EXPERIMENTAL APPARATUS
FOR THE MEASUREMENT OF
SOLID-VAPOR PHASE EQUILIBRIA

by

David D. Duston

A Thesis submitted to the Faculty and the Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Master of Science.

Signed: David D. Duston
David D. Duston

Golden, Colorado
Date: May 19, 1970

Approved:
A. J. Kidnay
Thesis Advisor

J. H. Gary
Head of Department

Golden, Colorado
Date: May 19, 1970

ABSTRACT

An experimental apparatus capable of making accurate measurements of solid-vapor pressures was designed, constructed and tested. The basic system consists of a copper equilibrium cell suspended in a constant temperature bath. The bath temperature is controlled by balancing liquid nitrogen refrigeration with a heater on proportional control.

Temperatures are measured with a calibrated platinum resistance thermometer and a Mueller Bridge. Vapor pressures are measured on three bourdon tube pressure gauges with ranges of 0 - 100 psi and 0 - 100 atm.

Step by step operating procedures for all the equipment and instruments are presented for use by future operators. After adding a gas chromatograph to analyze equilibrium vapor samples, future operators will use the system to obtain solid-vapor phase equilibria data.

Vapor pressures of carbon dioxide were measured from -75 to 0 deg C to test the equipment. The overall accuracy of the system is limited by the pressure measurements. Literature values of CO_2 vapor pressures were reproduced within ± 0.03 atm using the Heise 0 - 100 atm gauge and within ± 0.5 psi using the Heise and Seegers 0 - 100 psi gauges. The temperature of the bath can be measured accurately to ± 0.001 deg K. The temperature controller can be set to con-

trol within ± 0.003 deg K of a desired temperature. During a 12-hr temperature stability test run, the maximum deviation from the average temperature was ± 0.012 deg K.

ACKNOWLEDGEMENTS

The author wishes to express his sincere thanks for support from The Colorado School of Mines Foundation, Inc.

Grateful appreciation is extended to Professor Arthur J. Kidnay, thesis advisor, who gave valuable guidance during this study. Sincere thanks is extended to the Master of Science Committee members: Professors Arthur J. Kidnay, James H. Gary, and Daniel M. Bass, Jr.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

INTRODUCTION

Presently there is a lack of phase equilibria data, especially at low temperatures, and this information is needed for the successful and efficient operation of liquifaction and refrigeration cycles, as well as separation and purification units. These data are also needed for molecular interaction studies.

The purpose of this project was to design and construct an experimental apparatus capable of making accurate measurements of solid and liquid vapor pressures. The apparatus was tested by measuring the vapor pressure of CO_2 from -75 deg C to 0 deg C and comparing the data obtained with that in the literature. Carbon dioxide was chosen for comparison purposes because it is easily obtained in a pure state, and reliable vapor pressure data may be found in the literature.

In the future a gas chromatograph will be added to the system so that vapor phase composition can be determined, and thus, phase equilibria data obtained.

This thesis presents a complete description of how the apparatus was designed and constructed. Included are test run results describing the operating characteristics, and accuracy of the measurements made. The thesis also contains complete calibration data for the platinum resistance thermometer and pressure gauges, and complete operating instructions for the apparatus and instruments.

PROCESS FLOW

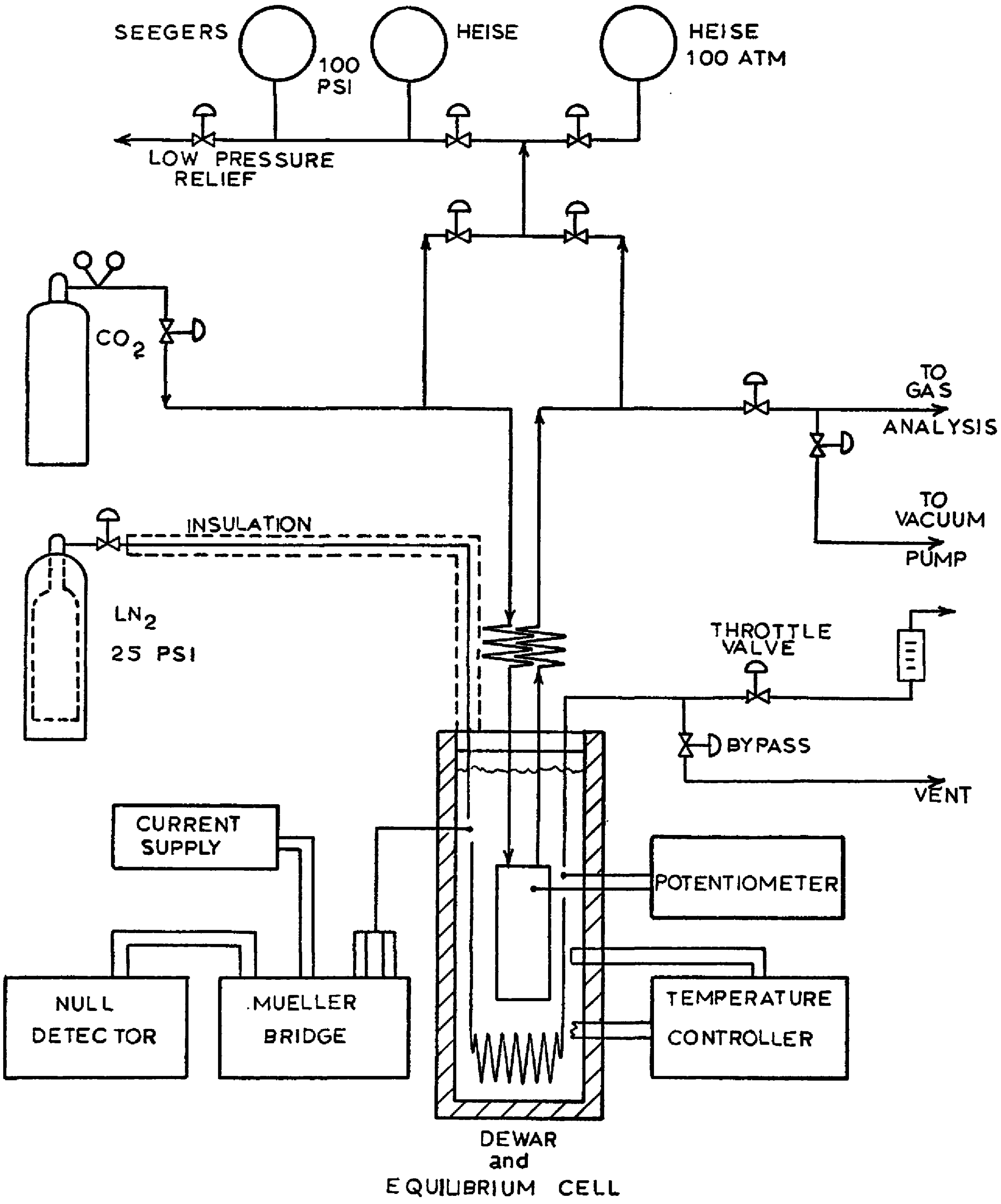
Figure 1 is a schematic diagram of the experimental apparatus. The basic system consists of a copper equilibrium cell suspended in a well-stirred constant temperature bath. The bath temperature is controlled by balancing excess refrigeration (liquid nitrogen) with a heater on proportional control. A calibrated platinum resistance thermometer and Mueller Bridge are used to measure the temperature of the bath. Any temperature differences between the bath and the interior of the equilibrium cell are detected by a copper-constantan thermocouple inside the cell with a reference junction in the bath.

Another commonly used system, generally referred to as a copper block cryostat, has a large copper equilibrium cell suspended in an evacuated container. The copper block has liquid nitrogen coils and heating elements wrapped around the outside with various arrangements for balancing refrigeration and heating rates to control the block temperature. A constant temperature bath has the following advantages over the copper block cryostat: (1) a well-stirred bath minimizes any temperature gradients in the equilibrium cell, (2) a large bath provides good thermal inertia for temperature stability, and (3) the bath arrangement costs less to build.

Figure 2 is a piping and instrumentation diagram for the

FIGURE 1

Experimental Apparatus for the Measurement of
Solid-Vapor Phase Equilibria
Process Flow Diagram



Symbol Index for Figure 2

A) Platinum resistance thermometer for controller

B) Calibrated platinum resistance thermometer

C) 125-w controller heating element, 32-in. long

D) LN_2 refrigeration coil, 1/4-in. copper tubing, 20-ft long

E) Feed preheater, 1/8-in. copper tubing, 9.5-ft long

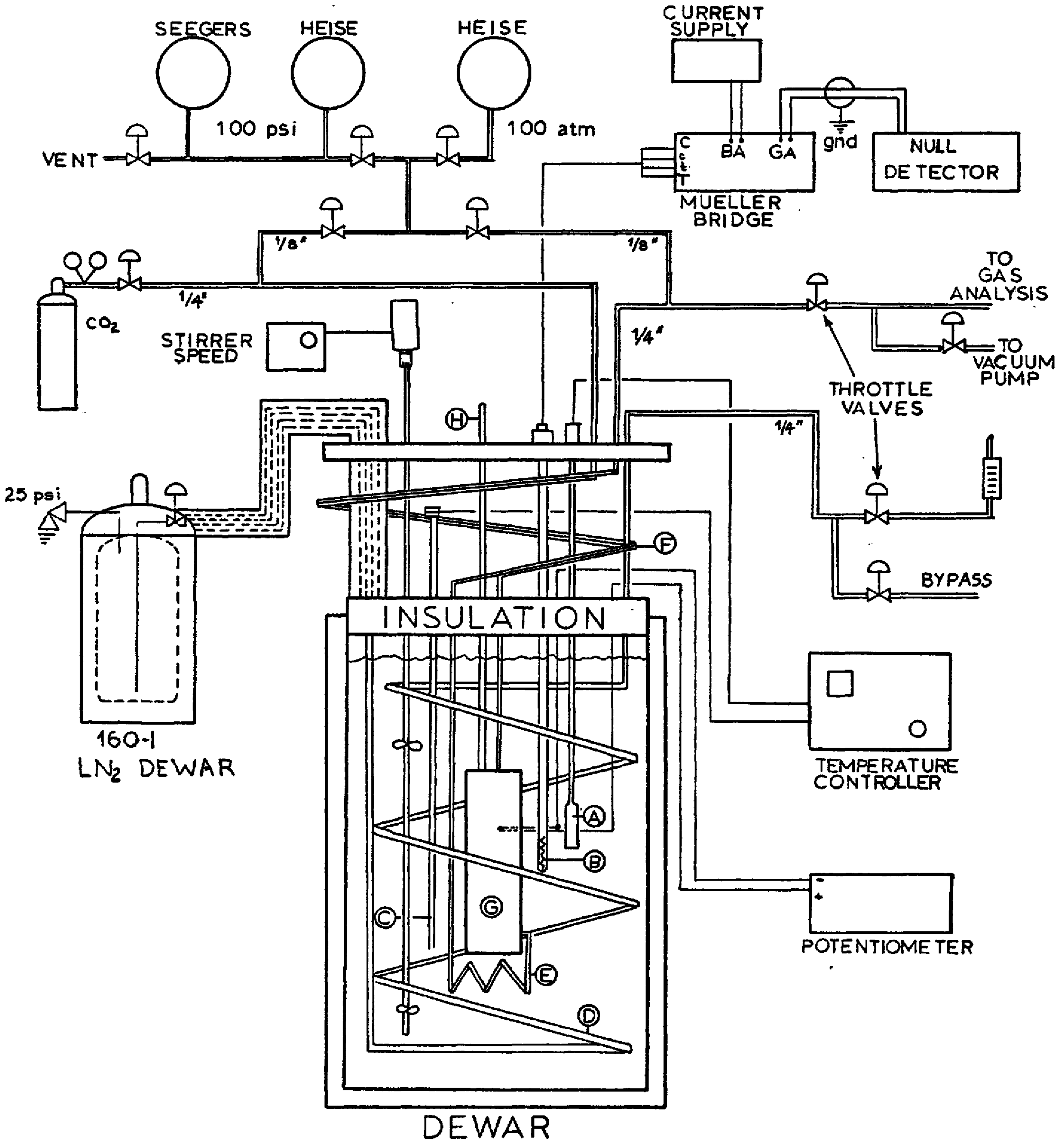
F) Inlet vs. exit streams counter current heat exchanger, 1/8-in. copper tubing, 8-ft long

G) Equilibrium cell

H) Fill line for equilibrium cell, 1/4-in. copper tubing, presently capped

FIGURE 2

Experimental Apparatus for the Measurement of
Solid-Vapor Phase Equilibria
Piping and Instrumentation Diagram



experimental apparatus. The bath is contained in a vacuum-jacketed cryogenic dewar 9 3/8 in. in diameter and 24-in. deep with a 27-liter full liquid capacity. Liquid nitrogen is fed from a 25 psi pressurized storage dewar through a 1/4-in. insulated copper transfer line to the bath. The total distance from the storage dewar to the bath is about 4 ft. The liquid nitrogen then enters 20 ft of 1/4-in. copper tubing in the bath where it vaporizes and exits close to the bath temperature. The nitrogen flow rate is controlled downstream of the bath with a 1/16-in. port throttle valve. From the throttle valve the nitrogen passes through a rotometer, and then is vented to the atmosphere. The rotometer was not in use for any of the test runs reported here. When large flow rates are required for rapid cool-down, the nitrogen bypasses the throttle valve and is vented to the atmosphere through a 1/4-in. globe valve.

Carbon dioxide, or any desired gas, is fed to the system from a high pressure regulator. After exchanging heat in a 1/8-in. counter-current heat exchanger 8-ft long, the CO_2 enters the bath and passes through 9.5 ft of 1/8-in. copper tubing and into the bottom of the equilibrium cell. The gas then exits the top of the cell, leaves the bath, and passes through the countercurrent heat exchanger. A throttle valve, 1/8-in. port, presently blocks any further gas flow, but in the future the gas will be taken to a gas chromatograph for analysis.

The vacuum pump is used to evacuate the system before filling the cell with the desired material.

The valve system for the pressure gauges allows pressure measurements on either the inlet or outlet side of the cell, and for measurement by either the 0-100 psi gauges or the 0-100 atm gauge. The low pressure relief valve allows venting the 0-100 psi gauges when making high pressure measurements on the 0-100 atm gauge.

EQUIPMENT DESIGN

The purpose of the section is to describe the design and construction of the equipment built for the experiment. Included in this section are the equilibrium cell, the refrigeration system, and supporting equipment.

Equilibrium Cell

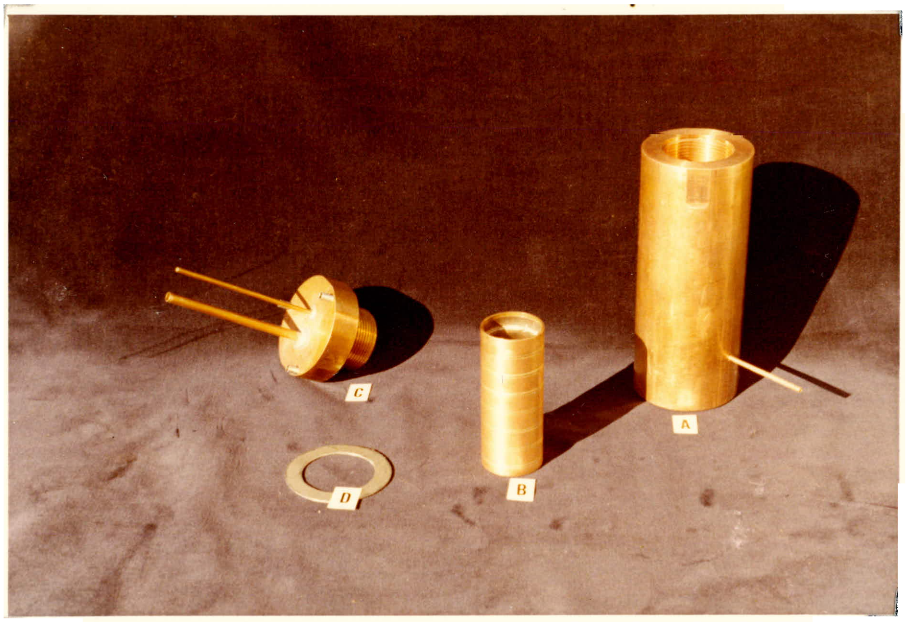
The equilibrium cell has four major parts: A) the cell block, B) the equilibrium tray assembly, C) the cell cap and, D) the lead sealing gasket (Photo 1).

The cell block (Figure 3) is a 6 3/4-in. long, 2 3/4-in. diameter copper block with an inner space bored to hold the equilibrium tray assembly. The 1/8-in. feed line enters 1/2-in. below the bottom tray and 1/2-in. above the bottom of the bore. The line is sealed with soft solder. The wall thickness is 5/8-in. on the sides and 3/4-in. on the bottom with 3/4-in. of S.A.E. threads for the cap.

