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METHODS OF CALIBRATION AND TESTING OF HYGROMETERS

ABSTRACT

This paper reviews the art of testing and calibrating hygrometers. It describes and discusses instruments which may serve as primary and secondary standards. The use of precision humidity generators for producing atmospheres of known humidity is outlined. The methods and techniques of obtaining fixed humidity points are given. Recommendations are made concerning further research to insure consistency and accuracy in hygrometric measurements.

CONTENTS

1. GENERAL INTRODUCTION

A variety of instruments are used in the measurement of the moisture content of air. Many of these are purely empirical and require testing and calibration. Some instruments have a theoretical basis. Even these sometimes require calibration for the highest accuracy. Then too, instruments operating on different principles, and, occasionally, instruments operating on the same principle, will yield divergent results. A method of test or calibration, or a standard against which other instruments may be compared, is necessary if consistent and accurate measurements of humidity are to be made.

The testing and calibration of hygrometers may be approached in either of two ways. An instrument or method that has a firm theoretical basis and is capable of giving highly accurate and reproducible absolute measures of the moisture content of air may be chosen as a standard. Hygrometers may then be calibrated by direct comparison with the standard when simultaneously exposed to various humidities. Alternately, atmospheres of known humidity may be produced and controlled. Hygrometers may then be exposed to the known atmospheres, or, the air of known humidity may be fed to the instruments under test.

2. HYGROMETER STANDARDS

2.1 Primary Standard

The gravimetric method of water vapor measurement is generally considered the most precise and accurate in hygrometry. In this method, the mass of water vapor admixed with a given volume of dry air is absorbed by a desiccant and then the volume of the dry air is measured directly. Since these quantities are fundamental, this method yields an absolute measure of the humidity. Because of this, and its relatively great inherent accuracy, the gravimetric method is often used as a primary standard against which other methods and instruments are compared. However, to achieve the inherent accuracy of the gravimetric method there must be careful attention to details. Measurements are time consuming, especially those involving low moisture contents. The results are average values. Hence it is usually necessary, when calibrating other instruments against the gravimetric method to employ a humidity generator that produces air of constant humidity. This method is principally used for research work of the highest accuracy or making fundamental calibrations.

The gravimetric method has a long and well established history of use. In 1845, Regnault(1) employed it to determine the density and vapor pressure of saturated water vapor in air. Subsequently, in 1888, Shaw(2) repeated some of Regnault's work as part of an extensive investigation on the hygrometric methods in use at that time. Awberry(3) utilized it to measure the water content of saturated air at elevated temperature while Awberry and Griffiths(4) used it as a standard for low temperature calibrations. Bartlett(5) and Saddington and Krase(6) measured the water content of gases saturated at high pressures with the gravimetric method while Goff et al.(7,8) utilized it to determine the interaction constant of moist air. Walker and Ernst(9) and Wexler(10) have utilized this method for calibrating and checking the accuracy of precision humidity generators. It has also been used extensively in investigations of the vapor pressures of liquids and solutions, particularly salt solutions(11-24).

An experimental set-up for making a moisture determination with the gravimetric method is shown in Figure 1. Air of constant water vapor content is produced by a humidity generator and a sample withdrawn through an absorption train, saturator and laboratory wet gas meter, etc. The moisture is absorbed by the train of U-tubes. The first U-tube removes all, or nearly all, of the water. If the absorbent in the first U-tube is near exhaustion or if the air flow is too rapid some moisture may remain in the effluent air. The second tube will remove the amount that is still left. The third U-tube serves as a guard to prevent water vapor from diffusing back from the saturator or gas meter. The first two tubes are weighed before and after a run to give the mass of water vapor removed from the air. The volume of the dry air emerging from the absorption train is measured by a laboratory wet gas meter. The gas meter, however, saturates the air that flows through, so that the indicated volume is that of moist air.(28) To insure that the air is completely saturated before entering the gas meter so that no changes in water level will occur due to evaporation, a saturator is inserted immediately upstream of the gas meter. This saturator may be a container or, preferably a series of containers, filled with water-washed gravel or pumice and moistened with water. Since the gas meter measures the volume of saturated air the indicated volume must be corrected to give the volume of dry air associated with the absorbed water vapor. The mass of dry air is obtained by multiplying the volume by the density.

The absolute humidity, in terms of mixing ratio r, mass of water vapor/unit mass of dry air, is given by

$$r = \frac{M_w}{V \times c \times \left(\frac{\rho}{1+.00367t}\right)\left(\frac{P-e_s}{760}\right)} \qquad (1)$$

where

M_W = mass of water vapor absorbed in the first two U-tubes, g

V = indicated gas meter volume, cm^3

c = calibration factor for gas meter (a function of rate of flow)

ρ = density of dry air at standard pressure and temperature (760 mm Hg and 0°C) = .001293 g/cm^3

t = temperature of the air in the gas meter, °C

P = absolute pressure of the air in the gas meter, mm Hg

e_s = saturation vapor pressure at temperature t, mm Hg

The procedure in making a run is as follows: The test gas is drawn through the absorption train, saturator, gas meter and flowmeter. The rate of flow is adjusted and controlled at a constant value by the vacuum control valve. After a predetermined volume of test gas has been sampled, the control valve is closed, the absorption tubes sealed and U-tubes Nos. 1 and 2 weighed.

Although this procedure appears to be simple, certain precautions should be observed to reduce and eliminate sources of error. A constant rate of flow should be maintained through the system. The wet gas meter is flow dependent so that the calibration constant (c in equation (1)) will depend on the flow. The rate of flow should be kept low, preferably below one lpm, if complete absorption of the water vapor from the sample air is to be assured. U-tube No. 1 is filled with anhydrous magnesium perchlorate, $Mg(ClO_4)_2$, while No. 2 and No. 3 are filled with phosphorous pentoxide, P_2O_5. Anhydrous magnesium perchlorate is a granular material, with an excellent drying efficiency(25,26) that is easy to handle while phosphorous pentoxide, which has the greatest known drying efficiency(27) is a powder that readily deliquesces and must be handled with care. In filling the absorption tubes, the desiccant should be packed loosely so that no appreciable pressure drop is introduced. Furthermore, it is desirable to insert glass wool plugs at intervals between the desiccant to avoid channeling of the air on passage through the tubes. It is well to remember that the maximum permissible pressure drop across a wet gas meter is about 0.3-inch water; hence the pressure drop through the system preceding the gas meter must be kept below this value. The gas meter must be carefully leveled, the water level properly adjusted, and only integral revolutions used as a measure of the volume.(29,30)

In making precision weighings of the absorption tubes such factors as buoyancy, change in weight of the internal air volume, change in external surface conditions, static change, and thermal gradient within the balance case contribute errors that may be easily overlooked. The use of an identical dummy absorption tube as a tare will compensate effectively for buoyancy. If this tare is treated and handled in a similar fashion as the tubes in the absorption train, then some of the other errors may be reduced to negligible amounts. The internal pressure within the tare is adjusted to that within the test absorption tube by momentarily opening it at the same time that the latter is sealed for a weighing. The tare and main tube should never be handled with bare hands, for moisture and oil from the hands will affect the weight. Both should be wiped with a damp cloth to remove static charge prior to insertion into the balance case. One technique for insuring that the balance pans do not accumulate static charge is to keep an ionizing source (e.g., a radioactive salt) within the case. Furthermore, the balance should be in a room that is maintained at a fairly constant temperature and where there are no sources of heat radiation that could induce temperature gradients, and hence convection currents, within the case. The relative humidity within the balance case should be constant, for changes in humidity may shift the balance rest point.

It is important that no hygroscopic materials be used in the experimental set-up other than, of course, the drying agents in the absorption train. Rubber and some plastics, for example, are sufficiently hygroscopic so that they act as moisture sources and sinks. For this reason, tubing and stoppers fabricated from such materials must not be used. The set-up should be made from glass or glass and metal. Seals, such as on the absorption tubes, are achieved with ground glass stopcocks. Pneumatic connections between components are made through mercury seals. Every effort must be made to eliminate the possibility of error from moisture sources or sinks.

A typical absorption tube weighs about 70 g. The duration of a gravimetric determination can be adjusted so that at least 0.2 g of water is absorbed. An analytical balance, with a capacity of 200 g and a sensitivity of 0.1 mg will weigh the absorbed water vapor with a sensitivity of 1/2000. Assuming that all precautions with regard to buoyancy, etc. have been taken, an accuracy in weighing of 1/1000 may be expected. If more water is absorbed greater accuracy may be obtained.

The accuracy of measurement of volume with the gas meter is limited at best to 1/500(29,30). The pressure measurement can be made with an accuracy of at least 1 mm water and the temperature measurement can be made to better than 0.1°C. Thus these two measurements will be better than 1/1000.

