Binary Solution

The total solution molar volume (solute + solvent) at a given solute mole fraction can be determined from these relations by addition of the component partial molar volumes. Figure 2 shows the total solution molar volume as a function of mole fraction for the sucrose - water binary system. The first derivative (dVm / dXa) can be determined from this relation, and represents the rate of change in the solution molar volume changes with respect to mole fraction. The molar volume quantities are solute and solvent specific, and knowledge of these relationships is required to solve the transport equations and determine the mass transfer coefficient.

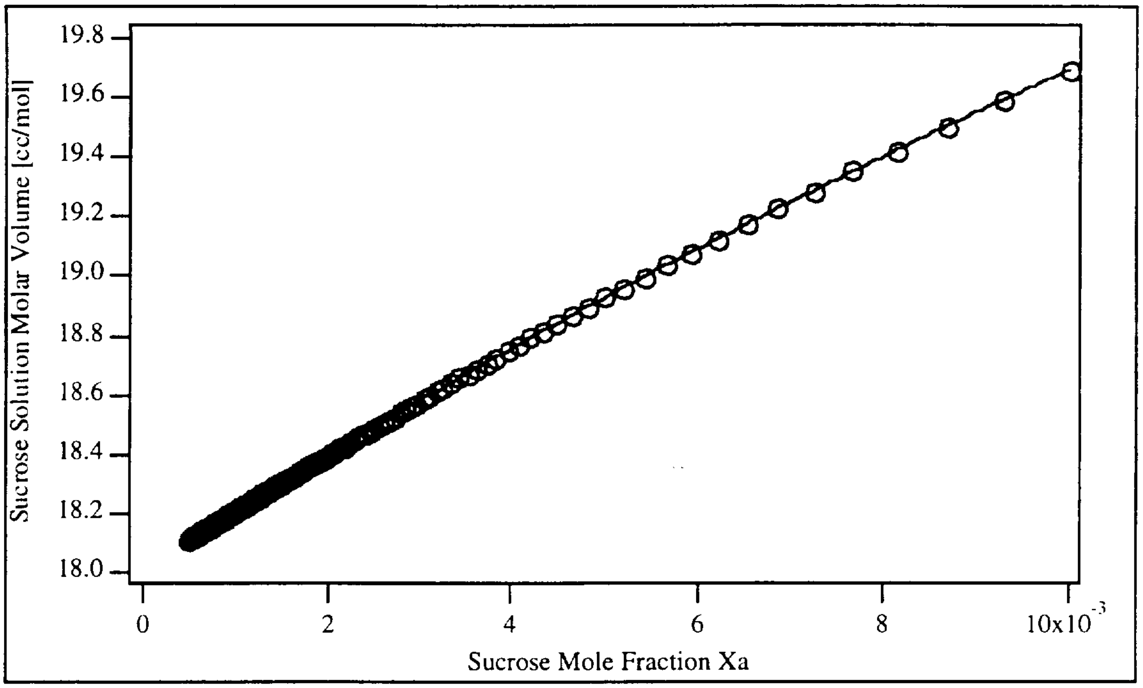

Figure 2 Solution Molar Volume Determined for Sucrose / Water Binary System as a Function of Sucrose Mole Fraction

MTA DEVELOPMENT ACTIVITIES

Several improvements have been developed for the MTA, including an upgraded fluid cell design, thinner membrane seal assembly, capability for application of additional driving potentials, development of a thermal model, and development of a printed circuit board for the Volumetric Flow Sensor interface electronics. Additionally, a demonstration version of the MTP experiment suitable for space flight in a glovebox environment has been designed. The Membrane Transport Cell (MTC) has also been designed for the collaboration with National Institute of Standards and Technology (NIST) and the Federal Bureau of Reclamation (FBR). Each of these activities are detailed in the following sections.

Improved Fluid Cell and Membrane Seal Assembly Design

An improved version of the MTA fluid cell has been designed. The design incorporates a thinner Membrane Seal Assembly, and an internal fluid cell geometry that is appropriate for fluid transfer operations in microgravity. The design is based on a 45° right triangle, the geometry that showed the best filling and draining performance during the DC-9 parabola experiments performed last year. Figure 3 shows a schematic of the fluid cell design.

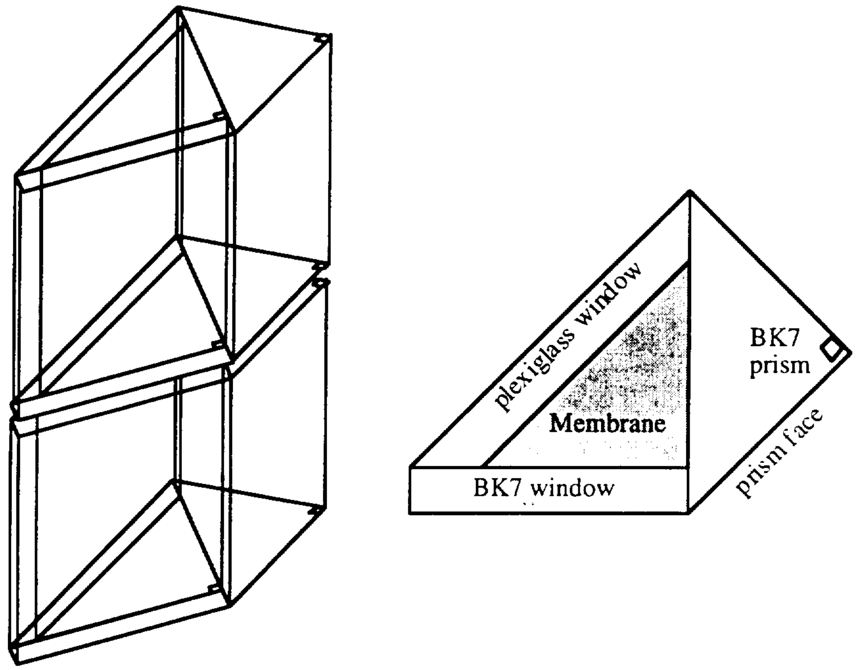

Figure 3 Improved MTA Fluid Cell Design

The prism and window legs of the right triangle form the interface to the refractometer system, and are constructed using BK-7 optical glass with an antireflection coating. The hypotenuse of the fluid cell triangle is constructed from Plexiglas, and provides the interface to the MTA Fluid Manipulation System. Specifications for these optical components were generated, and procurement activities initiated. The optical components must be custom-cut to precision dimensions, and have a lead time of several months.