The equilibrium tray assembly is 1 1/2-in. in diameter and contains seven equilibrium trays. The 1/2-in. tray spacing between each tray is filled with copper wool to provide more surface area for solid-vapor contacting. Gas flows through the cell from bottom to top through passages of 1/4-in. copper tubing extending 1/8-in. below and 1/4-in. above each tray. Passages are placed alternately on opposite sides of the cell. The tray assembly was constructed

PHOTOGRAPH

Equilibrium Cell



A) Cell Block

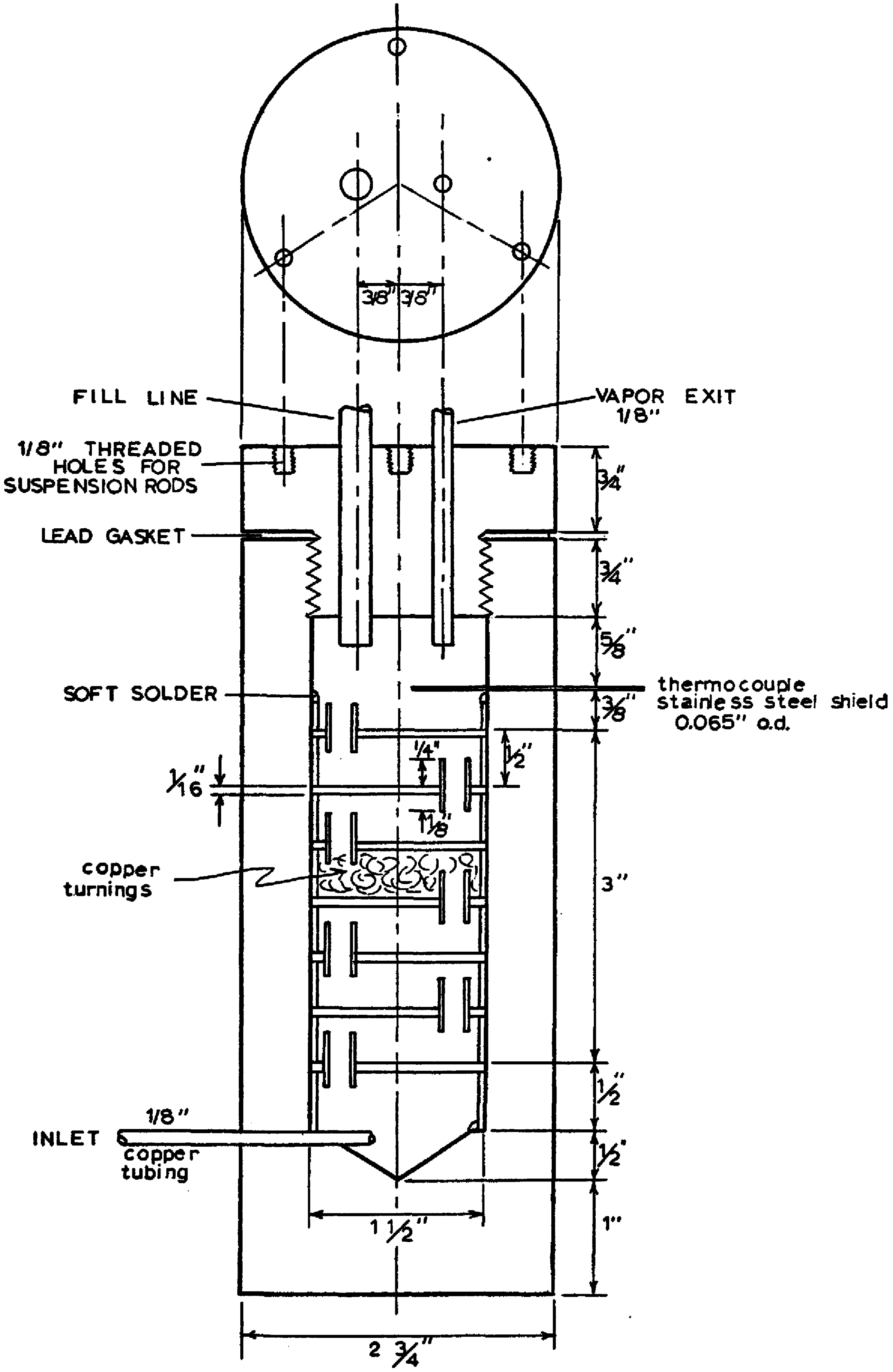
B) Equilibrium Tray Assembly

C) Cell Cap

D) Lead Sealing Gasket

FIGURE 3

Equilibrium Cell Assembly



by stacking 7/16-in. spacing rings alternately with the 1/16-in. thick trays and packing each space loosely with copper wool. The assembly was silver soldered together and placed in the cell block with soft solder seals at both the top and bottom. The total liquid capacity of the trays is about 200 cc.

The cell cap is 3/4-in. thick, plus 3/4 inches of S.A.E. threads. The 1/8-in. exit line and the 1/4-in. fill line are both copper tubing and sealed with soft solder. The cap also has three threaded holes for the stainless steel tubing which supports the cell in the bath. The tubing is 1/8-in., 304-stainless steel used to minimize the heat transferred to the cell. "Molykote" (Molydenum disulfide) was used as a thread lubricant to tighten the cap.

The lead sealing gasket is 1/16-in. thick and was used to avoid soldering the cap in place, and thus, allow easy opening of the cell in the future. Flats have been machined on both the cap and cell block so that a vice and wrench can be used to close and seal the cell.

The copper-constantan thermocouple is mounted in the exit vapor space 3/8 in. above the top tray. The thermocouple wire has a 304-stainless steel shield packed with magnesium oxide powder for insulation. Soft solder was used to seal the shield in the cell block.

The equilibrium cell was been hydrostatically pressure tested using equipment at the National Bureau of Standards in Boulder, Colorado. The system was pressurized to 2500 psig, at which point, a leak developed in the lead gasket. The pressure was dropped to atmospheric, the cap torqued down approximately 1/8 turn, and pressure re-applied to 1500 psig. No leak developed at this pressure.

The total weight of the equilibrium cell is approximately 12.5 lb, and was built this large to provide sufficient thermal inertia and temperature stability.

Refrigeration System

The bath is a 50 vol percent mixture of carbon tetrachloride (CCl_4) and chloroform ($CHCl_3$) contained in the cryogenic dewar. This mixture was recommended by Kanolt (1926) as a nonflammable liquid for cryostats. It has a freezing point of -81.4 deg C, and the mixture is a liquid at room temperature and atmospheric pressure. Also, the viscosity of the mixture does not hamper effective stirring at low temperatures.

A search was conducted to consider other possible fluids with a lower toxicity level than the CCl_4-$CHCl_3$ mixture. A suitable fluid should have at least -80 deg C freeze point, a low vapor pressure at room temperature, and it should be nonflammable and nontoxic. Using both a list of cryogenic fluids prepared by B. S. Kirk (1958) at the National Bureau of standards, and _Dangerous Properties of Industrial Materials_, Sax (1966), many possibilities were considered. The flammability of possible materials was considered to be more dangerous than the toxicity of the CCl_4-$CCHl_3$ mixture. No problems were encountered while running the equipment with this bath mixture.

Liquid nitrogen (LN_2), used for the refrigeration, was obtained from the Cryogenics Division of U. S. Welding in 160-l pressurized dewars. These dewars have vapor relief valve set at 25 psi and provide a constant flow of LN_2 which can be throttled to provide low flow rates for temperature control, or vented to the atmosphere at high rates for rapid cool down. The transfer line to the bath from the dewar is insulated with 3/8-in. rubber hose and 3/4-in. fiberglass.

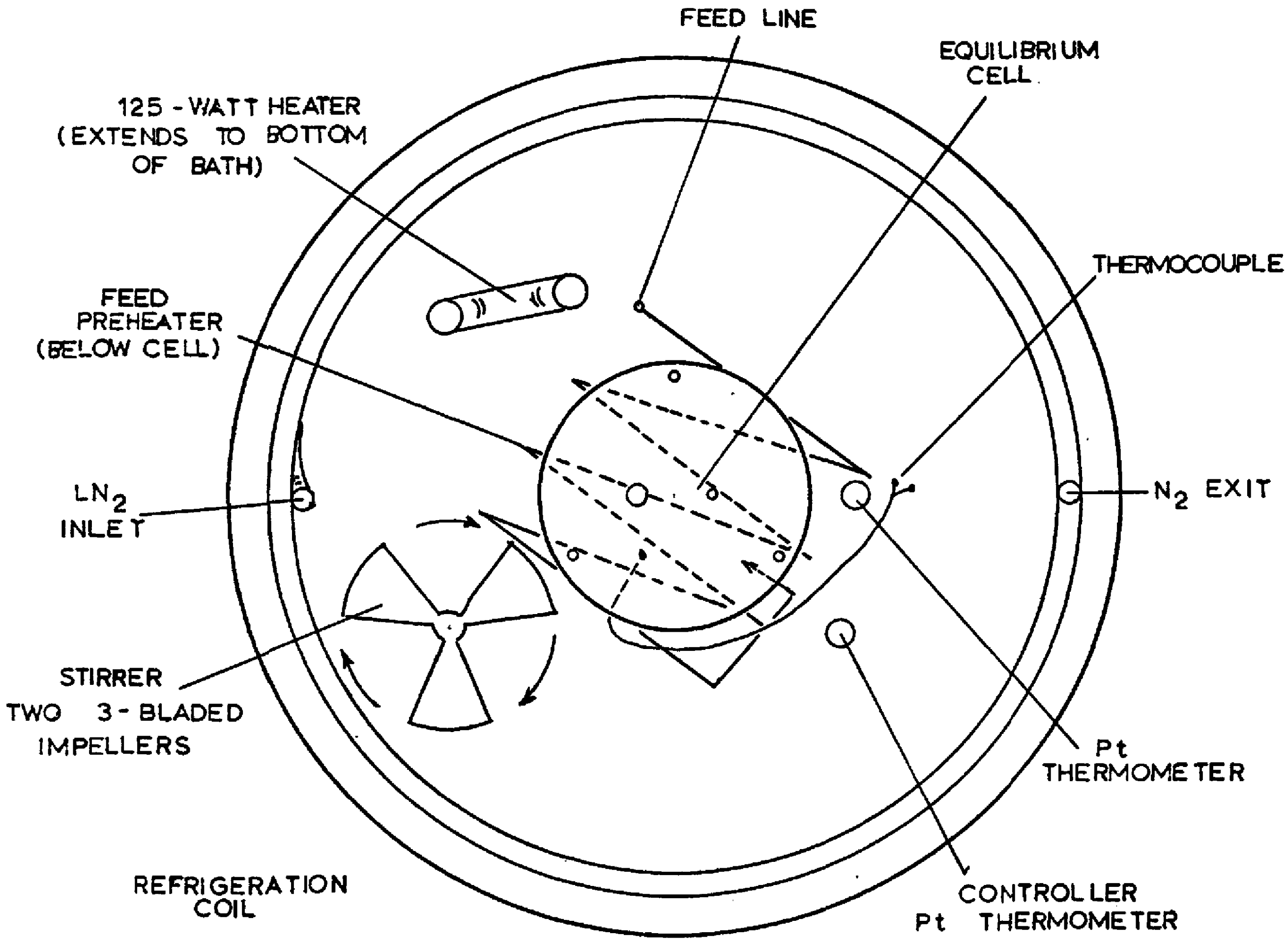
Excess refrigeration is balanced with a 125-w heater on proportional control. The heater was sized by calculating how much power would be required to change the temperature of the bath and the equilibrium cell by 0.2 deg C per min. This rate of change was estimated and the calculations are presented in the appendix.

Figure 4 shows the arrangement of equipment in the bath. The main objectives in placement in the bath were: (1) to keep heating elements as far as possible from temperature sensors, (2) to evenly distribute the refrigeration coil and heating element to minimize temperature gradients, (3) to keep moving parts away from the Pyrex tubing of the thermometer, and (4) to insure a well stirred bath.

The platinum resistance thermometer, Mueller Bridge, and null detector will be discussed in detail in the

FIGURE 4

Arrangement of Equipment in the Bath



"Instrumentation and Measurement" section.

Supporting Equipment

This section will be used to discuss and describe all supporting equipment i.e., equipment not directly related to the process flow, but inherent in the operation of the equipment. The following are discussed below: supporting framework, dewar support and lift system, overhead mounting plate.

The entire system is mounted in a 6-ft high, 4-ft wide, and 3-ft deep framework constructed with angle iron, and has a 4x3-ft front instrument panel and an 18x48-in. work bench. The framework is mounted on 4x6-in. blocks during operation, but it has caster wheels for easy moving. On either side chains are provided to hold the required gas storage cylinders upright.

The support and lift system for the bath dewar was designed to ease removal of the bath, and to provide stable support when in place. The dewar is lifted into place using a hand winch with 3/16-in. steel cable. The dewar can be removed by unscrewing the three wing nuts on the ring which fits over the top of the dewar.

The entire process flow system is supported by a 1/4-in. copper plate which in turn hangs from the frame by three 1/4-in. steel rods. This three-point system provides simple but stable support. The LN_2 transfer line passes through the plate insulated by a nylon bushing providing 1/2-in. of nylon plus the 3/8-in. of rubber insulation. The equilibrium cell hangs from the plate by three 1/8-in., 304-stainless steel rods with allen set screws at the top. The well for the platinum resistance thermometer has a beveled bottom shaped to fit the thermometer. This well is 1-in. deep and prevents excessive movement but does not hold the thermometer rigidly. The stirrer passes through a 1-in. hole in the plate providing ample room for adjusting the stirrer position and prevents transmission of vibrations to the plate.

At the right hand side of the apparatus is a power terminal capable of six 3-prong plugs thus giving a common ground to all instruments. The terminal has a total power "ON-OFF" switch and a break reset switch to be used if the system is overloaded.

INSTRUMENTATION and MEASUREMENTS

Temperature measurement, temperature control, and pressure measurement are the most important functions to be considered for these vapor pressure measurements. This section will describe the instruments used for each function and the calibration and operation of each. Discussed below are: 1) the platinum resistance thermometer, 2) the Mueller Bridge, 3) the temperature controller, and 4) the pressure gauges.

Platinum Resistance Thermometer

The platinum resistance thermometer used in this experiment is satisfactory as a defining standard in accordance with the text of the International Practical Temperature Scale of 1968. It is a four-lead resistor thermometer manufactured by Leeds and Northrup Company. The platinum wire element is mounted in an air-filled Pyrex tube, 7.35 mm in diameter, extending approximately 46 cm from the head. The sensitive portion is about 33-mm long with a temperature range of -183 to 500 deg C. The wire element has a resistance of 25.5071 absolute ohms at 0 deg C with a resistance change of about 0.1 ohm per degree C.

The thermometer should be protected from any mechanical shocks and excessive temperatures, both of which strain the platinum wire resistor and may change the characteristic constants of the thermometer.

The current flow through the thermometer when making measurements results in some heating of the resistor. Thus, the current used in making measurements is the same as was used for calibration, i.e., 1 ma. A current supply was built using 2 type D dry cells, a potentiometer, and a milliampmeter so that the current can be set at 1 ma.

The calibration for the thermometer is presented in the appendix. The table lists resistance ratios, i.e., the ratio of the resistance at the stated temperature to the resistance at 0 deg C at intervals of 1 deg K. A linear interpolation will not introduce an additional error greater than the equivalent of 0.0001 degree at temperatures above -200 deg C. The table also lists the reciprocal of the difference between successive resistance ratios to facilitate interpolation. The pertinent International Practical Temperature Scale (1968) formulas and characteristic constants are also given and discussed in the appendix.

Certain precautions must be observed if reliable temperature determinations are to be made with a resistance thermometer. The coil must be immersed to a depth sufficient to prevent significant error due to heat conduction down the thermometer leads and Pyrex tubing. The thermometer is presently immersed 11 inches (about 60%) and no heating is observed when the thermometer is raised to 7 inches immersion depth.

Making temperature measurements will be discussed in the next section after discussing the Mueller Bridge.

Mueller Bridge

The thermometer resistance is measured with a Rubicon Mueller Bridge. For a more complete discussion of the principles of the Mueller Bridge design than it is feasible to include here, the reader is referred to Mueller (1916).

Description: The bridge has an internal resistance range of 0 to 141.1110 ohms in steps of 0.0001 ohm. The 141.1110 ohm rheostat arm has one plug switch and five dial-type decade switches. The plug switch controls six 10-ohm, and one 70-ohm resistor and the five dial switches are calibrated in 1.0, 0.1, 0.01, 0.001, and 0.0001 ohm.

The bridge has a built-in mercury-contact commutator to eliminate the effects of lead resistance on the measurement. The function of the commutator is to reverse the thermometer leads in such a way that the average of resistance measured with the commutator in the N (normal) position and the R (reverse) position is the resistance of the thermometer.

The resistance of the leads is completely eliminated only if the N and R measurements are made at the same temperature. By making a series of four measurements, at equal time intervals in the order NRRN any change of the difference of the lead resistance is computable and the average of the four measurements is independent of any linear drift in temperature.

The commutator has eight mercury contacts each of which require a small drop of mercury on them before any measurement can be made. The contacts can be reached by removing the Phillips head screw on the commutator and lifting the cover. No more mercury than will be held by surface tension is placed on each post, and excess is removed.