It is apparent that the over-all accuracy is limited by the volume measurement. If a greater over-all accuracy is required a water aspirator can be substituted for the gas meter. A further refinement would be to use an oil aspirator. If an oil with negligible vapor pressure is chosen (say butyl phthalate) then the saturator may be eliminated too. In that case, equation (1) becomes

$$r = \frac{M_W}{V \times c \times \left(\frac{\rho}{1+.00367t}\right) \frac{P}{760}} \qquad (2)$$

The gravimetric method yields a measure of the humidity in terms of mixing ratio. Two fundamental quantities are determined directly: the mass of water vapor and the volume of dry air. The latter, through the known density of air, is converted into mass of air. Thus, the value of the moisture content of the air has been obtained in terms of an absolute definition by direct measurement. By recourse to the laws of gaseous behavior it is possible to convert from mixing ratio to such terms as density, vapor pressure, specific humidity, relative humidity or saturation deficit. However, the accuracy with which the humidity can be expressed in units or terms derived from the mixing ratio is limited by the degree of validity of the laws of gaseous behavior and vapor pressure. The accuracy with which the mixing ratio can be determined directly is limited only by the accuracy of the measurement of fundamental quantities.

2.2 Secondary Standards

The time, work, painstaking care, and skilled personnel required for setting up and using the gravimetric method precludes its general use except for fundamental calibration work. There is a need, therefore, for one or more types of instruments that could serve as secondary or working standards. The secondary standard is one which can be calibrated against the primary standard and then, in turn, used for routine calibrations. It would appear that an instrument, to be acceptable as a secondary standard, should directly measure the humidity of the air in terms of fundamental quantities, or should have a firm theoretical basis for its operation so that its indication can be related to the humidity through known physical laws. The microwave hygrometer, the dewpoint indicator and the psychrometer, within certain ranges and under prescribed conditions of use may be utilized as secondary standards.

3. PRECISION HUMIDITY GENERATORS

Several convenient and practical methods are available for producing atmospheres of known humidity with sufficient precision and accuracy that the use of auxiliary hygrometers for direct measurement is not required. Equipment incorporating these methods may be called precision humidity generators.

3.1 Pressure Humidity Apparatus

In this type of apparatus, a stream of air at an elevated pressure is saturated and the pressure of the saturated air is reduced as required to give any desired humidity. If the temperature is held constant during saturation and upon expansion, and the perfect gas laws are assumed to be obeyed, then the relative humidity, RH, at the lower pressure, P_t, will be the ratio of the absolute values of the lower pressure, P_t, to the higher pressure, P_s, that is,

$$RH = \frac{P_t}{P_s} \times 100 \qquad (3)$$

Water vapor-air mixtures depart from ideal gas behavior. Furthermore, air, when saturated with water vapor at high pressure, does not hold the same amount of moisture as at atmospheric pressure(5,31). Equation (3), therefore, does not strictly define the relative humidity, particularly at high values of P_s. Weaver(32,33) has shown that an empirical equation of the form

$$RH = 100 \times \frac{P_t}{P_s} \frac{(1 - KP_t + K'P_t{}^2)}{(1 - KP_s + K'P_s{}^2)}$$

where the constant K has a value of 0.00019 and K' is equal to 0.0000000014 when the pressure is expressed in pounds per square inch, more closely yields the true relative humidity. The magnitude of the ratio

$(1 - KP_t + K'P_t{}^2)/(1 - KP_s + K'P_s^2)$ does not exceed 1/4 of 1% when P_t is at atmospheric pressure and P_s is no greater than 150 psig. For these pressures, the relative humidity will be in the range of 10 to 100%.

The pressure method was used by Weaver and Riley(32) for the calibration of electrically conducting hygroscopic films employed in the measurement of water vapor in gases. Their equipment was designed for low rates of gas flow and was used under ambient room-temperature conditions. Wexler and Daniels(34) used the two-pressure principle in the design of a precision humidity generator that produced atmospheres of known relative humidity from 10 to 98% over a temperature range from -40° to +40°C with an accuracy of at least 1/2 of 1 percent relative humidity.

Figure 2 is a simplified schematic drawing illustrating the principle of operation of the apparatus, while Figure 3 is a block diagram and Figure 4 a schematic of a practical version of the apparatus. The apparatus is a continuous flow device. Air from a high pressure source is dried and cleaned by a low-temperature drying and filtering system. It is then heated in a warm-up unit prior to entering the humidifying system. Two pressure regulators in series reduce and control the pressure in the saturators at any desired value. After emerging from the humidifying system, the air passes through an expansion valve into a test chamber, where its pressure is maintained constant, usually at atmospheric pressure, and then allowed to exhaust into the room or a vacuum source. The drying and filtering systems are immersed in a bath of dry ice and Stoddard's solvent. The humidifying system, expansion valve and test chamber are immersed in a thermostatted bath whose temperature can be controlled at any desired value.

Instruments undergoing test or calibrations can be inserted into the test chamber or, alternatively, air from the test chamber can be fed to the test hygrometer. Provided one can assure complete saturation, the accuracy with which the pressure humidity apparatus can generate air of known relative humidity is limited by a) the accuracy with which the pressure is measured, b) the uniformity or constancy of the temperature from the final saturator through to the test chamber, and c) the degree of validity of the correction term of equation (4). By using suitable pressure measuring instruments, the accuracy of the pressure measurements can be made to 1 part in 500. The temperature can be held constant to at least 0.05°C. The correction term can be determined, by the gravimetric method, with corresponding accuracy. It is estimated that the pressure humidity apparatus will produce a relative humidity that is known to 1/2 of 1% or better (in percent relative humidity).

The question may arise as to whether complete saturation is obtained. This can be ascertained by a simple experiment. The apparatus has an external saturator which can be charged with water and operated at any desired temperature, or it can be maintained dry. If this external saturator is maintained dry, then the humidifying system within the thermostatted bath must provide all the moisture necessary to saturate the air at the bath temperature. The apparatus is operated, therefore, with the external saturator dry and the moisture content is measured by inserting a precision hygrometer in the test chamber, or by sampling the air and making a gravimetric determination. Water is added, now, to the external saturator and its temperature is adjusted to some value above that of the thermostatted bath. Without changing any other operating conditions, air is passed through the apparatus. Since the external saturator supersaturates the air with respect to bath temperature, the humidifying system within the thermostatted bath precipitates and condenses out the excess water. The moisture content is measured again and compared to the previous measurement. If the two are identical, they give sufficient assurance that complete saturation is obtained.

Basically, this equipment generates a known relative humidity. From a measurement of the temperature and pressure within the test chamber and with the application of the gas laws and the saturation vapor pressure of water the relative humidity can be converted to other units of humidity measurement.

3.2 Two-Temperature Humidity Apparatus

The method employed in this apparatus for producing atmospheres of known relative humidity is to saturate a stream of air with water vapor at a given temperature and then to raise the temperature of the air to a specified higher value. If t_s is the temperature of saturation, e_s the saturation pressure of water vapor at temperature t_s, t_t the elevated temperature, and e_t the saturation pressure of water vapor at temperature t_t, then the relative humidity, RH, at temperature t_t is

$$RH = \frac{e_s}{e_t} \times 100 \qquad (5)$$

In equation (5), the assumption is made that the absolute pressure of the air at the elevated temperature, t_t, is the same as the absolute pressure of the air at the saturation temperature, t_s. If these two pressures are not identical, then a pressure correction must be introduced. If P_s is the absolute pressure of the air at t_s, and P_t is the absolute pressure of the air at t_t, then the relative humidity is

$$RH = \frac{e_s}{e_t} \cdot \frac{P_t}{P_s} \times 100 \qquad (6)$$

The inherent accuracy of this method depends not only on the accuracy with which the temperatures and pressures are measured, but also on the completeness of saturation and on the degree of accuracy or validity of the temperature-vapor pressure relationship for water. The latter may be considered to have been established with sufficient certainty for most purposes in hygrometry(35,36). Both the temperature and pressure can be measured to an accuracy of at least 1/1000. The completeness of saturation can be assured by employing a recirculating scheme. Thus this method has considerable inherent accuracy. Its main limitation is the time required for changing from one relative humidity to another, for this involves a temperature change.

The two-temperature principle has been used successfully in research laboratory equipment. Shaw(2) used it in a laboratory set-up for investigating the performance of hygrometers. Wiegerink(37) constructed equipment, based on this principle, for conditioning materials at constant humidities and elevated temperatures. Wexler(38) developed an apparatus capable of producing any desired relative humidity over a wide range of temperatures. Burcham(39) described a humidity oven, operating over the temperature range of 30° to 100°C, in which he achieved relative humidities of 30 to 95%.

A simplified schematic diagram illustrating how the two-temperature method may be employed on an apparatus is shown in Figure 5. By means of a gas pump, air is circulated from a saturator into a test chamber and then back into the saturator. The temperature, t_s, of the saturator and the temperature, t_t, of the test chamber are maintained at the respective desired values by thermostatted baths. Complete saturation is achieved simply and efficiently by recirculation of air over water (or ice) in the saturator, in a closed system.

The design of a practical system, based on this method, is shown in Figure 6. It differs from the elementary design of Figure 5 in that the test chamber is controlled by means of a heater inserted in the air stream rather than by immersing the test chamber in a thermostatted bath. The elimination of a thermostatted bath for the test chamber, with the resultant simplification in design and construction, is made possible by the fact that the saturator must necessarily be maintained at a lower temperature than the test chamber, and hence the only requirement for achieving any desired test-chamber temperature is the introduction of the requisite amount of heat into the air stream.

It is sometimes desirable to be able to change rapidly the relative humidity from one discrete value to another. This can be achieved in this equipment by utilizing a number of identical but independent systems that are arranged in such a fashion that their test chambers may be interchanged easily and quickly. Thus if a different saturator temperature, t_s, is maintained in each of, say, four saturators, and if the same temperature, t_t, is maintained in each of four test chambers, then the relative humidity in each test chamber is different. By interchanging the test chambers, the relative humidities therein undergo discrete changes, as each test chamber now communicates with a different saturator.

