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MEASUREMENT AND CORRELATION OF WATER ADSORPTION EQUILIBRIA ON SILICA GEL, SORBEAD, AND ALUMINA USING A NOVEL EXPERIMENTAL ISOTHERM APPARATUS

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The design and operation of a novel, experimental volumetric isotherm apparatus is discussed. Water adsorption equilibria in nitrogen is measured over three adsorbents: silica gel 40, alumina F-200, and sorbead RF. This work concentrated on the adsorption behavior of water at low partial pressures ranging from 1 - 1000 Pa. The isotherm data for all adsorbents studied were measured over three orders of magnitude in both loading and partial pressure and also at three temperatures: 298, 323, and 348 K. In this study, initial efforts to measure and correlate water adsorption equilibria over different adsorbent materials are presented that span wide ranges of partial pressures and temperatures.

14. SUBJECT TERMS

Volumetric isotherm apparatus	Water	Adsorbate loading
Adsorption isotherms	Adsorption equilibria	Adsorbents
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PREFACE

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MEASUREMENT AND CORRELATION OF WATER ADSORPTION EQUILIBRIA ON SILICA GEL, SORBEAD, AND ALUMINA USING A NOVEL EXPERIMENTAL ISOTHERM APPARATUS

1. INTRODUCTION

Adsorption equilibrium data are needed to effectively operate and design adsorption-based separation or purification systems. One current advanced air purification technology being considered for military applications is pressure swing adsorption (PSA).[1,2] PSA is a well accepted commercial process for air purification, primarily used for air drying. In this process, typical specifications call for the reduction of water vapor concentrations from 30,000 to 3 ppm.[3,4] In order to design this type of apparatus, fundamental water isotherm data must be measured. This study looks at initial efforts in the design and development of a novel isotherm apparatus in order to measure and correlate low concentration water adsorption equilibria and evaluate adsorbent materials to determine their effectiveness in current as well as future air purification systems.

Although water adsorption isotherms have been measured at high to moderate vapor concentrations, there has been little work to explore the equilibrium data behavior at low concentrations and loadings. This study concentrated on the adsorption behavior of water at low partial pressures ranging from 1 - 1000 Pa. The isotherm data for the adsorbents studied were measured over three orders of magnitude in partial pressure and at three temperatures: 298, 323, and 348 K. Three adsorbents were examined in this study for their adsorption equilibria at the above conditions. They were chosen for their use in commercial drying and separation process. The first adsorbent studied was silica gel 40, a high surface area, large capacity material primarily used for industrial gas drying.[5,6] Next, an activated alumina, alumina F-200, was chosen for its hydrophilic property, large surface area, and use as a commercial sorbent in the drying of industrial gases and petrochemicals.[6] Finally, sorbead RF, a homogeneous mixed oxide composed primarily of silica (97%) and alumina (3%), was examined for its large surface area and use in commercial-regenerative air purification processes.

This work emphasizes the importance of measuring accurate and reproducible equilibrium data. An automated experimental isotherm apparatus was developed to greatly increase system reliability and improve the overall collection of data. The recirculating, volumetric isotherm system constructed was based on the design of Rudisill, et al., and incorporates a number of features to minimize equilibria data errors.[7] In this investigation, initial efforts to measure and correlate water adsorption equilibria over three adsorbent materials will be presented which span wide ranges of water partial pressures and temperatures.

2. EXPERIMENTATION

2.1 Adsorption Isotherm Measurement Apparatus.

A diagram of the experimental apparatus is shown in Figure 1. The configuration of the volumetric system is similar to that used by Kaul[8] and later by Mahle, et al. There are four subsystems that comprise the main isotherm apparatus: (1) the water delivery system; (2) the temperature control system; (3) the circulation and adsorption system; and (4) the vapor-phase analysis system. All four subsystems are automated with a computer-controlled interface using National Instrument's LabVIEW programming language. The data acquisition program was developed under contract at the U.S. Army Edgewood Research, Development and Engineering Center (ERDEC) and allows the system to be fully automated and measure multicomponent adsorption equilibria at a variety of different temperatures and concentrations.

Some of the important capabilities of this experimental apparatus are that: (1) a wide range of vapor-phase concentrations may be measured; (2) rapid achievement of equilibration is possible with the recirculation of the gas mixture; (3) multi-component equilibria is easily measured with the use of single or multiple gas chromatographic detectors; (4) multiple temperatures may be set to gather data for many isotherms; and (5) the system is fully automated with only the user input initiated at the beginning of an experiment. A current project is underway and is the subject of another report to modify the system and install a new high pressure circulation pump to measure the effects of pressure (up to 35 atm) on the adsorption equilibria of trace components.* Multi-component adsorption of gases in a variety of temperature and pressure ranges has been documented using a number of experimental techniques.[9] The technique used in this study is based on the volumetric method and is best suited to measure both single and multi-component equilibria. In the volumetric method, the amount and composition of the gas-phase mixture are measured both before and after adsorption and the amount of chemical loaded onto the adsorbent is calculated using the difference in these quantities. A more in depth procedure is described below.

2.1.1 Water Delivery System.

A schematic of the water delivery system is shown in Figure 2. The gas-phase concentration of water is controlled using a water delivery system consisting of: (1) a temperature controlled, insulated Valco valve enclosure to deliver liquid water at desired temperatures; (2) a 316 stainless steel chemical reservoir filled with approximately 500 ml of water; and (3) 3, 6-port Valco valves (Valco, DC6UWP) with different nominal loop volumes of 0.2, 2, and 20 µl to inject water into the system. The tubing connecting the water delivery

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* Maurer, S.M., Croft, D.T., and Fowler, D.L., Measurement of High Pressure Adsorption Equilibria of R134a on Silica Gel, U.S. Army Edgewood Research, Development and Engineering Center, Aberdeen Proving Ground, MD, unpublished data.

system with the rest of the adsorption apparatus was made from 1/16" (0.040" ID) 316 stainless steel tubing to allow a maximum flow rate of the circulation of gas through the valves.

2.1.2 Temperature Control System.

Shown in Figure 3 is a schematic of the temperature control system and adsorption bed used in this study. The design of the system allows the user to monitor and control a stable adsorbent bed temperature. A more rigorous discussion and analysis of this control system may be found elsewhere and is the sole topic of another study.[10] The general components of the temperature control system consist of: (1) a copper sleeve for heat conduction; (2) wrapped copper coils to flow heated or chilled water from a water bath to control temperatures below 323 K; (3) wrapped heating tape to heat and control temperatures above 323 K; and, (4) rock-wool insulation to minimize any heat loss from the system. The adsorption bed consists of a 2.5 inch long 3/8"-316 stainless steel tube with fine mesh screens placed at both ends. A copper sleeve and aluminum foil is wrapped around the 3/8" tube for heat conduction, and a thermocouple is inserted inside the copper sleeve for the temperature controller. A second thermocouple is inserted internally up to the mesh screen to directly monitor the adsorbent bed temperature. Another identical 3/8"-316 stainless steel tube is placed upstream and used as both a heat sink and heat exchanger for the circulating gas flow.

2.1.3 Circulation and Adsorption System.

Shown in Figure 1 is the main gas flow circulation system which employs two 4-way air-actuated valves (Whitey, SS-43YF2-125) to control the chemical-vapor direction path. The "purge" valve, V1, allows the user to either purge the system with a dry purge gas (nitrogen, air, or helium) or to isolate the system in a closed-loop configuration to circulate the gas. The "bypass" valve, V2, is used to direct the chemical vapor in a challenge mode through the adsorbent or to bypass the sample while constantly circulating the gas. The main gas circulation tubing connecting the valves and other integral parts of the system are made from 1/4"-316 stainless steel tubing. An insulated 6 liter stainless steel ballast (Biospherics Research Corp) is used to mix the gas mixture and enables the user to measure a vapor-phase concentration range of nearly four orders of magnitude. A metal bellows pump (Metal Bellows, Model MB41) is used to circulate the gas mixture through the entire system and is set to around 4 SLPM by adjusting the needle valve (Whitey, SS-22RF4). This enables the user to control the volume of gas that is used to sweep through the injection valve for the gas chromatograph and the chemical injection valves inside the valve box. The tubing connecting the adsorbent and bed side of the system was made from 1/8"-316 stainless steel tubing in order to both minimize the volume on the challenge side and allow maximum flow through the adsorbent.

