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Ernest O. Lawrence

Radiation Laboratory

HIGH-PRESSURE VAPOR-LIQUID EQUILIBRIUM APPARATUS

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Robert Lawrence Miner

(M. S. Thesis)

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July 1960

ABSTRACT

Equipment has been designed and built for the measurement of the high-pressure solubility of oxygen and nitrogen in liquid carbon dioxide near its critical temperature. The equipment is designed to operate at pressures up to 15,000 psi and from -40°C to the critical temperature of carbon dioxide, 31.1°C. Equilibrium is attained by circulating both the liquid and vapor streams. Sections of the circulation lines are blocked off to trap the samples. Auxiliary equipment is included for the following purposes: refrigerating and controlling the constant-temperature bath; measuring the equilibrium temperature and pressure; measuring the liquid level in the equilibrium vessel; determining the density of the samples; analyzing the samples; and calibrating the analytical system.

INTRODUCTION

Equipment and operating techniques for obtaining high-pressure vapor-liquid equilibrium data are described. The equipment has been designed to determine the solubilities of oxygen and nitrogen in liquid carbon dioxide near its critical temperature, 31.1°C. The purpose of this study is to determine whether or not the liquid retains any selectivity between the two gases as the solubility of the gases in the liquid increases rapidly near the critical temperature.

No data have as yet been taken, and some of the equipment has not been fully checked-out or calibrated. The project is being continued.

The problem of obtaining accurate vapor-liquid equilibrium data has been worked on by many researchers, sometimes without great success. Two major problems are encountered: one is the agitation of the fluids so that equilibrium is reached and the other is that of sampling the liquid and vapor phases without disturbing the equilibrium. Problems of pressure and temperature measurement, and analysis of the samples are usually considered of less importance, but they may also become major problems when high pressures are involved and high accuracy is desired.

Three major methods are commonly used to agitate the fluids: stirring, shaking, or circulating at least one phase. Stirring involves the introduction of a rotating shaft into the equipment, which creates problems of sealing the shaft at 15,000 psi. Shaking the vessel eliminates that problem, but is difficult to carry out in a liquid bath at -40°C. The equipment described uses a circulation system, not primarily because of the drawbacks of the other methods, but because it also gives a good sampling system.

Several researchers obtain their samples by opening a valve and releasing a little of each phase into their sampling equipment. They assume that there will not be enough time for any shift in the equilibrium because of the decreased pressure. This assumption is very dubious at best.

Other researchers,[1, 2] unwilling to make this assumption, keep the total pressure constant during sampling by moving mercury into the equilibrium vessel to replace the removed sample. This method is not applicable in this system because of the presence of high-pressure oxygen which may oxidize the mercury, and because mercury freezes at -38.9°C.

EQUILIBRIUM SYSTEM

In this equipment a recirculating system is used; both the vapor phase and the liquid phase are circulated. The vapor phase is circulated as a means of attaining equilibrium. Circulation of the liquid stream gains very little in terms of reaching equilibrium, but provides a convenient way to sample the stream. Both the liquid and vapor streams are sampled by blocking off a section of the circulation lines. The samples are then removed one at a time by a Toepler pump to the vacuum system where the mass and composition of the samples are determined. The system is designed to handle pressures up to 15,000 psi and temperatures from -40°C to the critical temperature of carbon dioxide, 31.1°C.

The equilibrium, recirculation, and sampling systems are discussed with reference to Fig. 1, which is a simplified flow-diagram of the equilibrium equipment. This equipment is contained in a constant temperature bath which includes refrigeration equipment. The bath is shown in Fig. 2.

The equilibrium vessel and the vapor and liquid pumps, P-1 and P-2, are described in detail in subsequent sections. The tubing and valves described in this section, as well as the loading section are Aminco* superpressure equipment. The many joints involved are sealed with the standard Aminco fitting, in which a 59 deg conical seating surface on the male tubing fits into a corresponding 60 deg female conical seat in the body. A gland nut forces these two together tightly. The manufacturer claims they seal easily to 100,000 psi.

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*American Instrument Company

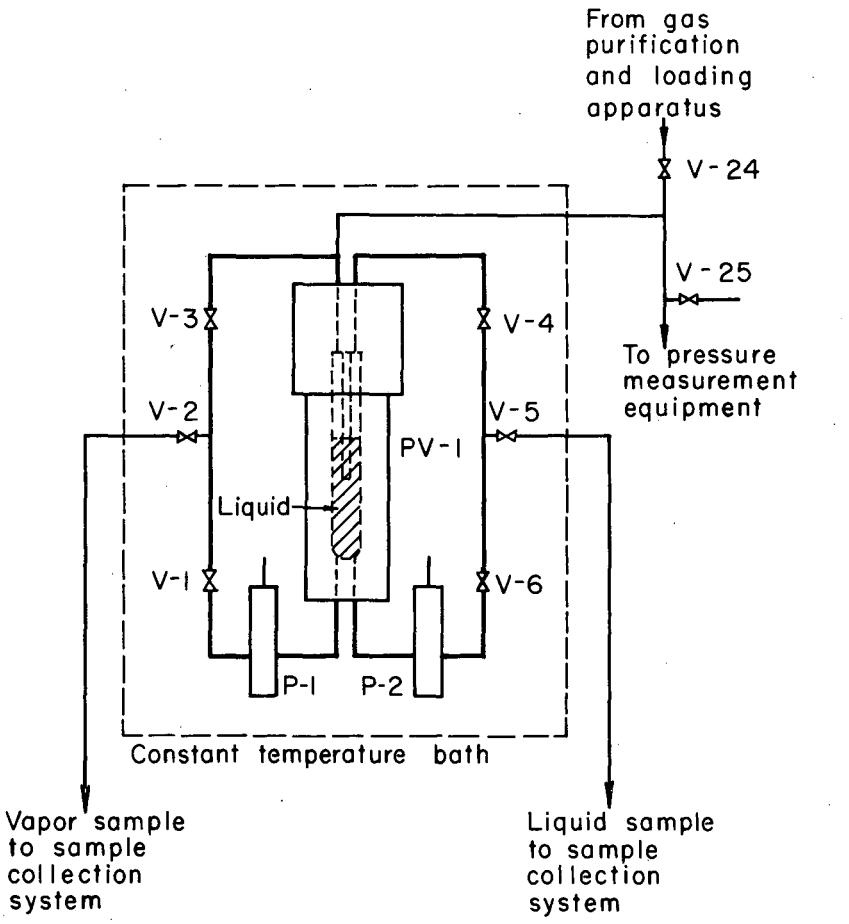

Fig. 1. Simplified flow diagram of equilibrium system.

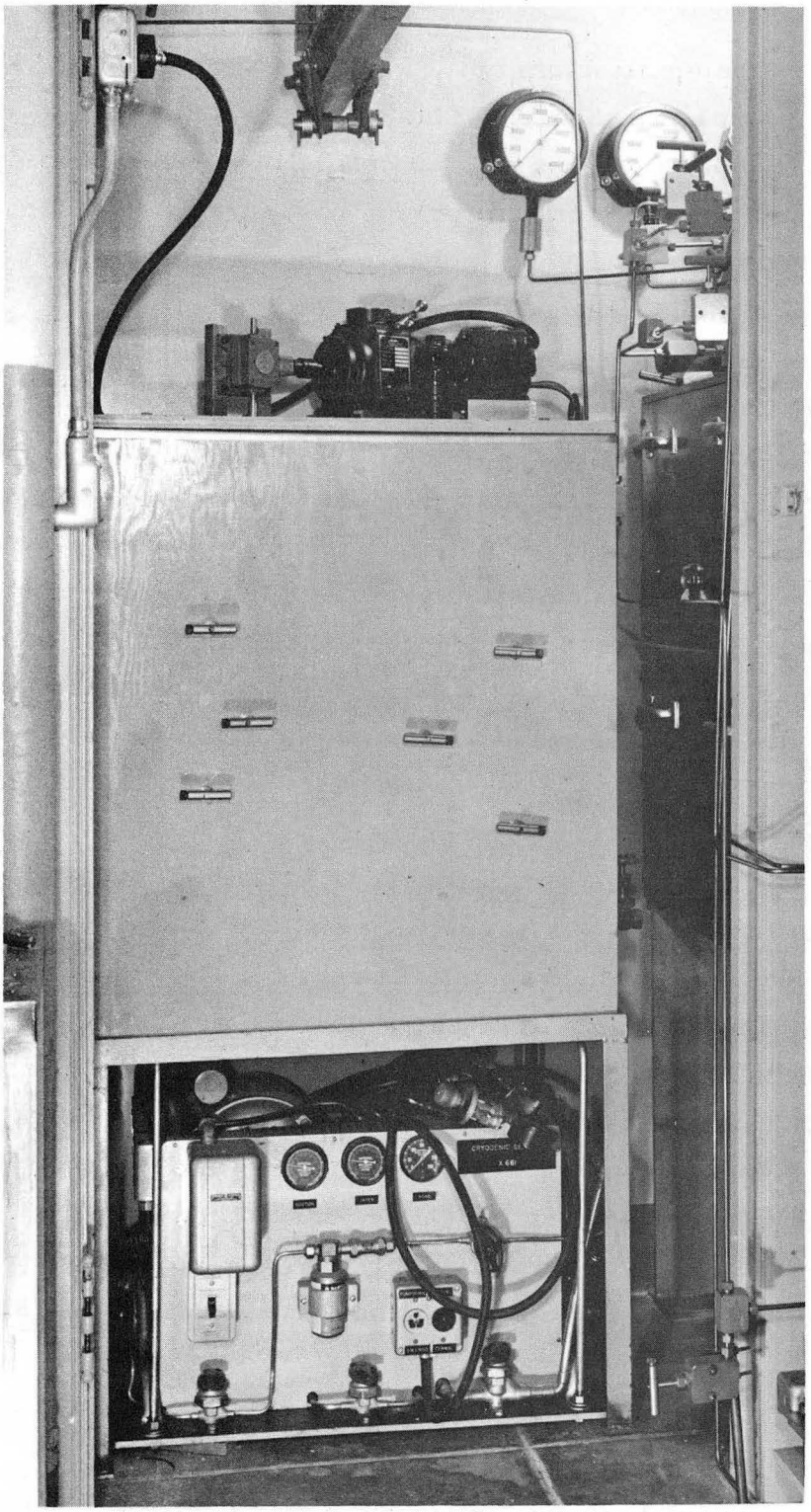

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Fig. 2. Main constant-temperature bath.

Equilibrium Cell

The equilibrium cell, PV-1, is shown in Fig. 4, and in longitudinal section in Fig. 3. This is a standard Aminco cell, catalog No. 41-4900. The body of the cell is of A. I. S. I. 403 stainless steel, designed for a maximum working pressure of 18,000 psi at 100°F. Wall thickness is 1 9/16 inches. The capacity of the cavity is approximately 200 cc. The vessel weighs 70 pounds.

The closure, an outside cap type, consists of five parts, (Fig. 3): (1) outside cap that screws onto the body of the vessel; (2) thrust bolts; (3) hardened-steel thrust ring that keeps the thrust bolts from marring the pressure head; (4) inner pressure head and, (5) gasket. Vent holes in the cap provide pressure relief in the event of gasket failure or leakage. A stainless steel delta gasket is used. As the pressure in the vessel increases, the pressure acts on the inside of the "delta" and changes the angle of contact between the gasket and its seats. This slight change in angle with rise in pressure tends to force the delta ring tightly against its seat and thereby insures a self-energized joint.

The bottom of the vessel is fitted with two standard Aminco tubing fittings for the vapor inlet and liquid outlet. The pressure head also has two Aminco tubing fittings, for the vapor outlet and liquid inlet. On the inside of the head at the liquid inlet, a piece of tubing has been attached to direct the liquid flow against the wall of the cavity. The pressure head also has a standard Aminco cone compression-type electrical fitting through which the two wires for the level indicator are introduced. This fitting seals the wires against the pressure by compressing a soapstone cone around them. Figure 3 does not show the electrical fitting because it is behind the thermowell in the pressure head.

A baffle has been attached to the thermowell to prevent liquid entrainment in the vapor stream.

Attached to the thermowell below the baffle is the level indicator (described in detail in a later section).