The arrangement is shown schematically in Figure 7 for two systems. The interchange of test chambers is effected by a special pneumatic switch. It consists of two ground and lapped plates, with suitable ports, to which the test chambers are attached and through which air may pass. A turn of the top plate with respect to the bottom plate advances each test chamber to a new position and connects each test chamber with a different saturator. Two such switches can be used instead of one, for greater convenience and versatility.

3.3 Divided Flow Humidity Apparatus

The principle of divided flow is employed in this apparatus to produce any desired humidity. Equipment, based on this principle, has been described by Walker and Ernst(9) for use at temperatures above freezing and by Glückauf(40) and Wexler(41) for use at temperatures below 0°C. A stream of dry air is divided accurately, usually by means of a proportioning valve, into two parts. One part is saturated with respect to water or ice; the other part is maintained dry. The two parts are then recombined in a test chamber and then exhausted into the room. The relative humidity is given by the ratio of the division.

Figure 8 is a simplified schematic diagram illustrating the principle of operation. By means of a proportioning valve, V, a flow of dry air is divided into two parts in a known ratio. One part is passed through a saturator, S, until it is completely saturated. The saturator shown in Figure 8 is designed solely for ice. It consists of a series of trays into which water can be poured and then frozen. Other types of saturators can be used equally well; the design is not limited to ice saturators. The air, after emerging from the saturator is then mixed in a mixing chamber, C_M, with the other stream that has been maintained dry, and then allowed to exhaust through a test chamber, C_T, into the atmosphere. The saturator mixing chamber, and test chamber are kept immersed in a constant temperature bath.

By direct measurement, the total pressure, P_s, in the saturator and the total pressure, P_c, in the test chamber are known. The fraction, X, of air flow that is directed through the saturator is given by the setting of the proportioning valve. Since everything is at a known constant temperature, the pressure e_s of the saturated water vapor within the saturator, is also known (by recourse to standard tables of vapor pressure). The relative humidity in the test chamber is determined by these known parameters.

Consider a unit mass of air entering the proportioning valve and dividing into two parts; one part passes through the saturator and is saturated with water vapor while the other by-passes the saturator and remains dry. The portion, X, of air emerging from the saturator, will contain Xr_s mass of water vapor, where r_s is the saturation mixing ratio, that is, mass of saturated water vapor per unit mass of dry air, at the saturator temperature. After the two streams recombine, the air will contain r mass of water vapor per unit mass of dry air. The total mass of the two separate streams is equal to the mass of the recombined stream, i.e.,

$$1 + Xr_s = 1 + r$$

or

$$X = \frac{r}{r_s} \qquad (7)$$

The relative humidity in the test chamber is defined by

$$RH = \frac{e}{e_s} \times 100 \qquad (8)$$

where e is the partial pressure of the water vapor in the test chamber. From Dalton's law of partial pressures, and assuming the perfect gas laws to apply, it follows that the mixing ratio of the air-water vapor mixture in the test chamber is

$$r = \frac{M_w}{M_a} \frac{e}{P_c - e} \qquad (9a)$$

and that the saturation mixing ratio in the saturator is

$$r_s = \frac{M_w}{M_a} \frac{e_s}{P_s - e_s} \qquad (9b)$$

where M_a = molecular weight of air

M_w = molecular weight of water

Therefore

$$\frac{r}{r_s} = \frac{e}{e_s} \frac{(P_s - e_s)}{(P_c - e)} \qquad (10)$$

By substituting equation (7) and (8) into equation (10), the relative humidity is obtained in terms of known quantities

$$RH = \frac{X\ P_c}{P_s - (1 - X)e_s} \times 100 \qquad (11)$$

If the pressure drop from the saturator to the test chamber is made sufficiently small, then P_s may be considered equal to P_c. Furthermore, at low temperature, say below 0°C, e_s is negligible compared to P_s.

Equation (11) therefore reduces to

$$RH = 100\ X \qquad (12)$$

At higher temperatures, where the saturation pressure of water is no longer negligible, the relative humidity in the test chamber should be computed by equation (11).

Only under the stated conditions of small pressure drops and low temperatures is the relative humidity given by the proportioning ratio, X. On the other hand, the proportioning ratio X is a precise value of the percent mixing ratio and so is a direct measure of the absolute humidity produced by the divided flow apparatus.

A divided flow apparatus, designed specifically for use at temperatures below freezing is shown schematically in Figure 9. It comprises the following functional units: (a) the drying system, (b) the proportioning system, (c) the humidifying system, (d) the mixing chamber, (e) the test chamber, (f) the cooling system, and (g) the thermostatting system for temperature control.

Air from a high pressure source is dried by freezing in a dry ice and Stoddard's solvent bath. The dry air is then brought to room temperature, its pressure reduced and controlled by a regulator, and passed through the proportioning system.

One type of proportioning system which is used consists of a valve which divides the air in a definite ratio by means of orifices. In one design of valve six orifices of equal cross-sectional area are so arranged that by a turn of the knob of the valve, the incoming air can be divided to produce any of seven ratios: 0, 1/6, 1/3, 1/2, 2/3, 5/6, and 1. These ratios are the fractions of air entering the valve that emerge through one of the exit channels. Since this exit channel is made to communicate with the saturating system, these ratios may be used as the values for X in equations (7), (9), (11), and (12). To assure that the air will divide in accordance with one of these given fixed ratios, the pressures downstream of the proportioning valve must be equalized. This is achieved by use of two variable resistances (pressure equalization valves) and a differential mercury manometer.

The two air streams, on leaving the proportioning system, flow through the humidifying system in parallel channels, into the mixing chamber where they are combined and centrifugally mixed, then into the test chamber and are finally discharged into the atmosphere. The saturators, mixing chamber and test chamber are immersed in a liquid bath that can be controlled at any desired temperature. For this particular apparatus, the temperature range is 0° to -40°C.

The divided flow apparatus is a continuous flow device in which the air speed through the test chamber can be adjusted and controlled. The rotation of the proportioning valve and the adjustment of the equalization valves are the only operations required for changing the relative humidity. The time involved is usually a matter of 1 or 2 seconds. This permits any hygrometer under test in the test chamber to be subjected to a discrete change in relative humidity, a desirable advantage in the study of lag characteristics.

3.4 Apparatus Employing Combined Principles

Each of the generators so far described is based on a single principle of operation. It is, of course, possible to combine several of the principles for humidity generation into one apparatus. For example, the pressure humidity apparatus can be made more versatile by separately controlling the saturator and test chamber temperatures. The advantage of this is that low relative humidities can be reached without the need of extremely high saturator pressures. The relative humidity is then given by

$$RH = 100 \frac{P_t}{P_s} x \frac{e_s}{e_t} \frac{(1 - K P_t + K'P_t)}{(1 - K P_s + K'P_s)} \qquad (13)$$

where

P_t = test chamber pressure

P_s = saturator pressure

e_s = saturation vapor pressure at the saturator temperature

e_t = saturation vapor pressure at the test chamber temperature

In a similar fashion, the divided flow apparatus can be designed so that the saturator system and test chamber are in separate temperature baths.

4. FIXED HUMIDITY POINTS

Very convenient methods exist for establishing atmospheres of known relative humidity which depend upon the equilibrium vapor pressure of water when a chemical is dissolved in it. The solution of a material in water lowers the vapor pressure of the water. The magnitude of the lowering depends on the concentration and temperature of the solution. These methods essentially provide fixed humidity points. They are ideally suited for controlling the relative humidity of a small space. Usually, little more is required than an enclosed space and an appropriate amount of chemical and water. Equilibrium conditions are more rapidly established, however, when air circulation or stirring, as by means of a fan or blower, is employed. When air circulation is used, the motor for driving the fan or blower is mounted externally to the test chamber to reduce any tendency for the chamber to warm up due to motor heat. The air circulation should be moderate, to reduce heating effects. In all these methods, the attainment of equilibrium depends on maintaining the chamber free of humidity sources or sinks. For this reason, the chamber should be fabricated from non-hygroscopic materials, preferably metal or glass. Materials, like wood, which are highly hygroscopic should not be used.

4.1 Saturated Salt Solutions

The saturated salt solution method is inexpensive, simple and produces relative humidities that are roughly independent of temperature. The decided advantage of a saturated solution is that it can be made without measuring either the amount of salt or water. Since the concentration is fixed, for a given temperature, the ambient relative humidity is fixed. A saturated solution therefore provides an easily attained fixed humidity point. It is only useful at temperatures above the freezing point of the solution. A sealed chamber is required for which a large glass jar or bell jar is often suitable. The salt solution is made up as a slushy mixture in a glass or enameled tray or in the glass jar, if used, with the solution spreading over as large an area as practicable. Distilled water and chemically pure salts must be used. Stirring the solution may accelerate the attainment of equilibrium.

Data for a number of saturated salt solutions have been compiled by various authors and in various handbooks(42,43,44). The salts listed in Table 1 have been particularly useful for hygrometer calibration work. The data in this table are based on dewpoint measurements(45). In general use, saturated salt solutions should not be expected to control the relative humidity to closer than about one percent relative humidity.