Calibration

The overall limit of error of the bridge, according to the manufacturer, is 0.002 percent of its setting or 0.00005 ohm, whichever is larger. At 0 deg C the bridge setting is 25.5071 ohm, therefore, the bridge error is 0.0051 ohm. This corresponds to approximately 0.051 deg C. In order to reduce this uncertainty, the Bridge was calibrated according to a procedure described by Riddle (1967, p.7).

Although a Mueller Bridge may be calibrated in any convenient unit of resistance, absolute ohms were required in this case because all measurements must be referred to the resistance of the thermometer at 0 deg C, i.e., 25.5071 absolute ohms. Regardless of the units of calibration, it is essential the bridge be self-consistent, that is, that the resistance change corresponding to each decade step be expressed in terms of a single unit of resistance.

To calibrate the bridge in terms of absolute ohms, a 10-ohm standard resistor was connected to the bridge, just as a four lead thermometer, and measured in terms of the X. of the 1-ohm decade. The standard resistor used was a Honeywell Rubicon, 10-ohm standard with a maximum error of

± 0.01 percent. The resistance measured by the Mueller Bridge was 10.0004 ohms.

After the value of X. is determined in absolute ohms, the resistance change corresponding to each decade is expressed in terms of absolute ohms. The method of calibration is to compare the resistance of each decade step with the resistance of the X (sum of all ten steps) of the next lower decade. This comparison is made by alternately including in the variable arm of the bridge either the step being calibrated or the X of the next lower decade. The lower decades of the bridge are used to make the variable arm balance an external resistance. From these alternate balances, a relation between the step being calibrated and the X of the next lower decade is obtained. The complete calibration consists of repeating this process for each decade step.

The external resistance required must remain adequately constant during the short time required for each comparison. A resistance box variable in 0.1 ohm steps up to 100 ohms was used as recommended by Riddle (1969, p.8). Steps in the calibration are presented in the appendix along with the resulting equations representing the relationships between each decade step.

The results of the Mueller Bridge calibration showed a maximum correction (in the range of measurements made) of +0.0007 ohm. However, under normal operating conditions temperature fluctuations of 0.005 deg C, or about 0.0005 ohms occur. Also, when making temperature measurements, 1 ma is used and the sensitivity at this current level is about 0.0002 ohm. For these reasons, it was felt to be unnecessary to try and apply a correction of 0.0007 ohm to the Muller Bridge measurements. This correction would be equivalent to an approximate increase in vapor pressure of 0.025 psi or 0.0015 atm.

Operation: Connect the four leads of the resistance thermometer to the four binding posts marked CctT. Connect the leads from the thermometer current supply to the BA binding posts. Using the shielded leads, connect the Null detector to the GA Post. Connect the ground post on the Null detector and the lead shield to a common ground. (The apparatus framework was found to be satisfactory.) Depress the 0 key on the Mueller Bridge and set the thermometer current supply at 1.0 ma. Zero the Null detector and set for maximum sensitivity.

Before making temperature measurements, it is necessary to balance the ratio arms of the bridge and to zero the bridge. Both these operations should be done once a day.

To adjust the ratio, insert the plug into position marked RATIO. Place the commutator in a neutral position, i.e., midway between N and R. Set the plug switch and the X1. and X.1 dials to 0. Balance the bridge by adjusting the lower three dials (X.01, X.001, X.0001) to minimize the deflection of the null detector as the 0 key is held down. Set the X1. and X.1 dials to R and depress the 0 key. If the deflection is the same as before, the ratio is in proper adjustment. If however, the deflection is different, adjust the ADJ. RATIO dial until the deflection is the mean of the two deflections. Return the X1. and X.1 dials to 0, and check the deflection again. It may be necessary to adjust the RATIO dial once more until the deflection is the same for the X1. and X.1 dials.

After having adjusted the bridge ratio to equality, insert the plug in the ZERO position and set the plug switch and all dial switches to 0. With the commutator in the N position, press the "O" button and balance the bridge using the ADJUST ZERO dial. Change the commutator to the R position and check the balance. If the bridge is not balanced, then the ratio equality adjustment is not correct and must be rechecked.

The current may be increased to 4 ma to obtain greater sensitivity while adjusting the ratio arm and zeroing the bridge. However, reset the current supply to 1 ma before making any temperature measurements.

The instrument is now ready to make a measurement. With the three position plug in the measure position, set commutator on N and balance the bridge with the rheostat dials. Set the commutator on R and rebalance the bridge. The average of the two readings thus obtained is the resistance of the thermometer, not including the resistance of the leads.

Temperature Controller

The controller, manufactured by Bayley Instrument Company, is a proportional controller with an overall control accuracy of 0.001 deg C from -200 to 100 deg C. The sensing element is a platinum resistance thermometer and the heating element, as discussed earlier, is the 125-w tubular probe.

This unit has a proportional bandwidth adjustment calibrated from 0 to 100, 100 being the maximum bandwidth and minimum gain or sensitivity of the instrument. At 100, the bandwidth is approximately 2 deg C and at 0 the bandwidth is approximately 0.01 deg C. This adjustment is used to reduce the sensitivity of the controller and permit operation without oscillation.

The instrument also has a gain control. The gain should be set at a maximum to get a stable control without oscillation of the control meter, but high enough to prevent low sensitivity and drift from the control point. The bandwidth and gain control settings were found by trial and error to work best with both set at 5.

The thermometer sensing probe is immersed 5 inches into the bath as recommended by the manufacturer.

Because operating the controller must be coordinated with other parts of the apparatus, setting the controller at a fixed temperature for control will be discussed in the "Experimental Procedure" section.

Pressure Gauges

Three bourdon tube pressure gauges are presently mounted: a Heise 0 - 100 psi, a Seegers 0 - 100 psi, and a Heise

0 - 100 atm. The manufacturers stated accuracy on both Heise gauges is ± 0.1 percent of the full scale reading. All three gauges have been calibrated at the National Bureau of Standards using a dead weight tester, and the test results are shown in the Appendix. The 0 - 100 atm Heise gauge and the 0 - 100 psi Seegers gauge have no calibration correction. However, the 0 - 100 psi Heise gauge shows deviations from 0.03 to 0.15 psi above the true pressure, and thus, a correction must be subtracted from reading on the gauge. A correction curve has been plotted and is also in the Appendix.

All three gauges have zero adjustments, but only the atmosphere gauge can be zeroed at 0 pressure and used as an absolute pressure gauge.

EXPERIMENTAL PROCEDURE

The following section describes the experimental procedure used in operating the equipment. The purpose of this section is not only to describe what was done, but to give a step by step procedure to be used by future operators.

Preparation

1) Fill the dewar with equal volumes of CCl_4 and $CHCl_3$ to 4 in. from the top. The total liquid volume rerequired is about 6.5 gal. When not in use the liquid can be stored in the dewar by placing a plastic cover under the ring clamp.
2) Connect a 160-1 liquid nitrogen dewar (U. S. Welding - LS 160) to the LN_2 transfer line and insulate the connection.
3) Lift the dewar slowly into place using the hand winch.
4) Place the platinum resistance thermometer in the well and connect the CctT leads to the corresponding posts on the Mueller Bridge.
5) Connect the thermometer current supply leads to the BA posts on the Mueller Bridge.
6) Connect the null detector to the GA posts on the Mueller Bridge using the shielded leads. Ground the null detector and lead shield. Allow 15 min. for the null detector to warm up.

7) Balance the ratio arms and zero the Mueller Bridge as described in the "Intrumentation and Measurement" section.
8) Connect the desired gas supply to the feed inlet line.
9) Zero the potentiometer and connect thermocouple leads.
10) Select a temperature to introduce liquid into the cell. Check the approximate vapor pressure at this temperature to be sure liquid can be formed.

Cool Down and Temperature Control

1) Turn on the stirrer and set the speed control on approximately 3. Check the platinum resistance thermometer for excessive vibration.
2) Start cool down to desired temperature by fully opening LN_2 bypass valve and opening LN_2 throttle valve about 10 turns. Fully open the liquid withdrawal valve on the LN_2 dewar.
3) Close the bypass valve when the desired temperature is reached, and adjust the throttle valve so that just enough refrigeration is supplied so that the bath temperature tends to drop slowly.
4) Turn on the temperature controller. Turn the Main Temperature Range dial up until the power output meter swings to the right, then back down on the dial until the meter swings left to zero.

5) Allow the instrument to bring the temperature back up by itself. Check the temperature; if it is slightly higher or lower than desired, adjust the Fine Temperature Control.

6) Check the controller power output. For the greatest sensitivity, the meter should read between 10 and 40. Make small adjustments in the LN_2 flow rate using the throttle valve to establish this condition.

Purge and Fill the Cell

1) Open the low pressure relief valve and the four pressure gauge valves on the front panel. Zero the pressure gauges, and record the barometric pressure. Close the relief valve.

2) Start the vacuum pump and evacuate the total system. Three to four minutes of pumping is usually sufficient. Close the valve to the vacuum pump.

3) Pressurize the system slowly with desired gas to approximately 80 psig.

4) Vent the system to about 5 psig using the low pressure relief valve.

5) Repeat steps 2, 3, and 4, four or five times.

6) Pressurize the system with the desired gas to about 10 psi above the vapor pressure at the bath temperature. Close the shut off valve on the feed line and observe the pressure change. (Allow several minutes for the temperature to come back to equilibrium.)

7) Repressurize the cell, and again observe the pressure change when the system is closed. Keep adding small amounts of gas to the system until the pressure remains constant.

Care must be taken to avoid overfilling the cell. If the cell is overfilled, the liquid vapor interface is outside the cell and this may result in errors in the vapor pressure measurement. Gas can be vented from the system through the low pressure relief valve to remove excess liquid.

Temperature Measurement

After filling the cell, allow several minutes for the system to come to equilibrium. Measure the resistance of the platinum thermometer as described in the Muller Bridge.

Pressure Measurement

When the pressure range is above 100 psig, close the valve to the 100 psi gauges and vent the gauges to about 5 psig. For a flow system, the pressure is measured on the inlet side of the cell by opening the valve marked "INLET" and closing the "EXIT" valve. The pressure is measured on the exit side of the cell by opening the "EXIT" valve and closing the "INLET" valve. For a non-flow system, both valves are open.

TEST RUN RESULTS

A total of six test runs was made with carbon dioxide to determine the system operating characteristics. The vapor pressure of carbon dioxide was measured from 198 to 268 deg K and compared with literature values to determine the error limits of the system. Data were also taken to determine temperature stability, cool down rates, LN_2 consumption, and temperature gradients between the cell and the bath.

Vapor Pressure Data Comparison

The carbon dioxide used in the experiment was Coleman grade (99.95 mole percent CO_2) and was obtained from Matheson Company, Inc. The observed vapor pressures were compared with National Bureau of Standards data (Meyers and Van Dusen, 1933, p. 409). The Meyers and Van Dusen data were chosen by Din (1956, p. 123) to represent the most accurate vapor pressure data for CO_2 available. The Meyers and Van Dusen data are also presented in Perry's Chemical Engineers Handbook 4th ed. and in the Handbook of Chemistry and Physics 45th ed.

To compare the vapor pressure data taken in this experiment with that of Meyers and Van Dusen, it was necessary to convert to a common temperature scale. The platinum resistance thermometer used in this experiment is calibrated on the 1968 International Practical Temperature Scale. However, the Meyers and Van Dusen data are based on the 1927 International Temperature Scale. In order to interpolate in the tables presented by Meyers and Van Dusen, the 1968 temperatures from this experiment were converted to the 1948 International Practical Temperature Scale using data presented by Hust (1969, p. 453). Below 630 deg C the 1948 and 1927 temperature scales are the same. Vapor pressures from this experiment are therefore compared at equivalent temperatures with vapor pressures from Meyers and Van Dusen. Note, the temperatures from this experiment were converted to the 1948 temperature scale only for comparison purposes. All temperatures reported here are based on the 1968 International Practical Temperature Scale.

Atmosphere Gauge: The vapor pressure data from the Heise 0 - 100 atm gauge are compared in Table 1 with the literature values. Figure 5 shows the deviation of the observed vapor pressures from the literature values as a function of temperature.

With the exception of two data points (run No. 1), all of the observed vapor pressures lie within 0.07 atm of the true or literature values. The manufacturers stated accuracy of the Heise gauge is ±0.1 percent of the full scale, which corresponds to an error of ± 0.1 atm.

The observed vapor pressures from the atmosphere gauge are generally high, and thus, the possibility of some systematic error is suggested. However, an error of + 0.03 atm (approximate average error) would correspond to + 0.48 psi and would have been seen as an obvious error in the same

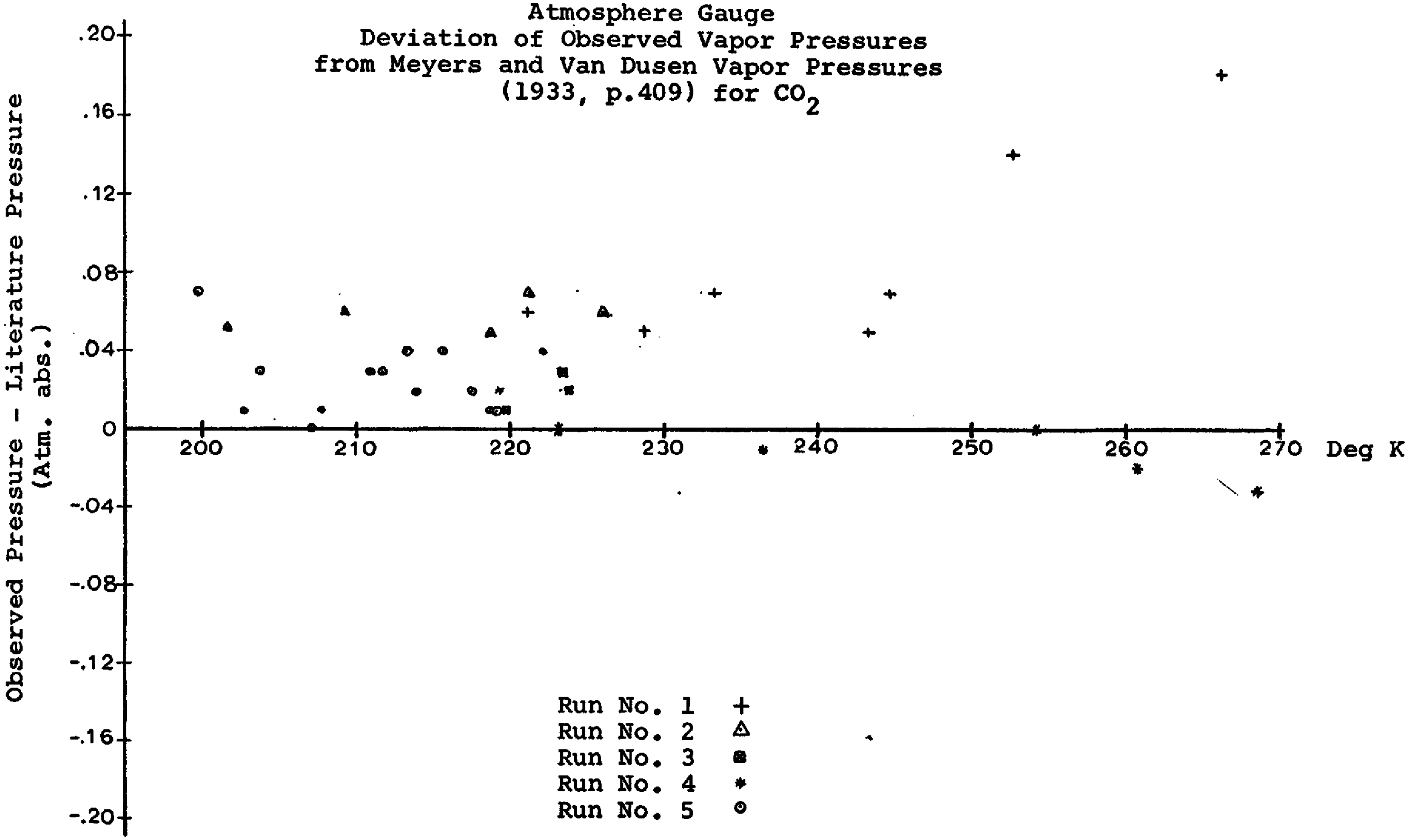
TABLE 1

Comparison of Observed Vapor Pressures of CO_2 using the Heise 0-100 Atm Gauge with Vapor Pressures from Meyers and Van Dusen (1933, p. 409).