2.1.4 Vapor-Phase Analysis System.

The vapor-phase analysis system consists primarily of a Hewlett Packard (HP) Gas Chromatograph (GC) Model 5880 with a Thermal Conductivity Detector (TCD) and a

Hayesep D column (6', 80/100 mesh). The carrier gas for the TCD and GC is helium (Matheson, UHP) and the oven temperature is set to 373 K. Gas samples are collected using a single 6-port Valco valve with a 1000 µl sample loop and are sent to the GC for analysis. Equilibration is determined by analyzing the gas samples until the vapor-phase concentrations are steady or reach a certain absolute or relative tolerance criteria.

2.1.5 LabVIEW Data Acquisition Program.

The entire isotherm program is fully automated under the LabVIEW programming language and is used to both control and monitor the system. The data acquisition system uses National Instrument's Signal Conditioning Extension for Instrumentation (SCXI) hardware consisting of: (1) the NB-MIO-16XL-18, a high performance multifunction board with analog (sixteen 16-bit ADCs with voltage inputs, two 12-bit DACs with voltage outputs, digital (eight lines of TTL-compatible digital I/O), and timing I/O (three 16-bit counter/timer channels) capabilities for the Macintosh NuBus; (2) the SCXI-1001, a 12-slot chassis to add plug-in boards and modules to control analog input/output signals, digital input/output signals, relays, or other DAQ board signals; (3) an SCXI-1120 module, 8-channel isolation amplifier with an attached SCXI-1328 isothermal, high accuracy-terminal block which allows the user to record thermocouples or other millivolt signals on eight channels and configure the gain settings for each channel independently; (4) an SCXI-1180 feedthrough panel with an attached SCXI-1302 terminal block that extends the I/O signals of the plug-in data acquisition board to the front of the SCXI chassis and allows the user to send output analog control voltages to various devices; (5) an SCXI-1160 module, 16-channel SPDT digital relay with an attached SCXI-1324 high-voltage terminal block that allows the user to control valve orientations, switch general purpose signals, and activate devices; (6) an SCXI-1121 module, 4-channel isolation amplifier with excitation and an attached SCXI-1328 isothermal terminal block, which allows the user to record signals for transducers requiring excitation such as strain gauges on four channels, and configure the gain settings for each channel independently; and (7) an SCXI-1161 module, 8-channel SPDT power relay that allows the user to switch power signals or activate external devices requiring large drive signals such as pumps, heaters, or motors.

The LabVIEW data acquisition system for the isotherm program allows the user to: (1) record all temperatures and pressures from the adsorption apparatus; (2) select the GC run time, GC retention time, and the GC retention time tolerance window for chemicals as well as collecting all integration data; (3) establish relative and absolute criteria for the equilibration of the vapor-phase concentrations; (4) select equilibration holdoff times and sampling intervals for the gas-phase analysis; (5) select file names for the data and log files to be written to disk; (6) select the mass vector profile by choosing the amount of chemical mass to be injected during each iteration; (7) select the isotherm temperatures for the experiment; and (8) control when to start or stop the experiment. Figure 4 shows a sample of the front panel of the isotherm program used as the operator interface. Figure 5 shows a small portion of the LabVIEW wiring diagram for the main program.

2.2 Materials.

The adsorbate examined in this study was water (Sigma-Aldrich, HPLC Grade) and used without further purification. The three adsorbents used in the experiments were: (1) silica gel 40 (Grace-Davison, 6/12 Mesh); (2) sorbead RF (Solvay Fluorides, 6/16 Mesh, Fines); and (3) alumina F-200 (Coastal Chemical, 7/14 Mesh). The sorbead RF was calcined at 823 K in air (sorbead RF-C) to investigate the effect of the heat treatment on the adsorption properties of this sample. Table 1 shows a tabulated listing of the adsorbents studied along with the names used in this report.

2.3 Experimental Procedure.

The experimental procedures utilized in this study will be described here. These procedures are similar to those used by both Rudisill, et al.,[7] to measure the multi-component equilibria of water and hydrocarbons on BPL activated carbon, and Mahle, et al.,[11] to measure the adsorption equilibria of refrigerant vapors on activated carbon. A pair of four-way valves controls the gas circulation path. The "purge" valve is used to determine if the system is: (1) either fed by dry nitrogen, air, or helium to purge the system and/or condition the adsorbent sample, or (2) in the closed-loop recirculation configuration. The "bypass" valve is used to circulate the gas mixture through the adsorbent (challenge mode) or to bypass the sample (isolate/bypass mode). The isotherm valve configurations and system events/procedures are outlined in both Tables 2 and 3.

The adsorbent sample is first heated in a moisture analyzer (Mettler, Model LJ16) for 30 minutes at 423 K and then weighed to get a dry sample weight, typically around 0.2 to 0.5 g. The adsorbent is then placed into the sample tube, covered with a small plug of glass wool, and inserted into the challenge side of the main circulation loop. Prior to initiating any experiment, the isotherm system is leak-tested by pressurizing the system to about 30 psia using dry nitrogen. The system pressure is monitored with a pressure transducer (Setra, Model 212FT, 0-30 psia) in both the challenge and bypass modes. The TCD is calibrated and checked once a week to ensure its accuracy. A pair of four-way valves controls the gas circulation path. The "purge" and "bypass" valves are positioned to direct the flow of nitrogen over the adsorbent at about 2 SLPM for about 30 minutes to remove any trace moisture that collected in the system during the transfer process. The adsorbent bed is then slowly heated to 423 K at a rate of 2 K/min, and held at 423 K for about 2 hours. The purge effluent is sampled with the GC until no water trace is detectable. After completing the sample drying procedure, the adsorbent bed is cooled to 348 K under a nitrogen purge flow of 1 SLPM with the water bath. The system is then depressurized to 1 atm, and both four-way valves were switched to bypass the adsorbent and put the system in its closed-loop configuration.

The computer program to control the system and automatically measure the isotherm data is then initiated. In order to properly operate the system, the following operational parameters must be selected: (1) isotherm temperatures; (2) chemical mass injected

into the system for each equilibrium point; (3) chemical loop volumes; (4) equilibration holdoff times and criteria; and (5) TCD calibration parameters. These values tend to vary from experiment to experiment and are adjusted as necessary depending on the adsorbent.

Once the adsorbent bed reaches its first desired isotherm temperature, the automated program begins the chemical procedure while the apparatus is in the bypass mode. Depending on the amount of chemical selected in the target mass vector, the computer program automatically selects the proper sequence and number of injections for each of the loops (high, medium, and low). These loop selections are based on the loop size and density of the water at the injection temperature and pressure. The measured vapor-phase concentration from the GC analysis system is used to calculate the amount of water injected into the system. After the proper sequence of loop iterations is finished, the program waits a user-specified equilibration holdoff time (30 minutes for water) to ensure that the liquid water has completely vaporized and equilibrated in the main bypass loop. Gas samples are taken at user-specified intervals until the vapor-phase concentrations are stable within a certain equilibration criteria. The amount of mass actually injected is then compared with the ideal target mass. If the actual mass is below the target mass by the user-specified tolerance (typically 25%), then the program re-calculates the next series of injections to achieve the desired target mass; however, if the actual mass is above or within the 25% tolerance of the target mass, the adsorbent bed is challenged with the chemical and the adsorption equilibria measurement is initiated.

The adsorbent bed is then challenged with the injected chemical mass by switching the bypass valve to "challenge" mode. An equilibration holdoff delay (wait time), typically about two hours for water, is then used prior to beginning the vapor-phase analysis. This prevents needless sampling when the system is not at equilibrium. After the equilibration wait time, gas-phase samples are taken at user-specified delay intervals to determine if equilibration has been established. Equilibration is determined by comparing the measured vapor-phase concentration of water with the user-defined relative and absolute equilibration criteria. If the vapor-phase samples fit the equilibration criteria, then a single isotherm point is established at the measured gas-phase concentration. The adsorbed phase loading is calculated by subtracting the difference between the actual injected mass and the mass of water in the vapor-phase. The vapor-phase concentration, adsorbate loading, adsorbent temperature, and system pressure are written and saved to a computer file.

The temperature for the next isotherm is changed by sending a new temperature set point from the computer. The system waits a user-defined time to allow the adsorbent temperature to stabilize. The program then waits for the equilibration holdoff delay, and vapor-phase concentrations are again sampled to determine if the system has equilibrated. The equilibrium adsorbate loading is determined at the vapor-phase concentration using the above procedures, and the next adsorbent temperature is selected. This process is continued until a point at all isotherm temperatures has been measured. The 4-way bypass valve is then changed to bypass the adsorbent, and the next target mass from the mass vector is injected into the system. The equilibrium measurements continue until all isotherm temperatures are completed

using all the mass vector target values. This "step-wise" programmed temperature profile, with the incremental addition of the adsorbate into a closed loop system, allows multi-point and multi-temperature equilibria to be easily measured.