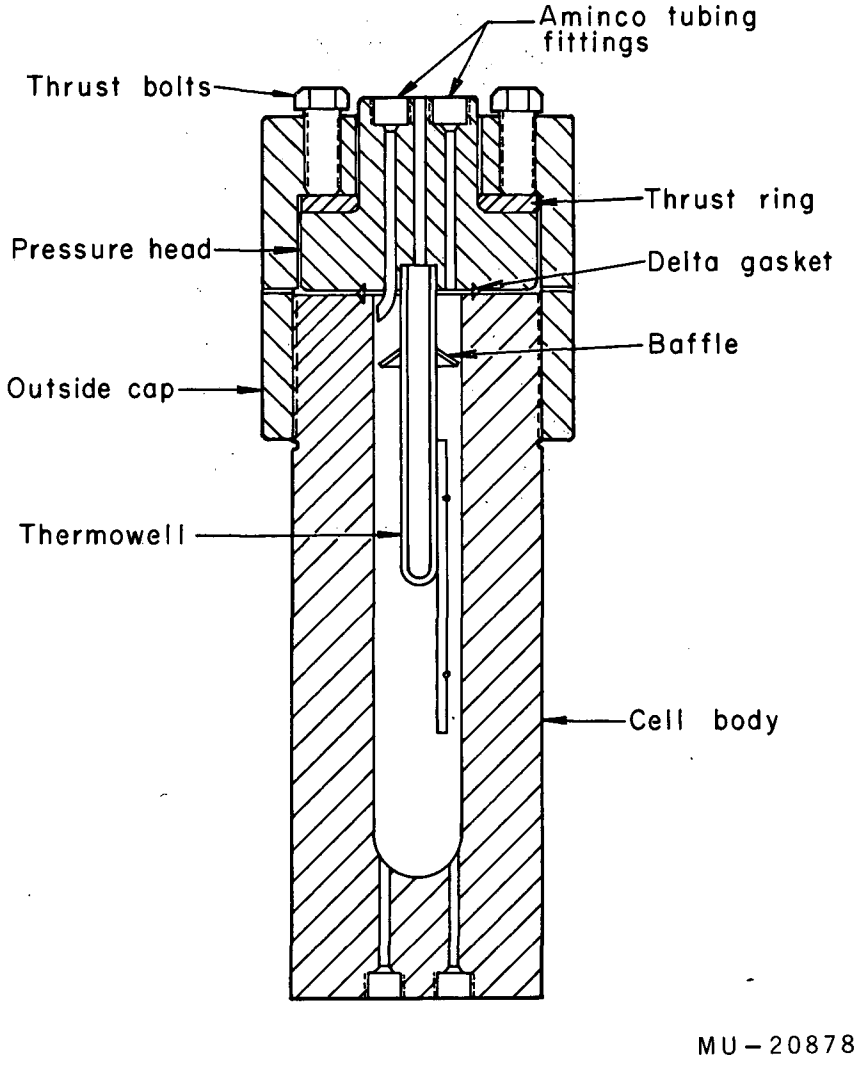

Fig. 3. Equilibrium cell, PV-1, longitudinal section.

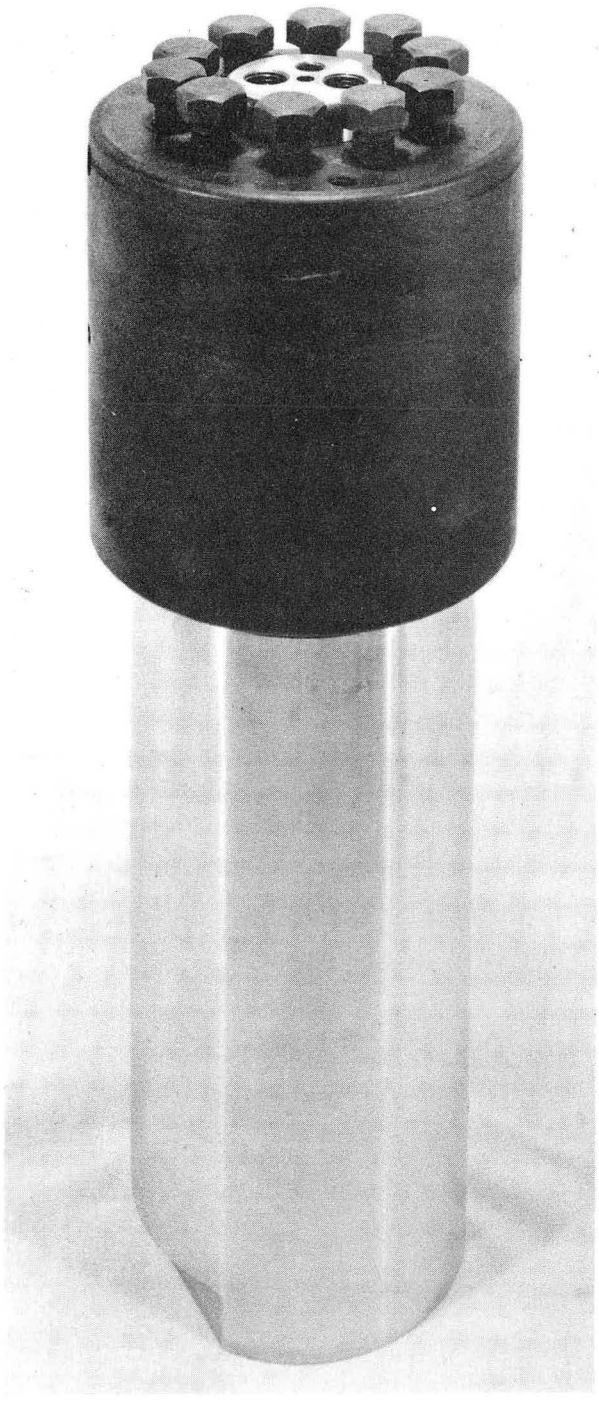

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Fig. 4. Equilibrium cell, PV-1.

In actual use, the vessel sits four inches off the bottom of the constant-temperature bath in a steel support in order that tubing can reach the connections at the bottom.

High-Pressure Vane Pumps

The design of pumps to circulate the vapor and liquid streams was the major design obstacle of this project because of the unique requirements. Pumps were needed which would withstand 15,000 psi internal pressure without substantial leaks; pump at very low rate, 25 to 300 cc/min; and produce a low head, one foot of fluid. The presence of high-pressure oxygen also created some materials problems. Leaks of any proportion could not be tolerated because they would continually change the equilibrium.

To introduce moving shafts, either turning or reciprocating, into a vessel containing gas at 15,000 psi is extremely difficult without creating leaks. Various schemes that could operate a pumping mechanism without direct drive, all involving some magnetic drive were proposed. The advantages of such a system seemed to be outweighed by the fact that such a system gives no positive indication that the pump is operating, therefore it was decided to use a rotating shaft.

The pump design used was conceived and developed by J. G. Dorward, Jr. of the Mechanical Engineering Department, Lawrence Radiation Laboratory, Berkeley. The liquid and vapor pumps are identical. A section through the pump cavity is shown in Fig. 5, and a longitudinal section is shown in Fig. 6. Figure 7 shows the exterior of the pump. This design is a variation of a vane pump. Cylindrical rollers act as the vanes for moving the fluid from inlet to outlet. The rollers are moved by a rotor mounted off-center with the cavity of the pump such that it is snug against the cavity on the bottom but has 0.1-in. clearance at the top of the cavity. This design creates a small volume to be occupied by fluid as the rollers move from inlet to outlet, but there is almost no volume below the outlet; therefore the roller pushes the fluid out of the outlet. The three rollers, which slide in grooves in the rotor, stay snug against the body of the cavity

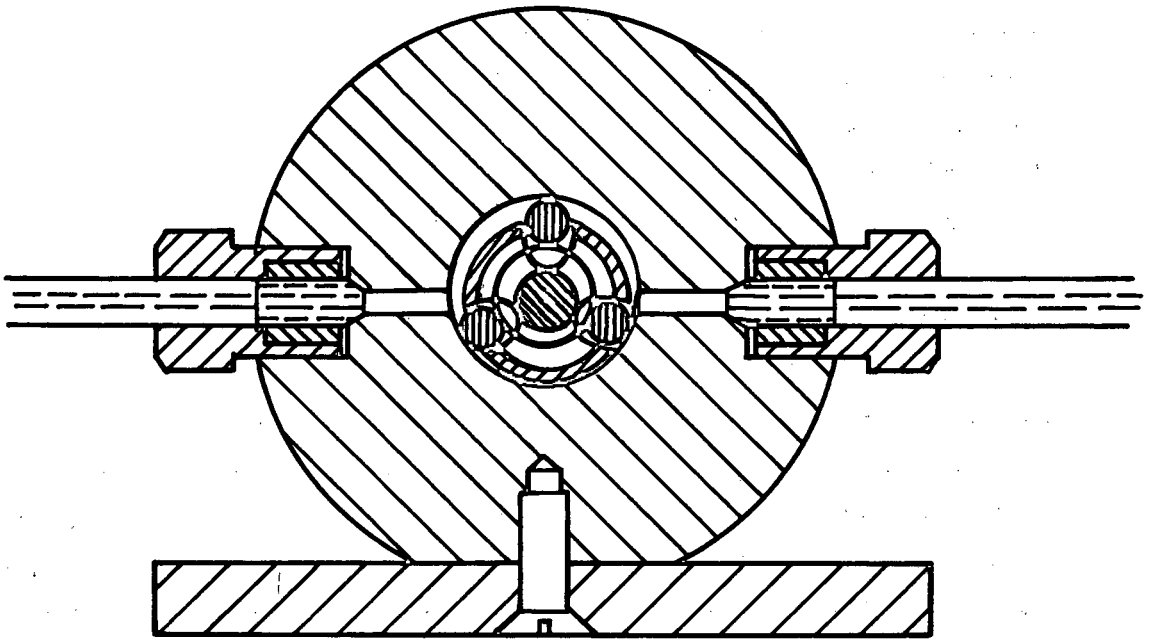

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Fig. 5. High-pressure vane pump, section through cavity.

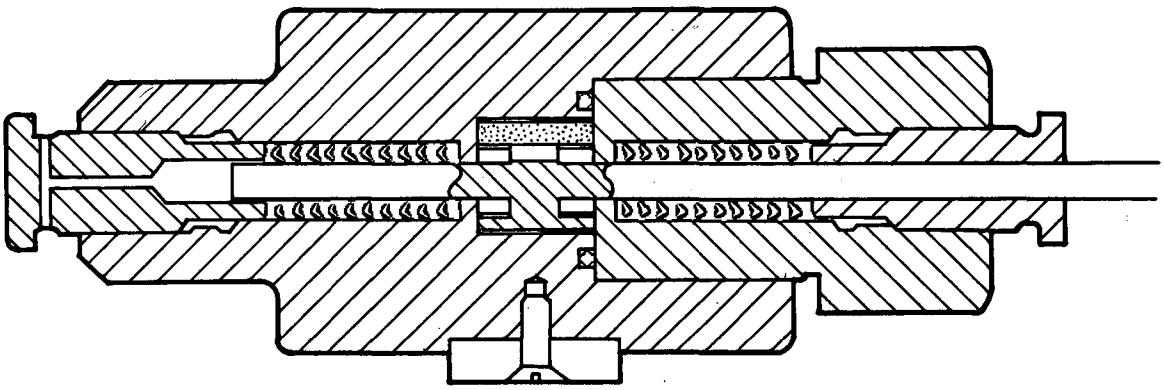

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Fig. 6. High-pressure vane pump, longitudinal section.

