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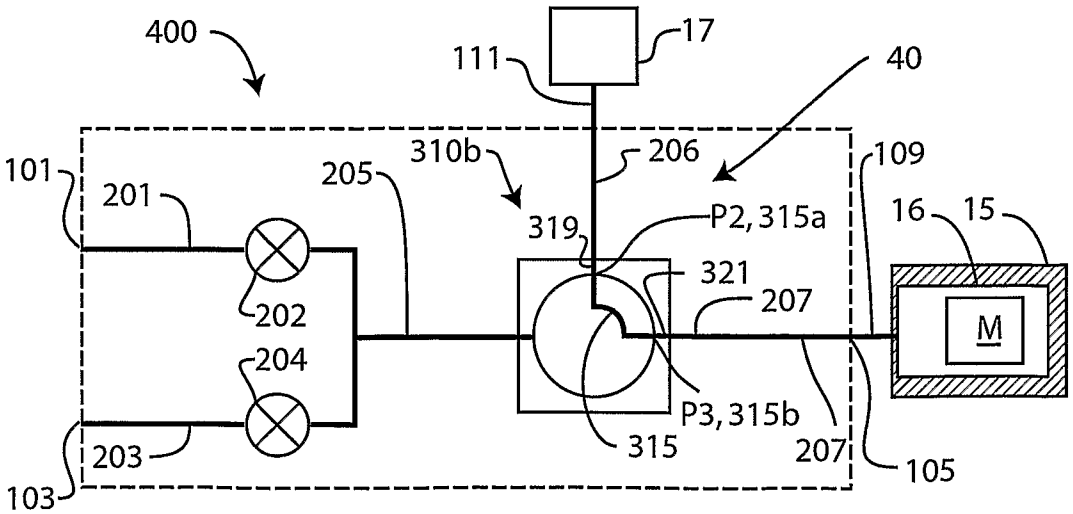
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(54) Title: METHOD AND APPARATUS FOR HANDLING SMALL QUANTITIES OF FLUIDS



(57) Abstract: The invention relates to a method and an apparatus for handling small quantities of fluids useful, for example, in measuring the gas and/or liquid sorption and desorption properties of substances such as hydrogen sorption by solid or liquid hydrogen storage materials. In one embodiment, low-volume rotary valves are used to dose samples in a sample holder. In another embodiment, a rotary valve is used as a dosing/bypass valve to both condition and measure samples. The invention also relates to an actuator for a rotary valve that has a manual override feature.

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METHOD AND APPARATUS FOR HANDLING SMALL QUANTITIES OF FLUIDS

TECHNICAL FIELD

[0001] The present invention relates to handling devices for fluids, including but not limited to gases or liquids, and specifically to the control of small quantities of fluids and to devices for performing measurements on small quantities of gases or liquids.

BACKGROUND ART

[0002] One common way to determine gas sorption properties of a material is to measure changes in pressure in a calibrated volume as gas is sorbed by a test sample of the material. The quantity of gas sorbed in each measurement is found from the equation of state of the gas. It is necessary to know three parameters to determine the quantity of gas sorbed: the pressure, temperature and volume of the gas. At constant volume and temperature, the quantity of gas sorbed is determined by measuring the change in pressure. From a known sample mass it is then possible to determine the mass concentration of gas that has been sorbed or desorbed by the sample. If the composition of the sample is well known, then the stoichiometry of gas in the sample may also be determined from the measured concentration.

[0003] Thus, for example, the pressure-composition-temperature characteristic curve (a "PCT" curve) of a sample may be obtained by dosing the sample with small "aliquots" of gas from a small volume or desorbed into a small volume such that only a small fraction of gas is sorbed or desorbed at one time. A sorption PCT curve is measured by increasing the pressure in each aliquot of gas applied to the sample in a step-wise fashion. Similarly, a desorption PCT diagram is measured by decreasing the pressure in a step-wise fashion, in the small volume into which the sample is desorbed. The conventional apparatus for performing such measurements is referred to as a Sieverts' device.

[0004] Typically, a gas dosing apparatus or Sieverts device involves dosing gas from a known volume using standard orifice and seal valves or on/off valves. Common examples of the types of valves are diaphragm valves or needle valves. These valves may be automated using pneumatic plungers or electrical solenoid mechanisms. One problem with these types of valves is that the diaphragm or stem moves in a lateral motion to open or close the valve, causing an internal volume change in the system as a whole. Volume changes on the order of

0.05 milliliters, for example, may cause significant measurement error if not taken into account when calculating the mass balance of a gas dosing system. This mass balance is critical when making specific types of measurements such quantifying the amount of gas sorption to or from a sample.

[0005] There are many problems and issues with conventional Sieverts' devices and with other prior art methods and devices for measuring sorption. Conventional devices must be operated for long periods of time taking many measurements, such as are required for generating a PCT curve. This may involve large numbers of repetitive operations, such as delivering aliquots in a PCT measurement, or switching between sorption and desorption in cycle-life measurements. It is important to obtain evenly spaced data points of sorption/desorption measurement along PCT curve. Without a detailed and even distribution of data points over the entire pressure range, the PCT curve will not be well resolved and certain portions may not be observed at all. Thus, for example, changes in the equilibrium plateau pressure identified with hydride phase transitions could be missed entirely.

[0006] Variations in air temperature in a room in which measurements are performed, or variations in the gas temperature throughout a measurement device, can produce significant errors in measuring the quantity of gases sorption or desorption from a material. Even if the surrounding air temperature is measured and introduced into the equation of state, the time lag between changes in the temperature of the surrounding air and the temperature of the gases in a Sieverts apparatus can be significant enough that the data can not be sufficiently corrected.

[0007] Small samples, such as those of 1 gram or less, and/or samples that adsorb or absorb only small quantities of gas, for example 50 milliliters STP or less, are difficult to investigate using typical volumetric devices that often have calibrated volumes and piping with volumes on the order of 10 milliliters or more. Thus, for example, standard on/off valves have internal volumes greater than 1 milliliter, especially when designed to operate at pressures greater than 30 atmospheres. However, to be able to measure gas sorption on very small samples using the Sieverts method, very small dosing volumes are required. For example, a pressure concentration temperature isotherm measurement on a 20 mg sample with 1 weight percent gas uptake under ambient conditions would require a dosing volume on the

order of 0.5 milliliters. This is much smaller that the standard valves' internal volume, without even considering the volume of any tubing, pressure transducers, or fittings.

[0008] Manual orifice-and-seat-type valves found in prior art devices are subject to inconsistent operator behavior. In particular, operators have a tendency to over-tighten valves during high-pressure experiments, resulting in valve seat damage causing the valve to leak. Manual systems have been known to operate for only a few experiments before the valves leak to the point that the data is seriously compromised.

[0009] Thus there is a need in the art for a method and apparatus that permits the accurate measurement of sorption characteristics using small quantities of sorption materials. The apparatus should preferably be easily automated, capable of operation at constant or measurable temperatures, and having repeatable volumes. There is also a need in the art for a dosing valve and other system components have very small internal volumes.

DISCLOSURE OF THE INVENTION

[0010] The present invention overcomes some of the problems of prior art valves and sorption measurement devices by providing an apparatus having a small dosing volume. In one embodiment, the apparatus is a measurement device. In another embodiment, the apparatus is a valve for dosing small quantities of fluid.

[0011] It is one aspect of the present invention to provide an automated apparatus that employs computer controlled operations and data collection.

[0012] It is another aspect of the present invention to provide an apparatus having a small dosing volume for dosing small quantities of gases and/or liquids using a rotary valve.

[0013] It is one aspect of the present invention to provide an apparatus having a combined dosing and bypass function.

[0014] It is yet another aspect of the present invention to provide an apparatus having a small dosing volume with small gas vessels, spacers, and small internal diameter gas lines (c.a. 0.15 mm diameter) to reduce the minimum working volumes to about 0.1 to 10 milliliters. This enables the measurement of gas sorption properties of small (< 1 gram) samples and samples with limited gas sorption capacities. In various embodiment the dosing

volume is approximately 0.01 milliliters, is less than approximately 0.05 milliliters, is less than approximately 0.1 milliliters, is less than approximately 0.5 milliliters, is less than approximately 1.0 milliliters, is less than approximately 5.0 milliliters, or is less than 1.0 liters

[0015] It is one aspect of the present invention to provide an apparatus having a small dosing volume to measure the sorption and desorption properties of a materials capable of gas or liquid sorption. In some embodiments, the apparatus is an apparatus for measuring the hydrogen adsorbing, absorbing or desorbing properties of hydrogen absorbing metal alloys or other compounds, hydrogen, oxygen, nitrogen, carbon-dioxide, methane and other gas adsorbing carbon materials, chemical compounds, and high-surface area absorbing substances.

[0016] It is another aspect of the present invention to provide an apparatus having a small dosing volume that can be attached to one of many different types of gas/liquid analyzers, gas/liquid manifolds, and gas sorption/desorption isotherm measuring instruments. In another embodiment, the apparatus performs measurement by applying precise aliquots of gas or liquid using an automatic rotary valve that can dose small quantities of gas or liquid (ca, 0.01 to 500 sml depending on the dosing volume and pressure). In yet another embodiment, the apparatus measures without a system volume change by dosing with a rotary valve, greatly improving the accuracy of gas/liquid uptake and release measurements.

[0017] It is yet another aspect of the present invention to provide an automated apparatus and method of measuring gas adsorption, absorption and desorption in materials.

[0018] It is one aspect of the present invention to provide an apparatus that may be attached to a gas or liquid manifold or any number of gas or liquid analyzing instruments.

[0019] It is another aspect of the present invention to provide better apparatus for measuring gas or liquid sorption and desorption properties of small samples of materials by dosing the sample with small quantities of gas or liquids.

[0020] It is yet another aspect of the present invention to provide an apparatus that has no change in system volume on filling a reservoir with a gas or a liquid and subsequently dosing the gas or liquid to a sample for sorption or desorption.

[0021] It is yet another aspect of the present invention to provide an apparatus having a rotary valve with a small slit in a plastic member that conducts gas from one port on a rotary valve to the next port. To switch between gas ports on the valve, parts of the rotary valve are rotated by either manually or automatically until the slit is aligned with a second set of ports. Because the valve opens and closes by rotating the sealing surfaces, there is no volume change associated with opening or closing the valve. In one embodiment, the slit and all gas connections are all very small, with volumes on the order of 0.1 to 1.0 microliters, and may therefore be much smaller than the total calibrated reservoir volume required for dosing.

[0022] It is one aspect to provide an apparatus connectable to a source of fluid or vacuum. The apparatus includes a sample holder having an internal volume, a dosing reservoir, and a valve having at least two ports and at least two positions. The at least two ports includes a first port fluidly connectable to the source, and a second port fluidly connected to the internal volume. The at least two positions includes a first position that fluidly connects the first port and the dosing reservoir, and defines a first enclosed volume including the internal volume, and a second position that fluidly connects the dosing reservoir and the internal volume to form a second enclosed volume. In one embodiment the valve includes two or more fluidly connected valves.

[0023] It is another aspect to provide an apparatus connectable to a source of fluid or vacuum. The apparatus includes a sample holder having an internal volume, a dosing reservoir, and a valve having at least two ports and at least two positions. The at least two ports includes a first port fluidly connectable to the source, and a second port fluidly connected to the internal volume. The at least two positions includes a first position that fluidly connects the first port and the dosing reservoir, and defines a first enclosed volume including the internal volume, and a second position that fluidly connects the dosing reservoir and the internal volume to form a second enclosed volume. The apparatus further includes a pressure measuring device, at least three ports including a third port fluidly connected to the pressure measuring device. The first position fluidly connects the dosing reservoir, the pressure measuring device, and the dosing reservoir, and the second position fluidly connects the second enclosed volume and the pressure measuring device.