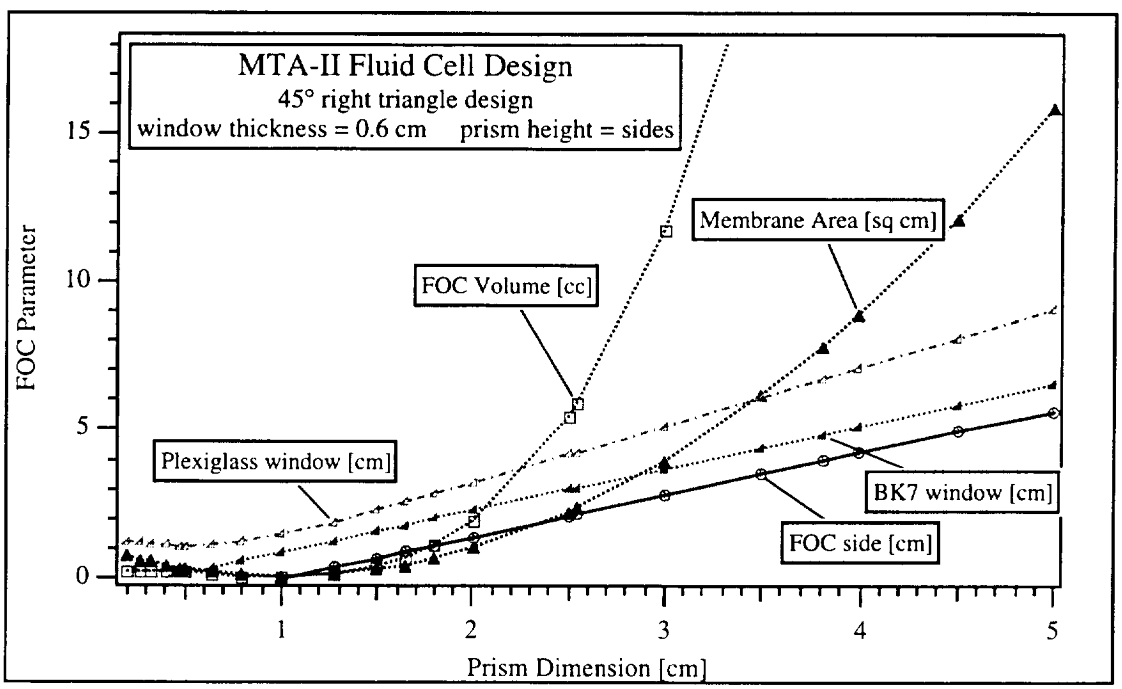

Figure 4 MTA Fluid Cell Parametrics for 45° Right Triangle Internal Geometry, with 6 mm Window Thickness

The dimensions of the optical components define several aspects of the fluid cell geometry, including: the membrane area available for osmotic transport, the total contained volume of fluid on each side of the membrane, and the area available for membrane sealing. Parametric calculations were performed to determine the relations among the various fluid cell parameters based on the 45° right triangle design. Figure 4 shows how the fluid cell parameters vary as a function of the triangle side dimension, for a window thickness of 6 mm.

Two separate sizes of fluid cells are in development, each having a different window thickness and overall dimension. Both designs are based on the 45° right triangle geometry, and will be tested and compared to determine optimal membrane sealing surface area, minimum seal thickness and optical obscuration, and filling and draining characteristics in planned microgravity aircraft experiments. The two cell designs will also be characterized in terms of osmotic performance, utilizing the membrane for osmotic transport while interfaced to the MTA profile refractometer and VFS systems.

Instrumentation for Application of Additional Driving Potentials

Instrumentation has been developed to allow the application of trans-membrane thermal and electrical driving potentials. In this design, the fluid cells are supported in compression between the two thermal reservoirs, with copper plates used to provide the interface to the electrical and thermal boundary conditions. The upgrade has been designed to accommodate both the MTA-I and the newer MTA-II Fluid Cell designs, either may be mounted within the support structure. Figure 5 shows a schematic diagram of the upgraded system, and how these driving potentials are applied.

The thermal boundaries for the MTA are defined by the two reservoirs, each connected to a temperature controlled circulation bath. The baths (Lauda M-3A) are listed as capable of controlling the circulation temperature to within 0.1°C. The reservoirs are interfaced to the MTA fluids through a copper plate sealed between the thermal and MTA fluid cell reservoirs. The temperature of the copper plate defines the thermal boundary condition for the MTA fluids. The high thermal conductivity of copper allows heat to be conducted from the circulation bath to the MTA fluids. Copper is also a good conductor of electricity, and the copper plate also serve as an electrode for imposition of the trans-membrane electrical potential, or for measurement of streaming potentials generated during osmotic transport operations.