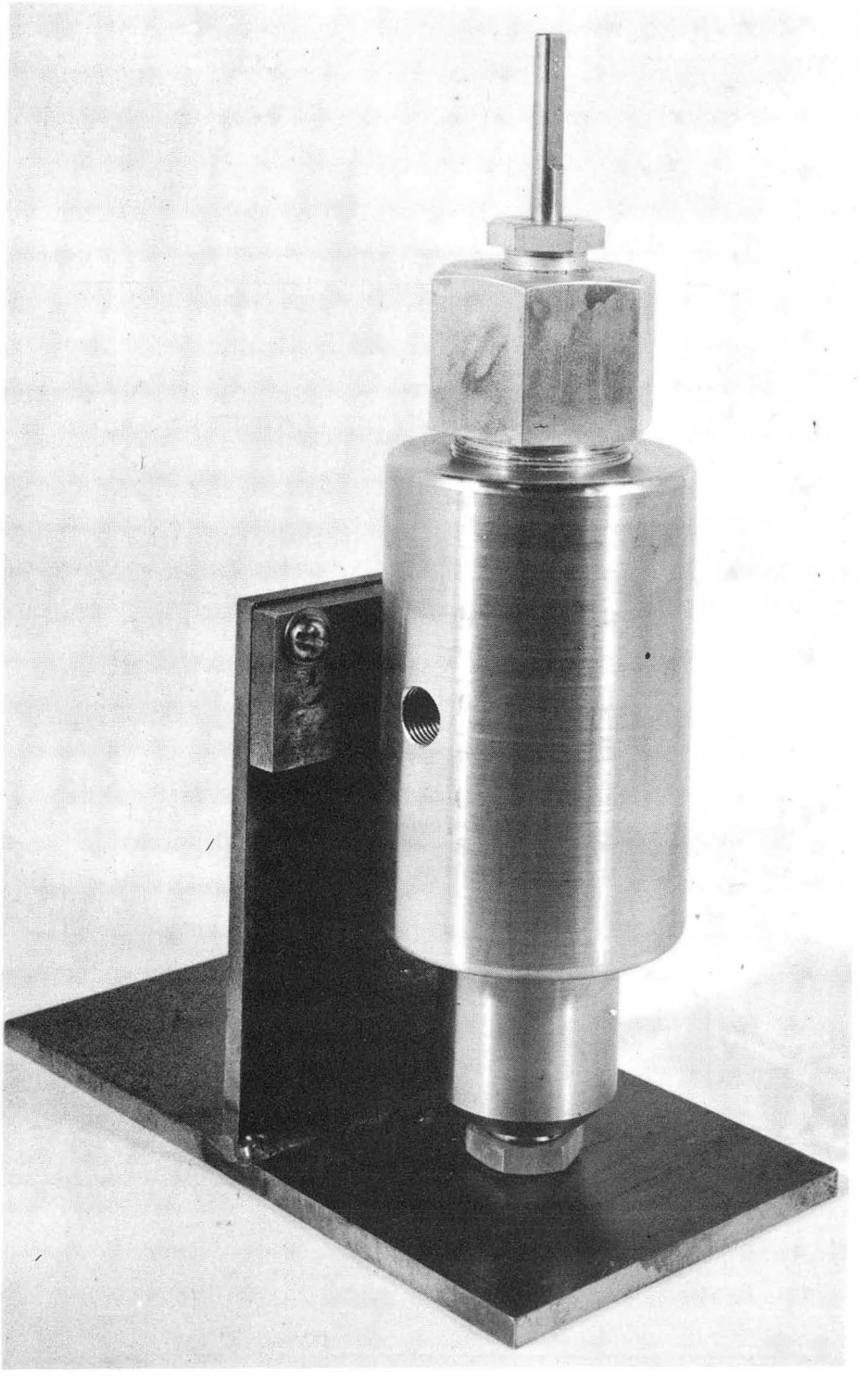

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Fig. 7. High-pressure vane pump.

because they are forced outward by a contact ring inside each end of the rotor. The inlet and outlet are 1/8-in. holes to standard Aminco fittings.

The rotor is driven by a shaft that passes out of the pump through packing. Because of the high pressure involved it is necessary to have a blind shaft on the other end of the rotor so that the end pressures will be equal, rather than having an imbalance of 15,000 psi on a 5/16-in. shaft, or approximately 1150 pounds force forcing the rotor against the end of the cavity. Such a force would obviously keep the pump from turning, therefore a blind shaft was included. Although it does not extend beyond the body of the pump, its end is subject to the external pressure because of holes drilled in the cap for that end.

Teflon V ring packing* was used for packing both ends of the rotor shaft. This is considered superior to other common packing because the internal pressure helps make the packing seal against the shaft. Pressure tends to make the V's straighten out, which forces them more tightly against the shaft.

One end of the pump must be removable so that the rotor can be installed: To achieve this one end is designed with a seal body which is bored to receive the shaft and packing. The joint between the seal body and the pump body must also be gas-tight and therefore a Teflon O ring is used.

The body of the pump is 304 stainless steel. The seal body and the two packing nuts are 303 stainless steel. The rotor is monel. The rollers are made of Rulon "A."†

Both pumps were tested for leakage with helium. At 25,000 psi, there was small leakage along the main shaft of each pump. At lower pressure there was no leakage.

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*C-VH rings, Crane Packing Co.

†Dixon Corporation

Each pump was tested pumping both water and air to determine the pumping rate and the effect of head on the rate. Both pumps pumped well with water. Against no head, the pumping rate was approximately 2 1/2 cc/revolution. Opposing one foot of head reduced this by a fairly constant 20 cc/min at all rates. For instance, a rate of 100 rpm produced only 230 cc/min rather than 250 cc/min, against one foot of head. The motor driving the liquid pump operates at 115 rpm which should give a pumping rate of approximately 270 cc/min.

When air was pumped, there was a large effect of opposing head. Against no head, the rate for each pump was 2.5 cc/revolution. One pump gave less head effect than the other because of differences in internal clearances, and was chosen as the vapor pump. When the pump opposes a five-inch liquid head, 150 rpm were required to obtain any flow. This effect, of an opposing head, is caused by fluid leakage within the pumping cavity. There probably is some leakage between the rollers and the rotor, but the greater leakage is almost sure to be around both ends of the rotor and rollers. Because these are revolving parts, and in the case of the rotor, metal on metal friction, there must be some clearance. The amount of leakage will be a function not only of the opposing head, but also of the properties of the vapor which will be very pressure-dependent. The greater density of the vapor at high pressure should decrease the leak rate. The level indicator in the equilibrium vessel, PV-1, should give some response when vapor circulation begins. The motor for driving the vapor pump has a variable speed transmission that can vary from zero to 1100 rpm.

Constant Temperature Bath

The equilibrium equipment is enclosed in a constant temperature bath (Fig. 1). Figure 2 shows the exterior of the bath. The bath is equipped to control temperatures ranging from -40°C to +31.1°C, the critical temperature of carbon dioxide. A refrigeration unit supplies the cooling. The temperature is controlled by the heat input to a blade heater. The bath fluid is trichloroethylene, chosen for its suitable viscosity over the specified temperature range.

The refrigeration unit is a package unit that has a single-stage compressor and is water cooled. The refrigerant is Freon 22. The temperature of the refrigerant in the cooling coils is controlled by the pressure regulator on the compressor. The flow of liquid refrigerant to the cooling coils is controlled by a thermal expansion valve that senses the degrees of superheat of the vapor leaving the cooling coils. The valve keeps liquid from flowing faster than it can be evaporated and thus protects the compressor cylinders from getting liquid feed which could blow a cylinder head off.

Because it is extremely difficult to control a refrigeration unit very closely, the temperature control of this bath is by heat input. A "Resistotrol"* temperature controller controls the power input to a blade heater. The manufacturer claims 0.01°C temperature control. The bath fluid is thoroughly stirred by a two-impeller stirrer.

The bath is a wooden box lined with four inches of polystyrene insulation on the bottom and sides. The inside is a stainless steel soldered box. The lid of the box is 3/4-in. plywood. The motors for driving pumps P-1 and P-2, and the stirring motor are located on the bath lid. Extending through the lid are the probe for the temperature controller and the thermopile (discussed in the section on temperature measurement).

The six valves located inside the bath, V-1 through V-6, are operated from outside the bath by valve stems extending through the bath wall. These stems are made leak-proof by O rings in grooves

*Hallikainen Instruments

on the shafts of the valve stems which seal against the brass sleeves extending through the bath wall. The sleeves seal against the metal lining of the bath with O rings. The high-pressure tubing and the cooling coils are extended through the bath walls in similar fashion.

Operation of Equilibrium System

The equilibrium vessel, PV-1, is filled by introducing the gases one at a time from the gas-purification and loading apparatus. The carbon dioxide is always introduced first, and at such a delivery pressure that it will liquefy at the temperature of the equilibrium bath. The loading of carbon dioxide is stopped when the gas-liquid interface rises to approximately the middle of PV-1, determined by the liquid level indicator, which will be discussed in greater detail in a later section.

Oxygen and nitrogen are introduced in turn, successively raising the total pressure of the system to levels which will result in oxygen and nitrogen being in approximately the desired ratio in the vapor phase. This ratio of the gases and the total system pressure will, of course, vary from run to run. During the loading of oxygen and nitrogen, the liquid-level indicator is regularly checked. This is done to insure that the quantity of liquid does not increase to the point of filling the entire equilibrium vessel as more gas is dissolved in the liquid at high pressure.

When the loading is completed, the loading apparatus is isolated by closing valve V-24. The vapor pump, P-1, and the liquid pump, P-2, are then started, and both streams are circulated while the system reaches thermal and chemical equilibrium. The liquid-level indicator is turned off because it is no longer needed, and because the energy input to it would interfere with the system reaching constant temperature.

The line from the equilibrium vessel to the pressure-measuring equipment is a dead space in the vapor system. Since the vapor in this line is not circulated, it is not of the same composition as that of the circulating vapor, and is therefore a source of error. However,

since the inside diameter of this line is less than 1/16 in., any diffusion along it will be very small. As an added precaution, this line is bled through valve V-25 after the system is approaching equilibrium. This bleeding upsets the equilibrium somewhat, and therefore delays the final approach to equilibrium, but the dead line is then filled with vapor almost identical in composition to the equilibrium vapor.

When the system has been circulated for a sufficient time to reach equilibrium, the temperature and pressure are measured which is discussed in later sections. Then pumps P-1 and P-2 are stopped. Valves V-1 and V-3 are closed, trapping the vapor sample, and valves V-4 and V-6 are closed, trapping the liquid sample. The samples are removed to the vacuum system one at a time by opening valve V-2 for the vapor sample and V-5 for the liquid sample (see section on sample collection).

GAS-LOADING AND PURIFICATION SYSTEM

The equilibrium system has been designed for pressures up to 15,000 psi. Gas cylinders, however, normally deliver gas at pressures up to 3.000 psi. Therefore some means was needed for increasing the pressure. Methods for compressing gases to these pressures all seemed to involve much leakage as well as contamination of the gas by the pumping fluid. A scheme has been devised for filling special loading vessels from cylinders at less than 100 psia pressure, but with the loading vessels cooled to liquid nitrogen temperature, 78°K. Both oxygen and nitrogen will liquefy under these conditions. The gases can develop up to 39,000 psi when they are warmed to room temperature.

The loading apparatus is shown in Fig. 8. A purification vessel is included for each gas, but the carbon dioxide system does not include a high-pressure loading vessel. Carbon dioxide is loaded directly from the cylinder to the equilibrium vessel, passing through the purification vessel. As it is desired to collect carbon dioxide liquid, this requires that the cylinder delivery pressure be equal to the vapor pressure of carbon dioxide at the temperature of the equilibrium bath. For the temperatures expected in this experiment, -40°C to 31.1°C (the critical temperature of carbon dioxide), this delivery pressure can vary between 146 psia and 1,075 psia.

During the loading of the oxygen and nitrogen, the high pressure vessels are enclosed in polystyrene foam vessels which hold liquid nitrogen. The gases are delivered to the cooled vessels at approximately 50 psig using pressure regulators at the cylinders. Considerable time required to liquefy enough gas to fill the loading vessels. In the case of nitrogen, less than 15°C of ΔT is available for cooling. For cooling the oxygen, about 30°C of ΔT is available at this delivery pressure. Higher delivery pressures would allow faster cooling, but would involve greater problems in holding a gas seal on the purification vessels.

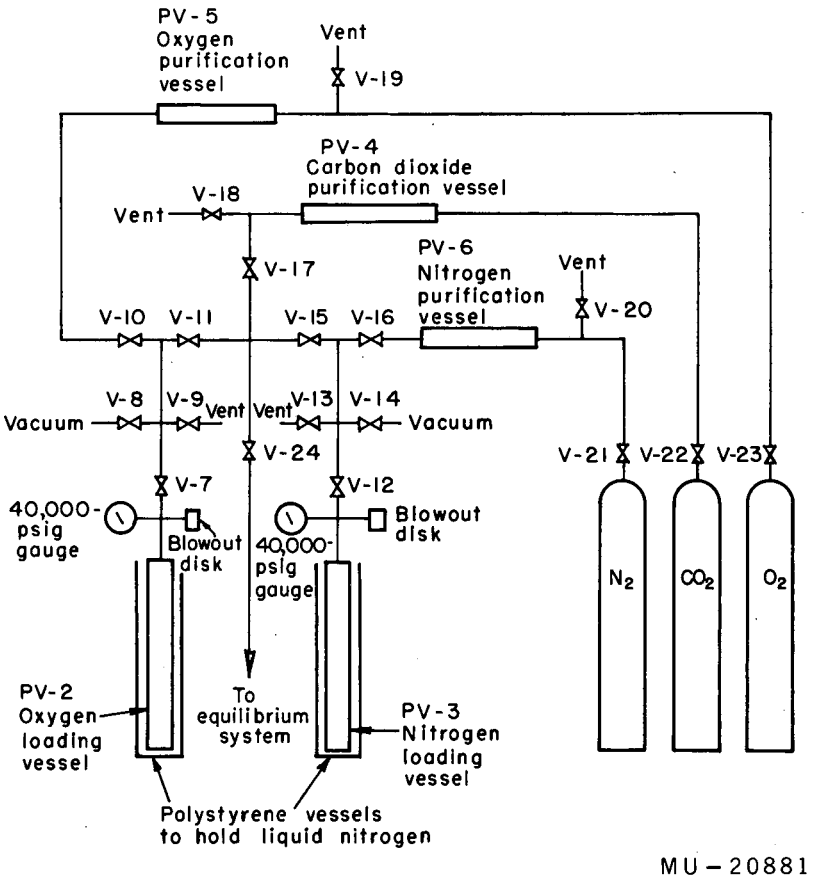

Fig. 8. Gas-loading and purification system.