[0024] It is one aspect to provide an apparatus connectable to a source of fluid or vacuum. The apparatus includes a sample holder having an internal volume, a dosing reservoir, and a valve having at least two ports and at least two positions. The at least two ports includes a first port fluidly connectable to the source, and a second port fluidly connected to the internal volume. The at least two positions includes a first position that fluidly connects the first port and the dosing reservoir, and defines a first enclosed volume including the internal volume, and a second position that fluidly connects the dosing reservoir and the internal volume to form a second enclosed volume. The apparatus further includes a plurality of sources, a passageway to fluidly connect each of the plurality of sources and the first port, and a plurality of on/off valves to control fluid communication between each of the plurality of sources and the first port.

[0025] It is one aspect to provide an apparatus connectable to a source of fluid or vacuum. The apparatus includes a sample holder having an internal volume, a dosing reservoir, and a valve having at least two ports and at least two positions. The at least two ports includes a first port fluidly connectable to the source, and a second port fluidly connected to the internal volume. The at least two positions includes a first position that fluidly connects the first port and the dosing reservoir, and defines a first enclosed volume including the internal volume, and a second position that fluidly connects the dosing reservoir and the internal volume to form a second enclosed volume. The apparatus further includes a passageway to fluidly connectable to the source and the internal volume, and an on/off valve to control fluid communication between the source and the sample holder. In one embodiment the valve has at least three positions including a third position that fluidly connects the first port and the internal volume. In another embodiment, the at least three ports is at least four ports including a fourth port fluidly connectable to the source, and the third position fluidly connects the third port and the fourth port. In yet another embodiment, the at least three ports is at least four ports including a fourth port fluidly connected to the sample holder, with the third position fluidly connects the first port and the fourth port.

[0026] It is one aspect to provide an apparatus connectable to a source of fluid or vacuum. The apparatus includes a sample holder having an internal volume, a dosing reservoir, and a valve having at least two ports and at least two positions. The at least two ports includes a first port fluidly connectable to the source, and a second port fluidly connected to the internal

volume. The at least two positions includes a first position that fluidly connects the first port and the dosing reservoir, and defines a first enclosed volume including the internal volume, and a second position that fluidly connects the dosing reservoir and the internal volume to form a second enclosed volume. The apparatus further includes an actuator operably engageable with the valve. In one embodiment, the actuator has a manual override to disengage the actuator and permit manual operation of the rotary valve.

[0027] It is another aspect of the present invention to provide a source of fluid or vacuum. The apparatus includes a sample holder having an internal volume, a dosing reservoir, and a valve having at least two ports and at least three positions. The at least two ports includes a first port fluidly connectable to the source, and a second port fluidly connected to the internal volume. The at least three positions includes a first position that fluidly connects the first port and the dosing reservoir, and defines a first enclosed volume including the internal volume, a second position that fluidly connects the dosing reservoir and the internal volume to form a second enclosed volume, and a third position that fluidly connects the first port and the internal volume.

[0028] It is an aspect of the present invention to provide device to measure sorption properties of a material sample, the device comprising: a sample holder having an internal volume for containing a material sample, a plurality of dosing reservoirs, and one or more valves operable to connect individual ones of the plurality of dosing reservoirs to the internal volume, each forming an enclosed volume.

[0029] It is an aspect of the present invention to provide a device to measure sorption properties of a material sample, the device comprising: a sample holder having an internal volume for containing a material sample, a dosing reservoir, a valve to fluidly connect the dosing reservoir and the internal volume to form an enclosed volume, two or more pressure measuring devices, and a valve to fluidly connect individual ones of the two or more pressure measuring devices to the internal volume.

[0030] It is one aspect of the present invention to provide an apparatus to control a rotary valve. The apparatus includes a frame, a mounting to attach the rotary valve to the frame, an actuator attached to the frame and operably engageable with a mounted rotary valve, and a manual override device to disengage the actuator and permit manual operation of the mounted

rotary valve. In one embodiment, the actuator is a pneumatic actuator. In another embodiment, the actuator is an electric actuator. In yet another embodiment, the apparatus includes a computer system to control the rotary valve when operably engaged

[0031] It is another aspect of the present invention to provide an apparatus to control a rotary valve. The apparatus includes a frame, a mounting to attach the rotary valve to the frame, an actuator attached to the frame and operably engageable with a mounted rotary valve, and a manual override device to disengage the actuator and permit manual operation of the mounted rotary valve. The rotary valve includes a rotatable member for operating the rotary valve, and the actuator includes a first member having a first end adapted to be connected to the rotatable member of the mounted rotary valve and a second end, and a knob attached to the second end. When the knob rotates upon rotation of the rotatable member of the mounted rotary valve. In one embodiment, the actuator includes a second member engageable with the first member, and the manual override device disengages the actuator by disengaging the first member and the second member. The manual override device may also includes a button that, when pushed, separates the interlocking portions of the first and second member.

[0032] These aspects, together with the various ancillary aspects, will become apparent to those skilled in the art from the following detailed description, are attained by the apparatus and methods of the present invention, embodiments thereof being shown with reference to the accompanying drawings, by way of example only, wherein:

BRIEF DESCRIPTION DRAWINGS

[0033] Figure 1 is a schematic of a measurement apparatus of the present invention;

[0034] Figure 2A is a schematic diagram of a first embodiment valve system of the present invention;

[0035] Figure 2B is a schematic diagram of detail of an alternative embodiment valve system of the present invention;

[0036] Figures 3A and 3B are schematic diagrams of a first embodiment of a rotary valve for use with valve systems of the present invention as a three-port, two-position valve, where

Figure 3A shows the rotary valve in a first position and Figure 3B shows the rotary valve in a second position;

[0037] Figures 4A and 4B are schematic diagrams of the valve system of Figure 2A or 2B incorporating the rotary valves of Figures 3A and 3B, respectively;

[0038] Figure 5 is a schematic of an alternative valve system of the present invention;

[0039] Figures 6A and 6B are schematic diagrams of a second embodiment of a rotary valve for use with valve systems of the present invention as a two-port, two-position valve, where Figure 6A shows the rotary valve in a first position and Figure 6B shows the rotary valve in a second position;

[0040] Figure 7 is a schematic diagram of a first embodiment of a dosing/bypass valve system of the present invention;

[0041] Figure 8 is a schematic diagram of a second embodiment of a dosing/bypass valve system of the present invention;

[0042] Figure 9 is a schematic diagram of a third embodiment of a dosing/bypass valve system of the present invention;

[0043] Figures 10A, 10B, 10C, and 10D are schematic diagrams of a third embodiment of a rotary valve for use with valve systems of the present invention as a four-port, four-position valve, where Figures 10A, 10B, 10C, and 10D show the rotary valve in a first, second, third, and fourth position, respectively;

[0044] Figure 11 is a pressure versus time plot obtained using a measurement device of the present invention;

[0045] Figure 12 is a PCT isotherm obtained using the measurements of Figures 11;

[0046] Figure 13 is a top view of one embodiment of a rotary valve actuator of the present invention;

[0047] Figure 14 is a side view of the embodiment of Figure 13;

[0048] Figures 15A, 15B, and 15C, which show one embodiment of a rotary valve actuator at different amounts of actuation;

[0049] Figure 16A is a sectional view A-A of Figure 14 showing a rotary actuator device and rotary valve in the automatic mode in a first position, Figure 16B is a sectional 16B-16B from Figure 16A, and Figure 16C is a schematic of the rotary valve;

[0050] Figure 17A is a sectional view A-A of Figure 14 showing a rotary actuator device and rotary valve in the automatic mode in a second position, Figure 17B is a sectional 17B-17B from Figure 17A, and Figure 17C is a schematic of the rotary valve;

[0051] Figure 18A is a sectional view A-A of Figure 14 showing a rotary actuator device and rotary valve being switched to a manual mode in the first position of Figure 16, Figure 18B is a sectional 18B-18B from Figure 18A, and Figure 18C is a schematic of the rotary valve;

[0052] Figure 19A is a sectional view A-A of Figure 14 showing a rotary actuator device and rotary valve switched to a second position in the manual mode, Figure 19B is a sectional 19B-19B from Figure 19A, and Figure 19C is a schematic of the rotary valve;

[0053] Figure 20A is a sectional view A-A of Figure 14 showing a rotary actuator device and rotary valve switched to a third position and reengaged in the automatic mode, Figure 20B is a sectional 20B-20B from Figure 20A, and Figure 20C is a schematic of the rotary valve;

[0054] Figure 21 is an embodiment of the invention that permits the selection of one of a number of dosing reservoirs;

[0055] Figure 22 is an embodiment of the invention that permits the selection of one of a number of pressure transducers; and

[0056] Figure 23 is an embodiment of the invention that permits the selection of one of a number of dosing reservoirs and the selection of one of a number of pressure transducers.

[0057] Reference symbols are used in the Figures to indicate certain components, aspects or features shown therein, with reference symbols common to more than one Figure indicating like components, aspects or features shown therein.

MODES FOR CARRYING OUT THE INVENTION

[0058] Although certain preferred embodiments and examples are disclosed below, it will be understood by those skilled in the art that the invention extends beyond the specifically disclosed embodiments to other alternative embodiments and/or uses of the invention and obvious modifications and equivalents thereof. Thus it is intended that the scope of the invention herein disclosed should not be limited by the particular disclosed embodiments described below. Thus, for example, in any apparatus disclosed herein, elements from different embodiments may be arranged in suitable combinations, and are not necessarily limited to any particular disclosed embodiment. In any method or process disclosed herein, the acts or operations making up the method/process may be performed in any suitable sequence, and are not necessarily limited to any particular disclosed sequence. For purposes of contrasting various embodiments with the prior art, certain aspects and advantages of these embodiments are described where appropriate herein. Of course, it is to be understood that not necessarily all such aspects or advantages may be achieved in accordance with any particular embodiment. Thus, for example, it should be recognized that the various embodiments may be carried out in a manner that achieves or optimizes one advantage or group of advantages as taught herein without necessarily achieving other aspects or advantages as may be taught or suggested herein.

[0059] Disclosed herein are apparatus and methods for handing and measuring fluid materials including, but not limited to, gases, liquids, and supercritical fluids, and referred to herein without limitation as fluids. Figure 1 is a schematic of a measurement apparatus **10** of the present invention. Measurement apparatus **10** includes a valve system **100**, a passageway **109** from the valve system into a sample container **16** of a sample holder **15** that may contain a material sample **M**, a passageway **111** from the valve system to one or more pressure measuring devices **17**, one or more temperature measuring devices **21**, and a computer system **19**. Valve system **100** includes one or more valves and passageways, and is used to control the passage of fluids between sample container **16** and one or more sources **12**. For illustrative purposes, Figure 1 shows source **12** as including a first source **11**, a second source **13**, although neither measurement apparatus **10** nor valve system **100** is limited to two sources and may, in alternative embodiments include only one source, or three or more sources.

[0060] Material sample **M** is, in general, any material that may exhibit pressure dependent changes including, but not limited to, a sorption material or materials to be measured for measuring bulk density, packing density, pore-size distribution, or surface area of non-sorbing materials.

[0061] As discussed subsequently, valve system **100** is operated to change the volume that encloses material sample **M** (and which would also preferably change the pressure within the material sample enclosing volume). In the embodiment of Figure 1, for example, first source **11** is a source of fluid at pressure up to 3,000 psi (20.7 MPa), or alternatively up to 5,000 psi (34.5 MPa), and second source **13** is a vacuum source. Pressure measuring device **17** may be, for example, a pressure transducer such as a Model 870B Micro-Baratron® capacitance manometer (MKS Instruments, Wilmington, Massachusetts), pressure transducers generally described as strain-gauge pressure transducers, or piezoelectric pressure transducer, and be a gauge pressure measuring device (measures with respect to open atmosphere), absolute (measures with respect to vacuum), or differential (measures with respect to a known reference pressure).