2.4 Graphical Presentation and Correlation of Adsorption Equilibria.

Adsorption equilibria are plotted as water partial pressure (Pa) versus adsorbed-phase concentration (mol of water/kg of adsorbent). Since the vapor-phase concentrations of water in this study ranged over nearly four orders of magnitude, the equilibria data are plotted on a logarithmic scale to clearly display all data.

One of the most common approaches used to correlate adsorption equilibria on microporous adsorbents is based on the Polanyi potential theory (pore-filling) approach. In this study, the water adsorption equilibria for all adsorbents were fit using the Dubinin-Astakhov equation (DAE):

$$\ln(p) = \ln(p_{sat}) - \frac{\beta E}{RT}(-\ln\Theta)^{1/m} \tag{1}$$

where p = partial pressure of the adsorbate (Pa), p_{sat} = saturation partial pressure of the adsorbate (Pa), T = adsorbent temperature (K), $\beta E/R$ = DAE correlation parameter, $\Theta = q/q_{sat}$ = fractional saturation loading, m = DAE correlation parameter, q = adsorbate loading (mol/kg), and q_{sat} = saturation adsorbate loading (mol/kg). $\beta E/R$, m, and q_{sat} are the DAE fit parameters and p, T, and q are the variables used to fit this correlation.[12] This three-parameter function is derived using a pore filling approach and has the advantage over other equilibria correlation approaches since it becomes the vapor-liquid equilibrium expression when the adsorbent is saturated.

The correlation of the water adsorption equilibria was performed using a commercial software package, SigmaPlot by Jandel Scientific. The package uses the Marquardt-Levenberg algorithm to find the coefficients (fit parameters) of the independent variables that give the "best fit" between the equation and the data.[13] The algorithm then optimizes the parameters by using a least squares analysis to minimize the variance between the measured and calculated values of the dependent variable:

$$\text{var} = \frac{1}{N}\sum_{i=1}^{N}[(\ln p)_{meas} - (\ln p)_{cal}]^2 \tag{2}$$

where $(\ln p)_{meas}$ is the measured partial pressure of water and $(\ln p)_{cal}$ is the calculated partial pressure.

3. RESULTS AND DISCUSSION

3.1 Water Adsorption Equilibria Data and Correlations.

Water adsorption equilibria data were measured at 1 atm in nitrogen and temperatures of 298, 323, and 348 K. The vapor-phase partial pressures ranged from 1 - 1000 Pa and the water loadings ranged from 0.1 - 10 mol/kg. All samples were initially heat treated *in-situ* at 423 K for approximately 2 hours prior to the start of an experiment.

3.1.1 Silica Gel 40.

Figure 6 shows the results of water adsorption equilibria on silica gel 40 at 298, 323, and 348 K in nitrogen. Two separate experiments were performed on this adsorbent at all three temperatures and plotted together to show the accuracy and reproducibility of the experimental system. The silica gel adsorption data shown in Figure 6 are listed in Table 4. These data span nearly three orders of magnitude in vapor-phase concentration and nearly two orders of magnitude in loading. The graphical representation of the data in Figure 6 is presented on a log-log scale in order to emphasize the low water concentration data, which is of great importance in the design of adsorption systems whose main mission is to deliver air at low dew points.

Also shown in Figure 6 is the least squares best fit for the DAE which shows that water adsorption on the silica gel is nearly linear. Table 5 shows the DAE fit parameters for water on silica gel 40 as well as all other adsorbents examined in this study. Of all the adsorbents studied, the silica gel 40 had the lowest capacity for water at the lowest vapor-phase concentrations by nearly an order of magnitude. This behavior is interesting especially since this same adsorbent shows the largest capacity for water at the highest gas-phase water concentrations.

3.1.2 Sorbead RF.

Figure 7 shows the results for water adsorbed on sorbead RF at 298, 323, and 348 K in nitrogen. The sorbead RF equilibria data shown in Figure 7 are listed in Table 6. These data span nearly three orders of magnitude in vapor-phase concentration and an order of magnitude in loading. Also shown in Figure 7 is the DAE fit which represents the measured data well. Table 5 shows the DAE fit parameters for water adsorbed on sorbead RF. The sorbead RF adsorbent is a mixed oxide which is composed of 97% silica and 3% alumina. One may expect the adsorption equilibria to match that of silica gel, but this adsorbent shows behavior similar to the silica in only the largest loadings and largest vapor-phase concentrations. It shows an adsorptive behavior more like the hydrophilic alumina materials at the low vapor-phase concentrations.

Figure 8 shows a comparison of water adsorption at 323 K in N_2 between sorbead RF and the calcined sorbead RF-C. Calcination of the sorbead RF at 823 K for 2 hours

drastically reduces the adsorption capacity of this material throughout the entire measured vapor-phase concentration range. The sorbead RF-C equilibria data are listed in Table 7. The surface areas are shown in Table 8 and were measured using a 3-pt Brunauer-Emmett-Teller (B.E.T.) analysis and were found to be 742 m^2/g and 643 m^2/g for the sorbead RF and sorbead RF-C, respectively. Although the surface area of the sorbead RF-C is decreased only 15% by the calcination, the capacity of this material is only slightly more than half of its uncalcined counterpart throughout the entire vapor-phase concentration range. The vapor pressure of water (460 Pa) over the calcined adsorbent must be approximately 6 times that of the uncalcined material (75 Pa) in order to develop the same loading of water (1 mol water/kg adsorbent). In fact, the 348 K isotherm on sorbead RF matches very closely with that of the 323 K isotherm on sorbead RF-C.

3.1.3 Alumina F-200.

Figure 9 shows the results of the adsorption equilibria of water on alumina F-200 at 298, 323, and 348 K in nitrogen. The alumina equilibria data shown in Figure 9 are listed in Table 9. These data measurements span nearly three orders of magnitude in the vapor-phase concentration and about an order of magnitude in loading. Also shown in Figure 9 is the best fit using the DAE. Table 5 shows the DAE fit parameters for water adsorbed on alumina. Of all adsorbents studied, the alumina F-200 exhibited the largest capacity for water at low vapor-phase concentrations, but appears to show the lowest capacities for water at the highest vapor-phase concentrations. This adsorption behavior is opposite to that seen earlier with silica gel. This fairly "flat" isotherm shows that it may be easier to strip adsorbed water off from the silica gel at lower water loadings than it is from the alumina. The alumina isotherms also appear to match closely with that of the sorbead RF although this material only has a small amount of alumina in its matrix.

3.2 Summary.

Water adsorption equilibria were measured in nitrogen at 1 atm at 298, 323, and 348 K over three different adsorbents: (1) silica gel 40; (2) sorbead RF; and (3) alumina F-200. A water isotherm for calcined sorbead RF-C was measured at 323 K. The Dubinin-Astakhov equation was used to correlate the equilibria data and provided a good fit to the measured data. Of all adsorbents studied, the silica gel had the lowest capacity for water at the lowest vapor-phase concentrations by nearly an order of magnitude; however, it also showed the largest capacity for water at the highest gas-phase water concentrations. In contrast, the alumina exhibited the largest capacity for water at low vapor-phase concentrations, but appears to show the lowest capacities for water at the highest vapor-phase concentrations. The adsorption behavior of the sorbead RF appears to fall between these two adsorbents. Also, calcination of the sorbead RF appears to drastically change the adsorption equilibria of this sample.

4. SUMMARY AND CONCLUSIONS

A novel automated data acquisition system was developed to measure adsorption equilibria over a wide range of temperatures and vapor pressures for moderately volatile adsorbates such as water.

Water isotherms over silica gel 40, sorbead RF, and alumina F-200 at 298, 323, and 348 K have been measured and correlated using the Dubinin-Astakhov equation.

Silica gel was found to have the lowest capacity for water at the lowest vapor pressures, but exhibited the largest capacity at the highest vapor pressures measured. Alumina was shown to have the lowest water capacity at the highest vapor pressures studied.