The amount of oxygen or nitrogen which is loaded into a loading vessel can be judged approximately by the pressure on the cylinder. The cylinder regulators for these gases read not only pressure, but also volume in standard cubic feet of gas. To fill a loading vessel full of liquefied gas requires 11.7 st. cu. ft of nitrogen or 15.1 st. cu. ft of oxygen. There is another check to determine when a loading vessel is full of liquid. For example, when oxygen is being loaded, valve V-7 can be closed, isolating the loading vessel from the oxygen cylinder. The loading vessel will contain liquid oxygen with oxygen vapor above it, at the delivery pressure. The pressure gauge, which is inside V-7, will register this pressure. If the loading vessel is not full of liquid, more will liquefy at this pressure until the pressure is reduced to 0 psig. If the pressure gauge does not show a pressure drop when V-7 is closed, then the vessel is full of liquid. The tubing and gauge above the loading vessel will not be cooled by liquid nitrogen and therefore only the loading vessel will fill with liquid.

No level-sensing devices have been installed in the loading vessels because the level is not critical. If the loading equipment is completely filled with liquid, three different measures protect against any overpressure problem: the equipment design, the pressure relief, and the operating procedure. Oxygen or nitrogen confined as liquid at liquid nitrogen temperature can only develop 39,000 psi when warmed to room temperature. The highest pressure part of this equipment, below valves V-7 and V-12, is nominally designed for 30,000 psi, but all these parts have been successfully hydrostatically tested at 40,000 psi. This part of the loading system is surrounded by 1/2-in. -steel [illegible] shielding. Included in each system is a blowout disk that will rupture at 29,000 psi ± 10%. The third protection is the loading procedure. As the vessel warms up and the pressure builds up, the valves that send the gas to the equilibrium system are opened. This is done as soon as the pressure gauge indicates a pressure greater than the pressure in the equilibrium system.

The only undesirable situation is that in which not enough gas is liquefied to give the final desired pressure. The loading vessel

must then be loaded a second time after its first load has been transferred to the equilibrium system. The experiment does not require measurement of the amounts of each gas loaded. Rough measurements are made in order that desired ratios of gases can be obtained. When the desired pressure is reached in the equilibrium system, the excess pressure can be released through the vent valves, V-9 for oxygen, V-13 for nitrogen.

Each gas before entering the loading vessel, passes through a purification vessel containing activated silica gel and "Drierite." These will remove oil and water vapor. The vessel for purifying carbon dioxide is designed for 14,000 psi, though 1,100 psi will be the maximum in use. The vessels for purifying oxygen and nitrogen are intended to hold only 150 psig because of the type of closures used. The bodies of the vessels are stainless steel pipe, threaded on the ends for stainless steel caps having Aminco tubing fittings. The caps are sealed with "Truseal"* seals made of Teflon.

The gas cylinders and purification vessels are each separated from the high-pressure parts of the system by a high-pressure valve, which could leak, and thus subject these parts of the system to pressures higher than those for which they are designed. Therefore the vent valve in each purification system should be opened as soon as that system is no longer in use. These valves are V-18, V-19, and V-20. If this venting procedure were omitted by mistake, no serious danger would exist. The carbon dioxide purification vessel is strong enough to take the pressure. The oxygen and nitrogen vessels are not this strong, but the seals are not capable of holding over 200 psi at a maximum, which is well below the strength of the vessels.

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*Flick-Reedy Company

PRESSURE MEASUREMENT

The equilibrium pressure within the equilibrium vessel, PV-1, is measured with the dead-weight gauge shown in Figs. 9 and 10. Figure 9 is a schematic drawing of the pressure measurement system and Fig. 10 is a photograph of the same system.

The piston of the dead-weight gauge has a small diameter, 0.130 in., so that the maximum working pressure of 15,000 psia can be balanced by a reasonable load of weights, 200 pounds. The piston was lapped to within 0.0002 in. of the cylinder diameter. In spite of the tight clearance, some of the oil used as the hydraulic fluid will leak out through the cylinder. A screw-driven oil makeup assembly has been put into the system to make up for the lost oil. When the oil makeup assembly has run its full length, this part of the system must be blocked off and more oil introduced from the oil reservoir while the oil makeup assembly is screwed back to the loaded position.

A level-sensing vessel, PV-8, has been included to indicate when more oil must be added. The vessel has four electrical contacts inside the vessel with approximately 2.3 ml. of volume between each successive pair. These contacts sense the level of the oil-mercury interface inside the vessel. Mercury is in the lower part of the vessel, oil in the upper part. When oil is lost at the piston, the oil-mercury interface rises. Each contact, when touching the mercury, completes a circuit with the other end which is grounded to the vessel. When each circuit is completed, a light on a panel is lit. The ideal controlled situation is for the lower two lights to be on, and the upper two off, indicating that the level is in the middle portion of the sensing vessel. When the third light is on, more oil is added until both the third and second lights go out.

Because the system for this project includes high-pressure oxygen, it was not desirable to have the gas in contact with either the oil or mercury used in the dead-weight gauge. Therefore an additional vessel, PV-7, was included which separates the fluid from the gas with a gas bellows which can expand and contract as the amount of fluid changes because of the makeup problem. The gas is on the

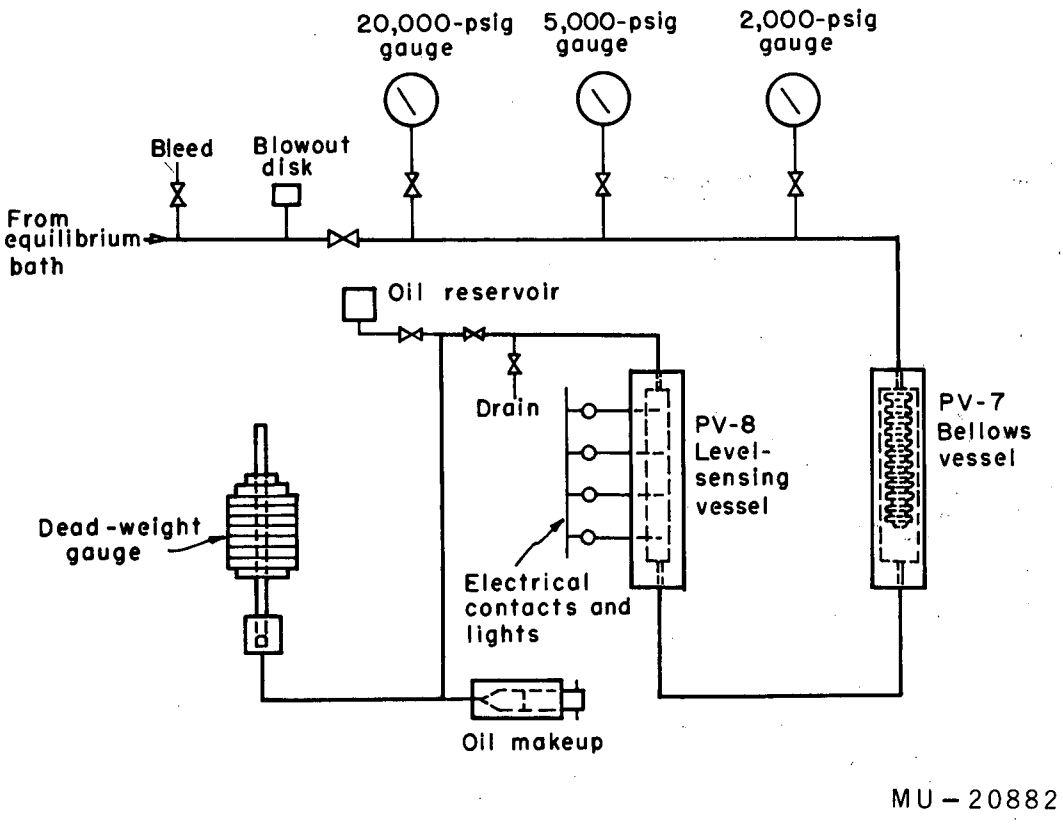

Fig. 9. Flow diagram of the dead weight gauge.

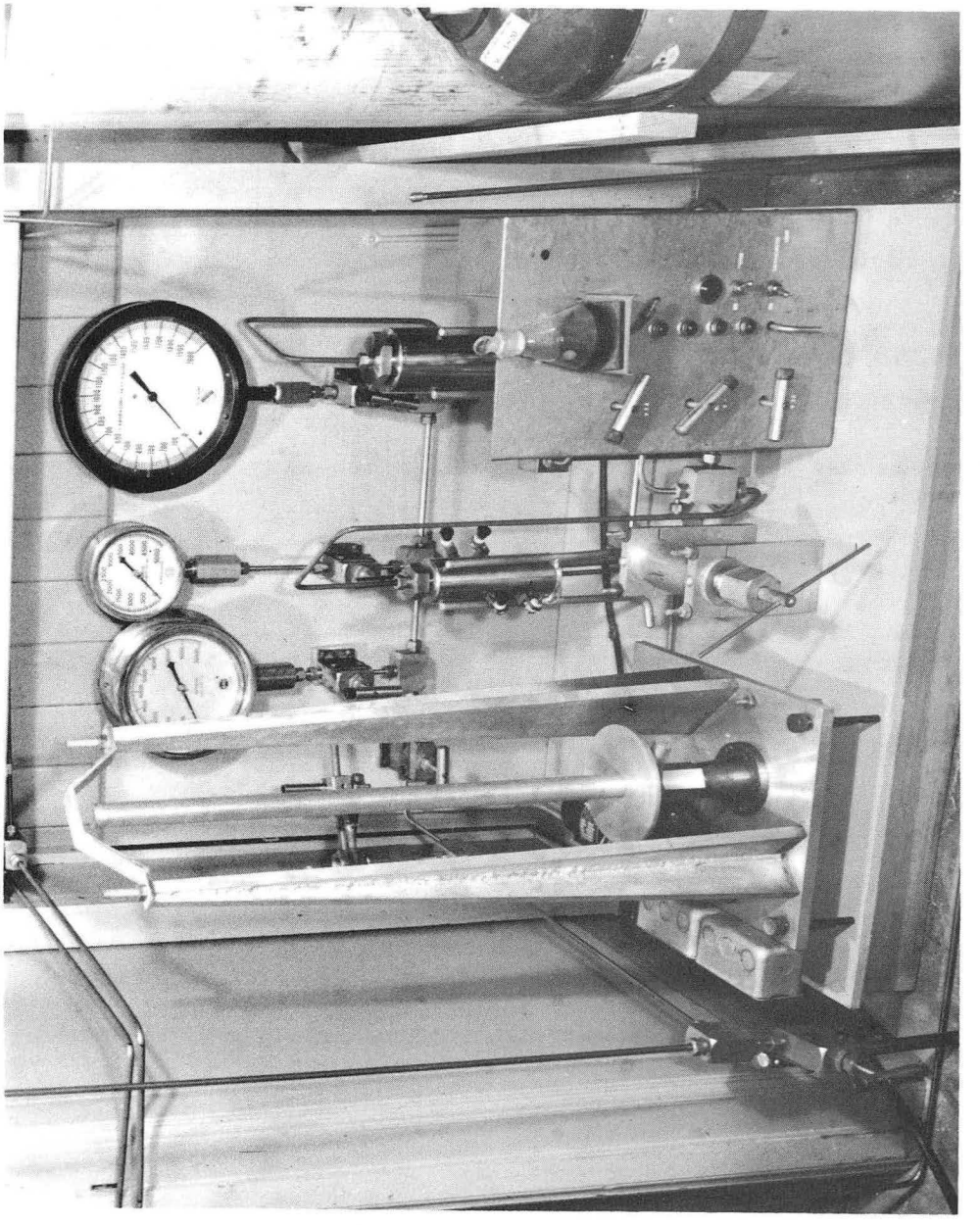

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Fig. 10. Dead weight gauge.

inside of the bellows and the fluid on the outside. The fluid around the bellows is again oil, to keep mercury away from the brass. At the bottom of PV-7 the oil contacts mercury. The line connecting PV-7 and PV-8 is filled with mercury. In summary, the entire chain of pressure transmission is from gas to brass bellows to oil to mercury to oil to the piston in the dead-weight gauge.