[0062] Thus, for example, Figure 1 shows material sample **M** within a volume that includes sample container **16** and passageway **109**. The volume of the reservoir surrounding material sample **M** includes the volume of sample container **16** and passageway **109**, and also includes a connected space within a portion of valve system **100** according to the operation of the valve system. Valve system **100** thus acts to change the reservoir enclosing a material sample **M**. In one embodiment, material sample **M** is contained within a first sample reservoir **30**, and the action of valve system **100** acts to combine the volume of the first sample reservoir with that of a dosing reservoir **20**, substantially contained within valve system **100**, to form a second sample reservoir **40**. In another embodiment, material sample **M** is contained within a second sample reservoir **40**, and the action of valve system **100** acts to reduce the volume of the second sample reservoir by that of dosing reservoir **20** to form a first sample reservoir **30**. Reservoirs **20**, **30**, and **40** are preferably either known, measured, or calibrated volumes that may be charged by a source including, but not limited to one of sources **11** or **13**.

[0063] The term "source" as used herein refers to a source of a fluid or of a vacuum, without limitation unless expressly stated herein. As used herein, the term "passageway" is a

broad term and is used in its ordinary sense and includes, without limitation except as explicitly stated, as any opening through a material through which a fluid may pass so as to act as a conduit. Passageways include, but are not limited to, flexible, inflexible or partially flexible tubes, bores through materials, or any other structure that can act as a conduit and any combination or connections thereof. The passageway materials or internal surfaces of passageways are preferably inert to material flowing therethrough. A passageway, as used herein, also includes separable portions that, when connected, form a passageway. In some embodiments, passageways are formed by connections that include, but are not limited to removable fittings, such as VCR fittings or bulkhead fittings, or by permanently coupling separate passageways to form longer passageway. The term "dosing reservoir" as used herein refers, without limitation and unless expressly stated herein, to an internal volume that may be used to selectively increase or decrease the volume of fluid within an internal volume of a sample holder, and thereby add or remove fluid that is in contact with the material sample. The act of combining or removing fluids using dosing reservoirs is a "dosing" operation that "doses" a material sample contained therein with a "dosing volume." The processes of sorption or desorption with the material sample depend on the change in fluid pressure at the material sample upon dosing.

[0064] In one embodiment, computer system **19** operates valve system **100** to obtain repetitive data. Thus, for example, software commands computer system **19** to simulate the manual operations that an experimenter would perform on an identical system with manual valves, and which may run for hours, days or months to obtain measurements on a material sample. Thus, for example computer system **19** may contain programming to provide aliquots to a material sample at every increasing or decreasing pressures and/or temperatures to obtain sorption data, such a PCT curve. Thus, for example, measurement apparatus **10** may control a commercial gas sorption analyzer such as PCTPro-2000 (Hy-Energy LLC, Newark, CA) and which is described, in part, in U.S. Patent Application Serial No. 10/440,069, filed May 17, 2003, GROSS, "METHOD AND APPARATUS FOR MEASURING GAS SORPTION AND DESORPTION PROPERTIES OF MATERIALS," the contents of which are incorporated herein by reference. The automatic operation of valves is well known in the field and includes, for example, air-operated or electrically controlled devices. In an alternative embodiment, some or all of valve system **100** is manually operated.

[0065] In one embodiment, one or more of some or all of valve system **100**, sample holder **15**, pressure measuring device **17** and connecting passageways are in one or more independently thermally insulated enclosures that include built-in heaters and temperature measuring devices such as thermocouples, rtds, thermostats or other temperature monitoring devices for temperature control. Thus, for example, Figure 1 shows a temperature measuring device **21** and heater or cooling elements **23** in contact with sample holder **15**. In one embodiment, the material sample and sample holder **15** is temperature controlled from high temperatures (up to approximately 1000°C) using heating elements to low temperatures such as the temperature of liquid helium or liquid nitrogen. In another embodiment, the fluid is maintained at a constant temperature slightly above room temperature by placing a portion of the valve system **100** within an insulated enclosure which is heated. In the preferred embodiment of the present invention, the heating is provided by an electric resistive enclosure heating element, however, other types of heating may also be used. The temperature is regulated using a software controller that may include PID temperature regulation, by computer system **19**, or by hardware temperature controlling devices such as thermostates that supplies power to the enclosure heating element through the enclosure heating element 110 V AC output device. Feedback for the software PID controller comes from an enclosure temperature measuring device **21** inside of the enclosure containing valve system **100** or sample holder **15**.

[0066] As described subsequently, measurement apparatus **10** may be used to determine effects of fluids from one or more of source **11** or **13** on material sample **M** with valve system **100** providing fluids, including a dose volume of known or measurable quantities of fluids, to the material sample, and performing measurements on the material sample, including but not limited to pressure or temperature measurement. Thus, for example, the fluid of first source **11** may include, but not limited to a gas, such as hydrogen gas, air, oxygen, nitrogen, krypton, argon, helium, ammonia, carbon monoxide, carbon dioxide, gaseous hydrocarbons, or methane, a liquid, such as water, acquiesce solutions, solvents, or liquid hydrocarbons; or a supercritical fluid, such as supercritical carbon dioxide, or a mixture thereof, such as humid air, or air with volatile hydrocarbons. The second source **13** is a vacuum source.

[0067] Valve system **100** provides fluid communication between two or more ports, with the embodiment of Figure 1 having a first port **101**, a second port **103**, a third port **105**, and a

fourth port **107**. Valve system **100** permits the transfer of fluids between ports, such as between either one of first port **101** (shown, for example, as arrow **G**) or second port **103** (shown, for example, as arrow **V**) and third port **105** (shown, for example, as double arrow **S**). In one embodiment, valve system **100** provides doses of fluids between two or more ports. Thus, for example, valve system **100** can transfer fluid or vacuum in dose reservoir **20** between port **101** and port **105**, or can transfer the same or a different volume of fluid in dose reservoir **20** between port **105** and port **103**. In an alternative embodiment, valve system **100** also provides direct fluid communication between selected ones of ports **101**, **103** and **105** without dosing.

[0068] Valve system **100** also selectively provides fluid communication between port **107** and one or more of ports **101**, **103**, and **105**. Pressure measuring device **17**, which is connected to port **107**, may thus selectively measure the pressure within sample holder **15** and one or more of first source **11** and second source **13**.

[0069] Although valve system **100** is well suited for use in measurement system **10**, neither the valve system, and its various component parts, or methods of operation is limited to any particular use, except as expressly stated below.

[0070] Computer system **19** controls the operation of valve system **100**, such as the fluid connections, and/or the control of doses, between different ports, and also collects and stores temperature readings from temperature measuring device **21** and pressure measuring device **17**. Thus, for example, computer system **19** can control the transfer of a dose of fluid – that is, an amount of fluid that is either predetermined or controlled by valve system **100**, or that has an amount that may be calculated based on measurements of the properties, such as temperature or pressure, of the fluid in measurement apparatus **10** or valve system **100**.

[0071] In some embodiments, it is preferred that the volume of dosing reservoir **20** is less than approximately 0.01 milliliters, less than approximately 0.05 milliliters, less than approximately 0.1 milliliters, less than approximately 0.5 milliliters, less than approximately 1.0 milliliters, less than approximately 5.0 milliliters, or less than 1.0 liters. The quantity (aliquot) of fluid in the dosing reservoir depends on the pressure, temperature and volume of the gas. It is thus advantageous to include components within measurement apparatus **10** having low internal volume including, but not limited to, electropolished stainless steel tubing

having an inner diameter of, but not limited to, 0.01 inches (0.25 mm), 0.02 inches (0.50 mm), 0.04 inches (1 mm), 0.06 inches (1.5 mm), or 0.08 inches (2 mm), low-volume rotary valves, short distances, and spacers within volumes (such as within a pressure measuring device **17**) to fill empty spaces to reduce internal volumes.

[0072] In a preferred embodiment, at least one of the valves of valve system **100** is a rotary valve. Rotary valves, such as Valvo injectors and valves (VICI Valco Instruments Co. Inc., Houston, TX) have very small internal volumes that do not change upon rotation, and are thus useful for low-volume dosing. One preferred type of rotary valve includes a small slit that conducts gas from one port on a rotary valve to the next port. To switch between gas ports on the valve, the valve is rotated until the slit is aligned with a second set of ports. Because the valve opens and closes by rotating the sealing surfaces, there is no volume change associated with opening or closing the valve. In one embodiment, the slit and all gas connections are all very small (typically on the order of 2 microliters), which is typically much smaller than the total dosing volume for making sorption measurements.

[0073] Rotary valves are known in the art having a number of ports and positions, permitting for a variety of configurations that may be used for dosing one or more samples with one or more sources. A rotary valve, in some embodiments, has the dual purpose of acting as the reservoir or part of a calibrated reservoir and the valve control device for dosing gas/liquids to a sample.

[0074] Figure 2A is a schematic diagram of a first embodiment valve system **200** of the present invention which may be generally similar to valve system **100**, except as further detailed below. Where possible, similar elements are identified with identical reference numerals.

[0075] Valve system **200** includes a first valve **202**, a second valve **204**, a third valve **210**, having a first port **211**, a second port **213**, and a third port **215**, each under the control of computer system **19**, and passageways **201**, **203**, **205**, **206**, and **207**. Passageway **201** connects port **101** and first valve **202**, passageway **203** connects port **103** and second valve **202**, passageway **205** connects the first and second valves to first port **211**, passageway **206** connects second port **213** to port **107**, and passageway **207** connects third port **215** to port **105**.

[0076] First valve **202** and second valve **204** are on/off valves that are electrically controlled by computer system **19** to control fluid communication between ports **101** and **103**, respectively, and third valve **210**. Examples of valves **202**, **204**, and any other on/off valve described herein, unless otherwise stated, include, but are not limited to, pneumatic diaphragm valves, pneumatic bellows valves, needle valves, plug valves, ball valves, or any kind of motorized or electrical solenoid valves including, but not limited to, miniture solenoid, piezo-electric, mems devices or micro-fluidic valves. Third valve **210** is a three port (**211**, **213**, **and 215**) valve having two positions – a first position that connects port **211** and **213**, and a second position that connects port **213** and **215**.

[0077] Valve system **200** may include additional valves or reservoirs. As an example, Figure 2B shows detail of an alternative valve system **200'** that is generally similar to valve systems **100** and **200**, except as follows. Valve system **200'** includes a valve **225** and a valve **227** in passageway **205**, and a passageway **221** between valves **225** and **237** that lead to a reservoir **223** that is connected to pressure measuring device **17**. Valve system **200'** allows system **10** to operate, for example, as a Sieverts' device.

[0078] In one embodiment, valve **210** is a rotary valve that is controlled by computer system **19**. Figures 3A and 3B are schematic diagrams of a first embodiment of a rotary valve **310** suitable for use as valve **210**, where Figure 3A shows rotary valve **310** in a first position **310a**, and Figure 3B shows rotary valve **310** in a second position **310b**. Rotary valve **310** may be generally similar to valve **210**, except as further detailed below. Where possible, similar elements are identified with identical reference numerals.

[0079] Rotary valve **310** is a three-port, two-position valve, where first position **310a** connects ports **211** and **213**, and second position **310b** connects ports **213** and **215**. More specifically, rotary valve **310** has a housing **311** with a surface **312** that on which a rotary element **313** can rotates as indicated by an arrow **R**. Rotary element **313** includes a passageway **315** having a first end **315a** and a second end **315b**. Housing **311** includes a first passageway **317** from first port **211** to an end **P1** on surface **312**, a second passageway **319** from second port **213** to an end **P2** on surface **312**, and a third passageway **321** from third port **215** to an end **P3** on surface **312**. Housing **311** and rotary element **313** are configured such that one or both of ends **315a**, **315b** either seat against surface **312**, or that each end **315a**,

315b aligns with one of end **P1**, **P2**, or **P3**, providing fluid communication with port **211**, **213**, or **215**, respectively, and thus connecting ports **211** and **213** or ports **213** and **215**. Rotary valve 310 may be for example, a Valco 4-port switching valve, Model DC4WM-HYE. In alternative embodiments, valve **310** may include additional ports and may be, for example, a four-port, three-position valve, where only three ports and two positions are used.