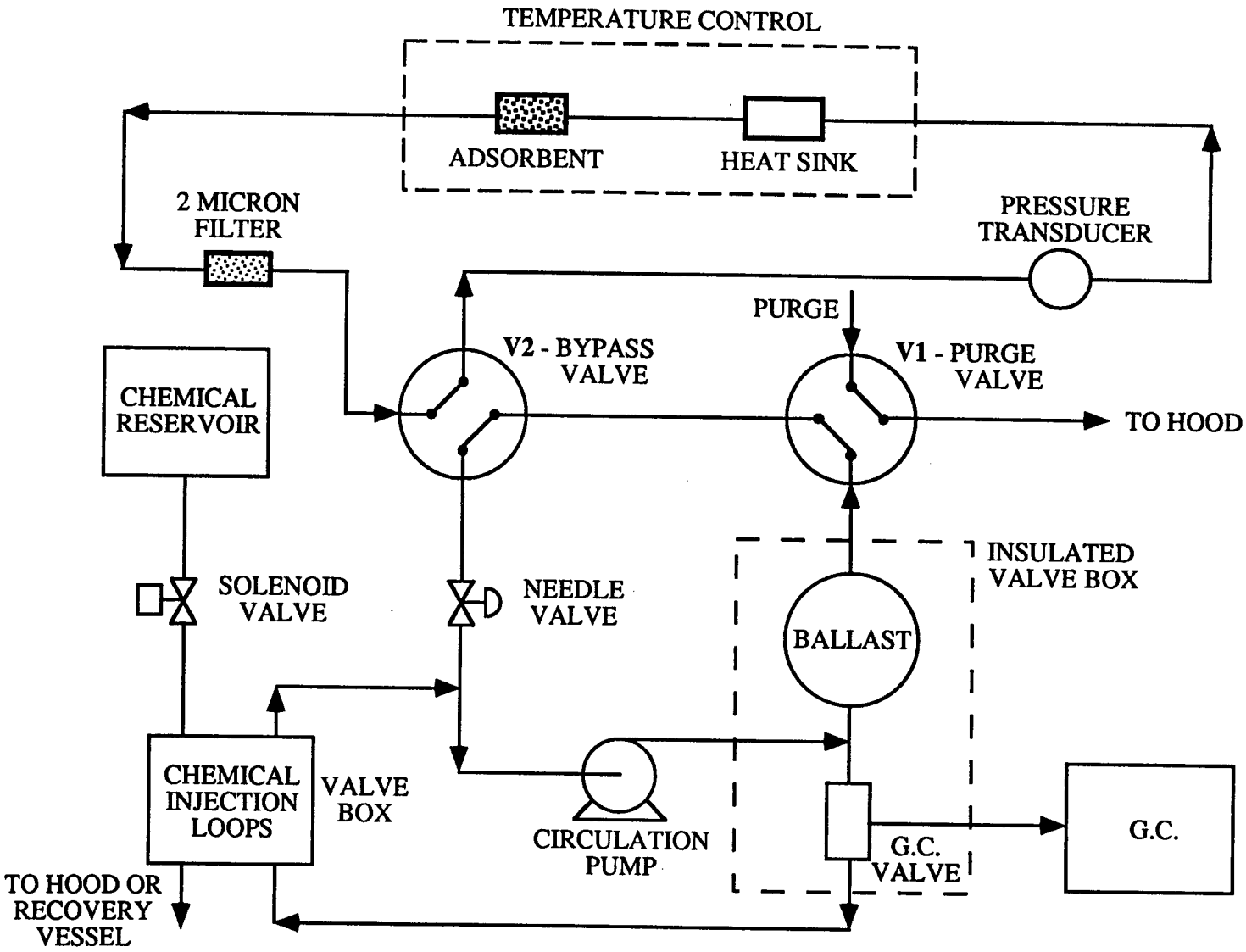


Figure 1. Volumetric Isotherm System Schematic (Isolate Bed Configuration)

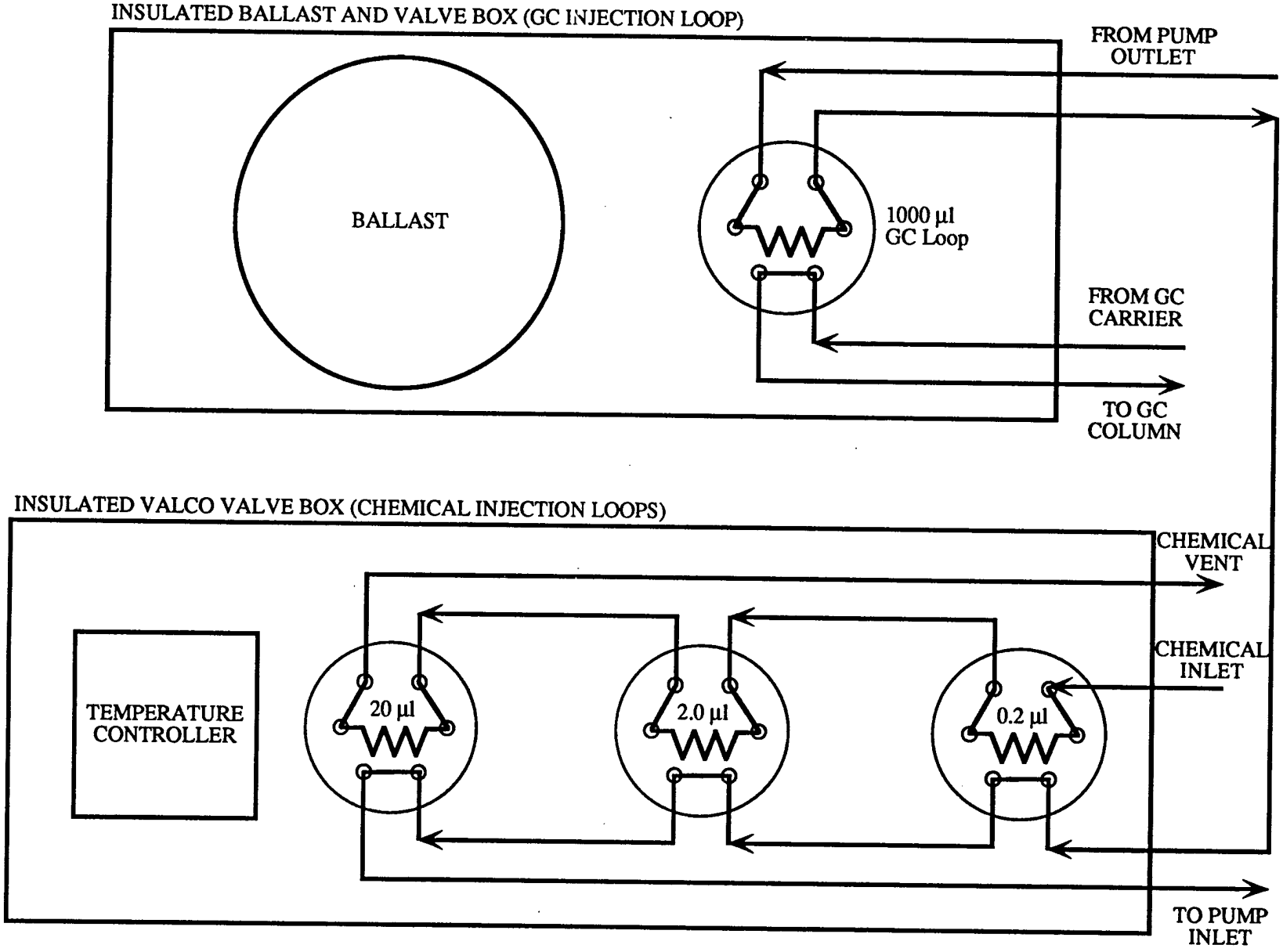
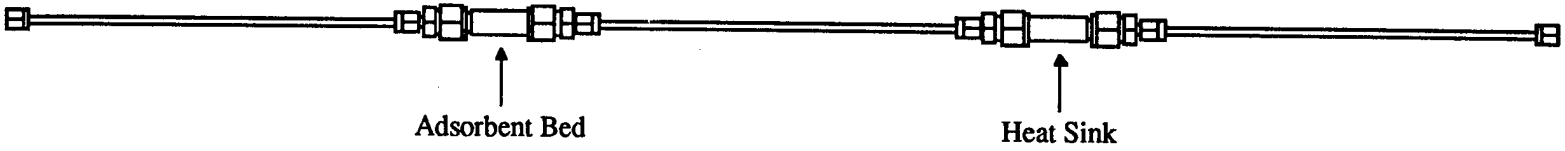