Three pressure gauges are included in the pressure measurement apparatus; they are for 20,000, 5,000, and 2,000 psig maximum readings. Each can be blocked off when the system pressure is too great for the gauge. The gauges are used only for measuring pressure during loading, but do not have the required accuracy for the final equilibrium pressure measurement. The gauges are very useful for a preliminary estimate of the pressure which determines how many of the larger weights must be placed on the dead-weight gauge for precise balancing.

Also included as part of the pressure measurement apparatus is the blowout disk which protects the entire equilibrium system from overpressure. It will rupture at 17,000 psig ± 10%.

The dead-weight gauge has not yet been calibrated. It is proposed to calibrate it against two accurately known pressures: a mercury column, and the vapor pressure of carbon dioxide at $0^{\circ}C$ (34.379 atmos).[3]

TEMPERATURE MEASUREMENT

The equilibrium temperature is assumed to be the same as the temperature of the constant-temperature bath. This is measured with a four-junction thermopile, consisting of four iron-constantan thermocouples connected in series to increase the voltage and thus the accuracy. The cold junction is in a stirred bath of ice and distilled water in a Dewar flask. The voltage is read on a potentiometer.

The thermopile was calibrated against a National Bureau of Standards thermometer over the range of -38 to +26°C with a total of 61 calibration points. The voltage-temperature relationship was not perfectly linear. All but four of the data points were within 0.1°C of the chosen line.

The assumption that the fluids are at the temperature of the bath fluid has been made because of the difficulties of introducing two additional wires into the equilibrium vessel. It would appear to be a good assumption, within the 0.1°C accuracy of the temperature measurement. The ideal operating arrangement would be for the fluids to reach equilibrium by circulating overnight, which is certainly sufficient time for thermal equilbrium. During this time there would be energy input to the fluids by the pumps, but this should be extremely small.

The thermowell in PV-1 is large enough to contain a single thermocouple. The temperature of the interior of the thermowell should be closer to the equilibrium temperature than to the bath temperature thus a thermocouple in this thermowell, when compared with the thermopile temperature, will give a partial check of the assumption of equal temperature.

SAMPLE COLLECTION

The liquid and vapor samples in the equilibrium system are at high pressure, up to 1,000 atmos. To be analyzed, they must be moved to glassware at approximately 1 atmos pressure. At 1 atmos both samples will be gases. Before analyzing the samples, a PVT (pressure-volume-temperature) measurement is made of each sample at approximately 1 atmos pressure for use in calculating the density of the samples at the equilibrium conditions. This density measurement and the measurement of the sample volumes are discussed in the next section.

The sample collection system consists basically of a pressure surge vessel, a Toepler pump for moving the gas, and a sample collection vessel (Fig. 11). The Toepler pump and sample collection vessel are glass, and connect to the metal parts with a glass-copper seal between stopcock D and valve V-25. A single line comes from the equilibrium system so that only one sample can be collected at a time.

The first step is to evacuate the entire system by connecting the top of the sample collection vessel to the vacuum manifold located on the analytical system (Fig. 12). This connection is made by ground-glass joints and rubber tubing and has proved quite leak-free. Valve V-26 and all the stopcocks, except E and F, are opened in order that the entire system is evacuated to valves V-2 and V-5 (Fig. 1), the valves to the vapor and liquid samples. V-26 is now closed, and V-2 opened, releasing the vapor sample into the pressure surge vessel, which is large enough (1.8 liters,) to reduce the pressure to approximately one atmos. Stopcock A is then closed and valve V-26 is opened.

The sample fills the entire sample-collection system plus the original sample space at a pressure less than 1 atmos. The next problem is to move all the gas into the sample collection vessel. The Toepler pump is capable of doing this. Because the volume ratios involved require many cycles, the Toepler pump is automatically controlled by a relay box. The lower chamber of the pump is a

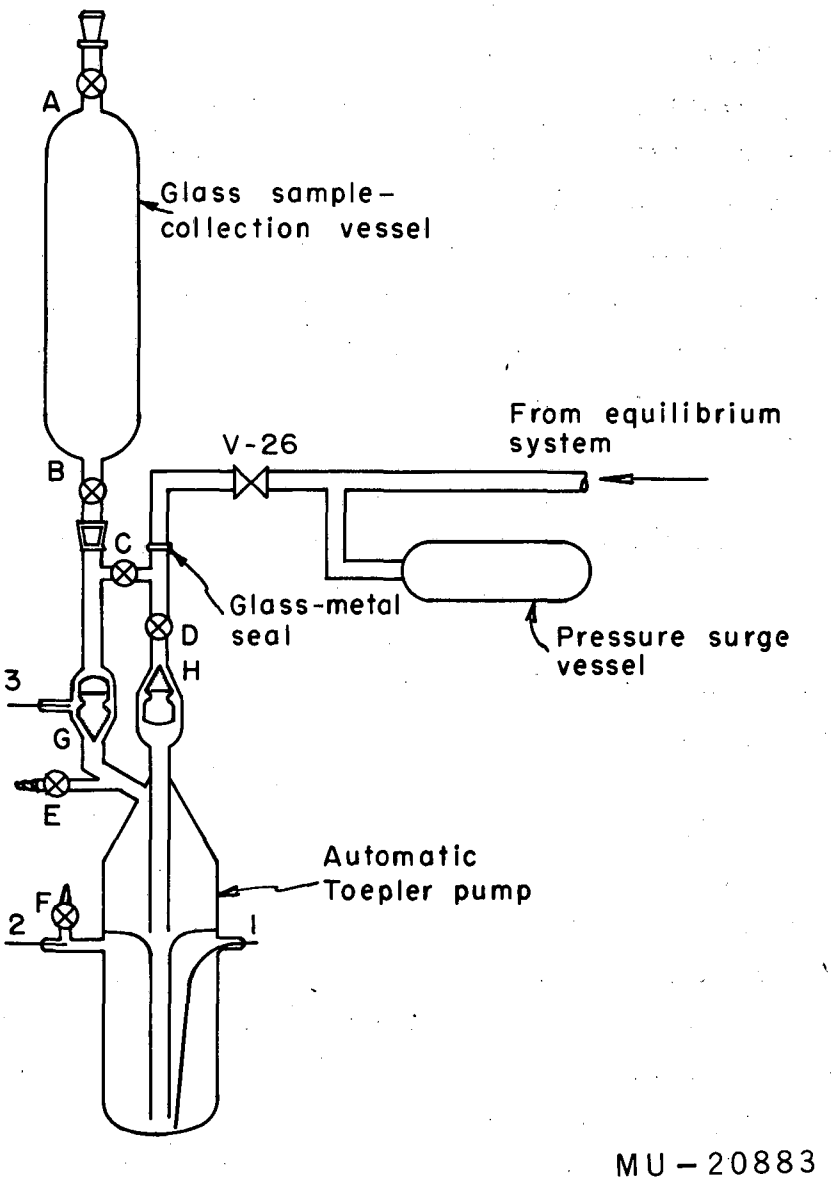

Fig. 11. Sample-collection system.

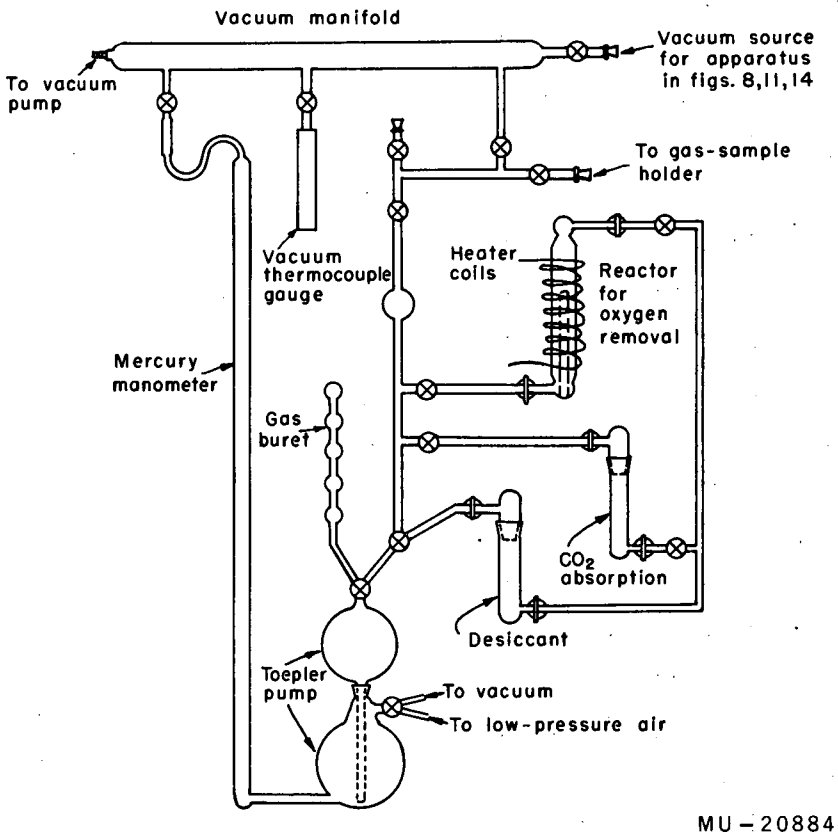

Fig. 12. Analytical system.

source of mercury which can move into the upper chamber through a diptube. The mercury is pushed up into the upper chamber by introducing low-pressure air through stopcock F. The mercury is brought down again by evacuating the air in the lower chamber through stopcock F. Three electrical contacts are provided: 1 the common, 2 the low level, and 3 the high level.

The cycle of pump operation is as follows: Stopcock C is closed, with B and D left open. The controller is started, introducing air at F so that the mercury rises into the upper chamber, cutting off the gas in the standpipe, and pushing all the rest of the gas in the upper chamber into the sidearm. The mercury float-valve in the sidearm, G, is fairly heavy and does not open until the pressure below is greater than above by several pounds. The mercury rises through this valve until it touches electrical contact 3. This makes a circuit with the common, and the controller shuts off the air and starts the vacuum pump, drawing the mercury back into the upper chamber and sealing valve G. The space above the mercury in the upper chamber is then at vacuum until the level drops below the end of the standpipe and more sample comes in through valve H until the pressure equalizes. The mercury drops in the upper chamber and rises in the lower chamber until it reaches electrical contact 2, which completes the other relay circuit. This shuts off the vacuum pump and again opens up the low pressure air starting the cycle again.

The net effect of the cycle is to move the gas from the upper chamber into the sample collection vessel, and introduce more gas into the upper chamber from the part of the system which must be evacuated. One cycle reduces that pressure by the ratio of the volume of the upper chamber of the Toepler pump to the volume of the whole system, which is primarily the pressure surge vessel plus the upper chamber. This ratio is about 1/3, thus evacuation is rather slow, but requires less than 25 cycles to reduce the pressure to 1/10,000 of the original. Considerable time is required for the evacuation of the sample, because much carbon dioxide is likely to solidify in the tubing during the original adiabatic expansion into the pressure-surge vessel.

Valve H is primarily a safety valve. In normal operation it will usually be open during all parts of a cycle until the late stages of evacuation. It closes only when the mercury rises in the standpipe to valve H. Its purpose is to prevent mercury from flowing into the rest of the system.

On the last pumping cycle, contact 3 is disconnected so that mercury will continue to rise beyond that point. The rise of mercury is controlled manually with stopcock F in order that the mercury rises through stopcock B to a calibration mark in the neck of the glass sample collection vessel. The mercury level is carefully brought to this mark. The entire vapor sample is then trapped in the collection vessel between stopcock A and the calibration mark. Stopcock B is closed, the mercury below it withdrawn into the Toepler Pump, and the collection vessel disconnected at the ground joint for the density measurement. A similar collection vessel is put in its place and the entire procedure repeated for the liquid sample.

Stopcock E is used for the addition of more mercury in case the total volume of mercury is not sufficient to rise above stopcock B. As long as the bore of stopcock E and the tube leading from it are full of mercury, addition of mercury causes no problems.

DENSITY MEASUREMENT

Although the primary objective of this equipment is to obtain data on the high-pressure equilibrium, the density of the saturated high-pressure samples is of value, and is obtained without much additional effort. The volumes of the sample spaces can be measured, and by PVT measurements at low pressure, coupled with the analysis results, the weights of the samples are calculated.