[0080] Figures 4A and 4B are schematic diagrams of a valve system **400**, where rotary valve **310** is used as valve **210** of valve system **200**, and which may be generally similar to valve systems **100** or **200**, except as further detailed below. Where possible, similar elements are identified with identical reference numerals.

[0081] An example of the use of valve system **400** in measurement apparatus **10** for dosing follows, where first source **11** and all valves and passageways contains hydrogen gas, second source **13** is a vacuum, and material sample **M** is to be tested for the ability to absorb or desorb hydrogen.

[0082] Figure 4A shows a pre-dosing configuration. Material sample **M** is in contact with hydrogen having contained within first sample reservoir **30**, which includes the space within sample container **16** not being taken up by material sample **M**, and the internal volumes of passageways **109**, **207**, and **321**. Valves **202** and **204** are operated to supply gas at a pressure that may be different from that in sample container **16**. Thus, for example, with valve **202** open ("on") and valve **204** closed ("off"), hydrogen may flow from source **11** toward pressure measuring device **17** through passageways **201**, **205**, **317**, **315**, **319**, **206**, and **111**. Alternatively, with valve **202** closed ("off") and valve **204** open ("one"), pressure measuring device **17** and the internal volume of passageways **201**, **205**, **317**, **315**, **319**, **206**, and **111** are evacuated. In either case, pressure measuring device **17** is capable of measuring the pressure within valve **310**.

[0083] When valve **310** is to rotated to position **310b**, as shown in Figure 4B, dosing occurs by changing the amount of gas in contact with material sample **M**. Specifically, in addition to the gas within first sample reservoir **30**, material sample **M** is brought into contact with the contents and volume of dosing reservoir **20**, forming second sample reservoir **40** from the internal volume fluid contained within passageways **315**, **319**, **206**, and **111**, and within pressure measuring device **17** and including the first sample reservoir **30**. Dosing reservoir **20**

includes the internal volumes of passageways **315**, **319**, **206**, and **111**, and the internal volume within pressure measuring device **17**, and thus the lengths and cross sections of the internal volumes should be kept small to have low dosing volumes. As an example 1/16 inch (1.6 mm) outer diameter electropolished stainless steel tubing with an 0.04 inch (1 mm) inner diameter. In addition to using small passageways, dosing reservoir **20** can be reduced further by filling unused internal volume within pressure measuring device **17** with solid material, such as a piece of metal placed within the unused internal volume.

[0084] Since the configuration of Figure 4B places pressure measuring device **17** in communication with material sample **M**, the change in pressure may be measured as a result of dosing the sample. The change in pressure in sample container **16** can be measured and, along with the temperature and the know volume, can be used to determine the change of fluid contained within or sorbed to the surface of material sample **M**. Pressure measuring device **17** may thus be used for the dual purpose of measuring the pressure of the fluid aliquot before dosing to or from the sample, as in Figure 4A, and then measuring the pressures drop/rise in the sample holder due to sorption/desorption, as in Figure 4B.

[0085] One example of a measurement that may be performed using valve system **400** in combination with a PCTPro-2000 (a commercial gas sorption analyzer) is shown Figures 11 and 12. The PCTPro-2000 is programmed to use valve system **400** to execute an automated sequence of doses of gas/liquid to a sample at increasing or decreasing pressures or at a constant pressure differential with respect to a previous dose's final measured pressure. By waiting after each dose until an equilibrium sorption/desorption pressure is obtained and then measuring this pressure the quantity of gas/liquid taken up or released from the sample can be calculated. This equilibrium pressure versus the cumulative uptake or release of gas/liquid can be plotted. In the case of a gas, this plot represents and equilibrium isotherm of the gas/liquid interaction with the sample.

[0086] Figure 11 is a pressure versus time plot obtained using a measurement device of the present invention, and Figure 12 is a PCT isotherm obtained using the measurements of Figures 11. The pressure of each dose is below the pressure in the sample holder causing material sample to desorption. Once the pressure in the reservoir is stabilized, the pressure is measured the quantity of gas or liquid is determined by knowing the calibration of the

reservoir volume and using gas/liquid pressure-temperature-volume relationships (such as the "ideal gas law").

[0087] More specifically, Figures 11 and 12 show a desorption isotherm of the release of hydrogen from a sample of a single sliver of $LaNi_5$ having a mass of approximately 45 milligrams. Dosing reservoir **20** has a volume of approximately 0.5 milliliters. The pressure data collected as a function of time is shown in Figure 11. This raw data was used to calculate the sample's gas concentration released that is plotted in the PCT isotherm shown in Figure 12.

[0088] More specifically, the quantity of gas ad/absorbed or desorbed for each measurement, N_j, is given by:

$$N_j = \frac{1}{RT} \sum_j (P_{Rj} V_R + P_{j-1} V_C - P_j (V_R + V_C)) \quad \text{EQ. 1}$$

where j is the dosing step, V_R is the dosing reservoir volume, V_C is the sample holder internal volume, P_{Rj} is the pressure measured in the dosing reservoir V_R at step j when the rotary valve is in a first position and the reservoir volume is in fluid communication with the source, P_{j-1} is the pressure measured in the second position inside of the second enclosed volume including the dosing reservoir and the internal volume $V_R + V_C$ at the previous measurement step j-1 where Pj-1 is then taken to be equal to the pressure inside of the first enclosed volume which is the internal volume Vc when the rotary valve is in the first position of measurement step j, P_j is the pressure measured inside of the second enclosed volume including the dosing reservoir and the internal volume $V_R + V_C$ at measurement step j when the rotary valve has been rotated into the second position, R is the universal gas constant, and T is the average gas temperature. When the change in pressure finally slows to a specified limit, this pressure reading P_j is taken as the equilibrium pressure P_{Ej} and the calculated quantity of gas sorbed N_j corresponding to the equilibrium pressure is taken as the equilibrium concentration N_{Ej} sorbed or desorbed in that aliquot measurement j. For PCT measurements the process is repeated. The sum of N_{Ej} is plotted versus P_{Ej} to form a PCT isotherm graph. The methods by which temperature and pressure measurements are used to determine PCT isotherms are described in

greater detail, for example, in U.S. Patent Application Serial No. 10/440,069, filed May 17, 2003, GROSS, "METHOD AND APPARATUS FOR MEASURING GAS SORPTION AND DESORPTION PROPERTIES OF MATERIALS."

ALTERNATIVE EMBODIMENTS

[0089] Figure 5 is a schematic of an alternative valve system **500** of the present invention which may be generally similar to valve systems **100**, **200** or **400**, except as further detailed below. Where possible, similar elements are identified with identical reference numerals.

[0090] Valve system **500** differs from the previously described valve systems in that it includes a single fluid port, port **101**, a two-port, two-position valve **510**, a passageway **501** from passageway **205** to a port **107a**, and a passageway **503** from passageway **207** to a port **107b**. Each port **107a** and **107b** may be attached to a pressure measuring device **17**. This embodiment permits the measure the pressure of the fluid aliquot before dosing to/from the sample (via port **107a**) and the pressure drop/rise in the sample holder due to absorption(adsorption)/desorption (via port **107b**).

[0091] In one embodiment, valve **510** is a rotary valve. Figures 6A and 6B are schematic diagrams of a second embodiment of a rotary valve **610** suitable for use as valve **510**, where Figure 6A shows rotary valve **610** in a first position **610a**, and Figure 6B shows rotary valve **610** in a second position **610b**. Rotary valve **610** may be generally similar to valves **210**, **310**, or **510**, except as further detailed below. Where possible, similar elements are identified with identical reference numerals.

[0092] Rotary valve **610** has a housing **611**, which is generally similar to housing **311**, except that it does not have a passageway **319**. Rotary valve **610** is a two-port, two-position valve, where Figure 6A shows the rotary valve in a first position **610a** and Figure 6B shows the rotary valve in a second position **610b**. The use of rotary valve **610** for valve **510** can result in a lower dosing volume, since the port for measuring pressure (such as port **213** of Figure 2) is eliminated, further reducing the volume of dosing reservoir **20** to the volume of passageway **315** which can be, for example, less than 0.1 milliliter. Alternatively a valve **210** could be used in place of valve **610**, with port **213** sealed off or provided with a sealed passageway of constant volume.

[0093] Alternative embodiments, referred to herein as dosing/bypass valve systems, provide for both dosing and dosing bypass by providing for direct contact of port **105** and either one of ports **101** and **103**. Figure 7 is a schematic diagram of a first embodiment of a dosing/bypass valve system **700** of the present invention which may be generally similar to valve systems **100**, **200**, **400**, or **500**, except as further detailed below. Where possible, similar elements are identified with identical reference numerals.

[0094] Dosing/bypass valve system **700** includes an on/off valve **703** within a passageway **701** than connects passageways **205** and **207**. Valve **703**, which is controlled by computer system **19** or, alternatively, is manually operated, provides a bypass to valve **210**, which may be a rotary valve. Valve system **700** is particularly useful for measurements where the material sample **M** must be prepared by directly exposing the sample to the fluid to a vacuum, as from one of sources **11** or **13**. Thus, for example, with valve **202** and **703** open ("on") and valve **204** closed ("off"), material sample **M** is exposed to the fluid provided by port **101** (for example, hydrogen gas). With valve **204** and **703** open ("on") and valve **202** closed ("off"), material sample **M** is exposed to the fluid provided by port **103** (for example, a vacuum).

[0095] Figure 8 is a schematic diagram of a second embodiment of a dosing/bypass valve system **800** of the present invention which may be generally similar to valve systems **100**, **200**, **400**, **500**, or **700** except as further detailed below. Where possible, similar elements are identified with identical reference numerals.

[0096] Dosing/bypass valve system **800** includes a valve **810** having at least four ports and three positions. More specifically, valve **810** has first, second, and third ports **211**, **213**, and **215**, respectively, and a fourth port **803**, and a passageway **801** that connects passageway **205** to port **803**. Valve **810**, which may be generally similar to valve **210** or **510** except as noted subsequently, includes a third position that connects ports **803** and **215**. As with valve **210**, valve **810** has a first position that connects that connects ports **211** and **213**, a second position that connects ports **213** and **215**, the operation of which have been described previously, and a third position that connects ports **803** and **215** and which is useful, in measurement apparatus **10**, in providing direct contact between material sample **M** and sources **11** or **13**.

[0097] Figure 9 is a schematic diagram of a third embodiment of a dosing/bypass valve system **900** of the present invention which may be generally similar to valve systems **100**,

200, **400**, **500**, **700**, or **800** except as further detailed. Where possible, similar elements are identified with identical reference numerals.

[0098] Dosing/bypass valve system **900** includes a valve **910** having at least four ports and three positions. More specifically, valve **910** has first, second, and third ports **211**, **213**, and **215**, respectively, and a fourth port **903**, and a passageway **901** that connects passageway **207** to port **903**. Valve **910**, which may be generally similar to valve **210**, **510**, or **810** except as noted subsequently, includes a third position that connects ports **903** and **211**. As with valve **210**, and **810**, valve **910** has a first position that connects that connects ports **211** and **213**, a second position that connects ports **213** and **215.** The third position that connects ports **903** and **211** and which is useful, in measurement apparatus **10**, in providing direct contact between material sample **M** and sources **11** or **13**.

[0099] In one embodiment, valve **810** or **910** is a rotary valve. Figures 10A, 10B, 10C, and 10D are schematic diagrams of a third embodiment of a rotary valve **1010** suitable for use as valve **810** or **910** where Figure 10A shows rotary valve **1010** in a first position **110a**, Figure 10B shows rotary valve **1010** in a second position **1010b**, Figure 10C shows rotary valve **1010** in a third position **1010c**, and Figure 10D shows rotary valve **1010** in a third position **1010d**. Rotary valve **1010** may be generally similar to valves **210**, **310**, **510**, **610**, or **810** except as further detailed below. Where possible, similar elements are identified with identical reference numerals.