4.2 Water-Sulfuric Acid Solutions

Water-sulfuric acid mixtures produce atmospheres of relative humidity that depend on composition and temperature(46,47,48,49,50,51). The concentration of the mixture, at a given temperature, determines the ambient relative humidity. The temperature effect, however, is small. The liquid may be exposed in a suitable tray in a sealed chamber to give the equilibrium vapor pressure of the mixture, or air may be otherwise brought into intimate contact with the liquid. Values of relative humidity, as a function of temperature and concentration, are given in Table 2. Collins' data(48) are used for temperatures of 20° through 75°C while Wilson's compilation(46) is used for 0°C.

To obtain a desired relative humidity, it is necessary to prepare a solution of proper concentration. In use, the concentration of the solution may change and some technique is needed to periodically check or measure the concentration. One scheme is to titrate a sample with a standard base of known concentration; another is to measure the density or specific gravity. Values of specific gravity, as a function of concentration, at 20°C assuming the density of water at 4°C as unity, are listed in Table 2 and are abridged from the Handbook of Chemistry and Physics(44). The concentration of the sulfuric acid solution can then be adjusted, if necessary, by the addition of a suitable amount of water or acid.

4.3 Water-Glycerin Solutions

Water-glycerin mixtures will similarly produce atmospheres of known relative humidity(52,53). The techniques employed with water-sulfuric acid mixtures work equally well with water-glycerin mixtures. An important advantage of water-glycerin mixtures over water-sulfuric acid is that they are non-corrosive. The relative humidities obtained from various water-glycerin solutions are given in Table 3. The values are based on the work of Grover and Nicol(53), who measured the vapor pressure at 20°C and applied Duhring's rule to compute the vapor pressures at other temperatures. Table 3 also contains values of specific gravity, at 20°C assuming the density of water at 4°C as unity, abridged from the Handbook of Chemistry and Physics(44). A measurement of the specific gravity of a glycerin-water mixture provides a check on the concentration.

5. HUMIDITY CHAMBERS

In response to a sensing element, such as a mechanical hygrometer, electrical hygrometer, or psychrometer, the humidity of a closed space may be raised by water, spray or steam injection, by exposure to a water surface or wet wicks, or by the introduction of saturated or high humidity air, or the humidity may be lowered by chemical absorption or the introduction of dry air. Either manual or automatic controls may be used to achieve the desired humidity. The basic feature about humidity chambers of this kind is that they require or depend upon auxiliary humidity measuring devices for an indication of the moisture content of the air. There are many chambers of this sort described in the literature(54-64). Most of them are meant to be used at room temperature, or, perhaps, elevated temperatures, for testing materials, and electrical instruments for the deleterious effects of high humidity. Some chambers have been designed for moisture absorption or permeability studies.

It will suffice to describe a typical, simple, humidity chamber in which the required humidity is obtained by circulating the air within the chamber, either over water or a chemical absorbent(54,56).

Figure 10 is a sketch of the humidity chamber. Two trays, each with a tight cover that can be raised and lowered by external manipulation, are placed in the chamber. One tray contains a chemical absorbent, such as sulfuric acid, silica-gel, or Drierite, while the other contains distilled water, preferably with exposed cotton or linen wicks. The cover of the appropriate tray is raised until a hygrometer indicates that the desired relative humidity has been attained. The cover is then dropped and since the chamber is sealed, the humidity remains constant. The chamber may be made automatic by using the output of a sensing element, through an appropriate circuit(62,63), to raise or lower the required cover.

6. DISCUSSION AND RECOMMENDATIONS

In making precision measurements of a physical quantity the accuracy and consistency of the results depend, in large measure, on a reference or standard against which the measuring instrument can be compared. In hygrometry, the gravimetric method of water vapor measurement is usually considered as the primary standard, for it is based on fundamental principles and is capable of relatively great accuracy. In order to use the gravimetric method for calibration work, a source of constant humidity is required. The results are time averages, and the times involved in making a gravimetric determination increase as the humidity decreases. Although the method has been used extensively, there appears to be a need for further research to prescribe the best equipment, techniques and procedures to be used for attaining reproducible, consistent and accurate humidity measurements. This need is particularly acute where low moisture contents are involved.

It is impractical to use the gravimetric method for routine calibration and testing. The time, care, and effort involved limit it to the calibration of secondary standards. The microwave hygrometer, the dewpoint hygrometer and the psychrometer are instruments that may prove suitable as secondary standards. However, each of these instruments needs to be investigated and improved as to performance and accuracy to the point where the construction can be specified and the conditions of use delineated to give an expected accuracy. These instruments have the virtue that rapid humidity measurements can be made, that they are potentially capable of considerable accuracy and have a theoretical basis of operation. These instruments can be used for routine calibration or for making precision measurements.

The fixed humidity points provided by saturated salt solutions are very useful where simple and inexpensive calibration techniques are required. Unfortunately, while there is a wealth of data for many salts, there is also considerable discordance among these data. This introduces a significant uncertainty as to the value of the relative humidity produced. Further research is required to establish definitively the values of relative humidity, as a function of temperature, for an adequate number of salts to give any desired relative humidity in, perhaps, 5% increments. In addition, work should be done to establish the conditions that must be met or controlled so that the experimentally determined values of relative humidity are realized within stated accuracies.

TABLE 1

Saturated Salt Solutions
Values of Relative Humidity Versus Temperature

Temperature	Relative humidity of saturated salt solution							
	$LiCl.H_2O$	$MgCl_2 \cdot 6H_2O$	$Na_2Cr_2O_7 \cdot 2H_2O$	$Mg(NO_3)_2 \cdot 6H_2O$	$NaCl$	$(NH_4)_2SO_4$	KNO_3	K_2SO_4
°C	%	%	%	%	%	%	%	%
0	14.7	35.0	60.6	60.6	74.9	83.7	97.6	99.1
5	14.0	34.6	59.3	59.2	75.1	82.6	96.6	98.4
10	13.3	34.2	57.9	57.8	75.2	81.7	95.5	97.9
15	12.8	33.9	56.6	56.3	75.3	81.1	94.4	97.5
20	12.4	33.6	55.2	54.9	75.5	80.6	93.2	97.2
25	12.0	33.2	53.8	53.4	75.8	80.3	92.0	96.9
30	11.8	32.8	52.5	52.0	75.6	80.0	90.7	96.6
35	11.7	32.5	51.2	50.6	75.5	79.8	89.3	96.4
40	11.6	32.1	49.8	49.2	75.4	79.6	87.9	96.2
45	11.5	31.8	48.5	47.7	75.1	79.3	86.5	96.0
50	11.4	31.4	47.1	46.3	74.7	79.1	85.0	95.8

TABLE 2

Relative Humidity Obtained from Water-Sulfuric Acid Solutions

% Sulfuric Acid by weight	Specific Gravity at $\frac{20^\circ}{4^\circ}$ C	Temperature, °C					
		0	20	25	30	50	75
		Relative Humidity, %					
10	1.0661	95.9	95.6	95.6	95.6	95.6	95.6
20	1.1394	87.8	88.0	88.0	88.0	88.2	88.5
25	1.1783	81.8	82.4	82.5	82.6	83.1	83.6
30	1.2185	73.8	75.0	75.2	75.4	76.2	77.2
35	1.2599	64.6	66.0	66.3	66.6	67.9	69.5
40	1.3028	54.2	56.1	56.5	56.9	58.5	60.5
45	1.3476	44.0	45.6	46.1	46.6	48.5	50.8
50	1.3951	33.6	35.2	35.7	36.2	38.3	41.0
55	1.4453	23.5	25.3	25.8	26.3	28.5	31.1
60	1.4983	14.6	16.1	16.6	17.1	19.0	21.4
65	1.5533	7.8	9.2	9.7	10.1	11.8	14.0
70	1.6105	-	3.4	3.7	4.1	5.4	7.2

TABLE 3

Relative Humidity Obtained from Water-Glycerin Mixtures

% Glycerin by weight	Specific Gravity at $\frac{20^\circ}{4^\circ}$C	Temperature, °C			
		0	20	40	70
		Relative Humidity, %			
20	1.0470	90.0	94.2	93.9	93.1
40	1.0995	82.2	86.5	86.6	86.2
60	1.1533	70.0	73.8	73.8	74.4
80	1.2079	49.6	51.7	50.9	50.5
90	1.2347	32.4	32.0	30.9	30.3