A U-tube mercury manometer is connected to the sample collection vessel (Fig. 11) at the ground joint above stopcock A. This manometer is fitted with stopcocks and ground joints in order that it can be evacuated on both sides of the mercury. The procedure is to attach the manometer, evacuate on both sides of the mercury, close the two stopcocks, and slowly open stopcock A, which releases the sample into the first leg of the manometer. The sample collection vessel with attached manometer is then submerged in a constant temperature water bath. Time is allowed for thermal equilibrium, and the heights of the mercury levels and the reference marks are then read with a cathetometer. The walls of the water bath are of plate glass in order that readings can be made through the bath with no distortion. The water-bath temperature is read with a thermometer to $0.1^{\circ}C$. The bath temperature is controlled with a simple relay controller, and controlled all parts of the bath at all times within the accuracy of the temperature measurement. The calculations of moles and weight of the samples are dependent upon the analytical results, and the calculation method is discussed at the end of the analytical section, which follows this section.

The volume of the sample collection vessels plus manometer must be calibrated. Weight limitations on the accurate balances available rule out using mercury for this calibration; therefore water should be used. Since water clings to the walls of a vessel when it is drained, it will be necessary to weigh the equipment dry, and then full of water. Once the over-all volume is determined, mercury can be used for calibrating the manometer. The final result desired is sample volume as a function of the position of the mercury-sample interface.

The volumes of the liquid and vapor sample spaces must also be calibrated. These spaces are each less than 10 cc. It is proposed to do this by PVT measurements of air in the sample spaces and in the calibrated gas buret of the analytical equipment. This buret is used in preference to the sample collection vessel. The gas buret has volumes as small as 10 cc, which will give greater pressures than the much larger sample collection vessel, and therefore reduce the percentage error in the pressure measurement.

The proposed procedure for the calibration of the vapor sample volume is detailed here. The procedure will be identical for the liquid sample space. For convenience, the sample lines and valves can be disconnected from the rest of the equipment. A hose connection can be connected to valve V-2 (Fig. 1). Rubber tubing can then join this connection to the ground joint on the analytical equipment, Fig. 12, labeled "To sample collection vessel." With V-2 closed, and V-1 and V-3 open, the sample space will be filled with air at room temperature and atmospheric pressure. Through the analytical equipment, evacuate all the apparatus up to valve V-2. Then close valves V-1 and V-3, measure the room temperature and the atmospheric pressure. Close the stopcock connecting the vacuum manifold to the analytical apparatus, and open valve V-2, releasing the air from the sample space into the evacuated analytical system. Now by proper operation of the manually operated Toepler pump, the entire sample can be moved into the gas buret, and a PVT measurement made. This procedure is explained in detail in the next section.

For these calculations, the compressibility factor for air must be known. Very precise compressibility factors are available for air as a function of temperature and pressure.[4] The moles of air, n, are calculated from the PVT data at the gas buret. Using this n, the volume of the sample space, V, is calculated from the atmospheric pressure and air temperature.

THE ANALYTICAL SYSTEM

Analysis of both the liquid and vapor samples is done in the vapor phase. Figure 12 is a flow diagram of the analytical apparatus, which is also shown in Fig. 13. The composition of a sample is determined by the stepwise removal of carbon dioxide and oxygen. A PVT measurement is made on the original sample and after each gas is removed. The nitrogen is determined by difference. The analysis is completely dry, and an absorption tube with a desiccant is in the absorption chain to remove any stray water vapor.

Carbon dioxide is removed by absorption with "Ascarite," a sodium hydroxide asbestos absorbent. Any water vapor present is absorbed by "Drierite," which is anhydrous calcium sulfate.

Oxygen is removed by reaction with active copper at approximately 550°C. The active copper is prepared by the reduction of cupric oxide with hydrogen according to the method of Dodd and Robinson.[5] The temperature of the reduction reaction, over 600°C, requires a quartz reaction vessel. A thermocouple in an internal thermowell proved quite reliable for measuring the temperature. The vessel is heated by a multiple-unit electric furnace, 422 watts maximum.

The sample is moved through the various parts of the equipment by a manually operated Toepler pump. Mercury rises through the dip tube from the lower chamber to the upper vessel when low pressure air is introduced above the mercury in the lower chamber. The mercury in the upper chamber drops when the lower chamber is evacuated. By appropriate changes of the three-way stopcocks during the rise and fall of the mercury, the gas can be completely moved from the gas buret to the absorption train or vice versa with only a few cycles of the Toepler pump.

For example, if the gas buret contains 50 cc of sample at 1 atmos, 5 cycles will reduce the pressure to 0.25 microns or 1/3, 040, 000 of the original gas. To move the gas in the opposite direction - from the absorption train to the gas buret - more cycles are required, because the volume of the absorption train is greater.

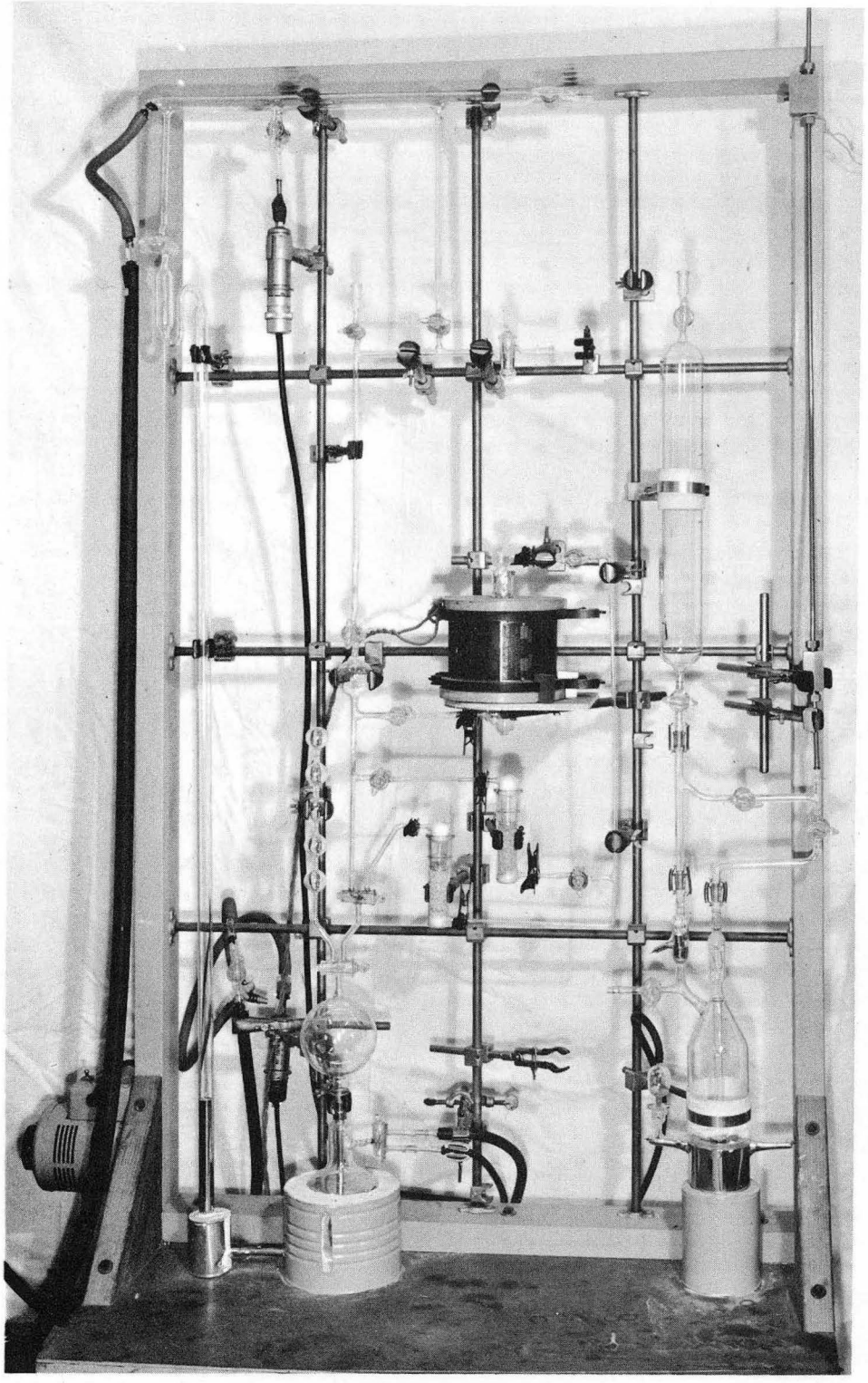

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Fig. 13. Analytical system and sample-collection system.

The gas buret is composed of five bulbs of approximately 10 cc each, connected by small tubing. The advantage of bulbs over a straight buret is that the point of measurement is in a small bore tube between bulbs. Any error in reading the height of the mercury meniscus results in a very small volume error. Five small bulbs instead of one large bulb also allows a choice of sample size. For example, the original sample may occupy 50 cc at approximately 1 atmos. After the carbon dioxide and oxygen are removed, the nitrogen may be only 1/10 the original number of moles. If the gas buret were a single 50-cc bulb, the pressure would be 1/10 the original, making the percentage error of pressure measurement 10 times the original measurement. Since five bulbs are available, the gas can now be moved into the top bulb, giving a pressure 1/2 the original, and an error twice the original.

In making a PVT measurement on the sample, the sample is moved into the gas buret with the Toepler pump. On the last cycle the mercury is pushed up through the three-way stopcock to the gas buret. The appropriate number of bulbs is chosen to give a reasonable pressure. Time must be allowed for the sample to reach the termperature of the surroundings. The mercury level is carefully adjusted to the mark below the desired bulb. The rise of mercury is controlled with the stopcock on the lower chamber of the Toepler pump which introduces air or evacuates the chamber. The three-way stopcock at the top of the upper chamber must remain wide open to the gas buret, since the pressure is measured by the difference in height of the mercury in the gas buret and in the manometer. The mercury levels are read with a cathetometer, and a correction is made for the capillary effect in the tubing of the gas buret.[3] The manometer is large enough, 18 mm i. d., so that no capillary correction is necessary. The temperature of the sample is assumed to be the same as that of the surrounding air. The temperature is measured to $0.1^{\circ}C$ with a thermometer suspended next to the gas buret.

Volumes of the bulbs of the gas buret were calibrated by weighing the mercury drained from the buret at various levels. These

calibrated volumes are listed in Appendix I. Error of volume measurement is less than 0.2%. Pressure and temperature measurements are accurate to 0.1%.

When the sample is first admitted to the equipment, previously evacuated, it is routed through the oxygen reaction vessel, which is then cold and thus unreactive, and then through the desiccant in order to remove any water vapor which might be present. With the use of the Toepler pump, the sample is moved through this circuit and into the gas buret. When a suitable amount of sample is in the gas buret, the excess sample remaining in the rest of the circuit can be removed through the vacuum manifold.

After the first PVT measurement, the original sample is moved several times by the Toepler pump through the "Ascarite" for removal of the carbon dioxide. It is then transferred to the gas buret for a second PVT measurement. Then the oxygen reaction vessel is heated to 550°C and the sample slowly passed through it several times. Following this, it is transferred to the gas buret for a last PVT measurement. For this PVT measurement, considerable time is required for the sample to cool to room temperature.

Two major sources of error must be guarded against with this equipment: incomplete removal of a component, and leaks. Both can be checked by the same procedure. After each absorption and PVT measurement, it is advisable to do a second absorption. If this result shows a decrease in gas, then the first absorption was not complete, and a third is advisable. If the second absorption shows an increase in gas, air has leaked into the system under low pressure, and the entire analysis must be discarded. The high-vacuum stopcocks showed no tendency to leak, but the ground joints on the vessels did,therefore they must be greased and fitted very carefully. The joints on the oxygen reaction-vessel were particularly susceptible to leaks because of the temperature change during the heating.

The analytical equipment is calibrated with a blending apparatus described in the section following this.

For calculating the moles of sample in each PVT measurement, the perfect gas law is not sufficiently accurate. Oxygen and nitrogen follow the perfect gas law near 1 atmos pressure with 0.1% accuracy, but the deviation of carbon dioxide is approximately 0.7%.[6] It is proposed to use the virial equation to correct for this deviation:

$$PV = nRT\left(1 + \frac{nB}{V}\right) \qquad (1)$$

B is the second virial coefficient for the mixture of gases being considered. The B's for the individual components are best calculated from precise compressibility data.[4] Guggenheim[7] gives a method for calculating the B's for the interaction of two different gases and the B's for mixtures of gases.