Run No.	Temp. IPTS 1968 (Deg. K)	Observed Vapor Pressure Atm. (abs)	Meyers and Van Dusen (Atm)	Error (Atm)	Error (PSI)	T(K)
1	221.274	6.30	6.24	+.06		
	228.801	8.47	8.42	+.05	—	
	233.723	10.20	10.13	+.07	+1.03	233.[illegible]
	244.920	15.02	14.95	+.07	—	
	243.478	14.30	14.25	+.05		
	252.757	19.34	19.20	+.14	+2.06	243.4[illegible]
	266.298	28.74	28.56	+.18	+2.65	[illegible]
2	202.267	1.87	1.82	+.05		
	209.153	3.10	3.04	+.06		
	218.888	5.70	5.65	+.05		
	221.236	6.30	6.23	+.07		
	226.010	7.62	7.56	+.06		
3	219.722	5.86	5.85	+.01		
	223.597	6.89	6.86	+.03		
	223.995	6.99	6.97	+.02		
4	219.469	5.81	5.79	+.02		
	223.027	6.71	6.71	0		
	236.520	11.20	11.21	-.01	-0.15	236
	254.437	20.22	20.02	0		
	260.880	24.47	24.49	-.02		
	268.542	30.36	30.39	-.03	-0.44	268
5	219.118	5.71	5.70	+.01		
	217.015	5.23	5.21	+.02		
	213.821	4.25	4.23	+.02		
	210.979	3.49	3.46	+.03		
	207.671	2.74	2.73	+.01		
	203.756	2.07	2.04	+.03		
	199.759	1.51	1.44	+.07		
	202.674	1.89	1.88	+.01		
	207.172	2.63	2.63	0		
	211.348	3.59	3.56	+.03		
	213.201	4.09	4.05	+.04		
	215.609	4.81	4.77	+.04		
	218.718	5.61	5.60	+.01		
	222.386	6.57	6.53	+.04		

FIGURE 5

Atmosphere Gauge
Deviation of Observed Vapor Pressures
from Meyers and Van Dusen Vapor Pressures
(1933, p.409) for CO_2



direction on the psi gauges. Since errors of this magnitude and direction were not observed on the psi gauges, errors must be due to only the atmosphere gauge.

If the test run data and the calibration data (Appendix B) for the atmosphere gauge are carefully compared, a consistent gauge error can be observed. The calibration data show that this gauge tends to read high, especially at low pressures, as 25 out of the 30 calibration points are positive or zero. The average error from the calibration is + 0.015 atm. A calibration curve was not plotted for the atmosphere gauge because most of the errors from the calibration were small and considered to be reading error.

It can also be seen from Table 1 or Figure 5 that errors for all data points of a given run deviate by no more than 0.03 atm from other points in that same run. With this information and the consistant readings between the calibration and vapor pressure data, it can be concluded that the atmosphere gauge has a reproducibility of approximately 0.03 atm.

PSI Gauges: Considerably more error was observed on the psi gauges. However, small systematic errors which cannot be detected on the atmosphere gauge are prominent on the psi gauges. Data from the first five runs is presented in Table 2 and Figure 6. Figure 6 shows the deviation of the observed vapor pressures from the literature values as a function of temperature. The vapor pressures measured during the

TABLE 2

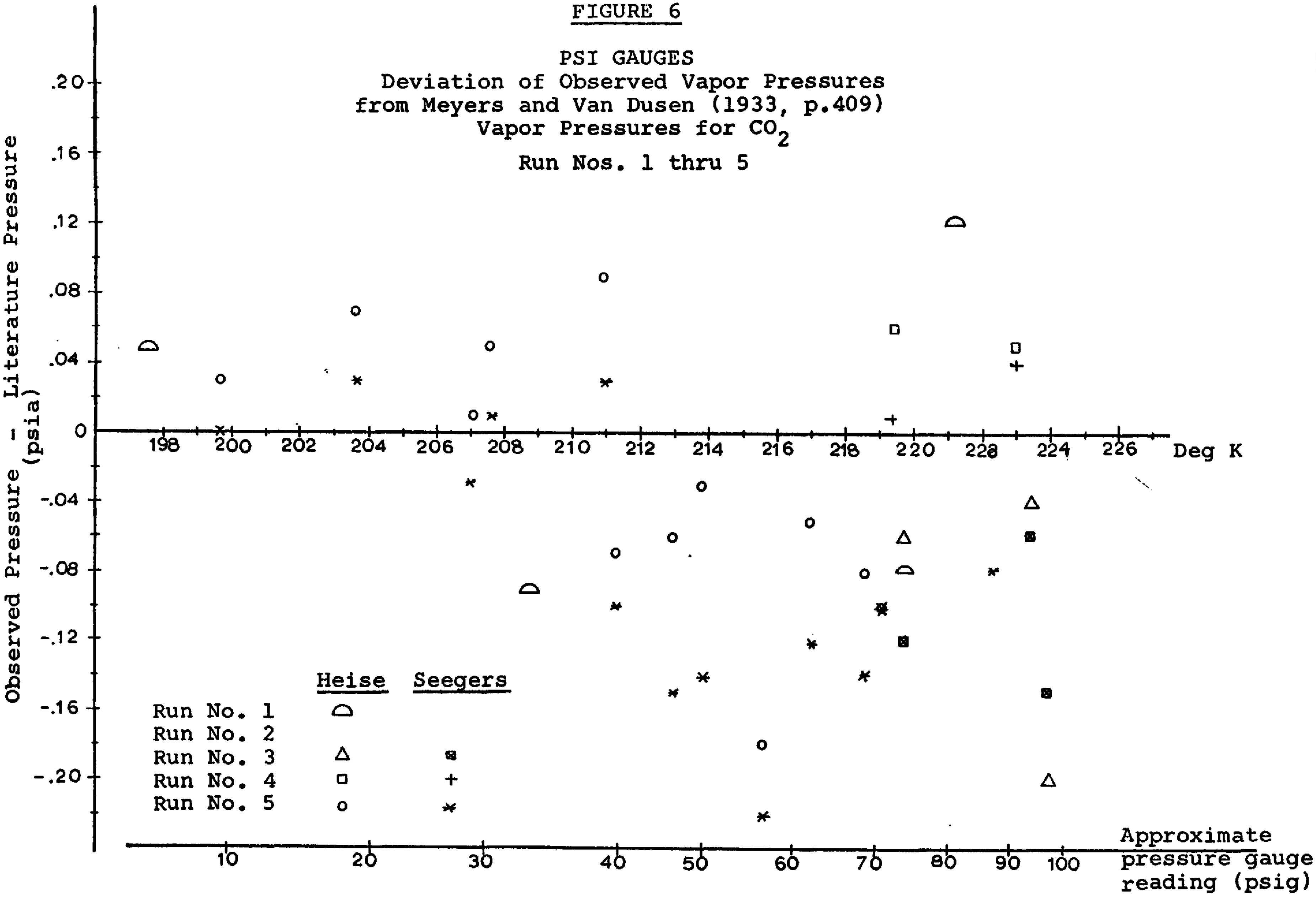
Comparison of Observed Vapor Pressures of CO_2 using the Heise and the Seegers 0-100 psi Gauges with Vapor Pressures from Meyers and Van Dusen (1933, p.405).

Run No.	Temp. IPTS 1968 (Deg K)	Observed Vapor Pressure (psia)		Meyers & Van Dusen (psia)	Error (psi)	
		Heise*	Seegers		Heise	Seegers
1	197.623	18.72	-	18.67	+.05	-
	208.886	43.73	-	43.82	-.09	-
	219.801	86.17	-	86.25	-.08	-
	221.274	91.83	-	9171	+.12	-
2	202.267	26.61	26.63	26.81	-.20	-.17
	209.153	44.37	44.41	44.65	-.28	-.28
	218.888	82.75	82.75	82.98	-.23	-.23
	221.236	91.23	91.22	91.56	-.33	-.34
	226.010	110.62	110.65	111.06	-.44	-.43
3	219.722	85.90	85.78	85.96	-.06	-.12
	223.597	100.78	100.78	100.82	-.04	-.05
	223.995	102.28	102.33	102.48	-.20	-.15
4	219.469	85.11	85.06	85.05	+.06	+.01
	223.027	98.60	98.59	98.55	+.05	+.04
5	219.118	83.70	83.70	83.79	-.90	-.90
	217.015	76.52	76.45	76.57	-.05	-.12
	213.821	62.13	62.04	62.16	-.03	-.14
	210.979	50.99	50.93	50.90	+.09	+.03
	207.671	40.18	40.14	40.13	+.05	+.01
	203.756	30.10	30.05	30.02	+.07	+.03
	199.759	22.14	22.11	22.11	+.03	0
	202.674	27.70	27.65	27.66	+.04	-.01
	207.172	38.68	38.64	38.67	+.01	-.03
	211.348	52.16	52.15	52.25	-.09	-.10
	213.201	59.44	59.35	59.50	-.06	-.15
	215.609	70.15	70.11	70.33	-.18	-.22
	218.710	82.28	82.22	82.36	-.08	-.14
	222.386	96.00	95.93	96.01	-.01	-.08

*NOTE: Calibration corrections have been applied to this Gauge

FIGURE 6

PSI GAUGES
Deviation of Observed Vapor Pressures
from Meyers and Van Dusen (1933, p.409)
Vapor Pressures for CO_2
Run Nos. 1 thru 5



first five runs were generally low and thus suggested the possibility of some systematic error in the system. As a result of these runs, possible sources of error were evaluated and the problem was found and corrected. Sources of error are discussed in the next section.

The low vapor pressures observed in the first five runs were caused by poor refrigeration distribution in the bath. All the LN_2 was vaporizing in the top 3 or 4 refrigeration coils in the bath causing lower temperatures in that region. Vapor in the exit line from the equilibrium cell was condensing and refluxing back to the cell. The problem was corrected by reversing the refrigeration coil, i.e., introducing the LN_2 to the bottom of the bath first. This corrected the problem in vapor pressure measurements as shown by Run No. 6 (Table 3 and Figure 7).

Reversing the refrigeration coil probably does not eliminate the 0.05 deg K temperature gradient, but places the gradient at the bottom of the bath where it will not affect vapor pressure or phase equilibria measurements. These measurements are not affected as long as the equilibrium gas is never cooled below the temperature at which it leaves the cell. In other phase equilibrium apparatus, heaters are sometimes used on the exit lines to ensure that cooling of the vapor does not occur. Therefore, as long as the cold region is in the bottom of the bath and does not create differentials between the thermometer and the inside of the cell, no problem will arise. However,

TABLE 3

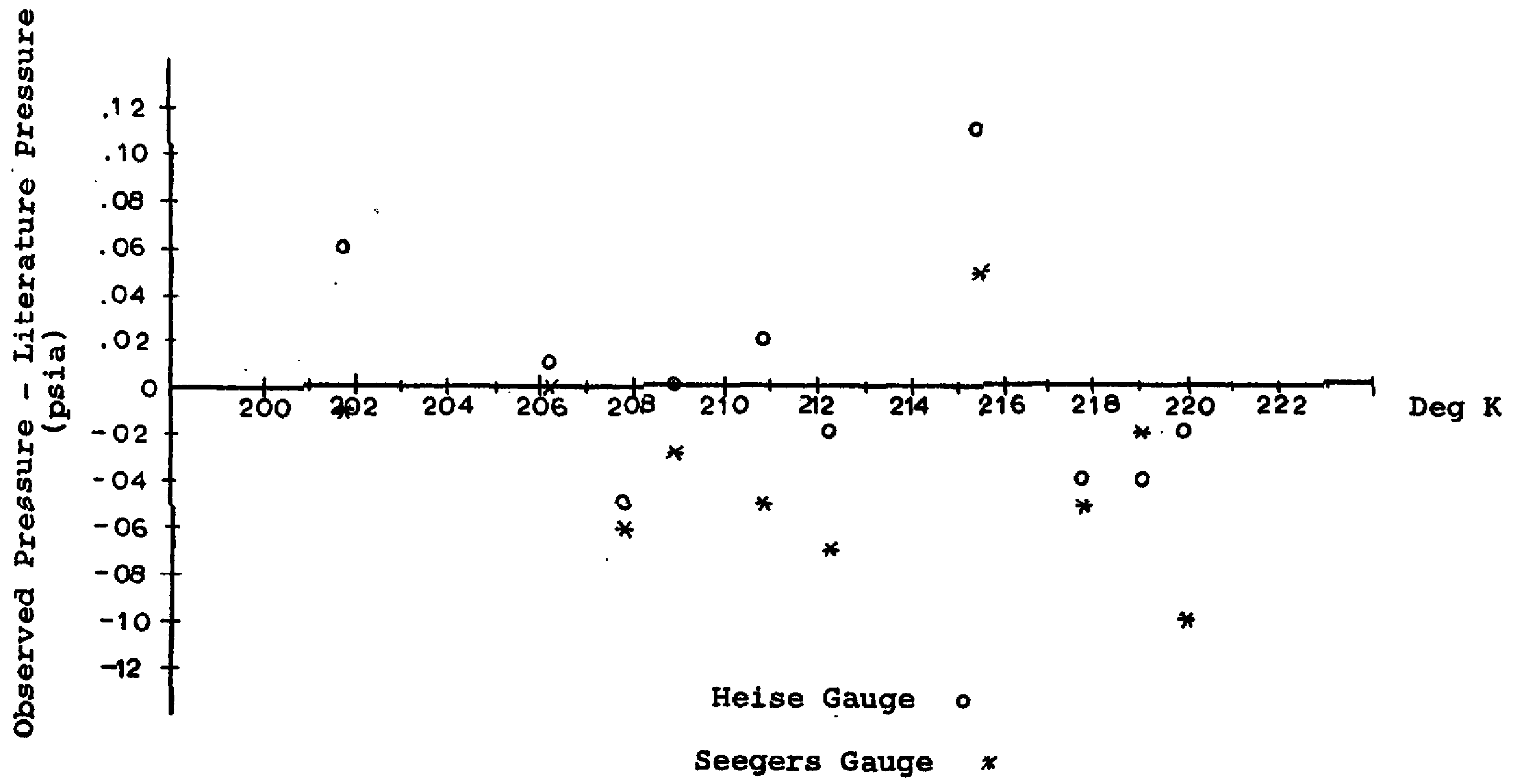
Comparison of Observed Vapor Pressures of CO_2 using the Heise and Seegers 0-100 psi Gauges with Vapor Pressures from Meyers and Van Dusen (1933, p.409) for Run No. 6.

Run	Temp. IPTS 1968	Observed Vapor Pressure (psia)		Meyers and Van Dusen	Error (psia)	
No.	(Deg K)	Heise*	Seegers	(psia)	Heise	Seegers
6	219.000	83.34	83.36	83.38	-.04	-.02
	215.525	71.73	71.67	71.62	+.11	+.05
	212.278	55.76	55.71	55.78	-.02	-.07
	210.838	50.42	50.35	50.40	+.02	-.05
	208.985	44.13	44.10	44.13	0	-.03
	206.137	35.85	35.84	35.84	+.01	0
	201.851	26.04	25.97	25.98	+.06	-.01
	207.997	41.04	41.03	41.08	-.05	-.06
	217.789	79.13	79.12	79.17	-.04	-.05
	219.971	86.83	86.75	86.85	-.02	-.10

*NOTE: Calibration corrections have been applied to this Gauge.

FIGURE 7

PSI Gauges
Deviation of Observed Vapor Pressures
from Meyers and Van Dusen (1933, p.409)
Vapor Pressures for CO_2
Run No. 6



this situation suggests that a thermocouple be placed at the bottom of the equilibrium cell to measure any temperature gradients between the top and bottom of the cell.

From Run No. 6 it can be concluded that Run Nos. 1 through 5 represented a system with some systematic error. However, when looking at all six runs the following conclusions about the psi gauges can be made.

1) The Seegers gauge consistently reads lower than the Heise gauge. Although corrections have been applied to lower the Heise gauge readings, discrepancies between the two gauges of as much as 0.10 psi still occur. These differences between the gauges are usually more than can be attributed to simple reading error. This suggests that both gauges should be recalibrated. The calibration on the Seegers gauge consisted of only three points, and a more complete calibration is desirable.

2) Considering Run No. 6, the gauges are reading within their expected accuracy. For this run, eight out of the ten data points had errors of ± 0.05 psi or less. Errors of this magnitude are considered as reading error.

Runs 1 through 5 show some relationship between error and temperature. At the higher temperatures the observed vapor pressures are low; and at the lower temperatures (solid region) the observed vapor pressures are high. This relationship is not as pronounced in Run No. 6, and no conclusion can be drawn.

Sources of Error: Possible sources of error are: 1) errors in the temperature measurement, 2) liquid-vapor or solid-vapor interfaces outside the equilibrium cell which are not at the measured temperature, 3) temperature gradients in the equilibrium cell and bath, 4) impurities in the sample gas , and 5) errors in the pressure gauge calibration.

To produce an error of 0.1 psi at 218 deg K would require an error in temperature of about 0.03 deg K or about 0.003 ohm. Both of these errors are an order of magnitude greater than is expected from the thermometer and Mueller Bridge calibrations. Therefore, an error in temperature measurement is unlikely to be a source of error.

If the cell were overfilled a liquid-vapor or solid vapor interface would be in the exit or inlet lines near the top of the bath. This would result in low vapor pressures if this portion of the bath was at a lower temperature. The thermometer was raised about 6 in. and a temperature 0.05 deg K colder was recorded. Incremental amounts of CO_2 were removed from the system. However, no changes in the observed vapor pressures were found that would indicate overfilling the cell.

