ABSTRACT: A method for precisely determining the volume of gases, irregular bodies and powdered materials, employing a variable volume hermetically sealed system including a reference compartment within which the material to be measured is placed. A predetermined gas pressure is established within said reference compartment when it is empty and again, the same pressure is established when the compartment contains the said material, a pressure detecting mechanism being employed to register the attainment of the said pressure.
METHOD FOR VOLUME MEASUREMENT

REFERENCE TO COPENDING APPLICATION

This application is a division of my copending application Ser. No. 603,034, filed Dec. 19, 1966, for Method and Apparatus for Volume Measurement new U.S. Pat. No. 3,453,881.

BRIEF DESCRIPTION OF THE INVENTION

This invention relates to a method of and apparatus for precisely determining volumes of gases, irregular bodies and powdered materials. More particularly, the present invention relates to a method of and apparatus for determining either the volume of an irregular sample by means of precise and accurate measurements of an amount of gas required to establish a predetermined pressure within a compartment varied in displacement volume by the placement of the sample therein or the volume of gas adsorbed by a sample by means of first precisely and accurately measuring the displacement volume of the sample as described above using a gas which is not adsorbed by the sample and then determining the displacement volume of the sample as described above using a gas which is adsorbed by the sample. The difference between these last two figures would represent the volume of gas adsorbed by the sample.

The type of apparatus employed here operates on the fluid mechanics principle that an increase or decrease in the volume of a container will cause a correspondingly inverse decrease or increase in the pressure of the gas within that container, assuming that the temperature of the entire system remains constant. This principle is commonly known as Boyle's Law and is represented mathematically by the following formula: \[ P_1V_1 = P_2V_2 \]

where \( P_1 \) and \( V_1 \) represent the initial pressure of the gas and volume of the container and \( P_2 \) and \( V_2 \) represent the final pressure of the gas and final volume of the container after a change in either the pressure or volume.

In the past, efforts have been made to use the above-mentioned law to determine the volume of irregular materials. One such effort employed a pair of equally variable volume containers joined together by a valving system and having a differential pressure gauge communicating with both. By placing a sample within one and varying the volume of both containers while maintaining as equal pressure in both, one could determine the displacement volume of the sample. However, only a conventional pressure detection mechanism was employed giving thereby only nominally accurate determinations of pressure within the two containers. Moreover, since two containers were used any error that occurred would be in effect multiplied by a factor of two thus doubling the inaccuracy of the entire system.

A first feature of the present invention resides in the provision of a new, unique and highly accurate method and means for determining the precise pressure within a system while employing only one reference compartment. Thus, the apparatus is capable of determining volumes to the third decimal point and possibly smaller and reducing the error multiplication factor to a figure approaching 1.

Another feature of the invention resides in the provision of an apparatus which is of relatively simple construction, easy to operate, and is extremely accurate in operation.

A further feature of the invention resides in the use of a pressure responsive bellows as a primary element of the pressure detection mechanism and the use of a suitable electric circuit connected to an incandescent lamp as a secondary element of the pressure detection mechanism.

A further feature of the invention resides in the fact that the system and method may be used not only to determine the precise volume of irregular materials, but also the precise volume of gas adsorbed by materials.

A further feature of the invention resides in the use of a method and means by which the volume of the system may be measurably increased or decreased.

Other objects, features and advantages of the present invention will become apparent from the following description, taken in conjunction with the accompanying drawings, in which:

FIG. 1 is a schematic view which will be used to explain the principle upon which the method and apparatus of the present invention are based;

FIG. 2 is a cross section of the housing of the pressure detection mechanism showing the bellows partially broken away.

APPARATUS

Generally, the apparatus of the present invention comprises a reference compartment of standard volume, means for measurably increasing or decreasing the volume of the compartment by increasing the volume of the related system, and means for accurately and precisely determining the pressure of the gas within the compartment and system. The present invention is practiced by first determining the volume of the entire system required to attain a predetermined pressure within the unoccupied compartment and system, then measuring the volume of the system required to attain that same predetermined pressure within the system while it is occupied by the irregular material, and then subtracting the figure representing volume of the system when occupied from the figure representing the volume of the system when unoccupied. The result represents the volume of the irregular material which occupied the compartment.