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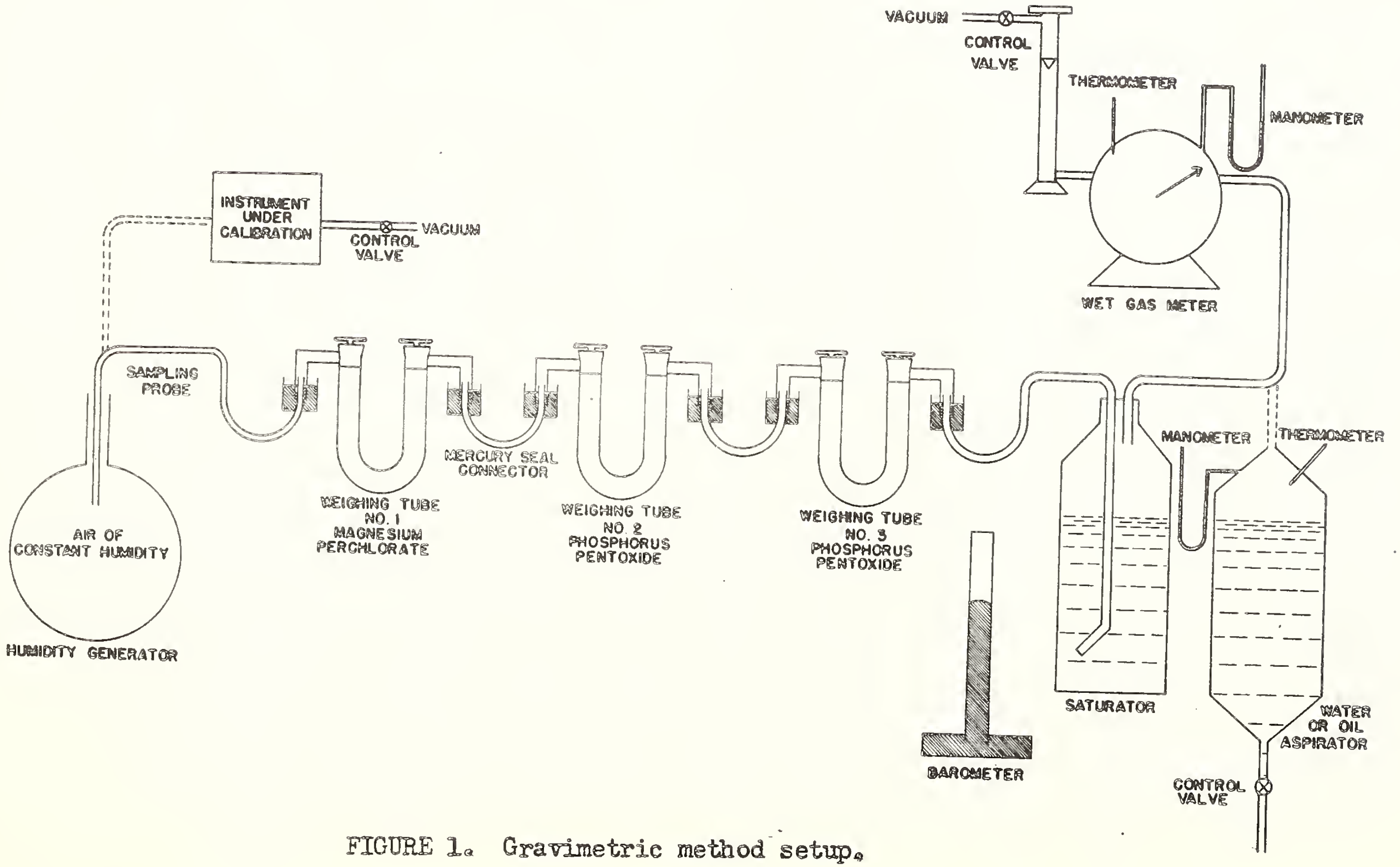

FIGURE 1. Gravimetric method setup.

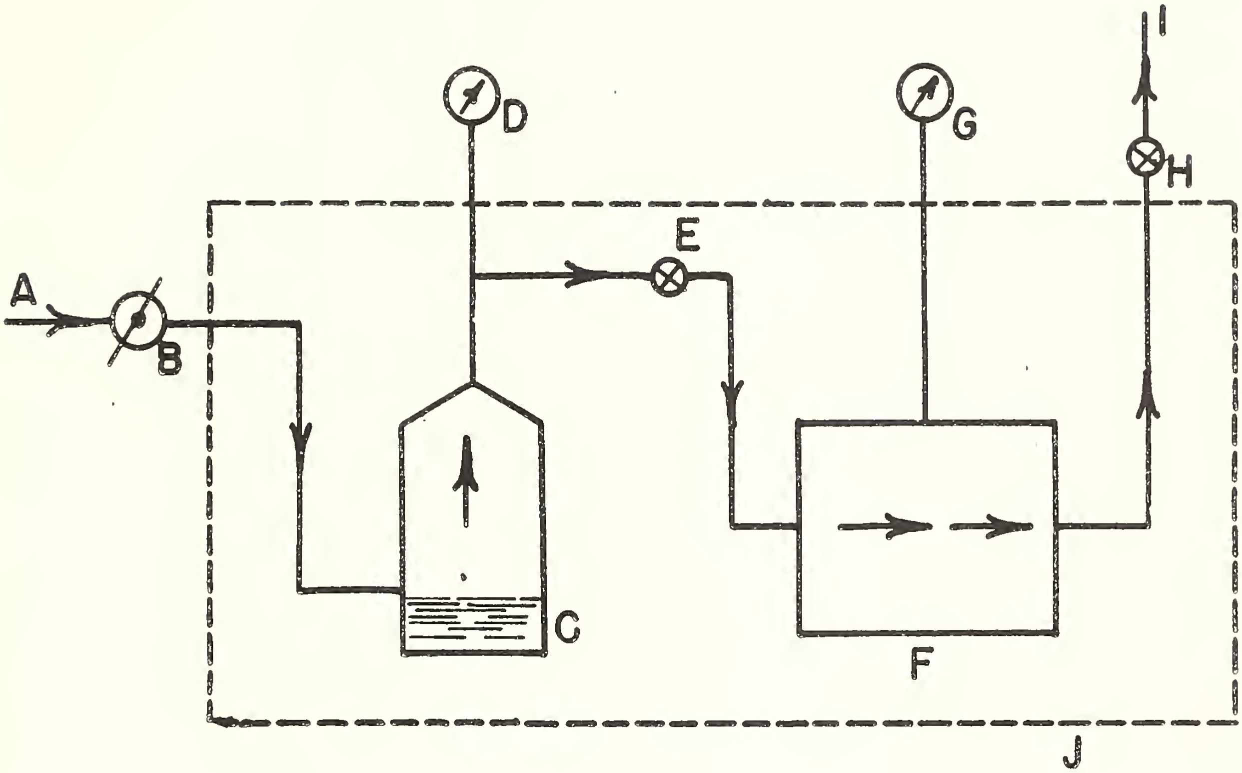

FIGURE 2. Simplified schematic drawing of the principle of operation of the pressure humidity apparatus.

A - High pressure air source	F - Test chamber
B - Pressure regulator	G - Pressure gage
C - Saturator	H - Exhaust valve
D - Pressure gage	I - Atmosphere or vacuum source
E - Expansion valve	J - Constant temperature bath

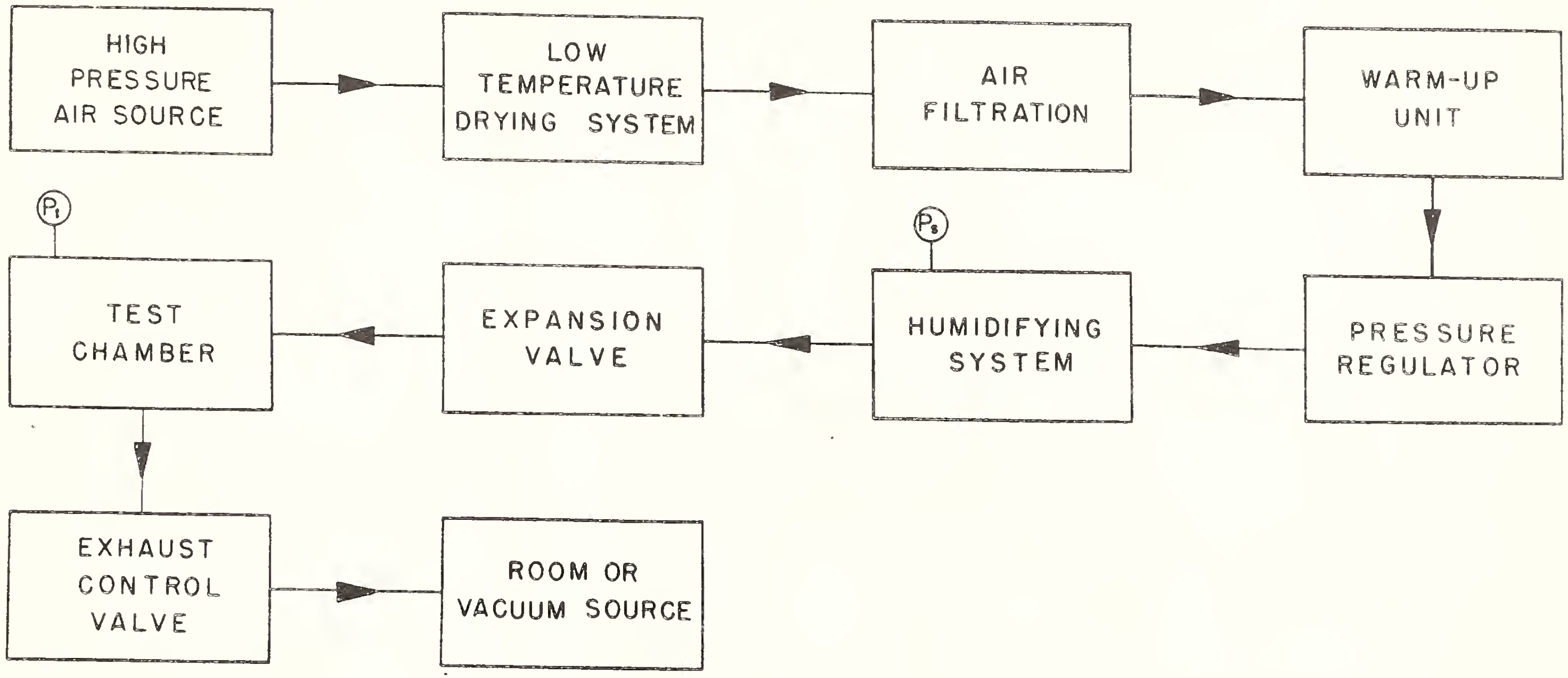

FIGURE 3. Block diagram of the pressure humidity apparatus.