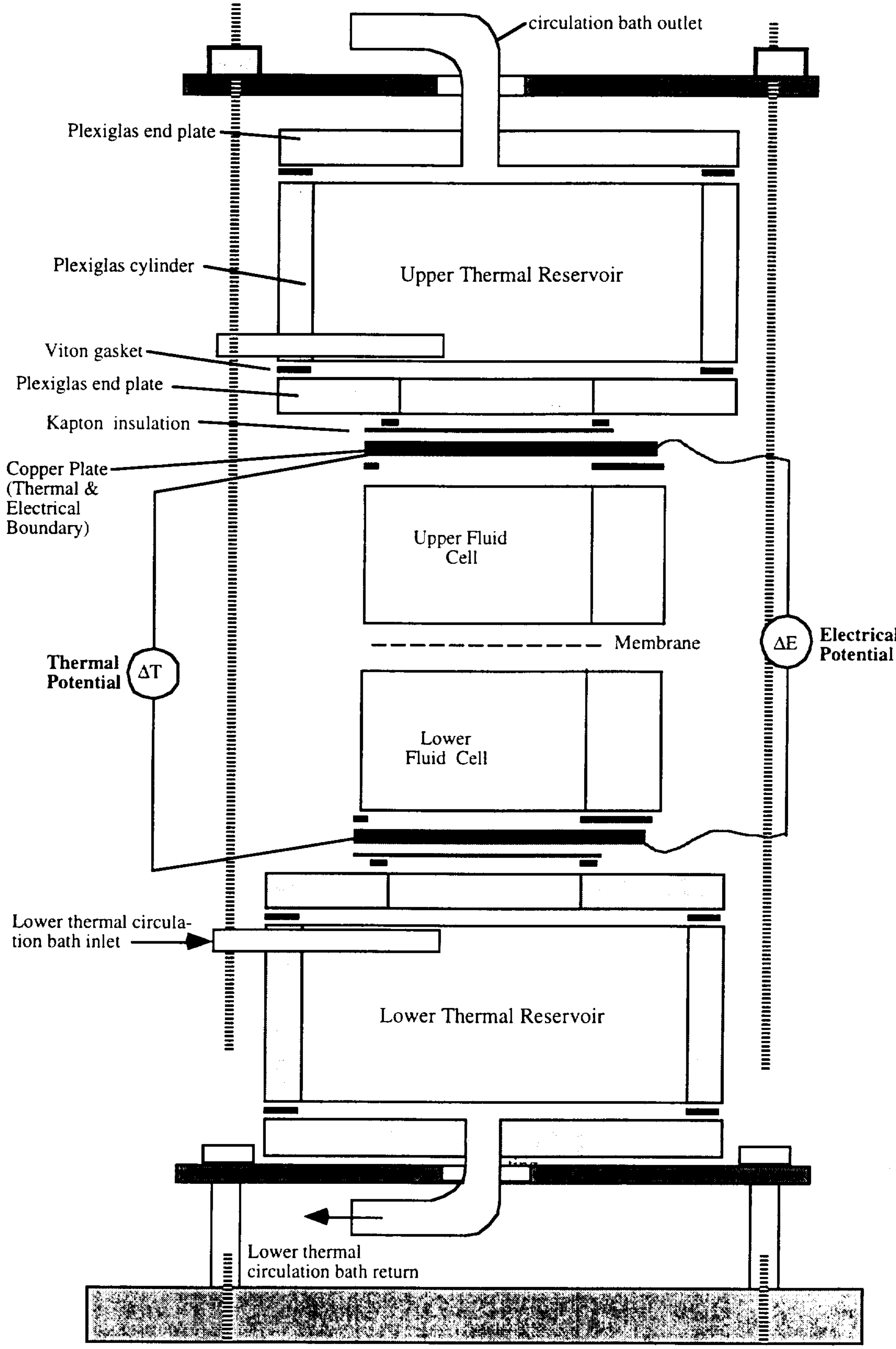

Figure 5 Schematic Diagram of MTA Driving Potential Upgrade

Commercially available Resistance Temperature Detectors (Pt-RTD, Omega Inc.) were procured, and the mechanical and electrical interfaces developed to allow computer acquisition of the circulation bath temperature data over time. The RTD's were joined to the end of a Luer fitting adapter, and sealed in place to prevent the circulating fluids from contacting the electrical connections. An electrical interface was developed using a Series 5B backplane, with modules to convert the RTD resistance measurement to a signal voltage, producing a linear voltage output with RTD temperature. Cables and software were developed to allow data acquisition using the MTP computer. The RTD's were calibrated using a precision thermometer, both submersed in a circulation bath. The bath temperature was systematically varied while recording the RTD output, and the reading from the precision thermometer. It was found that the bath temperature setpoint correlated very well with the precision thermometer reading. Figure 6 shows the RTD calibration data.