Rather than describe a particular embodiment of the invention, a detailed description of the pressure detection mechanism and a schematic embodiment of the entire system will be given. Thus, referring to FIGS. 1 and 2, the system 10 generally includes a sample cup 12 which has a threaded angular lip 14. Hermetically sealing cup 12 is a removable lid 16 threadedly received by lip 14. When lid 16 is properly positioned upon lip 14 of cup 12, there is created a reference compartment 18 of invariable volume. Apparatus 10 further includes a pump 20 interconnected by means of conduit 24 with reference compartment 18, three-way valve 42 and pressure detection mechanism 50. Valve 42 and mechanism 50 comprise integral and essential elements of this invention and will be discussed in greater detail in a later portion of this description. Pump 20 comprises an elongate cylinder 22 fitted with a piston 26 which is hermetically slidable therein. One end of cylinder 22 defines an orifice 28 to which conduit 24 is attached. Through the opposite end of cylinder 22 passes means for advancing and retracting piston 26. Such means may include a precision lead screw 30 which is journaled for rotation in end plate 32. A nut 34 is attached to piston 26 and engages the thread of lead screw 30 to advance and retract the piston as the lead screw is rotated. The piston 26 is prevented from rotating by pin 36 which is disposed in a slot in the cylinder wall. Thus, it will be seen that as hand wheel 38 is rotated, the piston is advanced and retracted.

Means are further provided for indicating the relative position of piston 26 within cylinder 22 so as to thereby indicate the volume in cylinder 22 swept by the piston 26. Such means may include a revolution counter 40 geared to screw 30 to indicate each complete revolution or portion thereof. Preferably, this counter should be capable of determining one thousandth of a revolution of screw 30. Thus, when hand wheel 38 is rotated, piston 26 is translated inwardly and outwardly, decreasing or increasing the total volume of the system 10 thus increasing or decreasing the total pressure of the gas within system 10. The revolution counter reading would increase with increasing volume and correspondingly decrease with decreasing volume.

Emptying into conduit 24 intermediate of reference compartment 18 and pump 20 is tubing 44 through which flows a volume of gas introduced into the system by three-way valve 42. Valve 42 has one of its three injection nozzles 46 connected to a source of inert gas such as helium under a determinable pressure, another nozzle 48 connected to a vacuum...
A suitable electric circuit \( S \) would then be connected between contact \( 60 \) and housing \( 54 \) so that upon electrical union between contact \( 60 \) and neck \( 64 \) current may flow from contact \( 60 \) through bellows \( 62 \) and base \( 63 \) to housing \( 54 \) and then through circuit \( 80 \) back to contact \( 60 \). Disposed in circuit \( 80 \) is an incandescent lamp \( 82 \) which will emit light upon the union of contact \( 60 \) and neck \( 64 \) completing the electrical circuit \( 80 \). Of course, for an electrical circuit to be completed, housing \( 54 \), neck \( 64 \) and shoulders \( 66 \) must be constructed from a suitable electrically conductive material.

After considerable use, it has become apparent that the present invention functions best if the system pressure is decreased to a predetermined pressure below atmospheric pressure. It has further become evident that reference pressures between 400 and 500 millimeters of mercury give an operation and result which is highly accurate and precise.

The predetermined pressure is that pressure within the system which will cause neck \( 64 \) to enter into electrical union with contact \( 60 \). Thus, this predetermined pressure is just slightly above or below the reference pressure of the pressure detection mechanism \( 50 \), depending on whether one chose to decrease or increase the pressure within compartment \( 28 \) and correspondingly system \( 10 \).

While a pressure responsive bellows has been disclosed as the most effective pressure detection mechanism, it should be understood that other type precise pressure detection mechanisms are equally within the scope of this invention. Other pressure detection mechanisms contemplated include an extremely accurate pressure indicator and a graduated manometer.

If the sample is activated so that under pressure it adsorbs air and under a partial vacuum it adsorbs air, the sampling gas must be inert. Helium has been found to be quite acceptable in that it is scientifically assumed that no adsorption occurs with its use. Therefore, if there is ever a question as to whether air may be adsorbed by the sample, it would be best to use helium as the gas.

If there is no possibility of adsorption, one can safely and accurately use air and expect quite satisfactory results. However, if air is used, it is strongly recommended that only decreases in pressure be used, since upon compression the moisture in the air is prone to form a condensate which would be detrimental to the system and, of course, destructive to the accurateness and precision of the test. Helium, on the other hand, will not condense under either compression or evaporation. Therefore, for another reason, helium is again recommended as the best sampling gas.

**METHOD FOR DETERMINING VOLUME**

Initially, we will assume an ideal condition in which the system is in perfect calibration, atmospheric pressure remains constant throughout the series of tests, and the gas of the system before and after evacuation is allowed to reach system temperature. First, a pressure of between 400 and 500 millimeters of mercury, preferably 450 millimeters of mercury, known hereinafter as the reference pressure, is established within the bellows \( 62 \) of pressure detection mechanism \( 50 \). Then, if lid \( 16 \) is threadedly driven onto cup \( 12 \) until reference compartment \( 18 \) is hermetically established, and valve \( 42 \) is open so as to equalize the pressure of the system with atmospheric pressure, and then closed, it will be evident that the system is closed at atmospheric pressure. Handwheel \( 38 \) is now rotated to retract piston \( 26 \), thus increasing the volume and lowering the pressure of the system according to the following formula:

\[ P_i V_i = P_f V_f \]

where \( P_i, V_i \) equals the initial pressure (atmospheric) times the initial volume of the system and \( P_f, V_f \) equals the final pressure times the final volume of the system where either the pressure or the volume is varied. If we always retract piston \( 26 \) until the pressure in the system is lowered to the point that neck \( 64 \) of bellows \( 62 \) is just expanded into electrical union with contact \( 60 \) within depression \( 54 \), the final pressure will equal the reference pressure initially.
created within bellows 62 plus a pressure differential sufficient to cause the neck 64 to enter into depression 56 and union with contact 60. The pressure differential will be constant throughout the operation of the device and thus, does not influence the results obtained. The pressure initially created within bellows 62 and the pressure differential required to cause neck 64 to enter depression 56 are known collectively hereinafter as the predetermined pressure. Therefore, letting $\Delta V$ represent the change in volume required to establish the same final pressure, $P_2$, when an irregular material $X$ having volume $V_x$ is added to the system $V_e$, the above formula may be expressed as: $P_1 V_e = P_2 (V_x + \Delta V_e)$, or

$$P_2 V_e - P_1 V_e = P_2 \Delta V_e \quad \text{or} \quad V_e = \frac{P_1 - P_2}{P_2 - P_1} \Delta V_e,$$

or finally:

$$V_e = \frac{P_2}{P_1} \Delta V_e.$$

Consequently, it becomes apparent that the volume $V_e$ equals the change in volume, $\Delta V_e$, required to attain the predetermined pressure, $P_2$, times a factor representing a proportion of final predetermined pressure to the difference between the initial pressure (atmospheric) and the final predetermined pressure.

Further, allowing $R_e$ to equal the reading of the counter 40 at the predetermined pressure without material $X$ in compartment 18; $R_0$ to equal the reading of the counter 40 at the same predetermined pressure with material $X$ in compartment 18; and $\alpha$ to equal the dial reading difference per cubic centimeter change in volume of the system, there may be expressed the following formula:

$$\alpha = \frac{R_e - R_0}{\Delta V_e} \quad \text{or} \quad \alpha \Delta V_e = R_e - R_0 \quad \frac{\Delta V_e}{\alpha} = \frac{R_e - R_0}{\alpha}$$

Preferably, $\alpha$ should equal a factor so that one revolution of hand wheel 3 equals one cubic centimeter change in the volume of the system.

Then, substituting this result in the previously mentioned formula, there results:

$$V_e = \frac{R_e - R_0}{\alpha} \frac{P_3}{P_1 - P_2}$$

or by allowing $\Delta R$ to equal $P_1 - P_2$ and $\Delta P$ to equal $R_e - R_0$,

$$V_e = \frac{\Delta R}{\alpha \Delta P} \text{ or } V_e = \frac{P_3}{\alpha \Delta P} \Delta R$$

It should be understood at this point that $\alpha$ is a mechanical correction factor which depends on the piston size, lead screw threads, and the gear ratio of the counter. For each system, $\alpha$ is a fixed quantity which does not vary with changes in temperature, pressure, and volume of the system.

Therefore, from the last formula, it may be seen that the volume of material $X$ equals the change in volume in the counter reading times a factor representing a proportion of final predetermined pressure to the product of lead screw pressure times $\alpha$. For simplicity's sake, this entire factor may be represented by $\beta$ which would therefore equal:

$$\beta = \frac{P_3}{\alpha \Delta P} \left( \frac{P_3}{P_1 - P_2} \right)$$

Then the volume of material $X$ would equal: $V_e = \beta R_0$.

Rather than compute $\beta$ for each use of the system by accurately establishing atmospheric pressure and the predetermined pressure, I have found that it is best to establish $\beta$ by determining the system volume change, $\Delta V_e$, for an object of known volume, $V_e$ Then the ratio of $V_e$ to $(R_e - R_0)$ would equal $\beta$, where $R_0$ is the reading of the counter 40 with the object of known volume, $V_e$ within compartment 18. Furthermore, it would be best to have $\beta$ approach one so that any error in the system would not be magnified by multiplication by a large $\beta$ factor. Thus, if after the comparison of $V_e$ and

$$\beta = \frac{P_3}{\alpha \Delta P} \left( \frac{P_3}{P_1 - P_2} \right)$$

(R$_2$-a-9), the $\beta$ factor is large, the predetermined pressure within the bellows may be reduced. Thus, by the following formula: $\beta = \frac{P_3}{\alpha \Delta P}$, the $\beta$ factor is reduced by reducing the predetermined pressure, $P_2$, which also changes $\Delta P$. By approaching 1 as a value for $\beta$, the system would read a volume of the irregular material $X$ as accurately as possible.