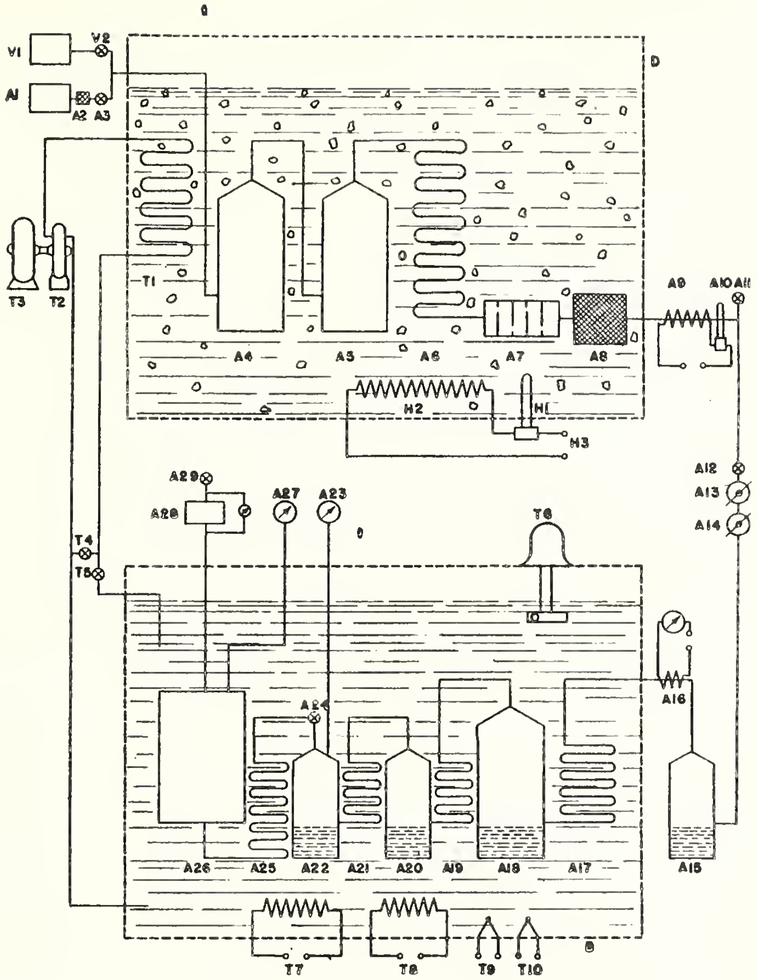

FIGURE 4. Schematic flow diagram of the pressure humidity apparatus.

A 1 - High pressure source
A 2 - Filter
A 3 - Valve
A 4 - Centrifugal water separator
A 5 - Centrifugal water separator
A 6 - Copper cooling coil
A 7 - Fin air dryer
A 8 - Low temperature filter
A 9 - Electric heater
A 10 - Bimetal thermoregulator
A 11 - Air reversal valve
A 12 - Shut-off valve
A 13 - Pressure regulator
A 14 - Pressure regulator
A 15 - External gross saturator
A 16 - Resistance thermometer and indicator
A 17, 19, 21, 25 - Copper coil heat exchangers
A 18, 20, 22 - Centrifugal saturators
A 23, 27 - Pressure gages
A 24 - Expansion valve
A 26 - Test chamber
A 28 - Linear flowmeter

A 29 - Exhaust control valve

B - Insulated liquid (varsol) constant temperature bath

D - Insulated dry ice bath

H 1 - Bimetal thermoregulator
H 2 - Electric heater
H 3 - Input voltage

T 1 - Varsol cooling coil
T 2 - Positive rotary displacement pump
T 3 - Motor
T 4 - Varsol by-pass valve
T 5 - Varsol control valve
T 6 - Centrifugal stirrer
T 7 - Constant electric heater
T 8 - Intermittent electric heater
T 9, T 10 - Thermistors

V 1 - Vacuum source
V 2 - Vacuum shut-off valve

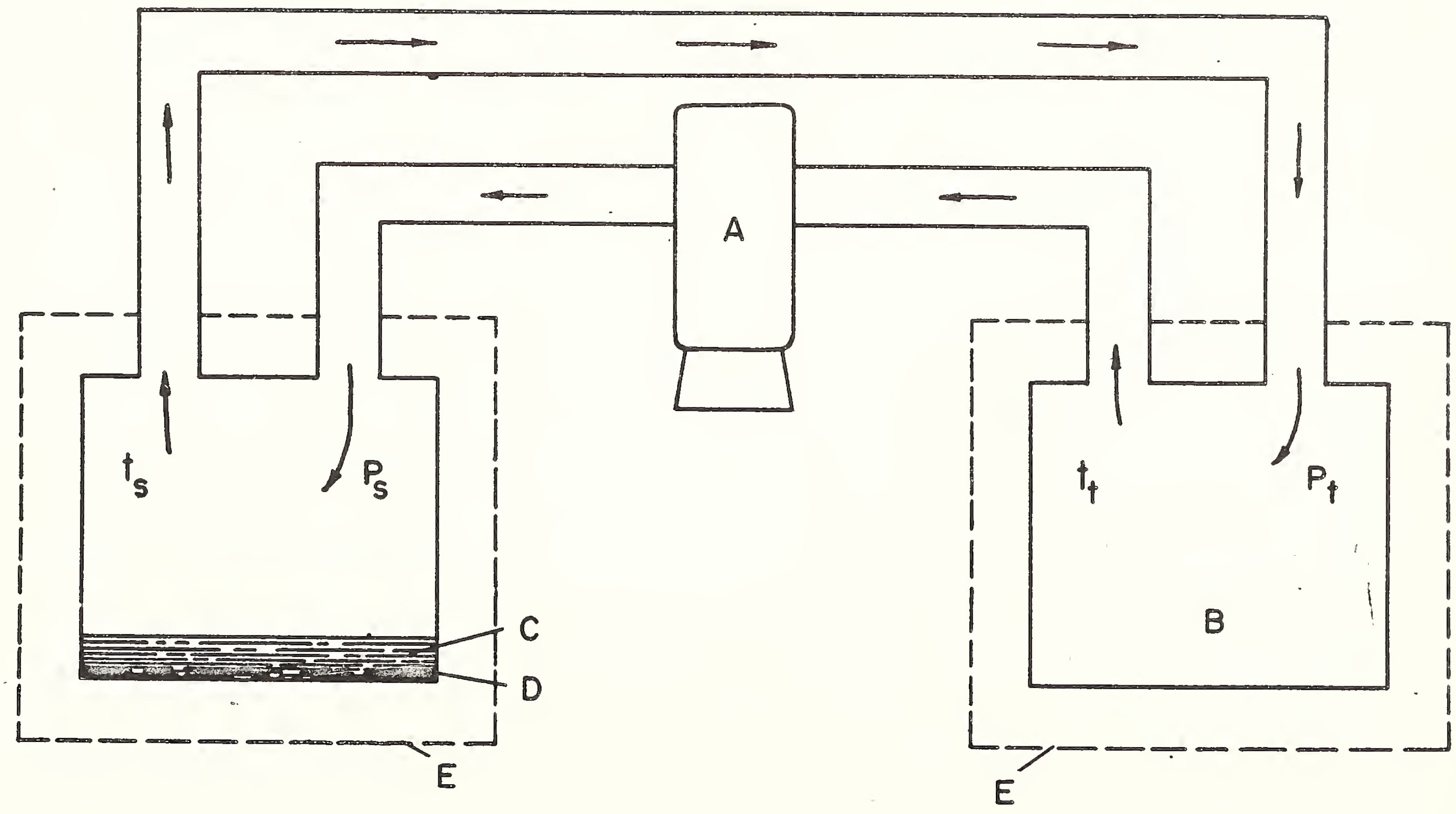

FIGURE 5. Simplified schematic diagram illustrating the two-temperature recirculating method of relative humidity production.
A, Gas pump; B, test chamber; C, water;
D, saturator; E, thermostatted bath.