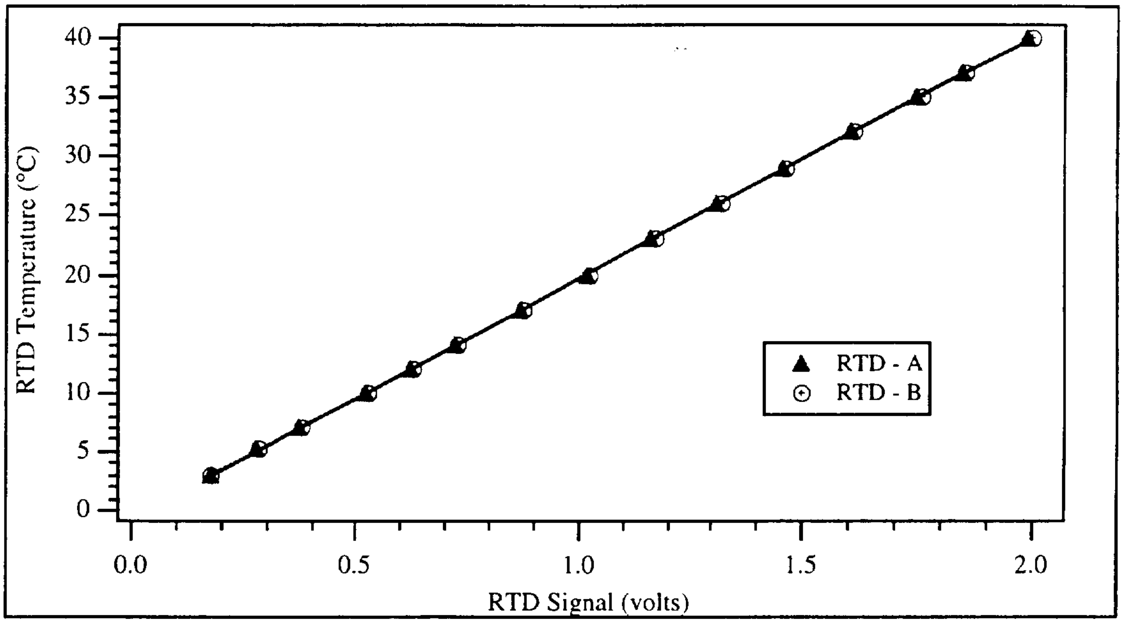

Figure 6 Platinum RTD Calibration Data

The circulation baths were interface to a cooling system to allow operation at sub-ambient temperatures. Figure 7 shows the system configuration for sub-ambient operation, where a small freezer and pumps are used to circulate cold fluid through the temperature control bath units.

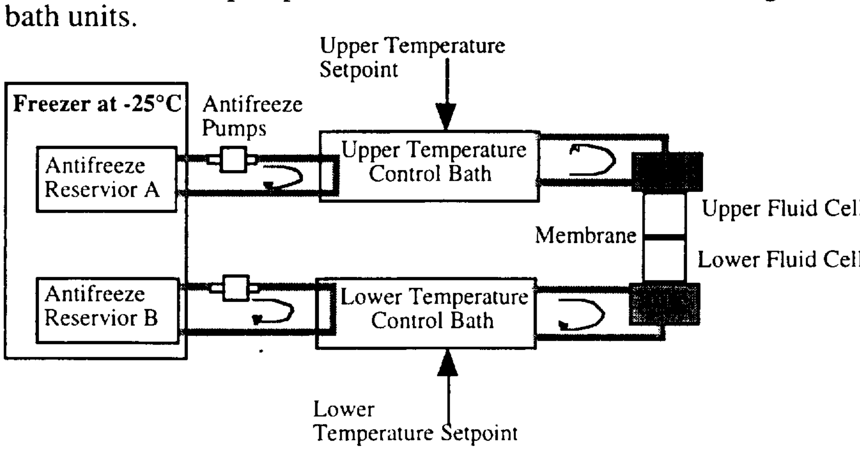

Figure 7 MTA Thermal Control System Schematic

Antifreeze solution (50% ethylene glycol) is contained in two reservoirs within the freezer, one for each circulation bath. A small pump is connected inline with each antifreeze reservoir and circulation bath, and used to pump the antifreeze solution through a cooling loop in the bath. This provides a cold sink for rejection of heat from the circulation bath fluid.

Software was developed to acquire the output signal from the RTD's, apply calibration factors, and record the data. Experiments were then performed to characterize the thermal performance of the system. Figure 8 shows data from an experiment with one side of the cooling system running at maximum. The data show that a temperature of 1°C is attained for a short time, and that a controlled temperature less than 10°C may be sustained for many hours. The ambient temperature is also shown, acquired from a thermocouple suspended in air near the system.

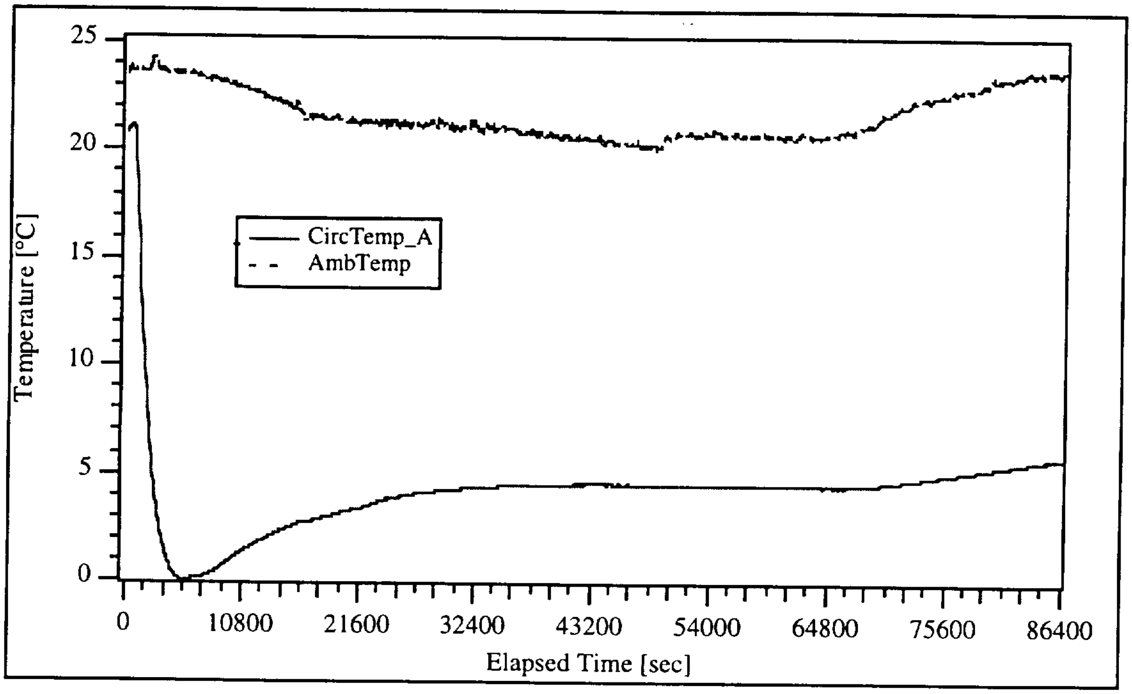

Figure 8 Thermal Control System Characterization Experiment

MTA Thermal Model

A model was developed to simulate the thermal behavior of the MTA fluid cell assembly. The initial version of the model shown is based on the MTA-I geometry. Subsequent versions of the model will be developed for the right triangle geometry of the MTA-II described in the previous section.