[0100] Rotary valve **1010** has a housing **1011**, which is generally similar to housings **311** or **611**, and includes a passageway **1001** from end **P4** on surface **312** to a port labeled **803/903**. Rotary valve **1010** is a four-port, four-position valve, where first position **1010a** connects ports **211** and **213**, second position **1010b** connects ports **213** and **215**, third position **1010c** connects ports **215** and **803/903**, and third position **1010d** connects ports **211** and **803/903**. Rotary valve **1010** has a housing **1011** within a surface **312** that on which a rotary element **313** can rotates as indicated by an arrow **R**. Housing **311** and rotary element **313** are configured such that one or both of ends **315a**, **315b** either seat against surface **312**, or that each end **315a**, **315b** aligns with one of end **P1**, **P2**, **P3**, or **P4** providing fluid communication with port **211**, **213**, **215**, or **803/903,** respectively, and thus connecting ports **211** and **213**, ports **213** and **215**, or ports **803/903** and **215.**

[0101] Rotary valve **1010**, which is a four-position valve, may be used either as valve **810** or as valve **910**. For use as valve **810**, the three positions of valve **810** described above correspond to positions **1010a**, **1010b**, and **1010c** respectively. For use as valve **910**, the three positions of valve **910** described above correspond to positions **1010a**, **1010b**, and **1010d** respectively.

[0102] Alternative embodiments include using the following uses of rotary valves having multiple ports and positions include, but are not limited to: 1) a rotary valve that can connect multiple ports to multiple sample holders, enabling the measurement of sorption properties of multiple samples. Such an embodiment may either use one pressure measuring device that is sequentially placed in fluid communication with individual sample holders, or may have multiple pressure measuring devices to obtain data from multiple sample holders, or may have one pressure measuring device per sample holder. 2) A rotary valve that can connect multiple ports having different dosing reservoirs, which may be generally similar to dosing reservoir **20**, to a sample holder. In one embodiment, the volume of the dosing reservoirs range from approximately 0.001 ml to approximately 1 liter, or more. These different dosing reservoirs may be selected manually or through the use of automation software, or 3) connecting multiple ports to multiple pressure measuring devices. This allows the measurement and dosing of gases or liquids over different ranges of pressures (for example 0.001 to 1.0 bar or 0.1 to 30 bar). These different pressure measuring devices may be selected manually or through the use of automation software. 4) connecting multiple ports to multiple pressure measuring devices and multiple dosing reservoir volumes. This allows the measurement and dosing of gases or liquids from a wide range of volumes (for example 0.001 ml to approximately 1 liter) over different ranges of pressures (for example 0.001 to 1.0 bar or 0.1 to 30 bar).

[0103] Examples of some of these alternative embodiments are shown in Figure 21 as an embodiment of the invention that permits the selection of one of a number of dosing volumes, in Figure 22 as an embodiment of the invention that permits the selection of one of a number of pressure transducers, and Figure 23 as an embodiment of the invention that permits the selection of one of a number of dosing volumes and the selection of one of a number of pressure transducers.

[0104] In the embodiment of Figure 21, more than one volume may be dosed. Thus, for example, Figure 21 shows, but the invention is not limited to, three dosing reservoirs **2111**, **2113**, and **2115** can be individually connected through a valve **2101** to port **213**. The different volumes may be obtained, for example, by providing different lengths of closed tubing to different ports. Valve **2101** is, for example, a rotary valve or a multiport valve or a manifold having several individual on/off valves, such as solenoid valves, that provides fluid communication between one of a plurality of input ports and one output port. The volumes of dosing reservoirs **2111**, **2113**, and **2115** of Figure 21 can each be different and range from 0.1 milliliter to 10.0 milliliters or more. The volumes are filled by selecting a volume via valve **2101** when ports **211** and **213** are connected. This provides a convenient method for selecting a range of doses. Valve **2101** may be manually operated or may be, for example, an electrically operated valve controlled by computer system **19**.

[0105] In the embodiment of Figure 22, more than one pressure measurement device may be used. Thus, for example, Figure 22 shows, but the invention is not limited to, three pressure measuring devices **17-1**, **17-2**, and **17-3**, which may each have different ranges or sensitivities, can be individually connected through a valve **2101** to port **213**. The three pressure measuring devices **17-1**, **17-2**, and **17-3** have ranges, for example, from approximately 0-1 Torr, (0 – 133 Pa) from 0-1000 Torr (0 - .133MPa), up to 100 psi (0.69 MPa), up to 250 psi (1.7 MPa), up to 1000 psi (6.9 MPa), up to 3000 psi (21 MPa), up to 5000 psi (34 MPa), or up to 10,000 psi (69 MPa). This embodiment permits increased sensitivity by changing pressure transducers during an experiment.

[0106] The embodiment of Figure 23 combines a system having more than one dosing reservoir and more than one pressure measurement device. Thus, for example, Figure 23 shows, but the invention is not limited to, three volumes **2111**, **2113**, and **2115** can be individually connected through a valve **2101-1** to port **213**, and three pressure measuring devices **17-1**, **17-2**, and **17-3**, which may each have different ranges or sensitivities, can be individually connected through a valve **2101-2** to port **213**.

ROTARY VALVE OPERATION

[0107] One embodiment of the present invention includes a valve actuator that can be switched between either an automatic dosing mode or a manual bypass (charge or discharge)

mode. Thus, for example, one embodiment includes a rotary valve actuator for valve system including but not limited to dosing/bypass valve systems **800** or **900**. The rotary valve actuator may be, but is not limited to, an electrical or pneumatic actuator.

[0108] Figures 13 and 14 are top and side views, respectively, of a first embodiment rotary valve actuator **1300** for operating a rotary valve **1350**, and Figure 16A is a cross-sectional view A-A of Figure 14. Rotary valve actuator **1300** includes a pneumatic actuator **1311** and a linkage that, under the control of computer system **19**, can rotate a rotary valve, including but not limited to one of rotary valves **310**, **610**, or **1010**, through two or more valve positions.

[0109] Rotary valve actuator **1300** includes a base **1301** having a first hanger **1303**, a second hanger **1307**, and a third hanger **1305**. Rotary valve **1350** has a rotary valve housing **1351**, two or more ports, indicated as ports **1352**, **1353**, **1354**, and **1355**, and an internal rotary element **1348** having passageways connect the valve ports. Rotary valve housing **1351** is restrained by second hanger **1307**.

[0110] An outer shaft **1325** is attached to rotary element **1348** by shaft adaptor **1347**, extends through a linkage arm **1331** which has a transverse slot **1344** facing housing **1350**, is rotatably restrained by hanger **1305**, and terminates at knob **1323**. Attachment of rotary element **1348** and shaft adaptor **1347** includes a slot **1346** in the shaft adaptor that accepts a tang **1349** of the rotary element. Shaft adaptor **1347** is fixed to outer shaft **1325** by a compression fit, transverse pin, or, alternatively, by a set screw (not shown). Knob **1323** is fixed to outer shaft **1325** by compression or, alternatively, by one or more set screws (not shown). Knob **1323** is thus connected to rotary element **1348**. Low slip coatings or sleeves may be included to reduce friction between rotating surfaces.

[0111] An inner shaft **1341** passes through and moves longitudinally within the interior of outer shaft **1325**, and extends from a button **1321** that protrudes through knob **1323** to an end **1342** proximal to valve **1350**. A spring **1345** extends from shaft adapter **1347** to end **1342**, providing a force on inner shaft **1341** that forces the inner shaft towards linkage arm **1331**. Inner shaft **1341** has a long rotation pin **1343** mounted transverse to the inner shaft centerline and extending radially beyond the otherwise cylindrical shaft. Rotation pin **1343**, which is forced by spring **1345** towards linkage arm **1331**, can fit within slot **1344**.

[0112] Linkage arm **1331** is attached to a linkage clevis **1333** by a rotary arm screw **1332**. A cylinder rod **1315** of pneumatic actuator **1311** is threaded into a rod clevis **1319**, and clevis pin **1335** forms the linkage between the pneumatic actuator and the linkage arm. Pneumatic actuator **1311**, which has an air supply connection controlled by computers system **19** (not shown), is rotatably attached by pin **1313** to hanger **1303**.

[0113] As described subsequently, hanger **1307** restrains rotary valve housing **1351**, permitting the rotary element **1348** to rotate. Thus, for example, hanger **1307** may retrain a rotary valve housing, including but not limited to housing **311**, **611**, or **1011**, permitting rotation of the corresponding rotary element **1348**, which can be, for example, rotary element **313**.

[0114] Rotary arm screw **1332** can be screwed more or less into linkage clevis **1333** to reduce or extend the length of rotary arm and therefore the radius of rotation. This length can be adjusted so that the rotation caused by pneumatic actuator **1311** matches the angular displacement required by rotary valve **1350**, including, but not limited to exactly 90 degrees. In addition, cylinder rod **1315** can be screwed more or less into rod clevis **1319** to extend or reduce the longitudinal motion of the cylinder rod. This adjustment provides a means to set the position of the rotating valve so that the internal slit in the rotating valve is aligned with the ports on valve **1350**.

[0115] Providing pressure to pneumatic actuator **1311** results in linkage arm **1331** rotating about rotary valve **1350**. The operation of pneumatic actuator **1311** is illustrated, in part, in Figures 15A, 15B, and 15C, which show the device **1300** at different amounts of actuation. Specifically, Figures 15A-15C show the actuation of pneumatic actuator **1311** at increasing amounts, such that, as cylinder rod **1315** moves increasingly outwards from the pneumatic actuator, linkage arm **1331** moves through 45 degrees. The operation of cylinder rod **1315** (and therefore rotary valve **1350**) is automated through the use of computer software within computer system **19**, in communications with a digital control device that opens and closes an air-operated valve that provides or releases air from the cylinder. Air pressure can be between 10 and 200 psi. When the gas pressure to the cylinder rod **1315** is relieved, a return spring (not shown) inside (or outside) of the cylinder rod causes the cylinder rod to return to its original

position. Likewise through the reverse action just described above the rotating valve and all connected components rotate 90 degrees back to the original position.

OPERATION OF THE PNEUMATIC ROTARY VALVE ACTUATOR

[0116] As described subsequently, rotary valve actuator **1300** has two modes of operation that are controlled by the position of button **1321**. With button **1321** in the "out" position (that is, away from rotary valve **1350**), rotary valve actuator **1300** is in a first, "automatic," mode of operation, where the operation of rotary valve **1350** is operably attached to, and controlled by, pneumatic actuator **1311**. In the first mode of operation, linkage arm **1331** is operably connected to rotary element **1348**, and changing the pressure of a fluid within pneumatic actuator **1311** causes a portion of rotary valve **1350** to move from one position to another as shown, for example, as the arrow **R** in Figures 3A, 6A and 10A. With button **1321** in an "in" position (that is, pushed in towards rotary valve **1350**), rotary valve actuator **1300** is an a second, "manual," mode of operation, where linkage arm **1331** is disengaged from rotary valve **1350**, permitting manual operation of the rotary valve which may occur, for example, by rotating knob **1323**.

[0117] The automatic operation of valve **1350** is illustrated with reference to Figures 15A, 15B and 15C, Figures 16A, 16B, and 16C, and Figures 17A, 17B, and 17C. Figure 16A is a sectional view A-A of Figure 14 showing rotary actuator device **1300** and rotary valve **1350** in the automatic mode in a first position, Figure 16B is a sectional 16B-16B from Figure 16A, and Figure 16C is a schematic of valve **1350**. Figure 17A is a sectional view A-A of Figure 14 showing rotary actuator device **1300** and rotary valve **1350** in the automatic mode in a second position, Figure 17B is a sectional 17B-17B from Figure 17A, and Figure 17C is a schematic of valve **1350**.

[0118] In the position of Figures 16A-16C, button **1321** is in a full "out" position, and rotation pin **1343** is engaged with transverse slot **1344**. Pneumatic actuator **1311** is thus linked with rotary element **1348**. Pneumatic actuator **1311** is in the retracted position of Figure 15A, and rotary element **1348** connects ports **1352** and **1355**.