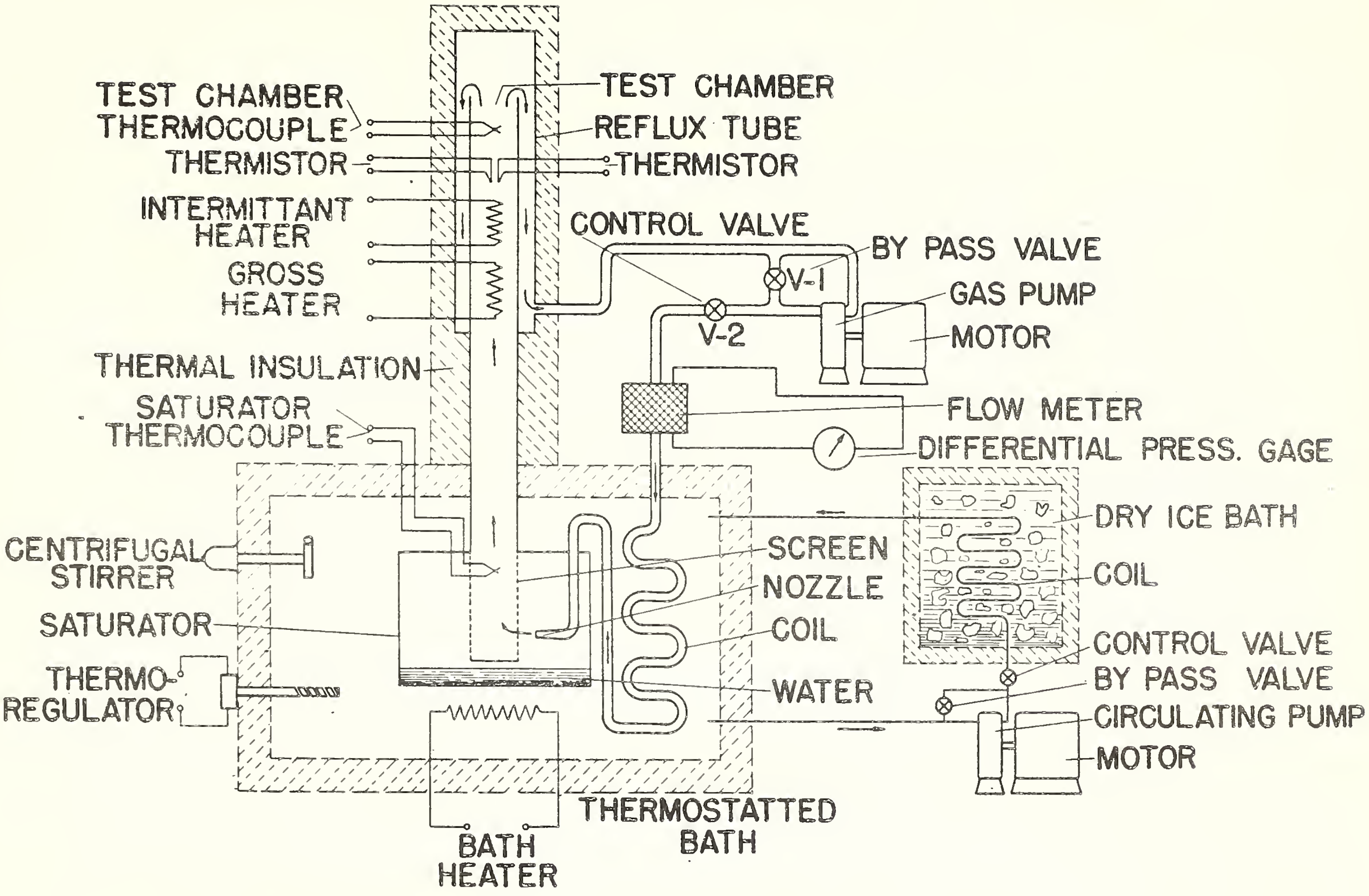

FIGURE 6. Schematic diagram of a practical two-temperature humidity apparatus.

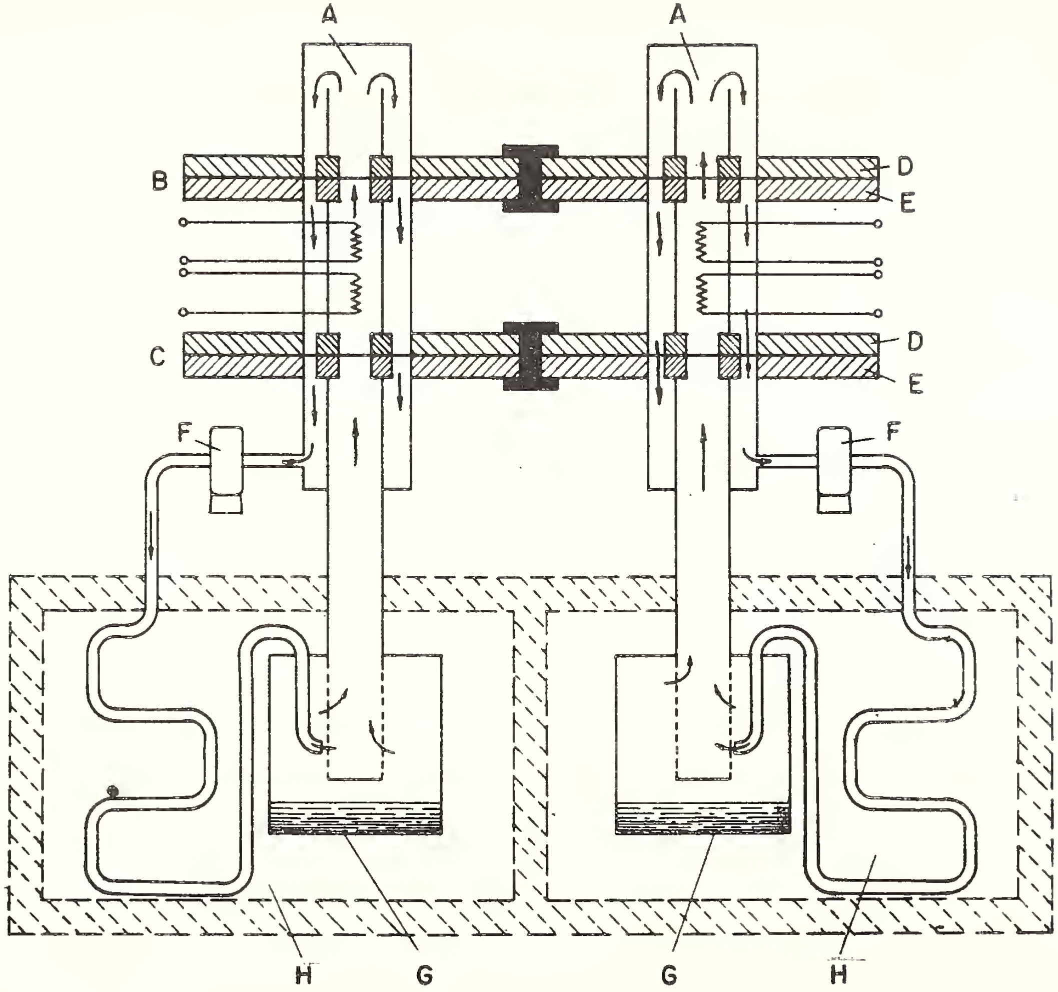

FIGURE 7. Schematic diagram of pneumatic switches for interchanging test chambers; only two of the four systems are shown; two-temperature humidity apparatus. A, Test chamber; B, upper switch; C, lower switch; D, top plate; E, bottom plate; F, gas pump; G, saturator; H, thermostatted bath.