The model is three dimensional, and includes 315 separate thermal nodes that are connected through a series of thermal conductors, and boundary conditions defined by the circulation bath reservoirs and ambient temperature. The nodes are located symmetrically about the MTA centerline, and configured as a series of stacked planes between the two thermal boundaries. The thermal conductance between nodes is defined by the thermal conductivity and heat capacity of the materials present at each location in the MTA. Figure 9 shows a diagram of the MTA thermal model, with nodes shown as dots and conductors shown as lines between the dots.

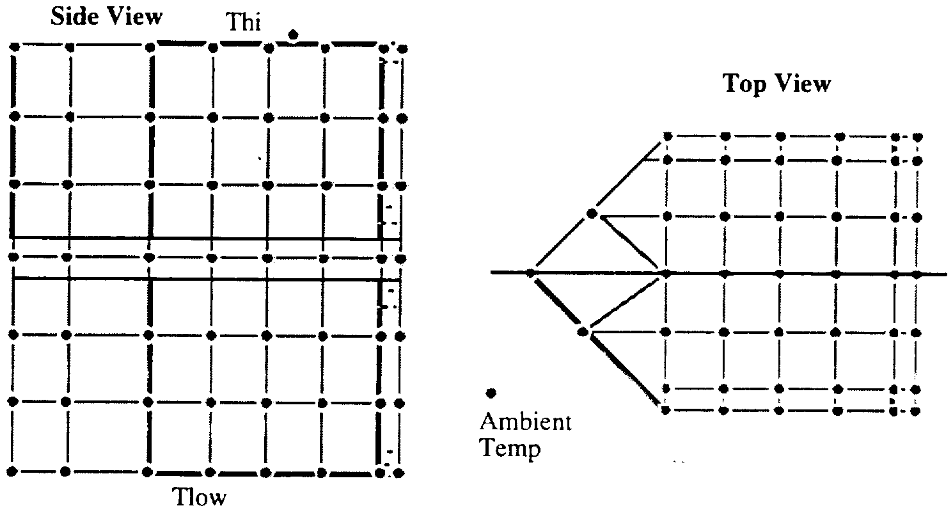

Figure 9 MTA Thermal Model Diagram Showing Node Positions

The MTA thermal model was developed using the Systems Integrated Numerical Differencing Algorithm (SINDA 85) application. The SINDA program was developed by Lockheed Martin, and has been used to create thermal models for many and varied spacecraft and flight instruments. The model is initialized with all components at ambient temperature. The transient temperature response is then predicted after imposition of thermal boundary conditions located at the upper and lower copper plates in the MTA. The current model assumes that the fluid thermal properties are those of a homogeneous solution, and that no convection occurs within the contained fluids. In the future the model will be upgraded to simulate stratified fluid layers in association with the membrane, as occurs when osmosis is active. The no convection assumption is valid as long as the fluid density gradient that forms is stably stratified with respect to gravity, that is, the higher density (generally lower temperature) fluid is present at the lower thermal boundary. This orientation is similar to the (-1g) gravimetric orientation described in prior reports for MTA osmosis experiments.

The transient response of the fluids is predicted, and output at regular intervals in the computation process. The model output is generated as a tabular listing of nodal temperatures as a function of time. Graphical techniques are currently being developed to visualize the temperature distribution present within the MTA.

The MTA model is three dimensional, and is useful for prediction of many aspects of the MTA thermal performance, including: thermal gradients present within the experiment fluids perpendicular to the membrane, the temperature distribution in the experiment fluids parallel to the membrane, determination of times to reach thermal steady state, the magnitude of wall effects, and how the various fabrication materials affect the temperature distribution. This information will also be applicable to the design and development of the MTA flight unit.

The model has been run for several different boundary conditions. Figure 10 lists the transient output for a central node in the upper and lower fluid cells, under conditions of 30°C at the upper boundary, and 10°C at the lower boundary, and 20°C ambient temperature.