It was established, however, that a temperature gradient existed in the bath. The excess cooling in the top of the bath was caused by all the LN_2 vaporizing in the top three of four coils of the refrigeration coil. As a result, a new refrigeration coil was built 9-ft long (about one-half as long as the original coil) with the LN_2 still entering the top and spiraling to the bottom of the bath. With the new coil installed the thermometer was again raised 6 in. and the temperatures in the top of the bath were 0.02 to 0.03 deg K colder. However, no change in vapor pressure data was noted. The shorter coil increased LN_2 consumption and was replaced with the original 20-ft coil.

It was then hypothesized that the vapor in the exit line was being condensed in the top portion of the bath. Although the equilibrium cell was not overfilled, the liquid-vapor interface being measured was outside the cell and in a cold spot. Two 710-ohm resistors were attached to the exit line in an attempt to heat the cold spot. Again no change in vapor pressure was observed.

The 20-ft refrigeration coil was then reversed so that LN_2 spiralled from the bottom to the top of the bath. When raised 6 in., the thermometer showed temperature deviations of only ± 0.0002 deg K from the normal measurement position. Therefore, with the cold spot around the exit vapor line eliminated, Run No. 6 was made.

An impurity such as water in the carbon dioxide would lower the observed vapor pressures. The carbon dioxide used in this experiment had a nominal purity of 99.95 mole percent CO_2. If the 0.05 percent impurity is assumed to be all water, and Raoult's Law is assumed, the liquid vapor pressure of the system would be lowered by 0.04 psi. If there was 0.10 mole percent water present, the liquid vapor pressure would be lowered by 0.09 psi. If the impurity was N_2, the vapor pressure would be higher than for pure CO_2.

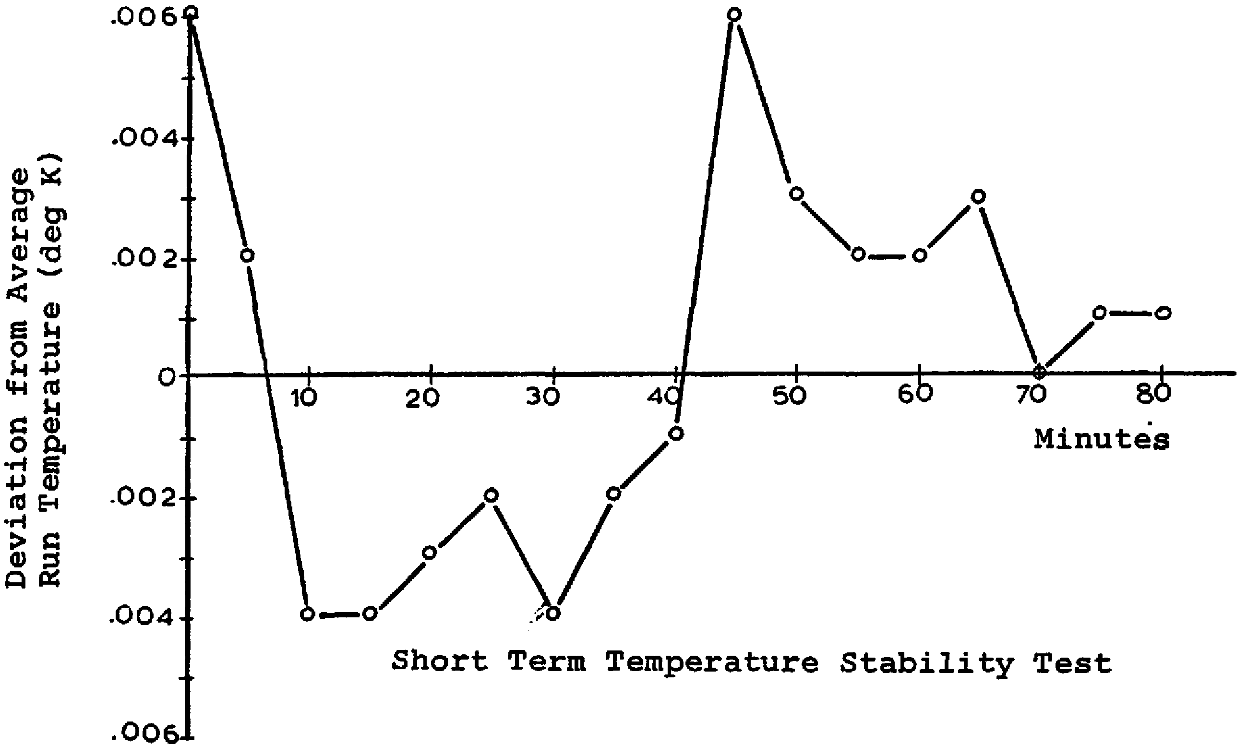
Errors in the pressure gauge calibrations could yield either high or low observed vapor pressure. These errors may also be dependent on the range of pressures being measured. Usually, the maximum error on a bourdon tube gauge occurs at either the high or low region of the scale.

Summary: To summarize the results of the vapor pressure measurements, the Heise atmosphere gauge has a reproducibility of ± 0.03 atm. The average error observed on this gauge was +0.03 atm with a maximum error of +0.07 atm. After a temperature gradient (which was small enough not to affect measurements on the atmosphere gauge) in the bath was eliminated, 80 percent of the data from the Heise and Seegers psi gauges had errors of ± 0.05 psi or less. This error can be attributed to uncertainty in reading the gauges.

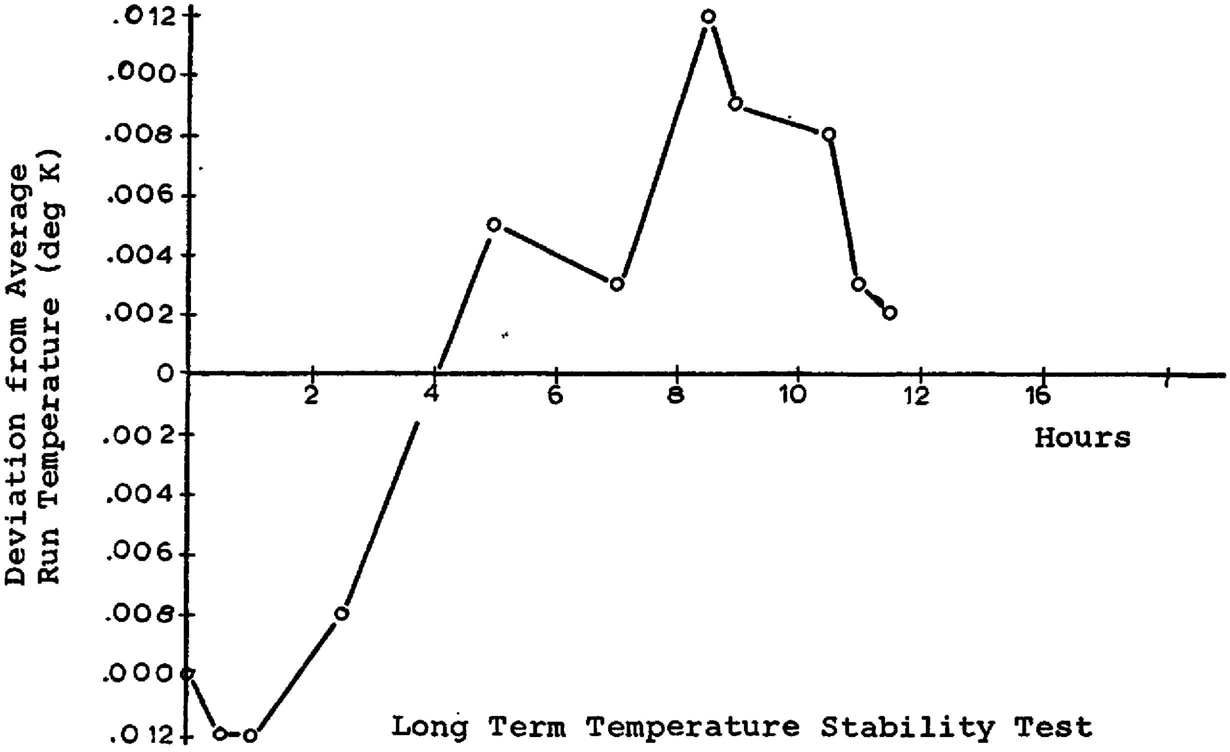
System Characteristics

Two tests were conducted to determine the temperature stability which can be expected for both short and long periods of time. For the short term temperature stability test, the temperature was measured every 5 minutes for 1 1/2 hours. The long term stability test lasted for 12 hours with the temperatures recorded about every 1 1/2 hours. Figure 8 shows plots of the deviation of each measured temperature from the average run temperature. The short term stability

FIGURE 8



Short Term Temperature Stability Test



Long Term Temperature Stability Test

test had maximum deviations of + 0.006 deg C and - 0.004 deg C, and the long term stability test showed a maximum deviation of ± 0.012 deg C.

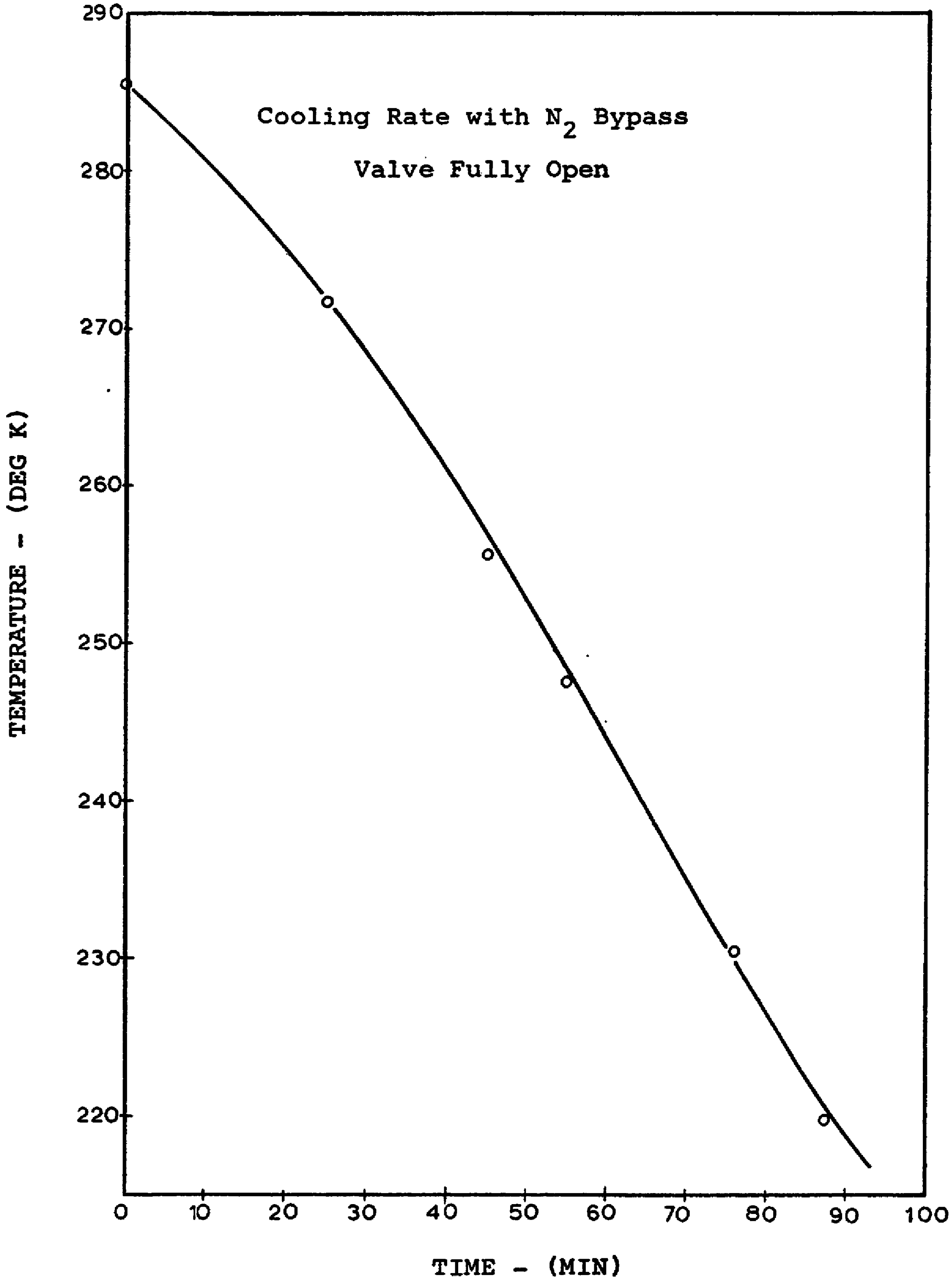
The stability tests represent the system operating by itself with no adjustments being made by the operator. Small changes can be made on the Fine Temperature Adjustment of the controller, and the temperature can be set within ± 0.003 deg K of the desired temperature.

Figure 9 is a plot of temperature vs. time to determine the rate of cooling using LN_2 with the bypass fully open. The average cool down rate is about 0.7 deg K per min. To heat the bath the 125-w heater from the controller was plugged into a 110 volt outlet. This heater was used only for short periods of time to heat the bath 5 or 10 deg K. The average heating rate was about 0.4 deg K per min. For faster heating of the bath, an auxillary 500-w heater will be installed and the 125-w heater will be used only with the controller.

Liquid nitrogen consumption varies between runs depending, of course on the time spent cooling to a given temperature vs. the time spent controlling at a set temperature. On the average a 160-l dewar of LN_2 was used for 25 to 30 hr. To cool down from 25 to -50 deg C required about 20 l of LN_2.

Differences in temperature between the inside of the equilibrium cell and the bath were measured with the copper-

FIGURE 9


Cooling Rate with N_2 Bypass Valve Fully Open
TEMPERATURE - (DEG K)
290
280
270
260
250
240
230
220
0
10
20
30
40
50
60
70
80
90
100
TIME - (MIN)

constantan thermocouple. With the Leeds-Northrup potentiometer the smallest temperature difference that can be detected is 0.002 mv or about 0.05 deg K. During maximum cool down rate the temperature inside the cell lagged the bath temperature by about 0.75 deg K. The cell would reach equilibrium with the bath within 2 to 3 min. after setting the bath temperature, and further temperature differences between the inside of the equilibrium cell and the bath could not be detected.

During the test runs it was noted that the outside of the bath dewar would get colder than expected. After the test runs had been completed the dewar was tested by filling it half full of LN_2. The LN_2 boiled vigorously indicating that the dewar does not have a good vacuum. It is, therefore recommended that the dewar be evacuated.

CONCLUSIONS

The temperature of the bath can be measured with a precision of ±0.001 deg K. The long term temperature stability test (12 hrs with no manual adjustments) showed fluctuations in temperature of ±0.01 deg K. The short term temperature stability test (1½ hrs) showed fluctuations of +0.006 deg K. Manual adjustments can be made with the temperature controller to set the temperature within ±0.003 deg K of the desired temperature.

The operating range of the apparatus is from -75 to 25 deg C. The low end of the operating range is limited by the freezing point of the CCl_4-$CHCl_3$ mixture (-81 deg C).

The Heise 0-100 atm gauge showed an average error in vapor pressure measurements of +0.03 atm, with a maximum error of +0.07 atm. The average calibration error for this gauge was +0.015 atm, thus indicating the gauge tends to read high. Although a calibration correction was not applied to this gauge, it can be noted that the average error in vapor pressure measurements can be reduced to +0.15 atm using the average calibration error as the correction.

Eighty percent of the data from the Heise and Seegers psi gauges have errors of ±0.05 psi or less. Calibration corrections were applied only to the Heise gauge, and hysteresis effects were neglected. The Mueller Bridge calibration was not considered, but if applied it would raise the literature vapor pressures by approximately 0.025 psi.

RECOMMENDATIONS

1) Recalibrate the Heise 0-100 psi gauge and the Seegers 0-100 psi gauge.

2) Install a differential thermocouple between the top and bottom of the equilibrium cell.

3) Install a refrigeration coil with better temperature distribution.

4) Calibrate the Mueller Bridge.

APPENDIX A

Platinum Resistance Thermometer Calibration

The Report of Calibration from the National Bureau of Standards for the platinum resistance thermometer is presented in this appendix.

U.S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS
INSTITUTE FOR BASIC STANDARDS
WASHINGTON D.C. 20234

REPORT OF CALIBRATION

PLATINUM RESISTANCE THERMOMETER
SERIAL NO. 1547841

SUBMITTED BY
COLORADO SCHOOL OF MINES
CHEMICAL AND PETROLEUM REFINING ENGINEERING

THIS THERMOMETER WAS CALIBRATED FOR USE WITH CONTINUOUS CURRENT OF 1.0 MA. THROUGH THE THERMOMETER.

THE FOLLOWING VALUES WERE FOUND FOR THE CONSTANTS IN THE INTERNATIONAL PRACTICAL TEMPERATURE SCALE(1968) FORMULAS:

ALPHA = 3.925435-03
DELTA = 1.496506
A4 =-5.316-07
C4 = 3.003-14

THE PERTINENT INTERNATIONAL PRACTICAL TEMPERATURE FORMULAS ARE GIVEN IN THE DISCUSSION ON THE FOLLOWING PAGES.

THE RESISTANCE AT 0 DEGREES C WAS FOUND TO BE 25.5071 ABSOLUTE OHMS. DURING CALIBRATION, THIS RESISTANCE CHANGED BY THE EQUIVALENT OF .0001 DEG C.