Figure 2. Insulated Ballast Box and Chemical Injection Loops Box

a) **Adsorption Bed Schematic:**



b) **Temperature Control System Schematic:**

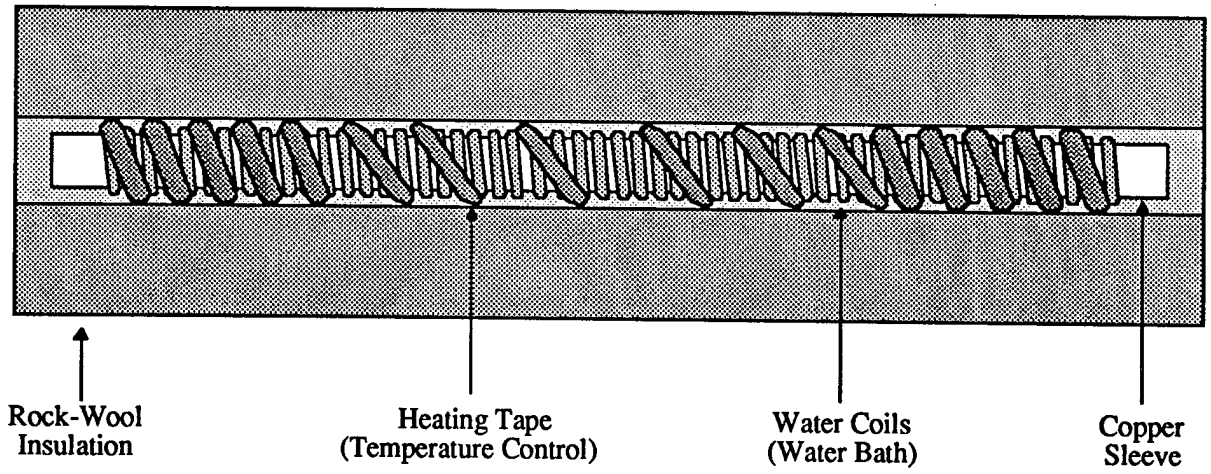


Figure 3. a) Isotherm Adsorption Bed and b) Temperature Control System Schematics