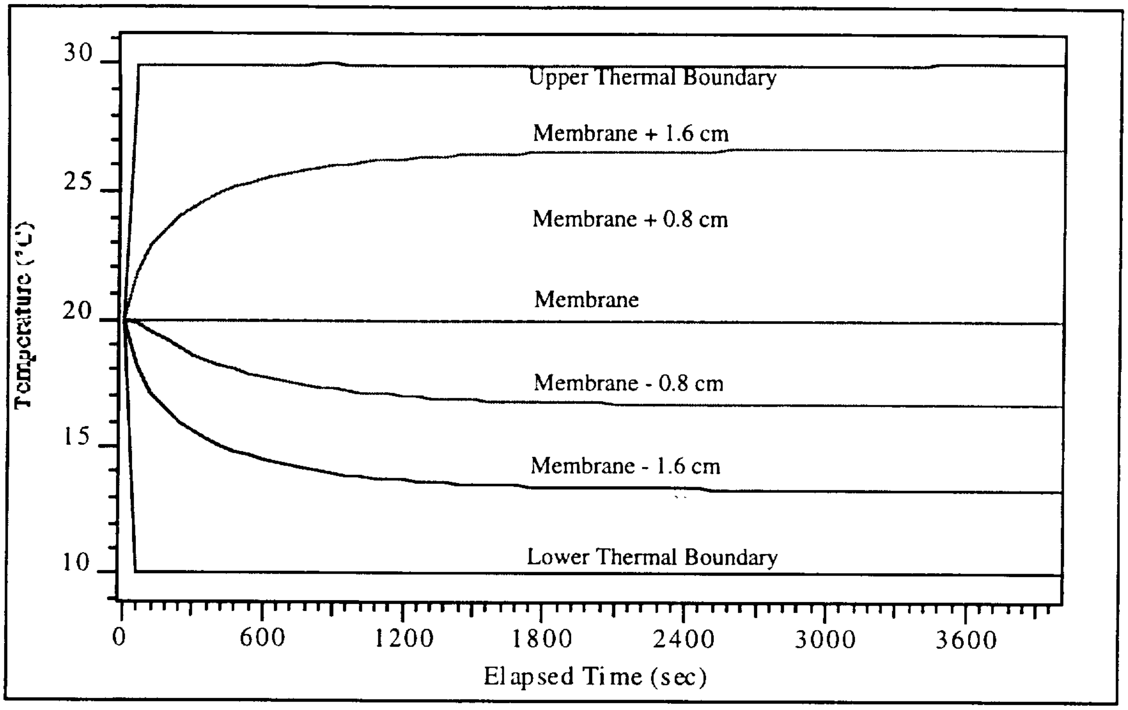

Figure 10 Transient Temperatures in a Central Node in the Upper and Lower MTA Fluid Cells: 30° Upper Boundary, 10° Lower Boundary, 20° Ambient Temperatures

The structure of the thermal gradients present within the experiment fluids relative to the boundary conditions and the membrane are of interest for characterization of the apparatus and detection of coupled transport in experiment fluids. The model predicts that at least an hour is required to reach thermal steady state within the MTA fluids, for these boundary conditions. Figure 11 shows the predicted steady state temperature distribution at two planes parallel to the membrane within the MTA fluids, for these boundary conditions. The distribution is substantially is one dimensional; that is the temperature variation at any cross section within the MTA is less than a few hundredths of a degree. The membrane has high thermal conductivity, and the temperature variation is even less at the membrane surface.

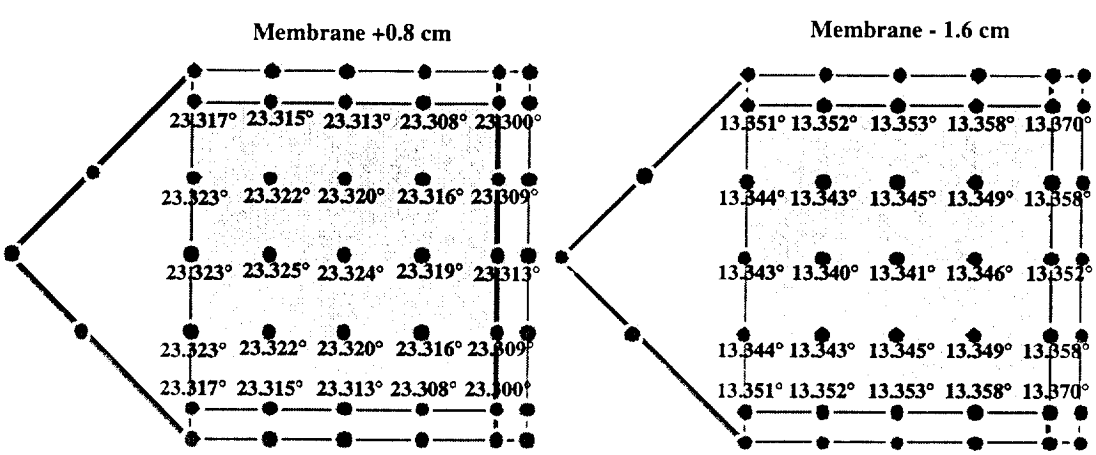

Figure 11 Membrane Node Temperatures At Two Planes Parallel to the Membrane Under Steady State Conditions in a Homogeneous Fluid. 30° Upper Boundary, 10° Lower Boundary, 20° Ambient Temperature

Volumetric Flow Sensor Interface Development

A printed circuit board (PCB) design and layout was generated for the Volumetric Flow Sensor (VFS) interface electronics circuit. Each PCB includes circuitry for two separate VFS sensor interfaces as well as voltage regulation, VFS signal integration and amplification, and a signal output voltage offset adjustment. A local vendor (Protosource Inc.) was used to fabricate the batch of circuit boards, and parts ordered to allow several VFS interface units to be built. The circuit boards have been received, and appear to have the proper and functional circuitry. The electronic parts have not yet been received.

These VFS interface circuits will be built and used in each of the membrane test units that are currently under development. Separate VFS units will be dedicated to each application, and the interface circuits optimized for the specific data acquisition functions.

Demo-MTA Microgravity Demonstration Experiment Development

The Demo-MTA has been designed as an apparatus for a microgravity glovebox demonstration experiment, and includes several key aspects of the MTP experiment concept. The experiment design includes a right triangle fluid cell design for microgravity fluid manipulation, and a VFS system for measurement of osmotic transport kinetics. Figure 12 shows a schematic of the Demo-MTA design.