THIS THERMOMETER IS SATISFACTORY AS A DEFINING STANDARD IN ACCORDANCE WITH THE TEXT OF THE INTERNATIONAL PRACTICAL TEMPERATURE SCALE OF 1968.

FOR THE DIRECTOR,
INSTITUTE FOR BASIC STANDARDS
Harmon Plumb
HARMON H. PLUMB
CHIEF, TEMPERATURE SECTION
HEAT DIVISION

TEST NO.199167
COMPUTED AUGUST 1969
JLR/UNIVAC

Temperatures between 0 °C and 631.74 °C on the new International Practical Temperature Scale of 1968 (IPTS-68) are defined by the indications (resistance values) of standard platinum resistance thermometers and the following expressions:

$$t = t' + M(t') \tag{1}$$

$$t' = \frac{1}{\alpha}\left(\frac{R_t}{R_o} - 1\right) + \delta\left(\frac{t'}{100} - 1\right)\frac{t'}{100} \tag{2}$$

$$M(t') = .045\left(\frac{t'}{100}\right)\left(\frac{t'}{100} - 1\right)\left(\frac{t'}{419.58} - 1\right)\left(\frac{t'}{630.74} - 1\right) \tag{3}$$

where t is the temperature, at the outside of the tube protecting the platinum resistor, in °C on the International Practical Temperature Scale of 1968 and R_t and R_o are the resistances of the platinum resistor at t° and 0 °C respectively, measured with a continuous current through the platinum resistor. The value of this current and the values of the constants α and δ found for this thermometer are given on the previous page. The value of M(t'), given by expression (3), is the same for all thermometers and is a function only of the quantity t'. The addition of the small value represented by (3) serves to make the IPTS-68 conform more closely to the thermodynamic scale than can be done with only the simple quadratic of expression (2).

An alternate form which is completely equivalent to expression (2) is

$$R_t = R_o\,(1 + At' + Bt'^2) \tag{4}$$

In some instances expression (4) is less difficult to calculate than (2). The constants A and B used in (4) are related directly to α and δ.

$$A = \alpha\,(1 + \delta/100) \tag{5}$$

$$B = -\alpha\delta/10^4 \tag{6}$$

CAUTION: The values of A, B, and δ on the new 1968 scale are distinctly different from the corresponding values on the old 1948 or 1927 scale. The values of α and R_o are also different but only trivially so.

Temperatures below 0 °C on the new 1968 scale are calculated using a standard reference table which gives values of R_t/R_o for a fictitious "mean" standard thermometer. This reference table and a specified deviation equation are combined to give the values for a particular thermometer. The standard reference table used for IPTS-68 is referred to as the "CCT-68" table. It is convenient to use the symbol W_t in place of R_t/R_o. For the special reference values of R_t/R_o tabulated in CCT-68 the special symbol $W_t{}^*$ is used. The table giving values of W_t for a particular thermometer from 0 °C down to -182.962 °C may be calculated from the following expressions,

$$W_t = W_t{}^* + \Delta W_t \tag{7}$$

$$\Delta W_t = A_4 t + C_4 t^3 \, (t - 100) \tag{8}$$

Expression (8) is the specified deviation equation in the range 0 °C to -182.962 °C. The constants A_4 and C_4 to be used in expression (6) for this particular thermometer are given on the first page.

A table calculated from the constants for this thermometer is on the following pages. If no value for C_4 is given, the table below 0 °C was calculated with an assumed value of this constant. The first column of the table gives values of temperature. Unless a different function is requested, the second column gives R_t/R_o (i.e. the ratio of the resistance at the stated temperature to the resistance at the ice point). The third column gives the inverse (reciprocal) of the difference between successive values in the second column. These reciprocal first differences are included to facilitate interpolation. The error introduced by using linear interpolation will be less than 0.0001 °C.

The range of this table does not imply that this thermometer is necessarily a satisfactory instrument over exactly the same range. The range was selected to cover an interval believed to include the needs of the majority of users of this type of thermometer.

AUGUST 1969 IPTS-68 TABLE FOR RESISTANCE THERMOMETER 1547841

TEMP. KELVIN	RESISTANCE RATIO	INVERSE DIFF.	TEMP. KELVIN	RESISTANCE RATIO	INVERSE DIFF.
			100	.286437	231.44
			101	.290755	231.58
			102	.295070	231.73
			103	.299383	231.88
			104	.303693	232.03
			105	.308000	232.19
			106	.312303	232.35
			107	.316604	232.51
			108	.320902	232.67
			109	.325197	232.84
			110	.329489	233.01
			111	.333777	233.18
			112	.338063	233.35
			113	.342345	233.52
			114	.346624	233.70
			115	.350900	233.87
			116	.355173	234.04
			117	.359442	234.22
			118	.363709	234.39
			119	.367972	234.56
			120	.372232	234.73
			121	.376489	234.91
			122	.380743	235.08
			123	.384994	235.25
			124	.389241	235.42
			125	.393486	235.59
			126	.397728	235.76
			127	.401966	235.92
			128	.406202	236.09
			129	.410435	236.25
			130	.414665	236.42
			131	.418891	236.58
			132	.423116	236.74
			133	.427337	236.90
			134	.431555	237.06
			135	.435771	237.22
			136	.439983	237.37
			137	.444193	237.53
			138	.448401	237.68
			139	.452606	237.83
90	.243133	230.46	140	.456808	237.98
91	.247471	230.51	141	.461007	238.13
92	.251806	230.58	142	.465204	238.27
93	.256143	230.66	143	.469398	238.42
94	.260477	230.74	144	.473590	238.56
95	.264809	230.84	145	.477779	238.70
96	.269139	230.94	146	.481966	238.84
97	.273467	231.06	147	.486151	238.98
98	.277793	231.18	148	.490333	239.12
99	.282115	231.31	149	.494512	239.26
100	.286437	231.44	150	.498689	239.39

AUGUST 1969 IPTS-68 TABLE FOR RESISTANCE THERMOMETER 1547841

TEMP. KELVIN	RESISTANCE RATIO	INVERSE DIFF.	TEMP. KELVIN	RESISTANCE RATIO	INVERSE DIFF.
150	.498689	239.39	200	.705008	244.86
151	.502864	239.53	201	.709090	244.95
152	.507037	239.66	202	.713171	245.04
153	.511207	239.79	203	.717251	245.13
154	.515375	239.92	204	.721329	245.22
155	.519541	240.05	205	.725405	245.31
156	.523705	240.18	206	.729480	245.40
157	.527866	240.30	207	.733554	245.49
158	.532025	240.43	208	.737626	245.58
159	.536182	240.55	209	.741696	245.67
160	.540337	240.67	210	.745765	245.76
161	.544490	240.79	211	.749833	245.85
162	.548641	240.91	212	.753899	245.93
163	.552790	241.03	213	.757963	246.02
164	.556937	241.15	214	.762027	246.11
165	.561081	241.27	215	.766089	246.19
166	.565224	241.38	216	.770149	246.28
167	.569365	241.50	217	.774208	246.37
168	.573504	241.61	218	.778266	246.45
169	.577641	241.73	219	.782322	246.54
170	.581776	241.84	220	.786376	246.62
171	.585909	241.95	221	.790430	246.71
172	.590040	242.06	222	.794482	246.79
173	.594169	242.17	223	.798532	246.88
174	.598297	242.28	224	.802582	246.96
175	.602423	242.39	225	.806630	247.04
176	.606546	242.49	226	.810676	247.13
177	.610668	242.60	227	.814721	247.21
178	.614789	242.70	228	.818765	247.29
179	.618907	242.81	229	.822807	247.38
180	.623024	242.91	230	.826849	247.46
181	.627139	243.01	231	.830888	247.54
182	.631252	243.12	232	.834927	247.62
183	.635364	243.22	233	.838964	247.70
184	.639474	243.32	234	.843000	247.78
185	.643582	243.42	235	.847034	247.86
186	.647688	243.52	236	.851067	247.95
187	.651793	243.62	237	.855099	248.03
188	.655896	243.72	238	.859130	248.11
189	.659997	243.82	239	.863159	248.19
190	.664097	243.91	240	.867187	248.27
191	.668196	244.01	241	.871213	248.35
192	.672292	244.11	242	.875239	248.43
193	.676387	244.20	243	.879263	248.51
194	.680481	244.30	244	.883286	248.58
195	.684572	244.39	245	.887307	248.66
196	.688663	244.49	246	.891327	248.74
197	.692751	244.58	247	.895346	248.82
198	.696836	244.67	248	.899364	248.90
199	.700924	244.76	249	.903380	248.98
200	.705008	244.86	250	.907395	249.06

AUGUST 1969 IPTS-68 TABLE FOR RESISTANCE THERMOMETER 1547841

TEMP. KELVIN	RESISTANCE RATIO	INVERSE DIFF.	TEMP. KELVIN	RESISTANCE RATIO	INVERSE DIFF.
250	.907395	249.06	300	1.106583	252.92
251	.911409	249.13	301	1.110536	253.00
252	.915422	249.21	302	1.114487	253.07
253	.919433	249.29	303	1.118437	253.15
254	.923444	249.37	304	1.122386	253.23
255	.927455	249.44	305	1.126334	253.31
256	.931460	249.52	306	1.130281	253.38
257	.935467	249.60	307	1.134226	253.46
258	.939472	249.68	308	1.138170	253.54
259	.943476	249.75	309	1.142113	253.62
260	.947478	249.83	310	1.146055	253.70
261	.951480	249.91	311	1.149995	253.77
262	.955480	249.98	312	1.153935	253.85
263	.959479	250.06	313	1.157873	253.93
264	.963477	250.14	314	1.161810	254.01
265	.967474	250.21	315	1.165745	254.09
266	.971469	250.29	316	1.169680	254.16
267	.975463	250.37	317	1.173613	254.24
268	.979456	250.44	318	1.177545	254.32
269	.983448	250.52	319	1.181476	254.40
270	.987438	250.60	320	1.185406	254.47
271	.991427	250.68	321	1.189334	254.55
272	.995415	250.75	322	1.193261	254.63
273	.999402	250.83	323	1.197187	254.71
274	1.003388	250.91	324	1.201112	254.79
275	1.007372	250.98	325	1.205036	254.87
276	1.011355	251.06	326	1.208958	254.94
277	1.015337	251.14	327	1.212880	255.02
278	1.019318	251.22	328	1.216800	255.10
279	1.023297	251.29	329	1.220718	255.18
280	1.027275	251.37	330	1.224636	255.26
281	1.031252	251.45	331	1.228552	255.33
282	1.035228	251.52	332	1.232458	255.41
283	1.039202	251.60	333	1.236382	255.49
284	1.043176	251.68	334	1.240295	255.57
285	1.047148	251.76	335	1.244206	255.65
286	1.051119	251.83	336	1.248117	255.73
287	1.055088	251.91	337	1.252026	255.80
288	1.059057	251.99	338	1.255934	255.88
289	1.063024	252.07	339	1.259841	255.96
290	1.066990	252.14	340	1.263746	256.04
291	1.070955	252.22	341	1.267651	256.12
292	1.074918	252.30	342	1.271554	256.20
293	1.078881	252.38	343	1.275456	256.27
294	1.082842	252.45	344	1.279357	256.35
295	1.086802	252.53	345	1.283257	256.43
296	1.090760	252.61	346	1.287155	256.51
297	1.094718	252.69	347	1.291052	256.59
298	1.098674	252.76	348	1.294949	256.67
299	1.102629	252.84	349	1.298843	256.75
300	1.106583	252.92	350	1.302737	256.83

AUGUST 1969 IPTS-68 TABLE FOR RESISTANCE THERMOMETER 1547841

TEMP. KELVIN	RESISTANCE RATIO	INVERSE DIFF.	TEMP. KELVIN	RESISTANCE RATIO	INVERSE DIFF.
350	1.302737	256.83	400	1.495908	260.79
351	1.306630	256.90	401	1.499741	260.87
352	1.310521	256.98	402	1.503573	260.95
353	1.314411	257.06	403	1.507404	261.03
354	1.318300	257.14	404	1.511234	261.11
355	1.322188	257.22	405	1.515062	261.20
356	1.326074	257.30	406	1.518890	261.27
357	1.329960	257.38	407	1.522716	261.36
358	1.333844	257.46	408	1.526541	261.44
359	1.337727	257.53	409	1.530365	261.52
360	1.341609	257.61	410	1.534188	261.60
361	1.345489	257.69	411	1.538009	261.68
362	1.349369	257.77	412	1.541829	261.76
363	1.353247	257.85	413	1.545649	261.84
364	1.357124	257.93	414	1.549467	261.92
365	1.361000	258.01	415	1.553283	262.00
366	1.364874	258.09	416	1.557099	262.08
367	1.368748	258.17	417	1.560913	262.16
368	1.372620	258.25	418	1.564727	262.24
369	1.376491	258.32	419	1.568539	262.32
370	1.380361	258.40	420	1.572350	262.40
371	1.384230	258.48	421	1.576160	262.48
372	1.388097	258.56	422	1.579968	262.57
373	1.391964	258.64	423	1.583776	262.64
374	1.395829	258.72	424	1.587582	262.73
375	1.399693	258.80	425	1.591387	262.81
376	1.403556	258.88	426	1.595191	262.89
377	1.407417	258.96	427	1.598993	262.97
378	1.411278	259.04	428	1.602795	263.05
379	1.415137	259.12	429	1.606595	263.13
380	1.418995	259.20	430	1.610395	263.21
381	1.422852	259.28	431	1.614193	263.29
382	1.426707	259.36	432	1.617990	263.37
383	1.430562	259.44	433	1.621785	263.46
384	1.434415	259.52	434	1.625580	263.54
385	1.438267	259.60	435	1.629373	263.62
386	1.442118	259.68	436	1.633165	263.70
387	1.445968	259.76	437	1.636956	263.78
388	1.449817	259.83	438	1.640746	263.86
389	1.453664	259.91	439	1.644535	263.94
390	1.457510	259.99	440	1.648322	264.03
391	1.461356	260.07	441	1.652109	264.11
392	1.465199	260.15	442	1.655894	264.19
393	1.469042	260.23	443	1.659678	264.27
394	1.472884	260.31	444	1.663461	264.35
395	1.476724	260.39	445	1.667242	264.43
396	1.480563	260.47	446	1.671023	264.52
397	1.484401	260.55	447	1.674802	264.60
398	1.488238	260.63	448	1.678580	264.68
399	1.492073	260.71	449	1.682357	264.76
400	1.495908	260.79	450	1.686133	264.84

AUGUST 1969 IPTS-68 TABLE FOR RESISTANCE THERMOMETER 1547841

TEMP. KELVIN	RESISTANCE RATIO	INVERSE DIFF.	TEMP. KELVIN	RESISTANCE RATIO	INVERSE DIFF.
450	1.686133	264.84	500	1.873439	268.99
451	1.689906	264.92	501	1.877156	269.07
452	1.693681	265.01	502	1.880871	269.16
453	1.697454	265.09	/503	1.884585	269.24
454	1.701225	265.17	504	1.888298	269.33
455	1.704995	265.25	505	1.892010	269.41
456	1.708764	265.33	506	1.895721	269.49
457	1.712531	265.42	507	1.899430	269.58
458	1.716298	265.50	508	1.903138	269.66
459	1.720063	265.58	509	1.906846	269.75
460	1.723827	265.66	510	1.910552	269.83
461	1.727590	265.75	511	1.914256	269.91
462	1.731352	265.83	512	1.917960	270.00
463	1.735113	265.91	513	1.921663	270.09
464	1.738872	265.99	514	1.925364	270.17
465	1.742631	266.07	515	1.929064	270.25
466	1.746388	266.16	516	1.932763	270.34
467	1.750144	266.24	517	1.936461	270.42
468	1.753899	266.32	518	1.940158	270.51
469	1.757652	266.40	519	1.943854	270.59
470	1.761405	266.49	520	1.947548	270.68
471	1.765156	266.57	521	1.951241	270.76
472	1.768906	266.65	522	1.954933	270.85
473	1.772655	266.74	523	1.958624	270.93
474	1.776403	266.82	524	1.962314	271.02
475	1.780150	266.90	525	1.966003	271.11
476	1.783895	266.99	526	1.969690	271.19
477	1.787640	267.07	527	1.973376	271.28
478	1.791383	267.15	528	1.977061	271.36
479	1.795125	267.23	529	1.980745	271.45
480	1.798866	267.32	530	1.984428	271.53
481	1.802606	267.40	531	1.988110	271.62
482	1.806344	267.48	532	1.991790	271.70
483	1.810082	267.57	533	1.995470	271.79
484	1.813818	267.65	534	1.999148	271.87
485	1.817553	267.73	535	2.002825	271.96
486	1.821287	267.82	536	2.006501	272.05
487	1.825019	267.90	537	2.010176	272.13
488	1.828751	267.98	538	2.013849	272.22
489	1.832481	268.07	539	2.017521	272.30
490	1.836211	268.15	540	2.021193	272.39
491	1.839939	268.23	541	2.024863	272.48
492	1.843666	268.32	542	2.028532	272.56
493	1.847391	268.40	543	2.032199	272.65
494	1.851116	268.49	544	2.035866	272.73
495	1.854839	268.57	545	2.039531	272.82
496	1.858562	268.65	546	2.043196	272.91
497	1.862283	268.74	547	2.046859	272.99
498	1.866003	268.82	548	2.050521	273.08
499	1.869722	268.90	549	2.054181	273.16
500	1.873439	268.99	550	2.057841	273.25