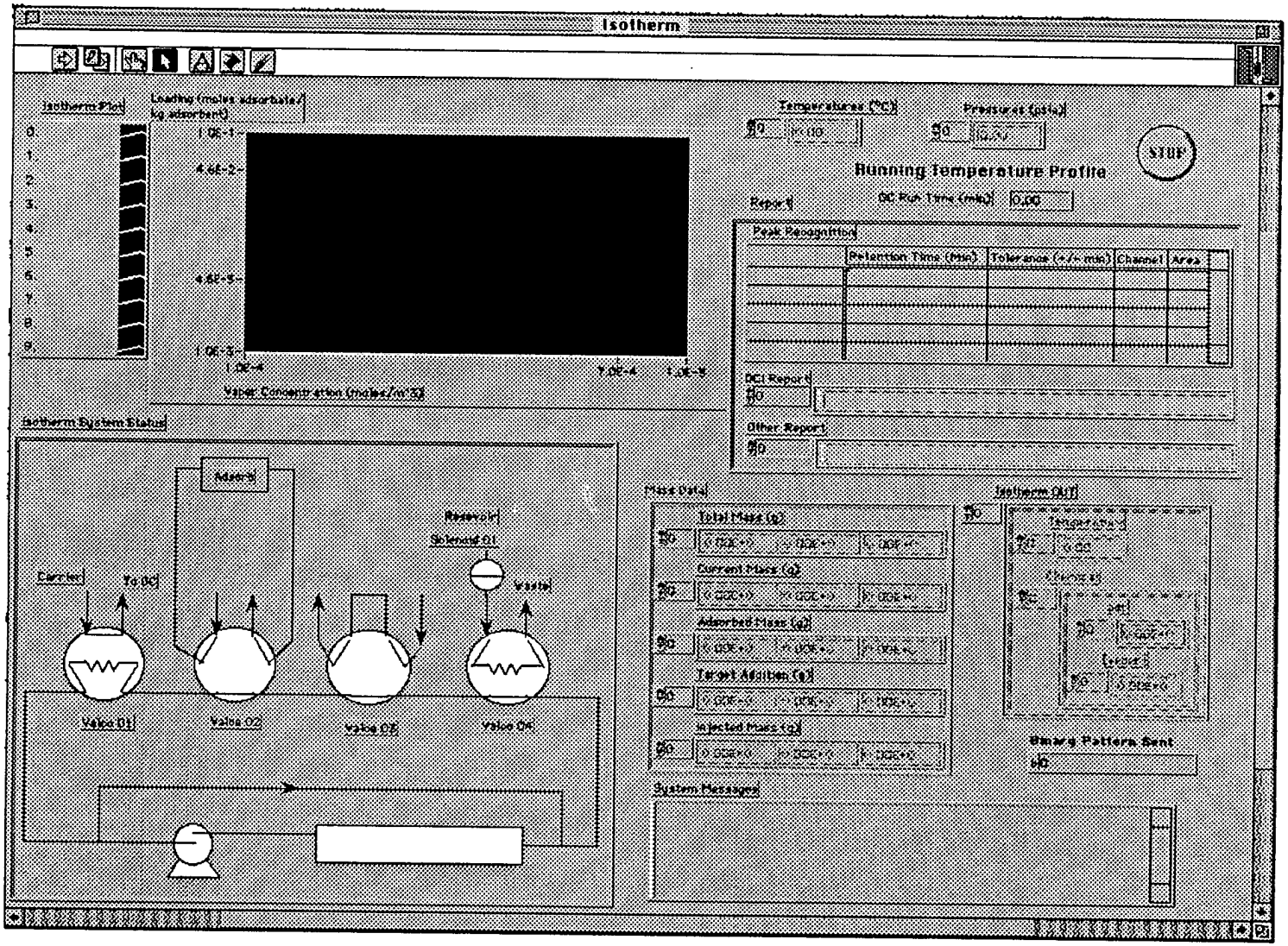


Figure 4. Isotherm Program Front Panel Using LabVIEW Data Acquisition System

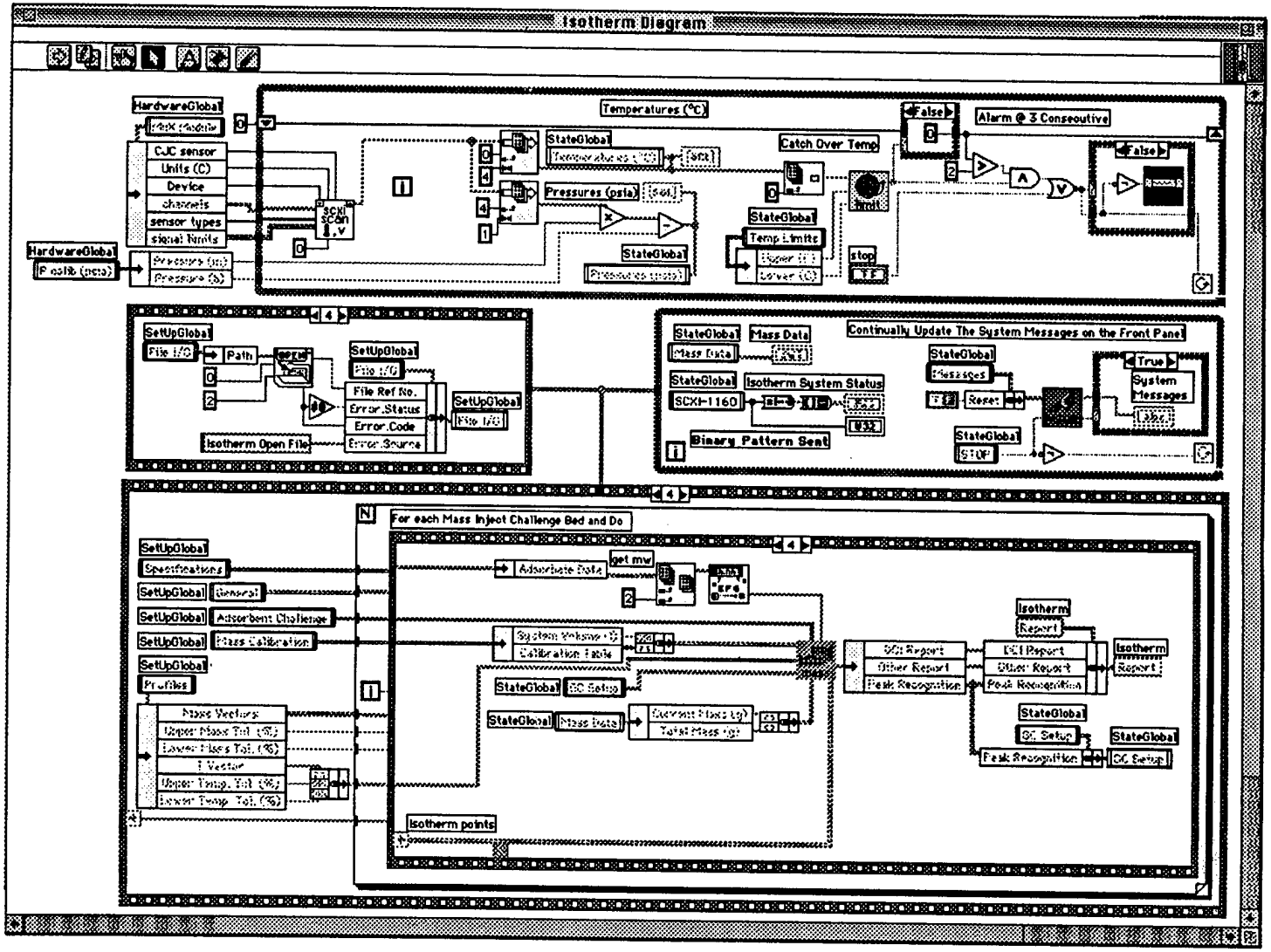


Figure 5. Isotherm Program Wire Diagram Using LabVIEW Data Acquisition System

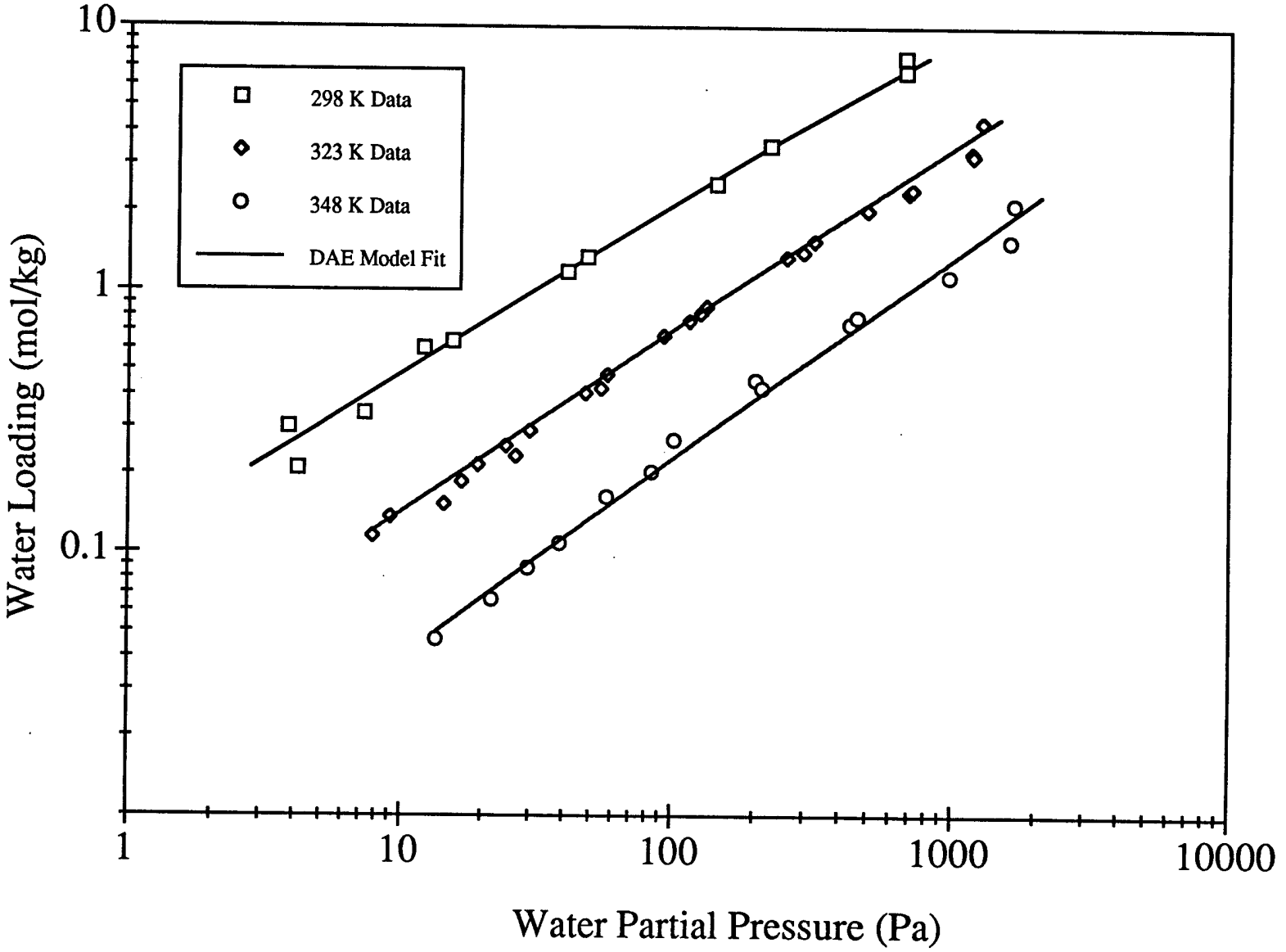


Figure 6. Water Isotherms on Silica Gel 40 at 298, 323, and 348 K in N_2 at 1 atm with best fit using Dubinin-Astakhov Equation

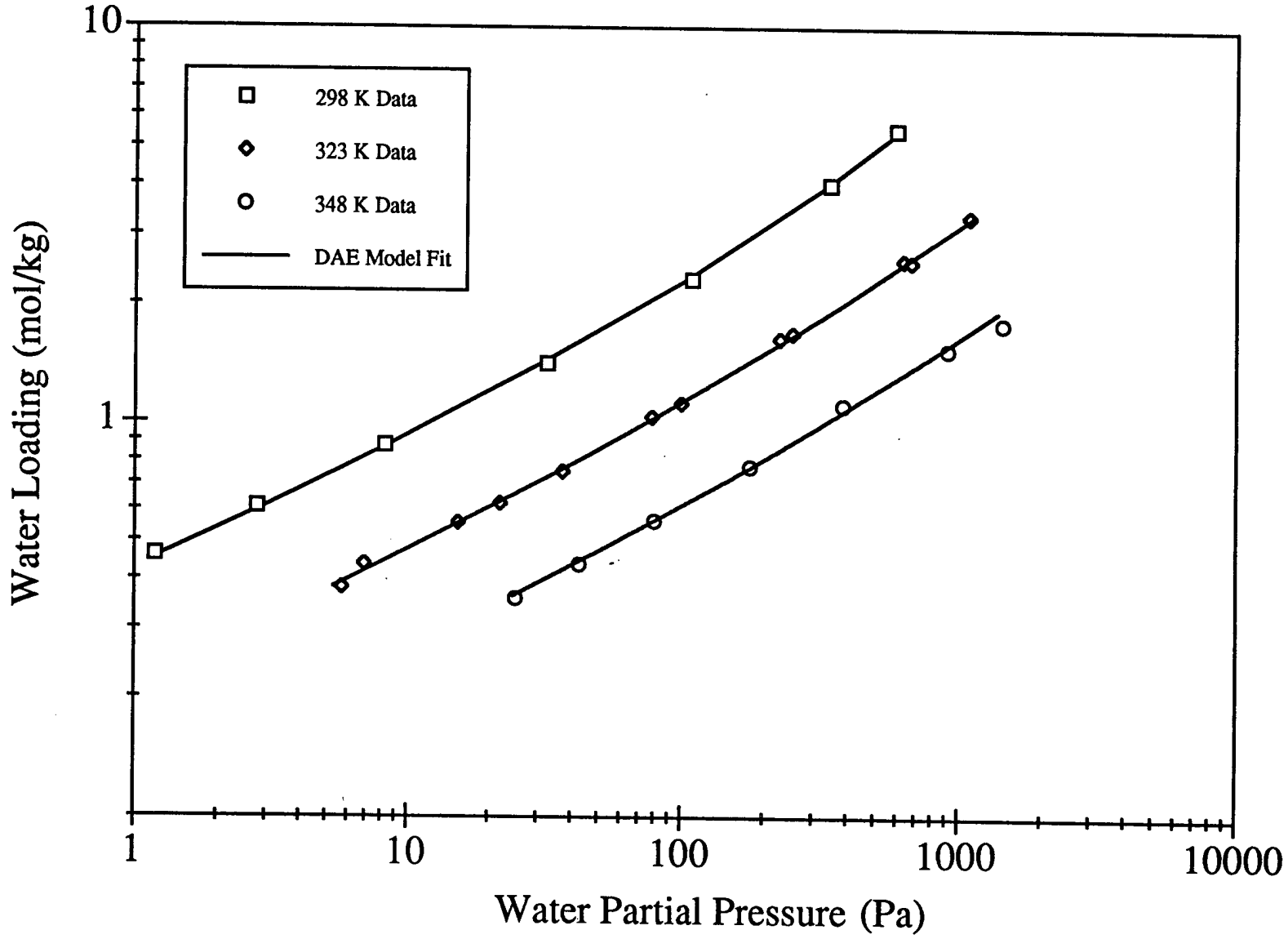


Figure 7. Water Isotherms on Sorbead RF at 298, 323, and 348 K in N_2 at 1 atm with best fit using Dubinin-Astakhov Equation