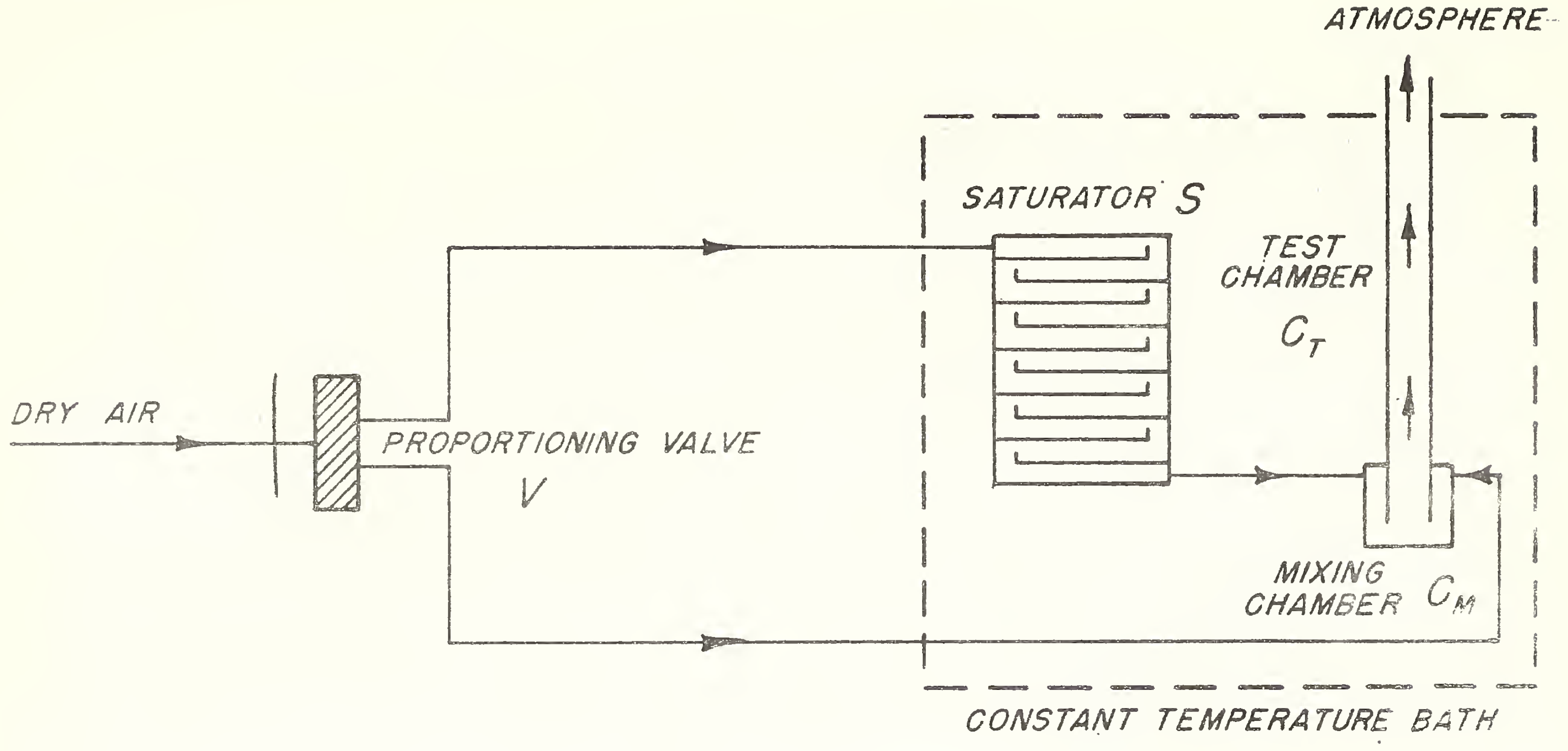

FIGURE 8. Simplified schematic diagram illustrating the principle of operation of the humidity apparatus.

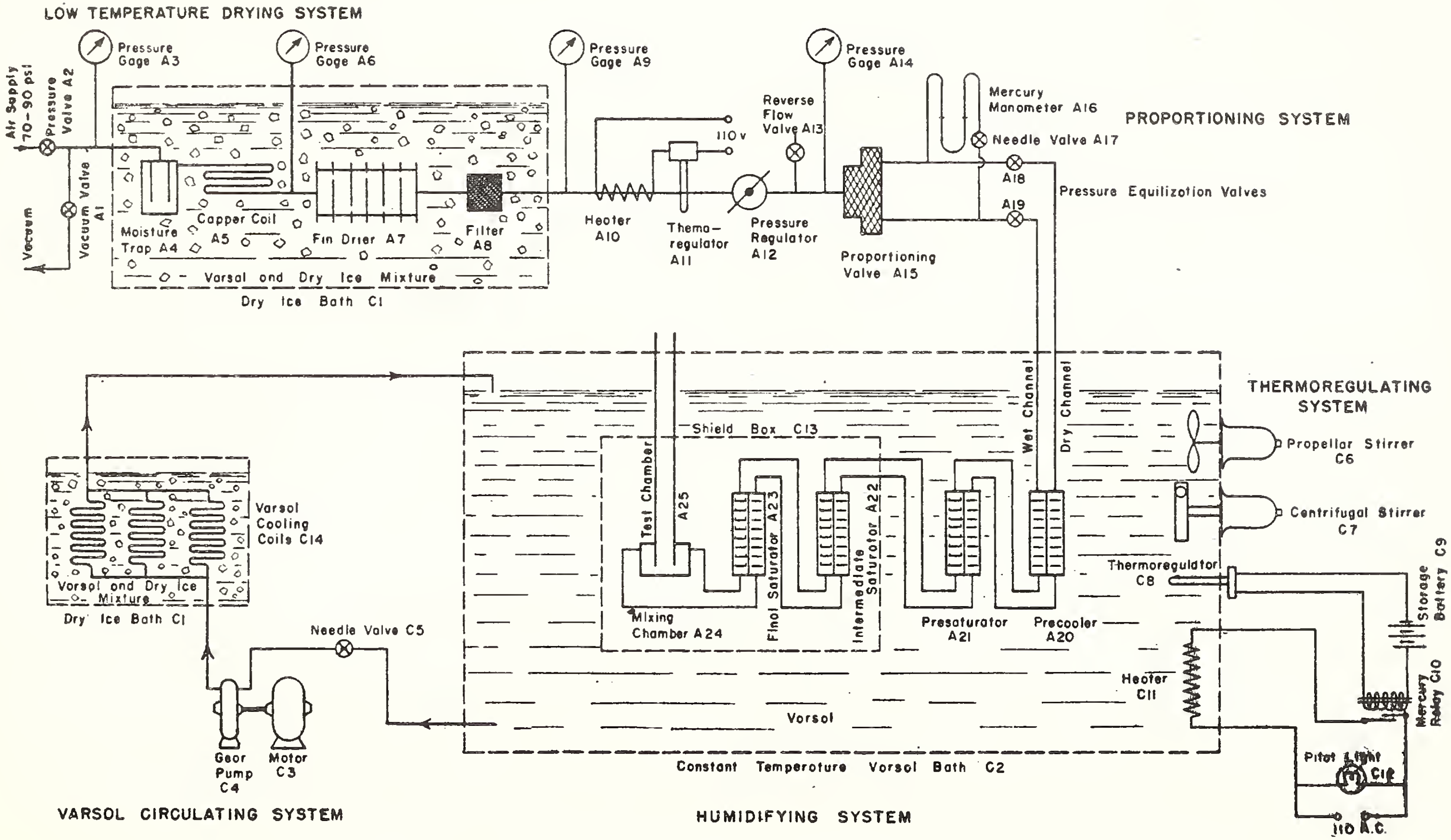

FIGURE 9. Schematic drawing of the functional units and component parts of the divided-flow humidity apparatus.

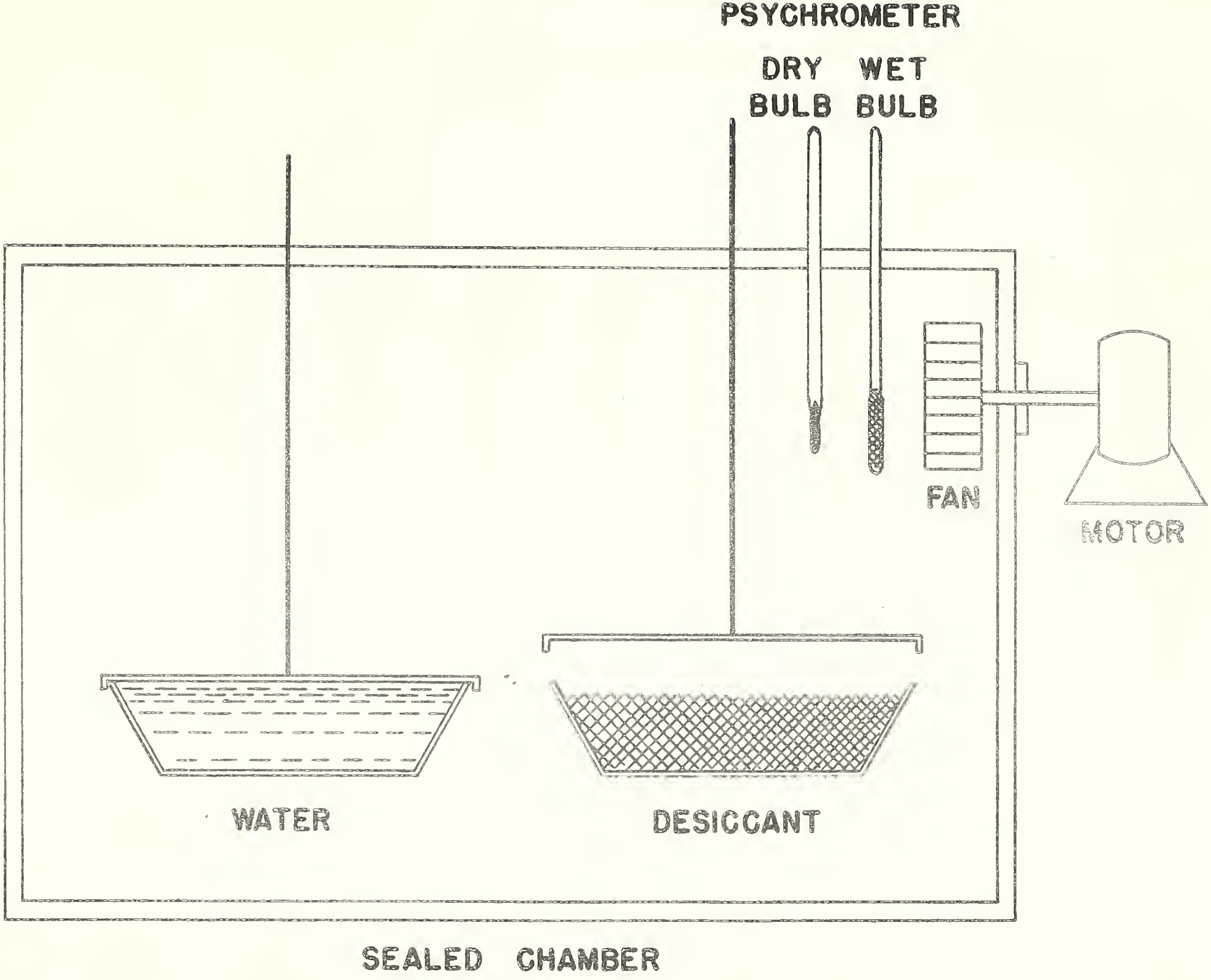

FIGURE 10 SIMPLE HUMIDITY CHAMBER