AUGUST 1969 IPTS-68 TABLE FOR RESISTANCE THERMOMETER 1547841

TEMP. KELVIN	RESISTANCE RATIO	INVERSE DIFF.	TEMP. KELVIN	RESISTANCE RATIO	INVERSE DIFF.
550	2.057841	273.25	600	2.239344	277.65
551	2.061500	273.34	601	2.242944	277.74
552	2.065157	273.42	602	2.246544	277.83
553	2.068813	273.51	603	2.250142	277.92
554	2.072466	273.60	604	2.253739	278.01
555	2.076122	273.69	605	2.257335	278.10
556	2.079775	273.77	606	2.260929	278.19
557	2.083426	273.86	607	2.264523	278.28
558	2.087076	273.95	608	2.268115	278.37
559	2.090726	274.03	609	2.271706	278.46
560	2.094374	274.12	610	2.275297	278.55
561	2.098020	274.21	611	2.278885	278.64
562	2.101666	274.29	612	2.282473	278.73
563	2.105311	274.38	613	2.286060	278.82
564	2.108954	274.47	614	2.289645	278.91
565	2.112596	274.56	615	2.293229	279.00
566	2.116237	274.64	616	2.296812	279.09
567	2.119877	274.73	617	2.300394	279.18
568	2.123516	274.82	618	2.303975	279.28
569	2.127154	274.91	619	2.307554	279.36
570	2.130790	274.99	620	2.311133	279.45
571	2.134425	275.08	621	2.314710	279.55
572	2.138060	275.17	622	2.318286	279.64
573	2.141693	275.26	623	2.321861	279.73
574	2.145324	275.35	624	2.325435	279.82
575	2.148955	275.43	625	2.329007	279.91
576	2.152584	275.52	626	2.332579	280.00
577	2.156213	275.61	627	2.336149	280.09
578	2.159840	275.70	628	2.339718	280.18
579	2.163466	275.79	629	2.343286	280.28
580	2.167091	275.87	630	2.346853	280.37
581	2.170714	275.96	631	2.350418	280.45
582	2.174337	276.05	632	2.353983	280.55
583	2.177958	276.14	633	2.357546	280.64
584	2.181579	276.23	634	2.361108	280.73
585	2.185196	276.32	635	2.364669	280.82
586	2.188816	276.40	636	2.368229	280.92
587	2.192432	276.49	637	2.371788	281.01
588	2.196048	276.58	638	2.375345	281.10
589	2.199662	276.67	639	2.378901	281.19
590	2.203275	276.76	640	2.382456	281.28
591	2.206883	276.85	641	2.386010	281.38
592	2.210493	276.94	642	2.389563	281.47
593	2.214108	277.03	643	2.393115	281.56
594	2.217717	277.11	644	2.396635	281.65
595	2.221324	277.21	645	2.400215	281.75
596	2.224931	277.29	646	2.403763	281.84
597	2.228538	277.38	647	2.407310	281.93
598	2.232140	277.47	648	2.410855	282.02
599	2.235742	277.56	649	2.414400	282.12
600	2.239344	277.65	650	2.417944	282.21

AUGUST 1969 IPTS-68 TABLE FOR RESISTANCE THERMOMETER 1547841

TEMP. KELVIN	RESISTANCE RATIO	INVERSE DIFF.	TEMP. KELVIN	RESISTANCE RATIO	INVERSE DIFF.
650	2.417944	282.21	700	2.593627	286.95
651	2.421486	282.30	701	2.597110	287.05
652	2.425027	282.39	702	2.600593	287.14
653	2.428567	282.49	703	2.604074	287.24
654	2.432106	282.58	704	2.607555	287.34
655	2.435643	282.68	705	2.611034	287.43
656	2.439180	282.77	706	2.614512	287.53
657	2.442715	282.86	707	2.617988	287.63
658	2.446249	282.95	708	2.621464	287.72
659	2.449782	283.05	709	2.624938	287.82
660	2.453314	283.14	710	2.628411	287.92
661	2.456845	283.24	711	2.631883	288.02
662	2.460374	283.33	712	2.635354	288.11
663	2.463902	283.42	713	2.638824	288.21
664	2.467430	283.52	714	2.642292	288.31
665	2.470955	283.61	715	2.645760	288.41
666	2.474480	283.71	716	2.649226	288.50
667	2.478004	283.80	717	2.652691	288.61
668	2.481526	283.90	718	2.656155	288.70
669	2.485048	283.99	719	2.659617	288.80
670	2.488568	284.08	720	2.663079	288.90
671	2.492087	284.18	721	2.666539	289.00
672	2.495604	284.27	722	2.669998	289.10
673	2.499121	284.37	723	2.673456	289.20
674	2.502636	284.46	724	2.676912	289.29
675	2.506151	284.56	725	2.680368	289.39
676	2.509664	284.65	726	2.683822	289.49
677	2.513176	284.74	727	2.687275	289.59
678	2.516687	284.84	728	2.690727	289.69
679	2.520196	284.94	729	2.694178	289.79
680	2.523704	285.03	730	2.697628	289.89
681	2.527212	285.12	731	2.701076	289.99
682	2.530718	285.22	732	2.704524	290.09
683	2.534223	285.32	733	2.707970	290.19
684	2.537726	285.41	734	2.711415	290.28
685	2.541229	285.51	735	2.714858	290.38
686	2.544730	285.60	736	2.718301	290.48
687	2.548231	285.70	737	2.721742	290.59
688	2.551730	285.79	738	2.725182	290.69
689	2.555227	285.89	739	2.728621	290.78
690	2.558724	285.98	740	2.732059	290.88
691	2.562220	286.08	741	2.735496	290.99
692	2.565714	286.18	742	2.738931	291.08
693	2.569207	286.27	743	2.742365	291.19
694	2.572699	286.37	744	2.745798	291.28
695	2.576190	286.46	745	2.749230	291.39
696	2.579680	286.56	746	2.752661	291.49
697	2.583168	286.66	747	2.756090	291.59
698	2.586655	286.76	748	2.759519	291.69
699	2.590142	286.85	749	2.762946	291.79
700	2.593627	286.95	750	2.766372	291.89

AUGUST 1969 IPTS-68 TABLE FOR RESISTANCE THERMOMETER 1547841

TEMP. KELVIN	RESISTANCE RATIO	INVERSE DIFF.	TEMP. KELVIN	RESISTANCE RATIO	INVERSE DIFF.
750	2.766372	291.89			
751	2.769797	291.99			
752	2.773220	292.10			
753	2.776645	292.19			
754	2.780064	292.30			
755	2.783484	292.40			
756	2.786903	292.49			
757	2.790320	292.60			
758	2.793737	292.70			
759	2.797152	292.81			
760	2.800566	292.90			
761	2.803979	293.01			
762	2.807391	293.11			
763	2.810801	293.21			
764	2.814210	293.31			
765	2.817619	293.42			
766	2.821025	293.52			
767	2.824431	293.62			
768	2.827836	293.73			
769	2.831239	293.82			
770	2.834641	293.93			
771	2.838042	294.03			
772	2.841442	294.13			
773	2.844841	294.24			
774	2.848238	294.34			
775	2.851634	294.44			

APPENDIX B

Pressure Gauge Calibrations

The two Heise gauges were calibrated together and the Seegers gauge was calibrated at a later date.

Calibration of Heise Gauges

The calibration was done by Rolf Prydz and A.J. Kidnay at the National Bureau of Standards, Boulder, Colorado on 12/31/70. A Ruska Instrument Company, Catalog No. 2400HL oil dead-weight tester was used for the calibration. The two Heise gauges calibrated were H35532 (0 to 100 psi) and C58810 (0 to 100 atm).

Barometric pressure at the start of the calibration was 623.1 mm Hg at 20 deg C; at the end of the calibration the barometric pressure was 623.7 mm Hg at 21.3 deg C. Thus the average barometer was 623.4 mm Hg at 20.8 deg C. When corrected for temperature and gravity, this is 0.8163 atm. Both Heise gauges were adjusted to zero when open to the atmosphere at the start of the calibrations.

The dead weight tester readings are believed accurate to the significant figures shown on the next page.

TABLE 4

Calibration Data for the Two Heise Pressure Gauges

Point	Dead Weight Tester Reading (Corrected) psi	atm	Heise Gauge H35532 psi	Heise Gauge C58810 atm	Remarks
1	29.97	2.039	30.00	2.09	
2	44.96	3.059	45.05	3.10	
3	59.94	4.079	60.05	4.11	
4	75.92	5.166	76.05	5.19	
5	95.90	6.526	96.05	6.55	
6	75.92	5.166	76.15	5.20	
7	59.94	4.079	60.15	4.11	
8	44.96	3.059	45.12	3.10	
9	19.98	1.359	20.15	1.39	
10	9.990	0.680	10.10	0.71	
-	open to atmosphere		0.10	0.00	Note Zero shift
11	145.85	9.925	-	9.91	
12	205.79	14.004	-	14.00	
13	305.70	20.802	-	20.85	
14	405.60	27.601	-	27.69	
15	495.52	33.719	-	33.75	
16	305.70	20.802	-	20.80	
17	145.85	9.925	-	9.89	
-	open to atmosphere		-	0.00	
18	605.42	41.197	-	41.25	
19	705.32	47.996	-	48.09	
20	805.23	54.794	-	54.80	
21	905.14	61.593	-	61.65	
22	1005.05	68.392	-	68.39	
23	1104.96	75.191	-	75.19	
24	1204.87	81.989	-	81.90	
25	1304.79	88.789	-	88.79	
26	1404.70	95.587	-	95.60	
27	1454.66	98.987	-	99.00	
28	1204.87	81.989	-	81.90	
29	905.14	61.593	-	61.60	
30	605.42	41.197	-	41.15	
	open to atmosphere		-	0.00	

TABLE 5

Heise Gauge H35532

Actual Pressure	Gauge Error
29.79	+0.03
44.96	+0.09
59.94	+0.11
75.92	+0.13
95.90	+0.15
75.92	+0.13*
59.94	+0.11*
44.96	+0.06*
19.98	+0.07*
9.99	+0.01*

*Since there was a zero shift of 0.10 psi, and since the values descending in pressure are higher by $\simeq$0.1 than the values for ascending pressure, it will be assumed that the zero shift took place as the pressures were dropped from 95.90 psig. Thus, all of the Heise gauge readings for descending pressures have been reduced by 0.10 psi in computing the gauge error.

FIGURE 10

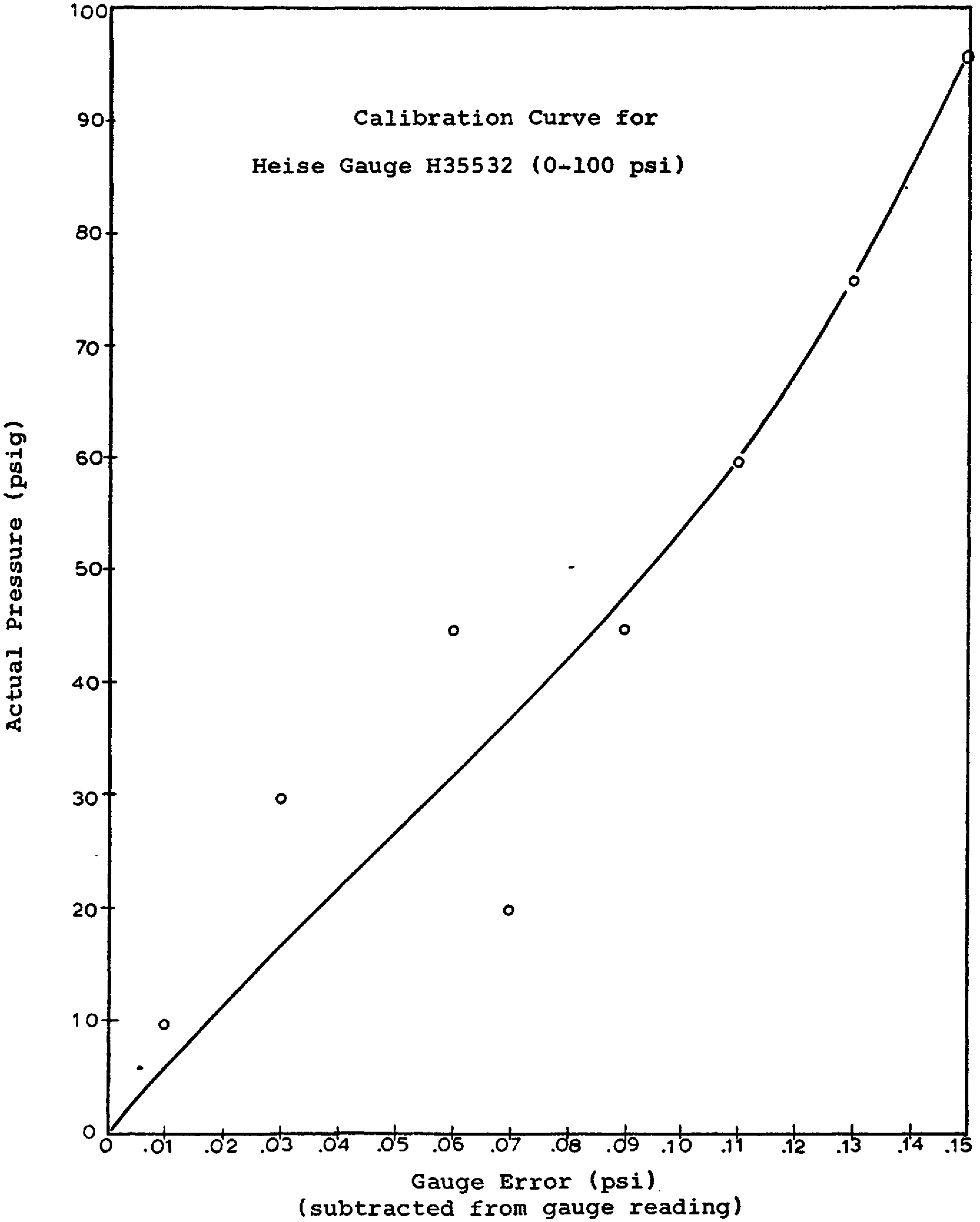

Calibration Curve for
Heise Gauge H35532 (0-100 psi)
Actual Pressure (psig)
Gauge Error (psi)
(subtracted from gauge reading)
0
10
20
30
40
50
60
70
80
90
100
0
.01
.02
.03
.04
.05
.06
.07
.08
.09
.10
.11
.12
.13
.14
.15

TABLE 6

HEISE GAUGE C58810

Actual Pressure atm	Gauge Error atm
2.039	+0.05
3.059	+0.04
4.079	+0.03
5.166	+0.02
6.526	+0.02
5.166	+0.03
4.079	+0.03
3.059	+0.04
1.359	+0.03
0.689	+0.03
9.925	-0.02
14.004	0.00
20.802	+0.05
27.601	+0.09
33.719	+0.03
20.802	0.00
9.925	-0.04
41.197	+0.05
47.996	+0.09
54.794	+0.01
61.593	+0.06
68.392	0.00
75.191	0.00
81.989	-0.09
88.789	0.00
95.587	+0.01
98.987	+0.01
81.989	-0.09
61.593	+0.01
41.197	-0.05
	Avg. = +0.015

TABLE 7

Seegers Pressure Gauge Calibration

The calibration of the Seegers 0 - 100 psi gauge was checked using an oil dead weight tester at the National Bureau of Standards, Boulder Colorado.

The gauge was set to zero at a barometric pressure of 615.2 mm Hg (corrected).

Date of calibration: 2/4/71

gauge (psig)	tester (psig)	
69.92	69.93	(going up)
89.90	89.91	(going up)
59.92	59.94	(coming down)

APPENDIX C

Results of the Mueller Bridge Calibration

The procedure used to calibrate the Mueller Bridge is described by Riddle (1969, p.7). The bridge was calibrated in absolute ohms using a Honeywell-Rubicon, 10-ohm standard resistor. The manufacturers stated error for this resistor is ± 0.01 percent of ± 0.001 ohm. In terms of X. of the 1-ohm decade of the Mueller Bridge, the resistance measured was 10.0004 ohms.

The equations obtained from the calibration are of the following form.

$$10_1 + a_1 = X. + b_1$$

$$10_2 + a_2 = X. + b_2$$

$$10_9 + a_9 = X. + b_9$$

$$10_x + a_x = X. + b_x$$

Where: $10_1, 10_2, \ldots 10_9, 10_x$ refer to successive steps of the 10-ohm decade,

a and b are obtained in the calibration.

The equations representing the calibration are presented below.