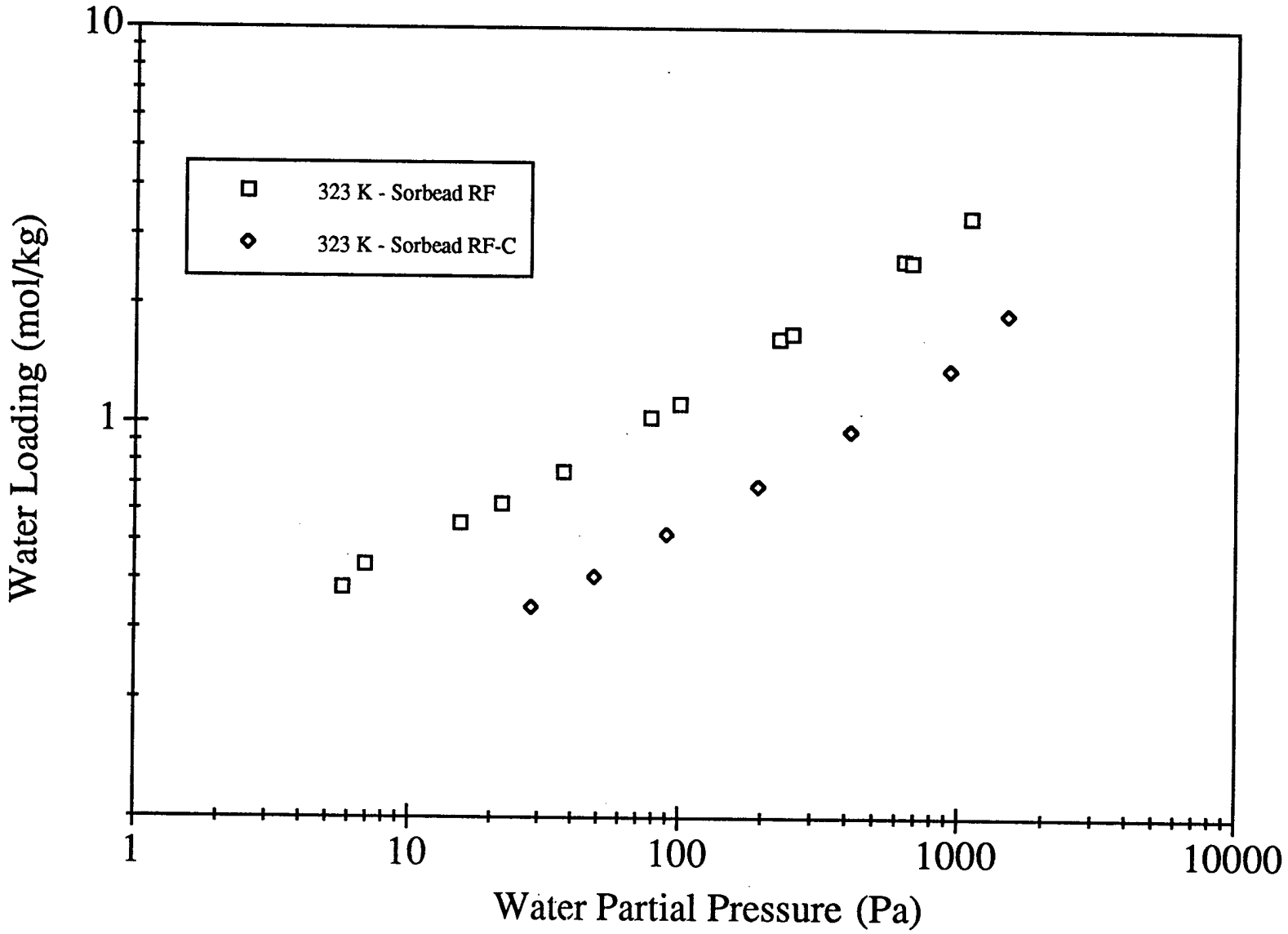


Figure 8. Water Isotherm Comparison on Sorbead RF and Sorbead RF-C at 323 K in N_2 at 1 atm

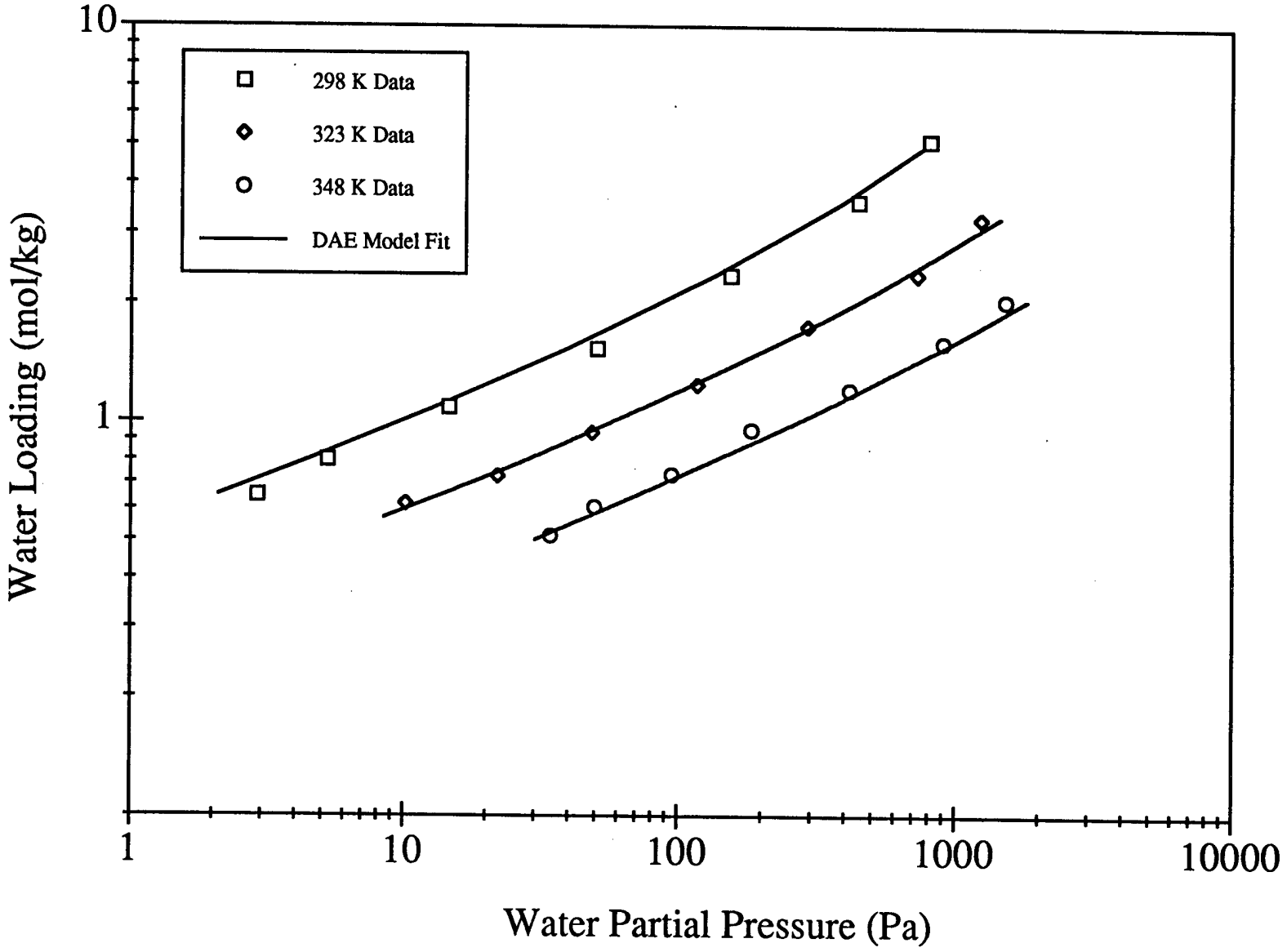


Figure 9. Water Isotherms on Alumina F-200 at 298, 323, and 348 K in N_2 at 1 atm with best fit using Dubinin-Astakhov Equation