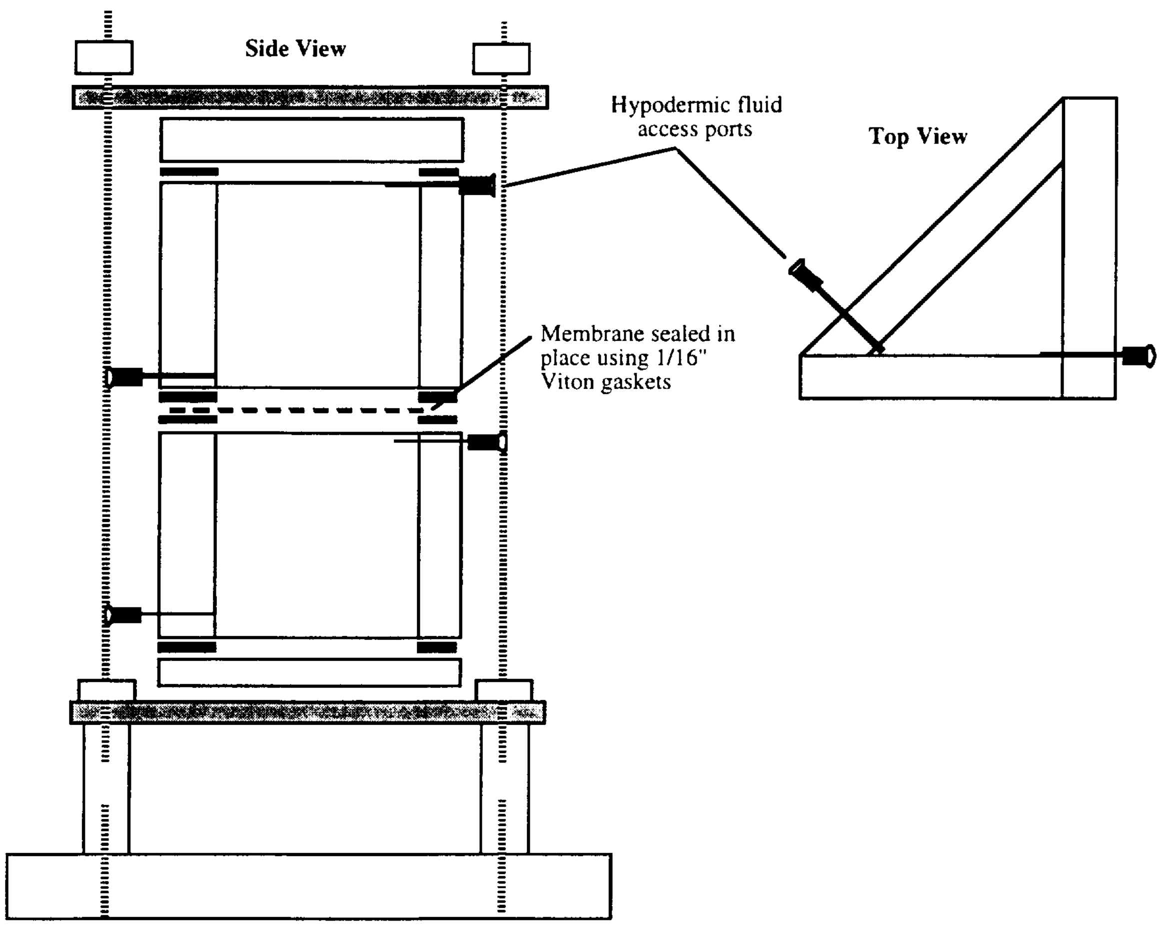

Figure 12 Demo-MTA Schematic Diagram

The fluid cell geometry of the Demo-MTA is based on the 45° right triangle design, similar to the MTA-II design described in a prior section of this report. The fluid cell is constructed entirely from Plexiglas, and does not include the fluid profile refractometer system. The Membrane Seal Assembly thickness in the Demo-MTA is not critical because there is no optical subsystem, and can be as thick as necessary to provide a tight seal. Fluid access ports are included in the design to allow filling and draining of the fluid cells. Current plans for the demonstration experiment are to use an astronaut to initiate the experiment by physically manipulating the experiment fluids using manual valves connected via tubing to syringes and overflow traps. The experiment solutions (water, sucrose, PEG) will be introduced into the Demo-MTA fluid cells on orbit within the glovebox containment facility. The filling and draining operations will be videotaped to assess functionality of the fluid cell design, and data collected from the Volumetric Flow Sensors and electrical interface to measure the kinetics of osmotic transport in microgravity.

Membrane Transport Cell (MTC) for LMA / NIST / FBR / NASA Collaboration

A collaboration has been established between Lockheed Martin Astronautics (LMA), the National Institute of Standards and Technology (NIST), the Federal Bureau of Reclamation (FBR), and NASA. The project has been named Membrane Transport Cell (MTC), and is based on technology from the MTP flight experiment development. The goal of the collaboration is to develop a prototype apparatus that will accurately measure the effective diffusive mass transfer coefficients of water through membranes. Experiments planned for the MTC will involve precision measurement of water transport kinetics from a compartment containing "solute-free" water into one containing the water solution, driven by osmosis. This measurement is useful for characterizing membrane performance in a way that is diagnostic for the various modes of transport of matter through a membrane. Alteration of the transport kinetics from a baseline value is then indicative of the underlying cause of the alteration. These measurements can provide a useful figure of merit for quickly characterizing new membranes, and for assessing relative alterations in membrane performance that result from storage, disinfection, and other treatments.

The MTC apparatus will be unique in the fact that no commercial device currently exists to perform these measurements. Membranes are used in a wide variety of applications, and an instrument to characterize membrane performance will be useful in many of these. The MTC thus represents a spinoff technology that is potentially viable in the commercial marketplace.

The collaboration activities include the build of a prototype Membrane Test Cell (MTC) apparatus, and development of instrumentation, software, experiment protocols, and analysis techniques necessary for measuring the kinetics of mass transfer through a membrane. In the MTC, two fluid compartments are separated by a semi-permeable membrane that is not permeable to the dissolved solute molecules. The single driving force for water transport will be the osmotic pressure (chemical potential) gradient present between the two fluid compartments. The data will be used to determine the time dependent, effective diffusive mass transfer coefficient of water through the membrane. Figure 13 shows the preliminary design schematic of the MTC apparatus.