[0119] In the position of Figures 17A-17C, button **1321** is in a full "out" position, and rotation pin **1343** is engaged with transverse slot 1344, as in Figures 16A-16C. Pneumatic actuator

1311 is in the extended position of Figure 15C, rotating outer shaft **1325** and rotary element **1348** by 90 degrees, and thus connecting ports **1352** and **1353**.

[0120] By pressing in button **1321**, rotary valve **1350** may be operated in a manual mode, independent of rotary valve actuator **1300**. To switch to manual mode, the operator pushes in button **1321**. Rotation pin **1343** thus moves out of transverse slot **1344**, disengaging linkage arm **1331**. (Transverse slot **1344** and the portion of linkage arm **1331** near the transverse slot are above and below the plane of sectional views of Figures **16B**, **17B**, **18B**, **19B**, and **20B**, and are indicated with dashed lines in those Figures). With linkage arm **1331** disengaged from outer shaft **1325**, rotary valve **1350** is free to rotate to any position by turning knob **1323**. Spring **1345** pushes against inner shaft **1341** so that when knob **1323** is turned to align rotation pin **1343** and transverse slot **1344**, for example by returning the knob to the original position or by rotating through 180 degrees, rotation pin **1343** will again move into transverse slot **1344** when button **1321** is not being pushed in. When button **1321** not being pushed in, rotation pin **1343** is forced into transverse slot **1344** by spring **1345** engaging outer shaft **1325** with linkage arm **1331**, and thus returning rotary valve **1350** to automatic mode.

[0121] The manual operation of valve **1350** is illustrated with reference to Figures 15A, 15B and 15C, Figures 18A, 18B, and 18C, Figures 19A, 19B, and 19C, and Figures 20A, 20B, and 20C. Figure 18A is a sectional view A-A of Figure 14 showing rotary actuator device **1300** and rotary valve **1350** being switched to a manual mode in the first position of Figure 16, Figure 18B is a sectional 18B-18B from Figure 18A, and Figure 18C is a schematic of valve **1350**. Figure 19A is a sectional view A-A of Figure 14 showing rotary actuator device **1300** and rotary valve **1350** switched to a second position in the manual mode, Figure 19B is a sectional 19B-19B from Figure 19A, and Figure 19C is a schematic of valve **1350**. Figure 20A is a sectional view A-A of Figure 14 showing rotary actuator device **1300** and rotary valve **1350** switched to a third position and reengaged in the automatic mode, Figure 20B is a sectional 20B-20B from Figure 20B, and Figure 20C is a schematic of valve **1350**.

[0122] In the position of Figures 18A-18C, pneumatic actuator **1311** and valve **1350** are in the first position of Figure 16, and button **1321** is being pushed by a user (not shown) into a full "in" position, causing rotation pin **1343** to be out of transverse slot **1344**, and thus disengaging

outer shaft **1325** and linkage arm **1331**. Pneumatic actuator **1311** is thus disengaged from rotary element **1348**, and valve **1350** can be operated by rotating knob **1323**.

[0123] In the position of Figures 19A-19C, knob **1323** has been rotated 90 degrees. Pneumatic actuator **1311** and linkage arm **1331** remain in the same position as in Figure 18, while rotating pin **1343** and transverse slot **1344** are at 90 degrees, with the rotating pin rigidly fixed on the end of inner shaft **1341**. Valve **1350** is in a position connecting ports **1352** and **1353**.

[0124] In the position of Figures 20A-20C, knob **1323** has been further rotated an additional 90 degrees, aligning rotating pin **1343** and transverse slot **1344**. Button **1321** is being pushed against spring **1345** and, upon release, rotating pin **1343** will be forced into transverse slot **1344**, engaging pneumatic actuator **1311** and linkage arm **1331**, returning valve **1350** into automatic mode. While pneumatic actuator **1311** remains in the same position as in Figure 18, the valve has been rotated by 180 degrees, connecting ports **1353** and **1354**.

[0125] Alternative embodiments of rotary valve actuator **1300** include, but are not limited to: different lengths of cylinders and rotary arm screws that can be used to provide a means to rotate the rotating valve other exact angles besides 90 degrees (useful if some valve other than a 4 port valve is desired to be used); a linkage with multiple slits at even or at not even angular spacing to provide a multitude of different actuator modes or positions using a multiport valve; a pneumatic cylinder that is a forward acting or return acting or double acting types; a pneumatic cylinder that is mounted to the right or to the left of the rotary valve actuator; and other devices to actuate the valve apparatus including, but not limited to, rotating pneumatic devices and linear motors.

[0126] One embodiment of each of the methods described herein may include a computer program that executes on a processing system, e.g., a one or more processors and memories that are part of an embedded system. Thus, as will be appreciated by those skilled in the art, embodiments of the present invention may be embodied as a method, an apparatus such as a special purpose apparatus, an apparatus such as a data processing system, or a carrier medium, e.g., a computer program product. The carrier medium carries one or more computer readable code segments for controlling a processing system to implement a method. Accordingly, aspects of the present invention may take the form of a method, an entirely hardware embodiment, an entirely software embodiment or an embodiment combining software and

hardware aspects. Furthermore, the present invention may take the form of carrier medium (e.g., a computer program product on a computer-readable storage medium) carrying computer-readable program code segments embodied in the medium. Any suitable computer readable medium may be used including a magnetic storage device such as a diskette or a hard disk, a game machine cartridge, or an optical storage device such as a CD-ROM.

[0127] Reference throughout this specification to "one embodiment" or "an embodiment" means that a particular feature, structure or characteristic described in connection with the embodiment is included in at least one embodiment of the present invention. Thus, appearances of the phrases "in one embodiment" or "in an embodiment" in various places throughout this specification are not necessarily all referring to the same embodiment. Furthermore, the particular features, structures or characteristics may be combined in any suitable manner, as would be apparent to one of ordinary skill in the art from this disclosure, in one or more embodiments. The term "comprising" as used herein is an open term.

[0128] Similarly, it should be appreciated that in the above description of exemplary embodiments of the invention, various features of the invention are sometimes grouped together in a single embodiment, figure, or description thereof for the purpose of streamlining the disclosure and aiding in the understanding of one or more of the various inventive aspects. This method of disclosure, however, is not to be interpreted as reflecting an intention that the invention requires more features than are expressly described herein. Rather, inventive aspects lie in less than all features of a single foregoing disclosed embodiment.

[0129] Thus, while there has been described several embodiments of the invention, those skilled in the art will recognize that other and further modifications may be made thereto without departing from the spirit of the invention, and it is intended to claim all such changes and modifications as fall within the scope of the invention. For example, any formulas given above are merely representative of procedures that may be used. Functionality may be added or deleted from the block diagrams and operations may be interchanged among functional blocks. Steps may be added or deleted to methods described within the scope of the present invention.

INDUSTRIAL APPLICABILITY

[0130] In addition to the uses of the present invention described herein, low volume dosing is useful for making may types of measurements including, but not limited to, desorption concentration measurements, kinetics measurements, sorption capacity measurements, pressure-concentration-temperature isotherm measurements, cycle-life measurements, porosity measurements, surface area measurements, density measurements, diffusion measurements, enthalpy of sorption or reaction measurements, entropy of sorption or reaction measurements, phase transition analysis measurements, activation energy measurements, moisture sorption measurements, interactions of pharmaceutical chemicals or packaging materials with moisture and gases, hydrate and solvate sorption measurements, stability, chemical reactivity, dissolution rate, and density of polymorphic forms of materials, Deliquescence and hygroscopicity measurements, desorption concentration measurements, kinetics measurements, and cycle-life measurements.

CLAIMS

I Claim:

1. An apparatus connectable to a source of fluid or vacuum, said apparatus comprising:

a sample holder having an internal volume;

a dosing reservoir; and

a valve having at least two ports and at least two positions, where said at least two ports includes

a first port fluidly connectable to the source, and

a second port fluidly connected to said internal volume,

where said at least two positions includes

a first position that fluidly connects said first port and said dosing reservoir, and defines a first enclosed volume including said internal volume, and

a second position that fluidly connects said dosing reservoir and said internal volume to form a second enclosed volume.

2. The apparatus of Claim 1, further comprising

a pressure measuring device,

where said valve has at least three ports, and where said at least three ports includes a third port fluidly connected to said pressure measuring device,

where said first position fluidly connects said dosing reservoir, said pressure measuring device, and said dosing reservoir, and

where said second position fluidly connects said second enclosed volume and said pressure measuring device.

3. The apparatus of Claim 2, where said valve has at least three positions, and where said at least three positions includes a third position that fluidly connects the first port and said internal volume.

4. The apparatus of Claim 3, where said at least three ports is at least four ports, where said at least four ports includes a fourth port fluidly connectable to the source, and where said third position fluidly connects said third port and said fourth port.

5. The apparatus of Claim 3, where said at least three ports is at least four ports, where said at least four ports includes a fourth port fluidly connected to said internal volume, and

where said third position fluidly connects said first port and said fourth port.

6. The apparatus of Claim 2, further including a system to control said pressure measuring device.

7. The apparatus of Claim 2, where said pressure measuring device includes a plurality of pressure measuring devices and one or more valves to fluidly connect individual ones of said plurality of pressure measuring device to said second port.

8. The apparatus of Claim 1, further comprising

a first pressure measuring device fluidly connected to said first port; and

a second pressure measuring device fluidly connected to said second port.

9. The apparatus of Claim 1, where said source includes a plurality of sources, said apparatus further including:

a passageway to fluidly connect each of the plurality of sources and said first port, and

a plurality of on/off valves to control fluid communication between each of the plurality of sources and said first port.

10. The apparatus of Claim 1, further including:

a passageway to fluidly connectable to the source and said internal volume; and

an on/off valve to control fluid communication between the source and said internal volume.

11. The apparatus as in any preceding claim, further including an actuator operably engageable with said valve.

12. The apparatus of Claim 11, where said actuator includes a manual override to disengage said actuator and permit manual operation of the valve.

13. The apparatus of Claim 11, where said actuator is a pneumatic actuator.

14. The apparatus as in any preceding claim, further including a system to control the temperature of said sample holder.

15. The apparatus as in any preceding claim, further including a system to control the temperature of said valve.

16. The apparatus as in any preceding claim, where said dosing reservoir has a volume of less than 0.1 milliliters.

17. The apparatus as in any preceding claim, where said dosing volume has a volume of from about 0.1 milliliters to about 10 milliliters.

18. The apparatus as in any preceding claim, where, when said first port is connected to the source, said first position charges said dosing reservoir from the source.

19. The apparatus as in any preceding claim, further including a computer system programmed to measure sorption or desorption properties of a material sample in the sample holder.

20. The apparatus as in any preceding claim, where said sample holder includes a plurality of sample holders each with an internal volume, and one or more valves to fluidly connect individual ones of said plurality of internal volumes to said third port.

21. The apparatus as in any preceding claim, where said valve includes two or more fluidly connected valves.

22. The apparatus as in any preceding claim, where said valve is a rotary valve.

23. The apparatus as in any preceding claim, where said valve includes two or more on/off valves.

24. The apparatus as in any preceding claim, where the fluid is a gas.

25. An apparatus connectable to a source of fluid or vacuum, said apparatus comprising:

a sample holder having an internal volume;

a dosing reservoir; and

a valve having at least two ports and at least three positions, where said at least two ports includes

a first port fluidly connectable to the source, and

a second port fluidly connected to said internal volume,

where said at least three positions includes

a first position that fluidly connects said first port and said dosing reservoir, and defines a first enclosed volume including said internal volume,

a second position that fluidly connects said dosing reservoir and said internal volume to form a second enclosed volume, and

a third position that fluidly connects the first port and said internal volume.

26. The apparatus of Claim 25, further comprising

a pressure measuring device,

where said valve has at least three ports, and where said at least three ports includes a third port fluidly connected to said pressure measuring device,

where said first position fluidly connects said dosing reservoir, said pressure measuring device, and said dosing reservoir, and

where said second position fluidly connects said second enclosed volume and said pressure measuring device.