10-Ohm Decade

a		b	(b-a)
$10_1 + 0.0461$	=	X. + 0.0468	+0.0007
$10_2 + 0.0648$	=	X. + 0.0655	+0.0007
$10_3 + 0.0705$	=	X. + 0.0711	+0.0006

1-Ohm Decade

$1_1 + 0.0122$	=	0.X + 0.0122	0.0000
$1_2 + 0.0114$	=	0.X + 0.0115	+0.0001
$1_3 + 0.0117$	=	0.X + 0.0116	-0.0001
$1_4 + 0.0117$	=	0.X + 0.0117	0.0000
$1_5 + 0.0103$	=	0.X + 0.0104	+0.0001
$1_6 + 0.0107$	=	0.X + 0.0108	+0.0001
$1_7 + 0.0133$	=	0.X + 0.0132	-0.0001
$1_8 + 0.0106$	=	0.X + 0.0106	0.0000
$1_9 + 0.0104$	=	0.X + 0.0105	+0.0001
$1_x + 0.0104$	=	0.X + 0.0104	0.0000

.1-Ohm Decade

$0.1_1 + 0.0068$	=	0.0X + 0.0068	0.0000
$0.1_2 + 0.0067$	=	0.0X + 0.0067	0.0000
$0.1_3 + 0.0066$	=	0.0X + 0.0065	-0.0001
$0.1_4 + 0.0065$	=	0.0X + 0.0064	-0.0001
$0.1_5 + 0.0063$	=	0.0X + 0.0063	0.0000
$0.1_6 + 0.0066$	=	0.0X + 0.0065	-0.0001
$0.1_7 + 0.0061$	=	0.0X + 0.0061	0.0000
$0.1_8 + 0.0059$	=	0.0X + 0.0050	0.0000

$0.1_9 + 0.0057$	$= 0.0X + 0.0057$	0.0000
$0.1_x + 0.0055$	$+ 0.0X + 0.0055$	0.0000

The external resistors required for calibration of the lower decades were not available. However, errors in the lower decade resistors are usually very small.

X. is known as a result of measuring the standard resistor. Since the measured value of the standard resistor was within the error of the resistor, X. will be assumed to be 10.0000 absolute Ohms. The above relations will then yield the resistances of 10_1, 10_2, 10_3 etc., and by adding these successively the resistance of 10, 20, 30 etc. can be obtained.

The values of 0.X and 0.0X may be found by the following equations:

$$0.X = \frac{X. + \quad (a-b)}{10}$$

$$= \frac{10.0000 + .0002}{10} \quad = 1.00002 \text{ ohm}$$

$$.0X = \frac{0.X + \quad (a-b)}{10}$$

$$= \frac{1.0002 + -.0001}{10} \quad = \quad .10001 \text{ ohm}$$

It can be seen that the largest and most significant errors occur in the 10-ohm decade. The largest correction to be applied is +0.0007 ohm.

APPENDIX D

Refrigeration Analysis

Presented below is an analysis of the refrigeration system which was used to determine the LN_2 consumption that could be expected, and to size the controller heating element.

I. C_p $N_2 \approx 0.25$ cal/g deg C
H_{vap} $N_2 \approx 1335$ cal/mole
ρ liquid N_2 at 76 deg K ≈ 0.8g/cc

Refrigeration capacity of 1 liter of liquid nitrogen leaving the system at 200 deg K as a gas.

$$\left(\frac{1335\ \text{cal}}{\text{mole}}\right)\left(\frac{1\ \text{mole}}{28\text{g}}\right)\left(\frac{0.8\ \text{g}}{\text{cc}}\right)\left(\frac{1000\ \text{cc}}{\text{liter}}\right) + \left(\frac{1000\ \text{cc}}{\text{liter}}\right)\left(\frac{0.25\ \text{cal}}{\text{g}\ °\text{C}}\right)\left(125\ °\text{K}\right)$$

$$= 63143\ \text{cal/liter}$$

II. Copper (Initial temperature 300 deg K)

$C_p \approx 4.8$ cal/mole deg K

assume 20 lb copper

$$(20\ \text{lb})(453.6\ \text{g})\left(\frac{4.8\ \text{cal}}{\text{mole}\ °\text{K}}\right)\left(\frac{1\ \text{mole}}{63.5\ \text{g}}\right)100\ °\text{K} = 68576\ \text{cal}$$

THIS REQUIRES: $\frac{68576}{63143} = 1.1$ liters LN_2

III. Carbon Tetrachloride - Chloroform mixture

$$\left.\begin{array}{l} C_p\ CCl_4 \approx 0.2\ \ \text{cal/g deg C} \\ C_p\ CHCl_3 \approx 0.23\ \ \text{cal/g deg C} \end{array}\right\}\ 0\ \text{deg C}$$

use $C_p \approx$ 0.22 cal/g deg C

$$\left.\begin{array}{l} CCl_4 = 1.49\ \text{g/cc} \\ CHCl_3 = 1.59\ \text{g/cc} \end{array}\right.\ \ 20\ \text{deg C}$$

dewar is 9 3/8-in. in diameter and 24-in. deep

$$\left(\frac{\pi \cdot 9.375^2}{4}\right)24 = 1657\ \text{in.}^3 \doteq 27200\ \text{cc}$$

average density = 1.54 g/cc
average C_p = 0.22 cal/g deg C

$$\text{liters of } LN_2 \text{ required} = \frac{921,536}{63143} \approx 15 \text{ liters}$$

IV) HEATER CAPACITY TO CHANGE TEMPERATURE OF BATH 0.2 °K

$$(27200\ cc)\left(\frac{1.54\ g}{cc}\right)\left(\frac{0.22\ cal}{g\ {}^\circ K}\right)\left(0.2\ {}^\circ K\right) = 1843\ cal$$

$$(20\ lb)\left(\frac{453.6\ g}{lb}\right)\left(\frac{4.8\ cal}{mole\ K}\right)\left(\frac{1\ mole}{63.5\ g}\right)\left(0.2\ {}^\circ K\right) = 137\ cal$$

$$\text{TOTAL} = 1980\ cal$$

Thus to change temperature 0.2 deg C per min requires

$$\left(\frac{1980\ cal}{min}\right)\left(\frac{69.79 \times 10^{-3}\ watts}{cal/min}\right) = 138\ watts$$

therefore use 125-watt heater.

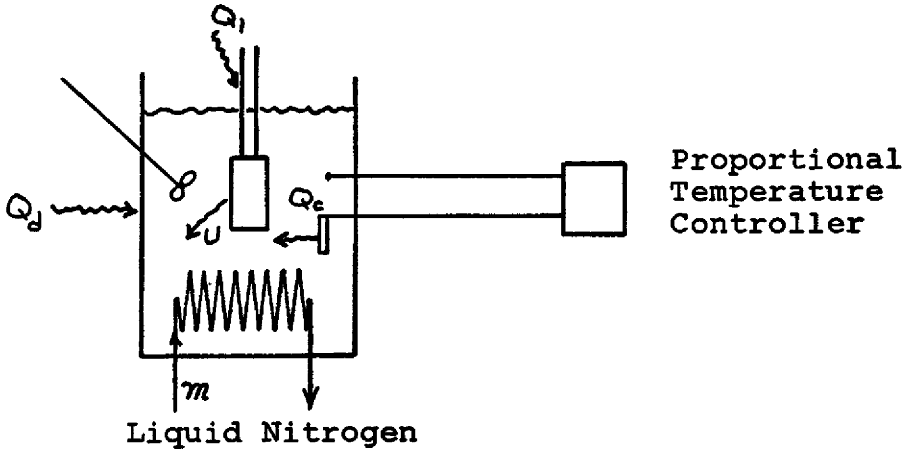
APPENDIX E

Equipment Suppliers

Carbon Tetrachloride and Chloroform	Chemistry Dept. CSM
Copper Cylinder (for cell) Copper Plate	Instrument Shop CSM " " "
Copper Tubing (1/8 in. and 1/4 in.)	McCombs Supply Co. 215 Wazee Market P. O. Box 5304 Terminal Annex Denver, Colo. 80217 Phone: 244-6674
Hoke Valves	James B. Drummond Co. 3201 S. Broadway Denver, Colo. 80110 Phone: 789-2281
Insulation (Tubular)	Steam Plant CSM
Liquid Nitrogen	United States Cryogenic Div. U. S. Welding 600 S. Santa Fe Drive Littleton, Colorado Phone: 777-6671
Swagelok Fittings and Whitey Valves	Denver Valve & Fitting Co. P. O. Box 15636 980 Simms Street Denver, Colorado 80215 Phone: 238-1319
Structural Angle Iron and Bolts	Murray Equipment Co. 1845 Federal Blvd. Denver, Colorado 80204 Phone: 433-3314
Tubular Heaters	Van Waters and Rogers, Inc. 4300 Holly Street Denver 16, Colorado Phone, 388-5651
Winch	Genuine Parts Co. 900 Washington Ave. Golden, Colo. 80401 279-4579

APPENDIX F

PROCESS CONTROL MODEL



Notation:

T = Temperature of the bath

T_c = Temperature of the equilibrium cell

T_{bp} = Boiling point of liquid nitrogen

V_b = Volume of the bath

ρ_b = Density of the bath

C_{pb} = Heat capacity of the bath

w = Weight of the equilibrium cell

C_{pc} = Heat capacity of the equilibrium cell

Q_r = Heat removed from the bath by LN_2

Q_l = Heat leak to equilibrium cell from outside the bath

Q_d = Heat leak into dewar

Q_c = Heat input by controller into bath

U = Overall heat transfer coefficient between equilibrium cell and the bath fluid

A = Surface area of the cell

m = Mass flow rate of liquid nitrogen

ΔH = Heat of vaporization of liquid nitrogen

$C_{p_{N_2}}$ = Heat capacity of gaseous nitrogen

Assumptions

1) The bath is perfectly stirred.

2) There are no temperature gradients in the equilibrium cell.

3) The heat capacity and density of the bath and equilibrium cell are constant.

Transient Equations:

Bath Fluid

$$\rho_b V_b C_{p_b} \frac{dT}{dt} = Q_d + Q_c + UA(T_c - T) - m(\Delta H) - mC^{\cdot}_{p_{N_2}}(T - T_{bp})$$

Equilibrium Cell

$$wC_{p_c} \frac{dTc}{dt} = Q_1 - UA(T_c - T)$$

Steady State Equations:

Bath Fluid

$$0 = Q_{d_{ss}} - UA(T_{c_{ss}} - T_{ss}) - m^{\cdot}_{ss}(\Delta H) - mC^{\cdot}_{p_{N_2}}(T_{ss} - T_{bp})$$

Equilibrium Cell

$$0 = Q_{1_{ss}} - UA(T_{c_{ss}} - T)$$

Deviation Variables:

$T = T' + T_{ss}$ $\qquad$ $Q_c = Q_c + Q_{c_{ss}}$

$T_c = T_c' + T_{ss}$ $\qquad$ $Q_1 = Q_1' + Q_{1_{ss}}$

$Q_d = Q_d' + Q_{d_{ss}}$ $\qquad$ $m = m' + m_{ss}$

(') refers to a pertabation from steady state

Dynamic Equations:

Bath Fluid

$$\rho_b V_b C_{p_b} \frac{dT'}{dt} = Q_d' + Q_c' + UA(T_c' - T')$$
$$- m'(\Delta H + C_{p_{N_2}} \cdot T_{ss} - C_{p_{N_2}} \cdot T_{bp})$$

Equilibrium cell

$$wC_{p_c} \frac{dT_c}{dt} = Q_1' - UA(T_c' - T')$$

Constants

$$a = \rho_b V_b C_{p_b}$$
$$b = (\Delta H + C_{p_{N_2}} \cdot T_{ss} - C_{p_{N_2}} \cdot T_{bp})$$
$$c = wC_{p_c}$$

Laplace Transforms

Bath Fluid

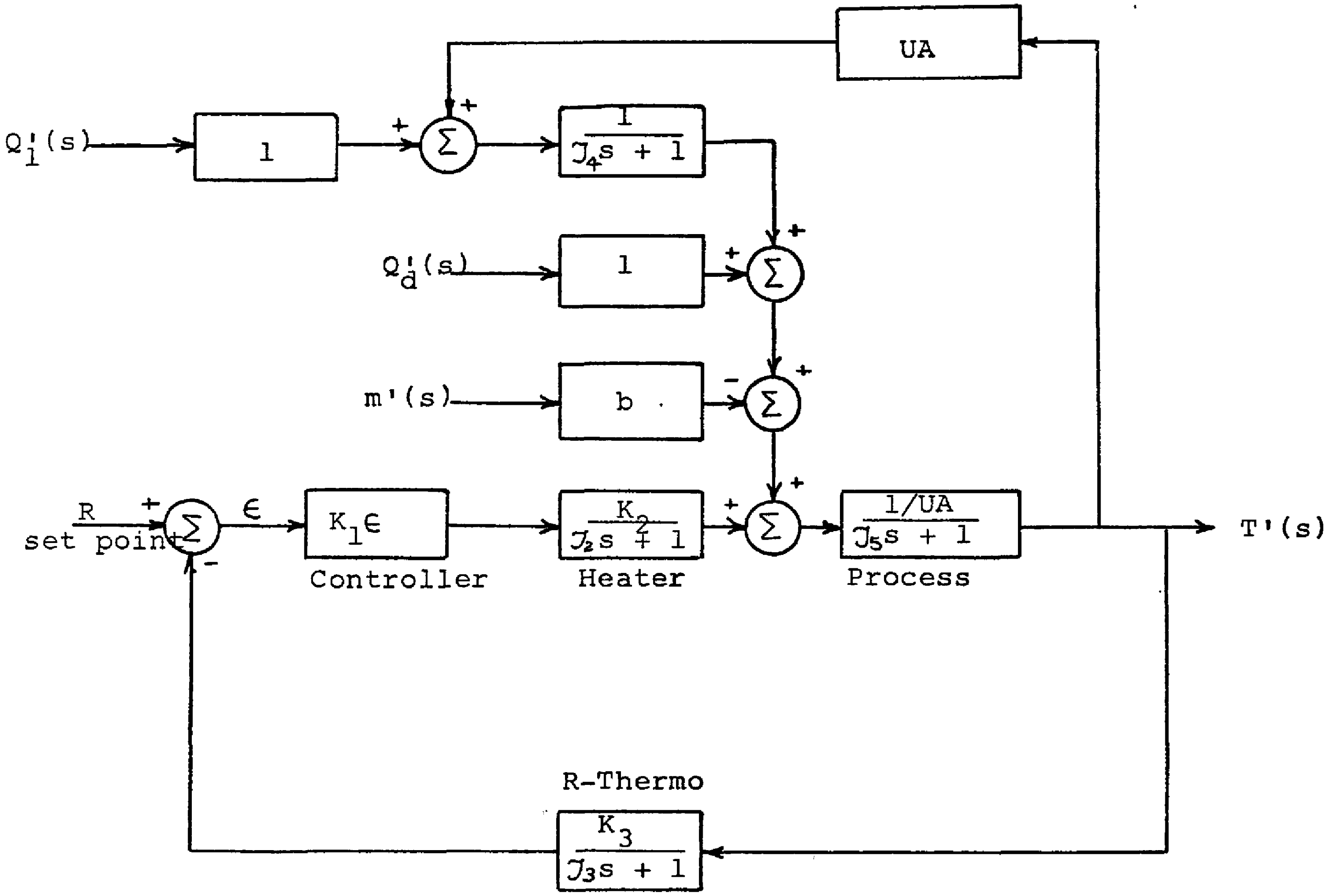
$$(as + UA)T'(s) = Q_d'(s) + Q_c'(s)$$
$$+ UAT_c'(s) - bm'(s)$$

Equilibrium Cell

$$(cs + UA)T_c'(s) = Q_1'(s) + UAT'(s)$$

FIGURE 11

Block Diagram



K_1 = controller gain

K_2 = heater gain

K_3 = measurement lag

τ_5 = a/UA

τ_4 = c/UA

REFERENCES

Din, F. ed., 1956, Thermodynamic functions of gases: London, Butterworths Scientific Publications.

Honeywell, Resistance standards and resistance bridges: Honeywell Rubicon Instruments, Bull. No.100, p. 10.

Hust, J. G., 1969, A compliation of historical review of temperature scale differences: Cryogenics, v. 9, n. 6, p. 443-455

Kanolt, C. W., 1926, Nonflammable liquids for cryostats: Bur. of Stds. Sci Paper No. 520, 619 (1926).

Kirk, B. S., 1958, List of Cryogenic Liquids: NBS File No. 58018, Proj. No. 8124, 12 p.

Meyers, C. H., and Van Dusen. M. S., 1933, The vapor pressure of liquid and solid carbon dioxide: NBS Jour. of Research, v. 10, p. 381-411.

Mueller, E. F., 1961, Wheatstone Bridges and some accessory apparatus for resistance thermometry: NBS Bull., Scientific Paper No. 288, v. 13, p. 547.

Riddle, J. L., 1969, Notes to supplement resistance thermometer reports on the International Practical Scale of 1968: NBS, Washington, D. C., Ap 1, 1969, 15 p.

Sax, N. I., 1966, Dangerous Properties of Industrial Materials: Reinhold Publishing Corp., N.Y.