In practice, the foregoing information is utilized by first establishing a reference pressure of preferably 450 millimeters of mercury within bellows 62. Then, enclosing compartment 18 by threadedly securing lid 16 to cup 12 and setting counter 40 at a standard initial point, $R_0$, from which all measurements are taken by sweeps of piston 26 within cylinder 22 will begin. Then, permitting the entire system to move to equilibrium with atmospheric pressure by first opening valve 42 to atmospheric pressure, waiting a period of time approximating 15 to 30 seconds during which time the system may adjust, and closing valve 42. The first value for the system is now obtained by rotating handwheel 38 thus retracting piston 26 until light 82 is illuminated. At that first illumination, a reading should be taken from counter 40 and recorded as $R_1$.

To establish a $\beta$ factor, the counter is then returned to the initial point $R_1$, valve 42 is opened to atmospheric pressure, and lid 16 is removed from cup 12. An object $K$ of known volume, $V_e$, preferably known to the third decimal point, is then placed in cup 12. The above-mentioned procedure is then followed until light 82 is illuminated. The counter reading at that first illumination is then recorded as $R_2$. The above procedure employed in the selection of the predetermined pressure must be recalculated on each sample in order to determine a factor which is usable close to 1. The operator may proceed in the precise and accurate determination of the volume of an irregular material since $\beta$ remains constant so long as the surrounding environment (pressure and temperature) remains constant.

The volume of the irregular material is determined in much the same fashion as the other volumes were determined. The counter 40 is first returned to its initial point $R_1$, valve 42 is opened to atmospheric pressure and lid 16 is removed from cup 12. If the known volume object is in the cup at this time, it must be removed. The sample of unknown volume is then placed in the cup 12 and the lid 16 is replaced. After allowing the system to come to equilibrium with atmospheric pressure, valve 42 is closed. Piston 26 is then retracted until light 82 is first illuminated. A reading should be taken from the counter 40 at that time and recorded as $R_3$. The volume of the sample may then be determined by the formula: $V_e = \beta R_3 = \beta (R_3 - R_0)$.

If $\beta$ equals unity, as would be preferred, and the mechanical correction factor is such that one revolution of the lead screw gives a one cubic centimeter change in the system volume, and the counter 40 is adjusted to read zero when there is no sample in compartment 18, the volume of the sample may be read directly from the counter in cubic centimeters. Further, if the counter provides sufficient calibration, the volume may be accurately and precisely read to the third decimal point. One factor, which may destroy the accurateness of this series of tests, is a significant change in atmospheric pressure during the series of determinations. To combat this factor, it is suggested that nozzle 49 be connected to a calibrated pressure pump which would supply air at a definite and accurate pressure. Thus, each time the system was moved to equilibrium with "atmospheric pressure" the pressure would be equal to the last equilibrium established. Therefore, each increase in volume required to reduce the pressure of the system to the predetermined pressure would begin at a uniformly equal ini-
METHOD FOR DETERMINING ADSORPTION AND DESORPTION

In determining the amount of a specific gas adsorbed or desorbed by a specific sample of material due to a pressure change at constant temperature, first determine the volume of the sample as previously described using helium as the initial sampling gas. The predetermined pressure should be lower than atmospheric pressure for adsorption measurement and less than atmospheric pressure for desorption measurement. The figure resulting from the test indicates the volume of that sample with no adsorption or desorption taking place. Next, evacuate the system and introduce the gas for which an adsorption or desorption factor is desired. Determine the volume of the sample. This example will represent the volume of the sample and the volume of that gas adsorbed or desorbed by the sample. Then, by subtracting the volume determined from each helium from the "volume" as determined with the adsorbed or desorbed gas, or vice versa, a result is given representing the volume of the gas adsorbed or desorbed by that sample while varying the pressure of the system from the initial pressure to the predetermined pressure. The amount of gas adsorbed or desorbed in moles can be calculated by the following formula: \( m = PV/R T \), where \( P \) is the predetermined pressure, \( V \) is the difference in volumes which are determined by the use of helium and the adsorbed or desorbed gas, \( R \) is the gas constant and \( T \) is the operation temperature. Then the amount of gas adsorption or desorption due to a pressure change may be represented as moles of gas per unit volume of material or per unit mass of material.

It will be apparent that particular embodiment of the invention shown and described herein is of illustrative character and that various modifications in construction and arrangement of parts and sequence of steps may be made within the spirit and scope of the following claims.

Having thus described the invention, what I claim and desire to be secured by Letters Patent is:

1. A method for determining the volume of a gas adsorbed by a sample of material due to a change in gas pressure including the following steps:
   a. introducing into a volumetrically variable system containing a sample of material to be secured by Letters Patent is;