27. The apparatus of Claim 26, further including a system to control said pressure measuring device.

28. The apparatus of Claim 26, where said pressure measuring device includes a plurality of pressure measuring devices and one or more valves to fluidly connect individual ones of said plurality of pressure measuring device to said second port.

29. The apparatus of Claim 25, where said source includes a plurality of sources, said apparatus further including:

a passageway to fluidly connect each of the plurality of sources and said first port, and

a plurality of on/off valves to control fluid communication between each of the plurality of sources and said first port.

30. The apparatus of Claim 25, further including:

a passageway to fluidly connect the source and said internal volume; and

an on/off valve to control fluid communication between the source and said internal volume.

31. The apparatus of Claim 25, where said at least two ports is at least three ports, where said at least three ports includes a third port fluidly connectable to the source, and where said third position fluidly connects said third port and said fourth port.

32. The apparatus of Claim 25, where said at least two ports is at least three ports, where said at least three ports includes a third port fluidly connected to said internal volume, and where said third position fluidly connects said first port and said fourth port.

33. The apparatus as in any preceding claim, further including an actuator operably engageable with said valve.

34. The apparatus of Claim 33, where said actuator includes a manual override to disengage said actuator and permit manual operation of the valve.

35. The apparatus of Claim 33, where said actuator is a pneumatic actuator.

36. The apparatus as in any preceding claim, further including a system to control the temperature of said sample holder.

37. The apparatus as in any preceding claim, further including a system to control the temperature of said valve.

38. The apparatus as in any preceding claim, where said dosing reservoir has a volume of less than 0.1 milliliters.

39. The apparatus as in any preceding claim, where said dosing reservoir has a volume of from about 0.1 milliliters to about 10 milliliters.

40. The apparatus as in any preceding claim, further including a computer system programmed to measure sorption or desorption properties of a material sample in the internal volume.

41. The apparatus as in any preceding claim, where said sample holder includes a plurality of sample holders each having an internal volume, and one or more valves to fluidly connect individual ones of said plurality of internal volumes to said third port.

42. The apparatus as in any preceding claim, where, when said first port is connected to the source, said first position charges the dosing reservoir from the source.

43. The apparatus as in any preceding claim, where said valve includes two or more fluidly connected valves.

44. The apparatus as in any preceding claim, where said valve is a rotary valve.

45. The apparatus as in any preceding claim, where said valve is two or more on/off valves.

46. The apparatus as in any preceding claim, where the fluid is a gas.

47. A device to measure sorption properties of a material sample, said device comprising:

a sample holder having an internal volume for containing a material sample;

a plurality of dosing reservoirs; and

one or more valves operable to connect individual ones of said plurality of dosing reservoirs to said internal volume, each forming an enclosed volume.

48. The device of Claim 47, where at least one of said plurality of dosing reservoirs has a volume less than 0.1 milliliters.

49. The device of Claim 47, where at least one of said plurality of dosing reservoirs has a volume of from about 0.1 milliliters to about 1 liter.

50. The device of Claim 47 including a pressure measuring device fluidly connectable to said internal volume.

51. A device to measure sorption properties of a material sample, said device comprising:

a sample holder having an internal volume for containing a material sample;

a dosing reservoir;

a valve to fluidly connect said dosing reservoir and said internal volume to form an enclosed volume;

two or more pressure measuring devices; and

a valve to fluidly connect individual ones of said two or more pressure measuring devices to said internal volume.

52. The device of Claim 51, where said dosing reservoir has a volume of less than 0.1 milliliters.

53. The device of Claim 51, where said dosing reservoir has a volume of from about 0.1 milliliters to about 1 liter.

54. An apparatus to control a rotary valve, said apparatus comprising:

a frame;

a mounting to attached the rotary valve to said frame;

an actuator attached to said frame and operably engageable with a mounted rotary valve; and

a manual override device to disengage said actuator and permit manual operation of the mounted rotary valve.

55. The apparatus of Claim 54, where said actuator is a pneumatic actuator.

56. The apparatus of Claim 54, where said actuator is an electric actuator.

57. The apparatus of Claim 54, further comprising a computer system to control the rotary valve when operably engaged.

58. The apparatus of Claim 54, where the rotary valve includes a rotatable member for operating said rotary valve, and where said actuator includes:

a first member having a first end adapted to be connected to the rotatable member of the mounted rotary valve and a second end; and

a knob attached to said second end,

where said knob rotates upon rotation of the rotatable member of the mounted rotary valve.

59. The apparatus of Claim 58, where said actuator includes a second member engageable with said first member, and where said manual override device disengages said actuator by disengaging said first member and said second member.

60. The apparatus of Claim 59, where said first member and said second member include interlocking portions, where said actuator engages the rotatable member of the mounted rotary valve by interlocking said first member and said second member.

61. The apparatus of Claim 60, where said manual override device includes a button that, when pushed, separates said interlocking portions.