The results desired from the calculation are n_1, n_2, and n_3, the number of moles of nitrogen, oxygen, and carbon dioxide. The PVT measurements made on the analytical system are for three- and two-component mixtures and a single component, therefore, the first calculation yields n_A, n_B, n_C, defined as follows

$$\begin{aligned} n_A &= n_1 + n_2 + n_3 \\ n_B &= n_1 + n_2 \\ n_C &= n_1 \end{aligned} \qquad (2)$$

For solution, the virial equation is used in the form

$$n = \frac{PV}{RT} - \frac{n^2 B}{V} \qquad (3)$$

where the B used will depend upon which components are present in the n. A trial and error solution is used, with n_A, n_B, and n_C calculated from the data with the perfect gas law. This will give estimates of n_1, n_2, and n_3 good to better than 1%. These n's are then used to calculate the appropriate B's, and using the approximate n's on the right hand side, new n's are calculated. Because of the high accuracy of the first approximation and the small effect of the second term, a repeat trial should not be necessary in order to get an accuracy of

at least 0.05%. The mole fractions of the three gases are then calculated from the n's.

When the mole fractions have been calculated, the final calculations can be made of the total moles of the liquid and vapor samples. The measurement of the PVT data on these samples was discussed in the section on density measurement. The virial equation is again used. The B's for the mixtures can be calculated exactly by the Guggenheim[7] method, since the mole fractions are known. The B's will not be the same as those for the calculation of analytical results because the temperatures are different. The moles of samples are then calculated using Eq. (3) in the manner previously described.

The weight of the sample is calculated by

$$W = \sum_{i=1}^{n} y_i n M_i \qquad (4)$$

where M is the molecular weight, and y the mole fraction. The density of the sample is then the weight of sample divided by the volume of the sample space.

GAS-BLENDING APPARATUS

In order to calibrate the analytical apparatus, it is necessary to have blends of the three gases: oxygen, nitrogen, and carbon dioxide for which the compositions are known with high accuracy. The design of Maimoni[8] seemed quite adequate for, although it is basically designed for two-component blends, it is applicable to three components.

The apparatus, (shown diagramatically in Fig. 14) was bedded in an aluminum frame with Weatherban Wall Sealer* (see Fig. 15). The apparatus has two calibrated burets in which the volumes of the pure components are measured. At the time of measurement, each buret acts as one leg of a mercury manometer with the other leg open to the atmosphere. After the pressure and volume of the individual gases are determined, the burets are interconnected for blending.

This design gives accurate measurements of pressure, volume, and temperature, and has no dead spaces for gas to be trapped.

The diameters of the tubes in the different sections of the burets were chosen to minimize the percentage error in the PV product by the following scheme: all the readings are made with a cathetometer, reading the mercury level in the tubes. The mercury level determines both the volume and the pressure. Assuming a constant error in reading the mercury level, a larger tubing will give a larger error in the volume, but will give a smaller capillary effect on the pressure. Although a correction is made for the capillary effect,[3] a small uncertainty in tubing diameter results in greater error at small tubing diameter because the capillary effect is greater. Therefore the diameter of the tubing is selected in order that the percentage error in reading the pressure is about the same as the percentage error in reading the volume. This point is discussed in more detail by Cook.[9]

The volumes of the burets were calibrated by weighing the mercury drained from each section. The tubing in each section used for measurement is precision-bore tubing so that the volume change along any of these pieces can be taken as linear. Two points were

*Minnesota Mining and Manufacturing Co.

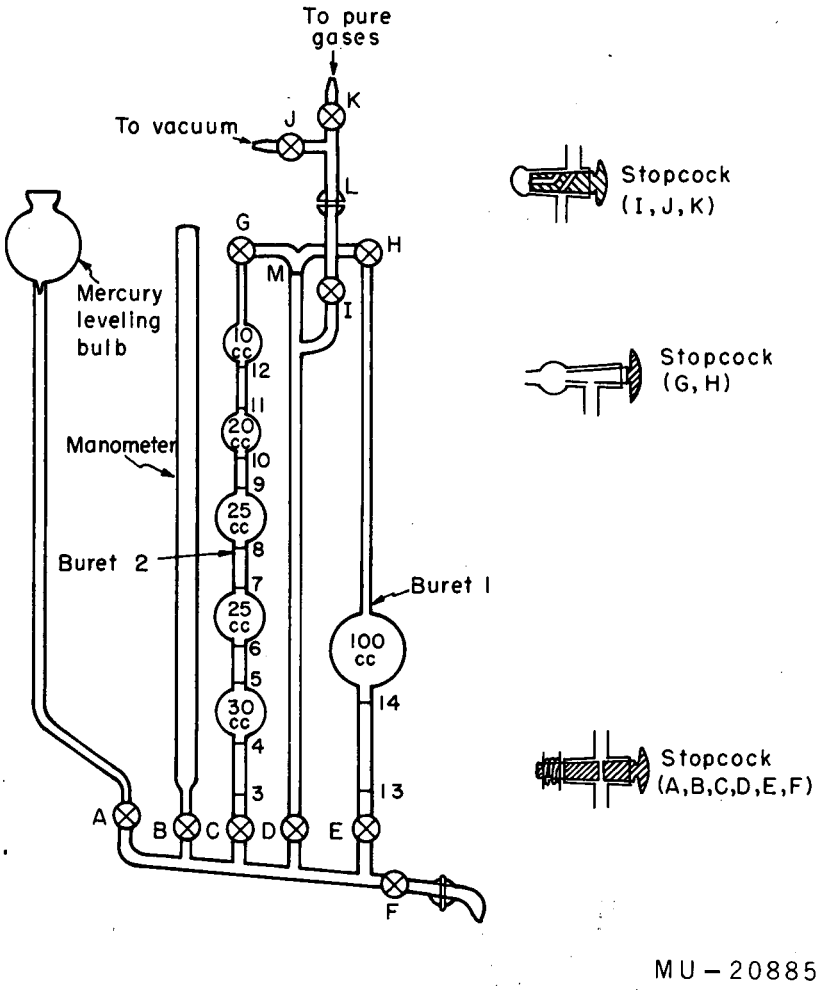

Fig. 14. Gas blending apparatus.

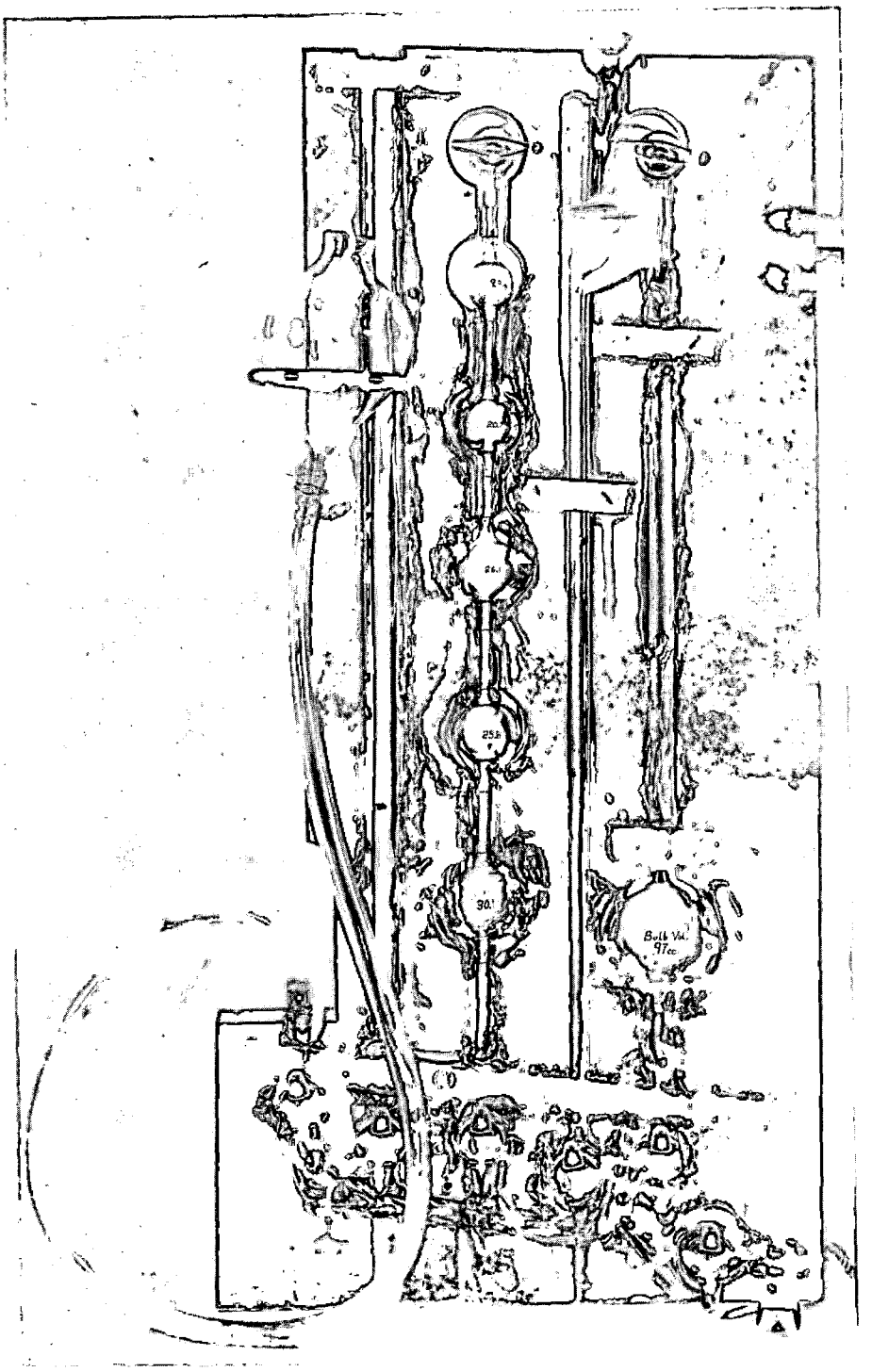

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Fig. 15. Gas blending apparatus.

calibrated within each section of tubing. To avoid gas bubbles, the apparatus was evacuated before being filled with mercury. Total volume error, including both calibration error and error in reading the mercury level during operation, is estimated at 0.06% maximum. The volume calibrations are listed in Appendix I.

The apparatus is connected to the vacuum system manifold and pumped out before admission of the gases to be blended. The gas that is to have the higher concentration in the final blend is admitted to buret 1.

The leveling bottle is used to place the mercury level in buret 1 within the calibrated section of precision-bore tubing above stopcock E. The first gas is then admitted to this buret. The pressure of the gas is adjusted to be near atmospheric. Stopcock H is closed and the system is evacuated prior to introducing the second gas into buret 2. After the second gas is admitted, the mercury level in buret 2 is adjusted to fall within the proper calibrated section to give the desired volume ratio between the two gases. Stopcock G is closed and the system above stopcocks G and H is again evacuated. Note that the construction of stopcocks G and H as shown in Fig. 14 is such that there is no dead space, even in the bore of the stopcocks.

Once the system is evacuated, stopcocks A and D are opened, allowing the mercury to rise to point M and to stopcock I, which is then closed. At this point the blending apparatus is charged and ready for the measurement of the pressure, temperature, and volume of the gases in the burets. This is accomplished by connecting each of the burets in turn to the manometer tube, by opening stopcocks B and C or E.

The blending apparatus is disconnected from the vacuum system at joint L and is immersed in the constant-temperature water bath used in the density measurement. The mercury levels in the two burets and the manometer tube are read with a cathetometer to the nearest 0.1 mm. The atmospheric pressure is measured with a cathetometer on a U-tube manometer in which the vacuum side is less than 1 micron (0.001 mm Hg). The measurement is made to 0.1 mm.

The blending apparatus is now removed from the water bath for the mixing operation. The manometer is isolated by closing stopcock B. Stopcocks A, G, and H are opened. By proper control of stopcocks C and E and the height of the leveling bottle, the samples are transferred back and forth between burets 1 and 2 for mixing. The mixing operation takes considerable time because at no time can all the gas be moved into a single chamber. Maimoni[8] found, with a similar apparatus, that as much as 40 minutes was required for adequate mixing.

For transferring the mixed sample to the analytical apparatus, ground joint L is again connected. The rubber tubing which previously connected to the pure gases is now connected to the analytical apparatus at the joint marked "To sample collection vessel" in Fig. 12. Stopcocks I and K are opened, and the system evacuated through the analytical system. The analytical system is then isolated from the vacuum manifold. The mercury below stopcock I is then lowered through stopcock D. When the mercury level has dropped, the mixed blend can then pass through stopcocks I and K to the analytical apparatus. The Toepler pump in the analytical apparatus is used to move sufficient sample into the gas buret.