Table 1. Adsorbent Nomenclature and Properties

Adsorbent Name	Common Name	Mesh Size	Adsorbent Appearance	Manufacturer
Silica Gel 40	Silica Gel 40 Silica Gel	6x12	Transparent	Grace-Davison Chemical
Sorbead RF	Sorbead R (Fines) Sorbead R	6x16	Orange-Brown	Solvay Fluorides
Calcined Sorbead RF	Sorbead RF-C Sorbead R-C	6x16	Transparent	Solvay Fluorides
Alumina F-200	Alumina	7x14	White	Coastal Chemical

Table 2. Isotherm System Valve Configurations

Valve Configuration	Valve Mode Orientation	Purge/Bypass[1] Valve - V1	Bed/Bypass[2] Valve - V2
1	**Purge Bypass**	Purge	Bypass
2	**Purge Bed**	Purge	Bed
3	**Isolate Bed**	Bypass	Bypass
4	**Challenge Bed**	Bypass	Bed

[1] Purge/Bypass Valve (V1): Purge = Purge Gas On; Bypass = System Isolated

[2] Bed/Bypass Valve (V2): Bed = Circulation/Flow Over Bed; Bypass = Circulation/Flow in Bypass

Table 3. Isotherm System Event Table

Event Number	Isotherm System Event	Valve Mode Orientation	Pump/Purge[1] Mode	Chemical Loop[2] Valves Mode
1	**Purge Bypass**	Purge Bypass	Purge (On)	Fill (Off)
2	**Purge Bed**	Purge Bed	Purge (On)	Fill (Off)
3	**Depressurize**	Purge Bed	Purge (Off)	Fill (Off)
4	**Isolate**	Isolate Bed	Pump (On)	Fill (Off)
5	**Fill Chemical**	Isolate Bed	Pump (On)	Fill (On)
6	**Inject Chemical**	Isolate Bed	Pump (On)	Inject
7	**Equilibrate Wait**	Isolate Bed	Pump (On)	Fill (Off)
8	**Bypass Mass**	Isolate Bed	Pump (Off)	Fill (Off)
9	**Challenge**	Challenge Bed	Pump (On)	Fill (Off)
10	**Equilibrate Wait**	Challenge Bed	Pump (On)	Fill (Off)
11	**Bed Mass**	Challenge Bed	Pump (Off)	Fill (Off)

[1] Pump/Purge: Pump = Circulation (On/Off); Purge = Purging (On/Off)

[2] Chemical Loop Valves: Fill = Chemical Fill Mode - On/Off; Inject = Chemical Inject Mode

Table 4. Adsorption Isotherm Data for Water on Silica Gel 40

298 K Water Adsorption Isotherms:

p (Pa)	q (mol/kg)	p (Pa)	q (mol/kg)
3.805	0.302	48.295	1.339
4.120	0.210	144.087	2.543
7.277	0.341	225.254	3.535
12.078	0.604	671.618	7.670
15.428	0.640	673.480	6.775
40.936	1.178		

323 K Water Adsorption Isotherms:

p (Pa)	q (mol/kg)	p (Pa)	q (mol/kg)
14.418	0.153	1181.800	3.243
26.533	0.233	9.102	0.136
54.414	0.423	19.210	0.216
115.283	0.764	47.685	0.406
496.578	2.022	133.253	0.866
7.836	0.115	323.181	1.545
16.716	0.186	1272.058	4.324
29.903	0.291	24.378	0.255
57.361	0.477	92.694	0.670
126.638	0.816	258.904	1.335
295.623	1.399	696.480	2.358
715.139	2.413	1167.437	3.325

Table 4 (con'd). Adsorption Isotherm Data for Water on Silica Gel 40

348 K Water Adsorption Isotherms:

p (Pa)	q (mol/kg)	p (Pa)	q (mol/kg)
13.537	0.047	1612.555	1.541
29.583	0.087	21.708	0.066
57.428	0.163	38.566	0.108
101.241	0.269	83.926	0.204
201.183	0.454	212.243	0.425
433.796	0.745	458.056	0.793
968.126	1.133	1664.919	2.134

Table 5. Dubinin-Astakhov Equation (DAE) Fit Parameters for Water Adsorption

Adsorbent	q_{sat} **(mol/kg)**	$\beta E/R$	m
Silica Gel 40	16.719	514.744	1.05
Sorbead RF	23.506	272.879	0.638
Sorbead RF-C	13.863	195.898	0.569
Alumina F-200	16.241	315.018	0.604

Table 6. Adsorption Isotherm Data for Water on Sorbead RF

298 K Water Adsorption Isotherms:

p (Pa)	q (mol/kg)	p (Pa)	q (mol/kg)
1.189	0.461	109.089	2.317
2.794	0.610	344.970	4.016
8.233	0.875	597.031	5.521
32.424	1.412		

323 K Water Adsorption Isotherms:

p (Pa)	q (mol/kg)	p (Pa)	q (mol/kg)
5.720	0.380	15.391	0.555
21.917	0.622	36.987	0.749
78.023	1.032	99.585	1.118
228.324	1.635	253.663	1.684
633.363	2.589	675.800	2.568
1095.133	3.346	1094.977	3.342
6.908	0.436		

348 K Water Adsorption Isotherms:

p (Pa)	q (mol/kg)	p (Pa)	q (mol/kg)
25.055	0.356	385.607	1.107
42.548	0.436	911.870	1.535
79.849	0.561	1450.601	1.786
178.266	0.774		

Table 7. Adsorption Isotherm Data for Water on Sorbead RF (Calcined)

323 K Water Adsorption Isotherms:

p (Pa)	q (mol/kg)	p (Pa)	q (mol/kg)
28.251	0.339	411.742	0.954
48.434	0.405	929.254	1.363
89.611	0.520	1488.266	1.886
192.443	0.690		

Table 8. Sorbead RF/Sorbead RF-C Surface Area Measurement and Heat Treatment

Adsorbent	Calcination Temperature (K)[1]	BET Surface Area (m^2/g)[2]	p (Pa) (q = 1 mol/kg)[3]
Sorbead RF	None	741.57	75
Sorbead RF-C	823	642.78	460

[1] Adsorbents were calcined in air at 823 K for 2 hours.
[2] Adsorbents were pretreated *in-situ* at 523 K under vacuum prior to surface area analysis.
[3] Adsorbent isotherms measured at 323 K for loading of 1 mol/kg.

Table 9. Adsorption Isotherm Data for Water on Alumina F-200

298 K Water Adsorption Isotherms:

p (Pa)	q (mol/kg)	p (Pa)	q (mol/kg)
2.902	0.650	155.321	2.354
5.253	0.801	448.297	3.609
14.646	1.086	815.431	5.140
50.774	1.536		

323 K Water Adsorption Isotherms:

p (Pa)	q (mol/kg)	p (Pa)	q (mol/kg)
10.152	0.619	293.740	1.748
22.027	0.728	733.703	2.360
48.579	0.938	1243.705	3.266
117.776	1.243		

348 K Water Adsorption Isotherms:

p (Pa)	q (mol/kg)	p (Pa)	q (mol/kg)
34.359	0.513	417.414	1.207
49.713	0.606	909.429	1.591
95.032	0.735	1524.405	2.037
183.981	0.953		

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GLOSSARY

B.E.T	Brunauer-Emmett-Teller (Surface Area Analysis)
m	Dubinin-Astakhov Equation Correlation Parameter
N	Number of Data Points in Variance Calculation
p	Partial Pressure of the Adsorbate (Pa)
p_{sat}	Saturation Partial Pressure of the Adsorbate (Pa)
q	Adsorbate Loading (Moles/Kilogram)
q_{sat}	Adsorbent Saturation Capacity (Moles/Kilogram)
R	Gas Constant
T	Temperature (Kelvin)
var	Variance
$\beta E/R$	Dubinin-Astakhov Equation Correlation Parameter
Θ	q/q_{sat} (Fractional Saturation Loading)