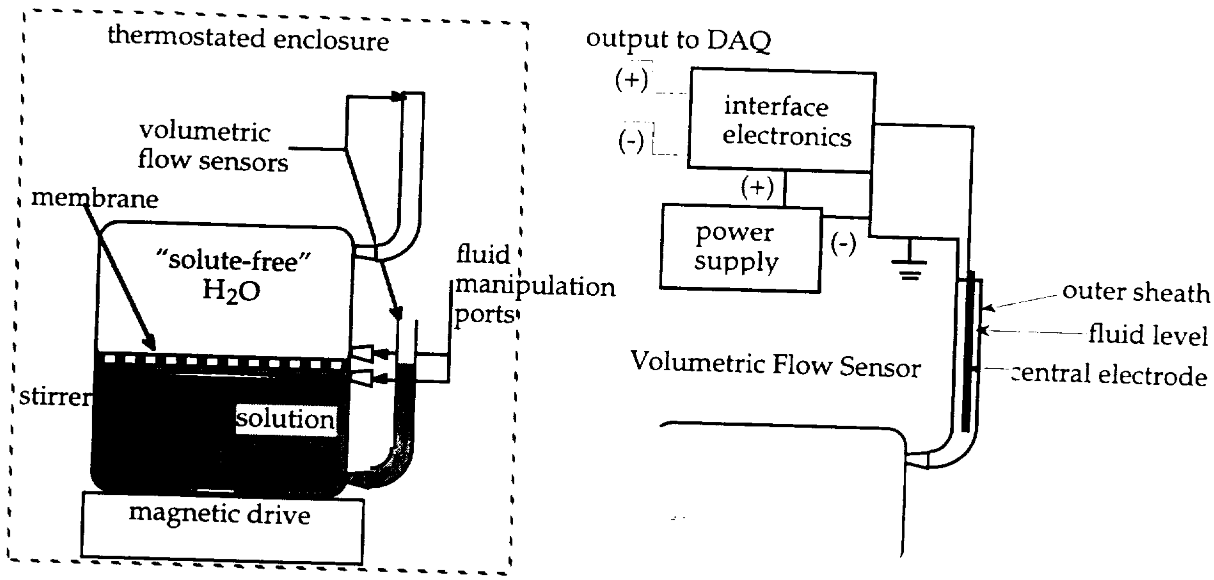

Figure 13 Membrane Transport Cell Schematic Diagram

Progress has been made in the design of the MTC fluid cells, and for a special version of the Volumetric Flow Sensor that will provide sub-microliter resolution for the MTC kinetic measurements.

The project description that follows was excerpted from the proposal to NIST and FBR for support of the MTC collaboration.

> The collaborative effort proposed is to build a Membrane Transport Cell (MTC) apparatus for precision measurement of water transport kinetics through a membrane. The support side of the membrane will be facing the "solute-free" H_2O. That cell will be pre-filled. At time zero the solution side cell is quickly filled and measurements of the water flux through the membrane are continuously made. The resulting data should have a characteristic time-lag form, as shown in Figure 14. When the rate of volume change is constant, the proportionality constant between the flux and the osmotic driving force is the effective water permeability coefficient through the membrane. The time lag, θ, is related to the thickness of the separating layer and the water diffusion coefficient through it. The diffusion coefficient combines with the water solubility to yield the permeability coefficient. Since the RO and NF membranes are not homogeneous films, extracting all the parameters will require further analytical modeling development.
>
> Measurement of the unsteady state gas and/or vapor transport ("time-lag") through membranes has historically been a very useful tool for characterizing pure component permeability, solubility, and diffusivity through membranes. Such measurements have been more problematical to perform for liquid transport through membranes.

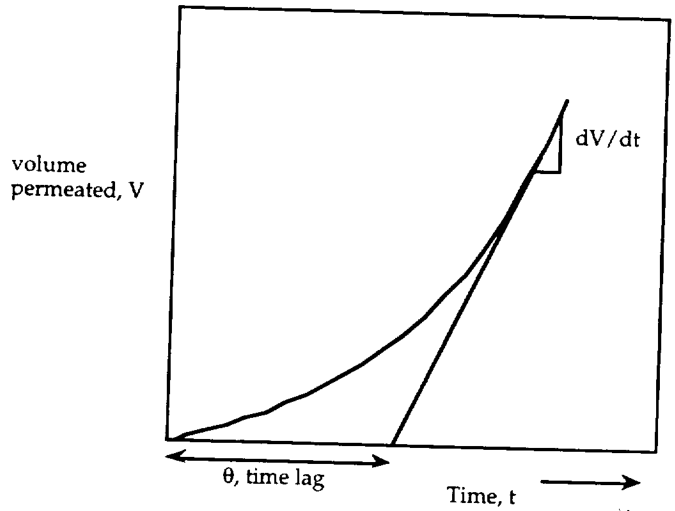

Figure 14 Anticipated Flow Kinetics and Analyses in the MTC

Recently, NASA has supported the development of an apparatus to study diffusion in unstirred layers separated by a semi-permeable membrane under microgravity conditions. This work was performed by Mr. Larry Mason at Lockheed Martin Astronautics, Denver, CO. Mr. Mason's instrumental focus was laser diffraction for determining the refractive index profile (correlating to concentration), but his design is also fully-automated and includes fast fill and emptying (without significant air bubbles), and high sensitivity level indicators that provide precise measurement of solvent flow kinetics. These latter characteristics support optimism that the design can be used for measuring liquid mass transfer properties through membranes in a time lag approach. Future apparatus development could also include solute concentration measurements for solute/membrane combinations that are not 100% rejecting of solute.