Calculation of the moles of each gas from the PVT data is best done using compressibility data which is available[4] for each of the gases used here.

LEVEL INDICATOR

It is important to have some indication where the liquid level is in the equilibrium vessel, PV-1. The level indicator described here indicates whether the level is between two specific points in the vessel. As long as the level is somewhere within the three-inch control region, there is no need to know it more accurately.

Figure 16 shows the details of the level indicator, which uses two glass enclosed thermistors* as the sensing elements. Figure 17 shows the details of the electrical circuit for making the level determination. The principle of the indicator is that the electrical resistance of a thermistor changes as its temperature changes. When current is passed through a thermistor, the temperature rises, and the temperature reached is determined by the heat transfer to the surrounding fluid. The heat transfer is a function of the fluid's properties.

Several ways of incorporating this principle into a usable sensor are apparent. The one chosen is to measure the difference in resistance of two thermistors, A and B, located at different levels in the equilibrium vessel. The thermistors are parts of opposing legs of a wheatstone bridge. Forming the other two legs of the bridge are variable resistors, C and D, of 100 ohm maximum resistance each. A vacuum-tube voltmeter, G, is used to measure the imbalance of the bridge. Located in the circuit external to the bridge is a large variable resistance, E, to control the total current in the circuit, which is measured by an ammeter, F. Power is supplied from two six-volt auto batteries.

With the current set at approximately 40 milliamperes (ma), the two variable resistors, C and D, are adjusted to balance the bridge so that the voltmeter, G, reads essentially 0. This adjustment must be made when it is known that both thermistors are in the same medium. The thermistors are approximate equal. Any change in

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*VECO 23A1 1/2 in. glass probe thermistors, 100 ohms at 25°C. Victory Engineering Co.

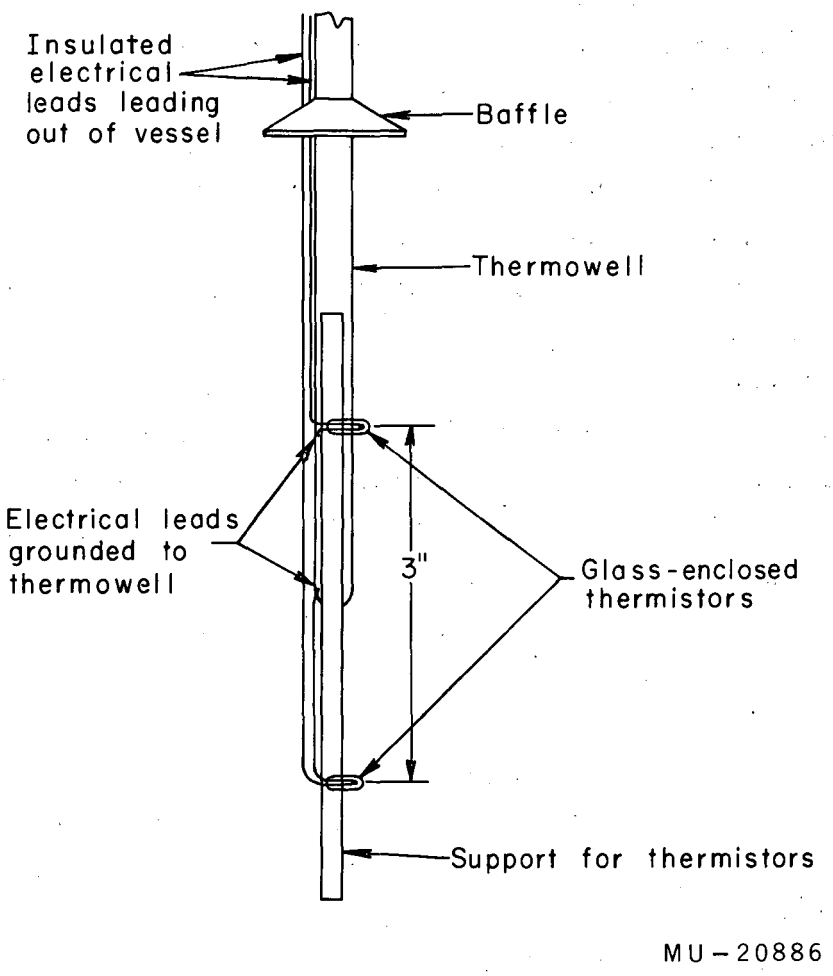

Fig. 16. Detail of level indicator.

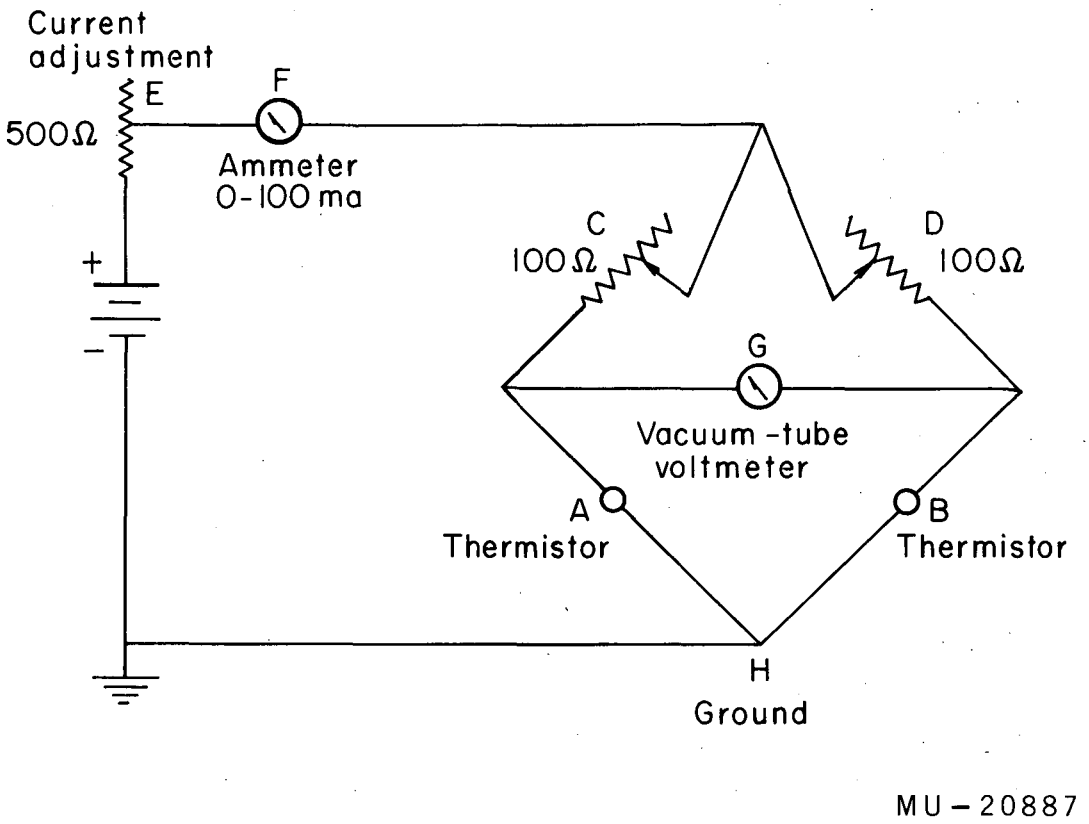

Fig. 17. Electrical circuit for level indicator.

the surrounding medium, such as an increase in density due to increased pressure, will cause approximately the same resistance change in both thermistors, and thus leave the bridge balanced. Only when the two thermistors are subjected to different surroundings should their resistances differ, causing an imbalance in the bridge. A direct voltmeter reading is used to measure bridge imbalance, rather than the change of resistance required in one variable resistance to restore the bridge to balance.

Tests of thermistors confirm that they are adequately sensitive to phase difference even when the vapor phase is quite dense at high pressure. Total circuit current of 40 ma was found to give proper sensitivity. During a test, the bridge was balanced with both thermistors in water at $0^{\circ}C$. When both thermistors were moved to water at $25^{\circ}C$, there was no detectable imbalance. When both were moved to normal heptane at $0^{\circ}C$, the bridge imbalance was 0.04 volts. When one thermistor was in water at $0^{\circ}C$ and one in normal heptane at $0^{\circ}C$, the bridge imbalance was 0.3 volts. Therefore some imbalance results from a change in the surrounding medium because the thermistors are not perfectly identical, but this imbalance is an order of magnitude less than the imbalance caused by putting the thermistors in different liquids. Putting one thermistor in air resulted in a much greater imbalance.

A metal supporting strip has been soldered to the thermowell in PV-1. The lower thermistor, A, is in a groove which is 3 1/2 in. from the bottom of the cavity. Thermistor B is in a groove 6 1/2 in. from the bottom. One lead from each thermistor is connected to the thermowell for ground, corresponding to point H in Fig. 17. The other lead from each thermistor passes out of the top of the vessel through one Aminco electrical connection. The pressure seal is made by imbedding both wires in a soapstone cone which is compressed until it seals. All other parts of the circuit are outside the constant temperature bath.

When loading the cell, carbon dioxide is introduced until the pressure rises to 100 psia. This is below the vapor pressure of

carbon dioxide at the minimum bath temperature (-40°C), and therefore no liquefaction will occur. With the current set at 40 ma, the variable resistors C and D are adjusted to give 0 voltage. Then the pressure is increased to just above the vapor pressure of carbon dioxide at the termperature of the constant temperature bath. Condensation should begin at this time, since it is controlled by heat transfer. A sudden bridge imbalance should appear when the liquid level reaches the first thermistor. The carbon dioxide is turned off, and the liquid and vapor pumps are turned on for a minute to fill the liquid line and clear the vapor line. This may drop the liquid level below the thermistor, in which case the bridge will return to balance. More carbon dioxide should then be introduced until the imbalance appears again.

When the oxygen and nitrogen are introduced, and the pressure raised to a high level, enough of these gases may dissolve in the liquid to increase its volume to the point where it reaches the upper thermistor, causing the bridge to balance again. This is quite unlikely if the loading of carbon dioxide is stopped soon enough after the level reaches the first thermistor. But if this condition occurs, it is intolerable, for if the liquid level is above this, there may be no vapor phase at all. Either the total pressure can be reduced by venting some gas until the imbalance reappears, or the entire loading can be repeated, with some carbon dioxide being vented after the level first reaches thermistor A.

APPENDIX I

Calibrated Volumes

Analytical Apparatus Gas Buret. These volumes are to the calibration mark below each bulb.

One bulb	10.07 cc	Four bulbs	40.20 cc
Two bulbs	20.00 cc	Five bulbs	50.05 cc
Three bulbs	30.11 cc		

Maximum error estimated at 0.15%.

Tubing between bulbs is 0.35 cm i. d.

Blending Apparatus. These volumes are referred to the upper mark of each pair of marks in the sections of precision bore tubing between bulbs as numbered in Fig. 14.

Meniscus between points	Volume	Precision bore tubing i. d.
3 & 4	126.75 cc + 0.648 cc/cm below 4	0.910 cm
5 & 6	92.61 cc + 0.652 cc/cm below 6	0.914 cm
7 & 8	62.49 cc + 0.038 cc/cm below 8	0.900 cm
9 & 10	32.65 cc + 0.387 cc/cm below 10	0.700 cm
11 & 12	10.96 cc + 0.222 cc/cm below 12	0.532 cm
13 & 14	107.80 cc + 0.639 cc/cm below 14	0.900 cm

Maximum error estimated at 0.06%.

APPENDIX II

Record of Engineering Drawings

The major pieces of high pressure equipment were either purchased from the American Instrument Company or designed at the Lawrence Radiation Laboratory, Berkeley, California. The drawings for the latter are listed here for future reference.

High Pressure Loading Vessels, PV-2 and PV-3

10J2393	10J5012
10J2382	10J5032

High Pressure Vane Pumps, P-1 and P-2

10J2743	10J2701	10J2751
10J2732	10J2691	10J3021
10J2722	10J2681	10J4151
10J2711	10J2761	

High Pressure Bellows Vessel, PV-7

10J2333	10J2673A	10J4042
10J5022	10J2322	10J5012

High Pressure Level Sensing Vessel, PV-8

10J2363	10J5032
10J2351	10J5012

Dead-Weight Gauge Cylinder and Piston

10J4161
10J4171

NOMENCLATURE

B = second virial coefficient, cc/mole

M = molecular weight

n = moles

P = pressure, mm of Hg

R = gas constant, 6.237×10^4 cc, mm Hg/g mole, ^{o}K

T = absolute temperature, ^{o}K

V = volume, cc

y = mole fraction

z = compressibility factor

Subscripts

1 = Nitrogen

2 = Oxygen

3 = Carbon dioxide

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