62. An apparatus or device substantially as shown and described.

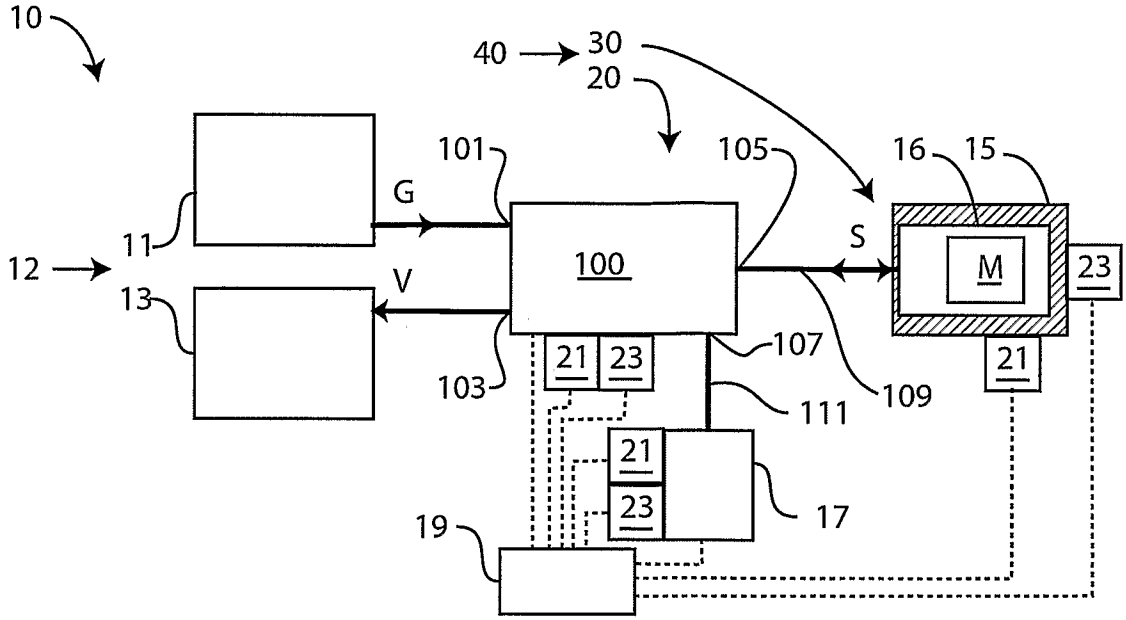


FIG. 1

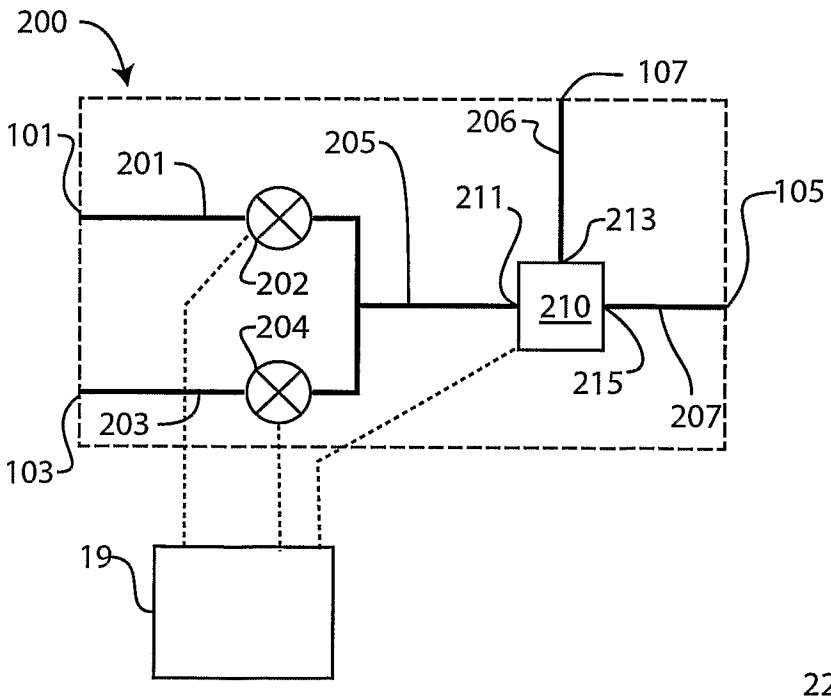


FIG. 2A

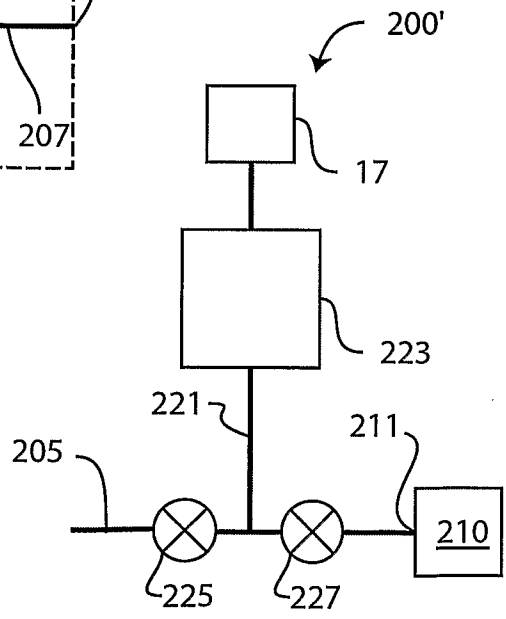


FIG. 2B

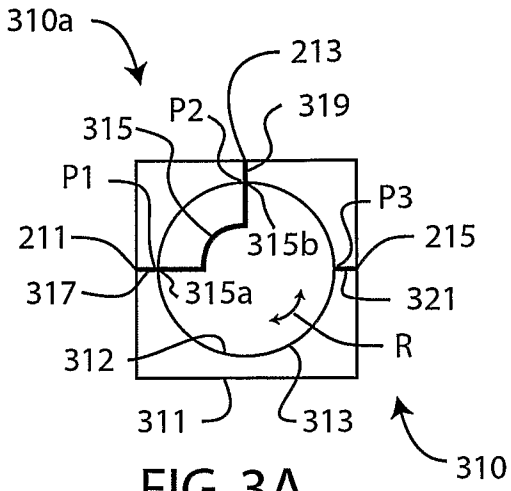


FIG. 3A

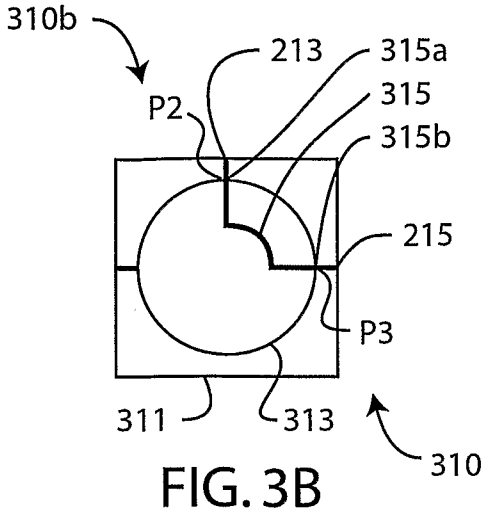


FIG. 3B

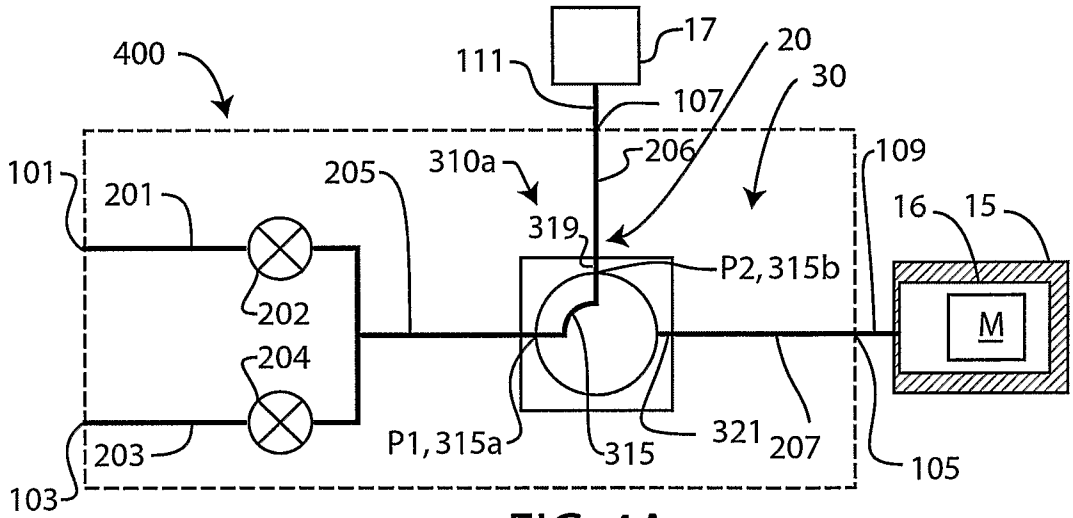


FIG. 4A

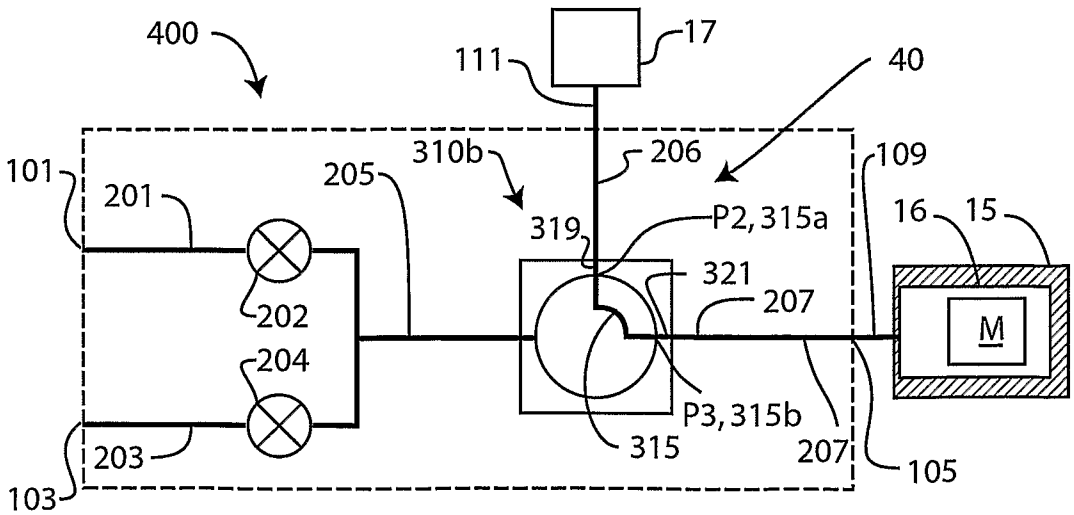


FIG. 4B

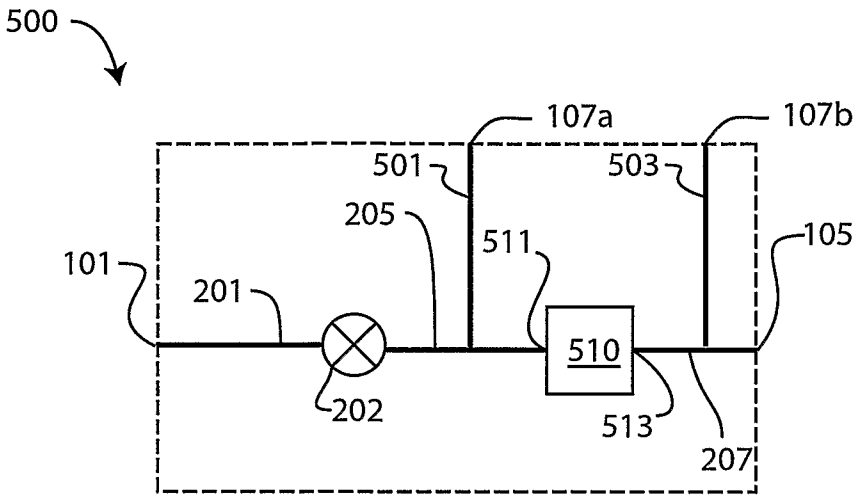


FIG. 5

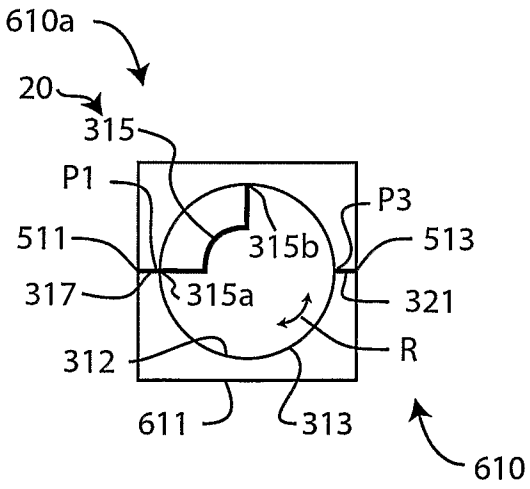


FIG. 6A

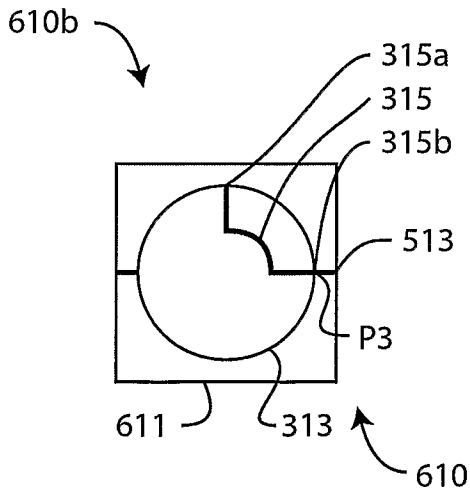


FIG. 6B

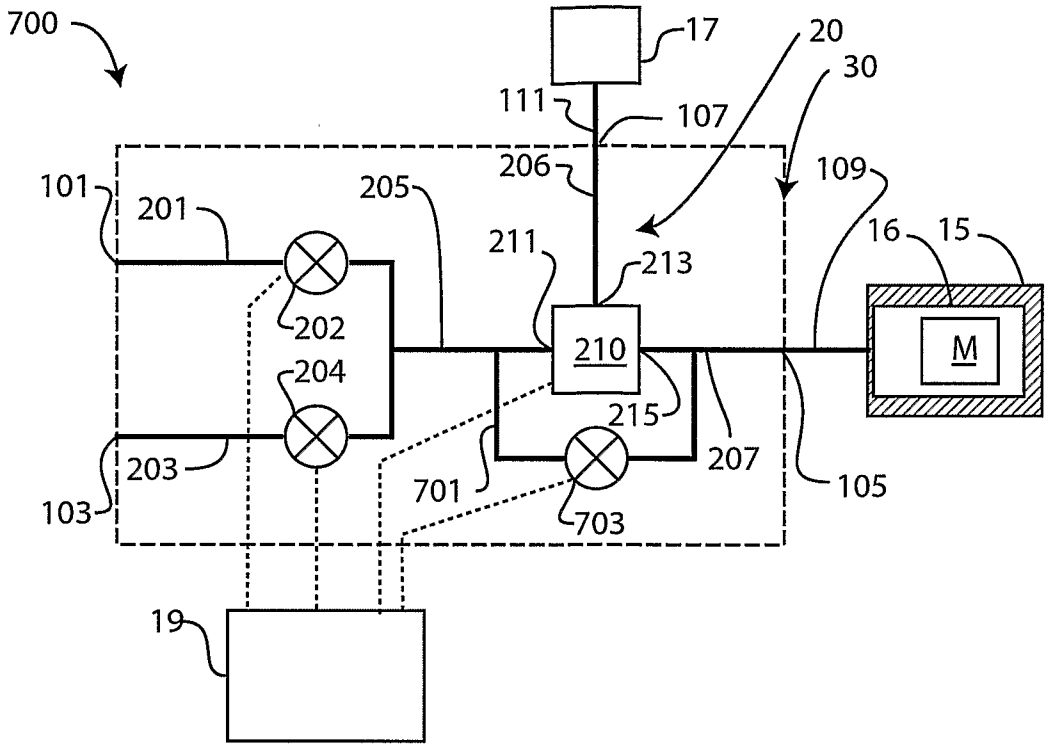

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FIG. 7

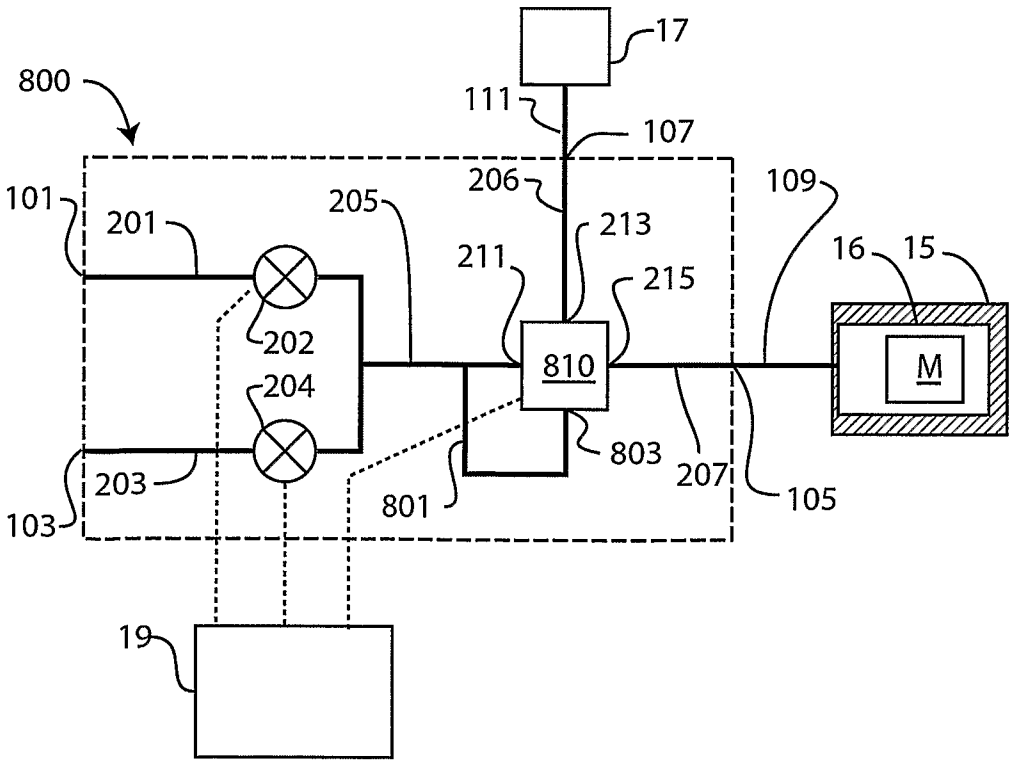

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FIG. 8

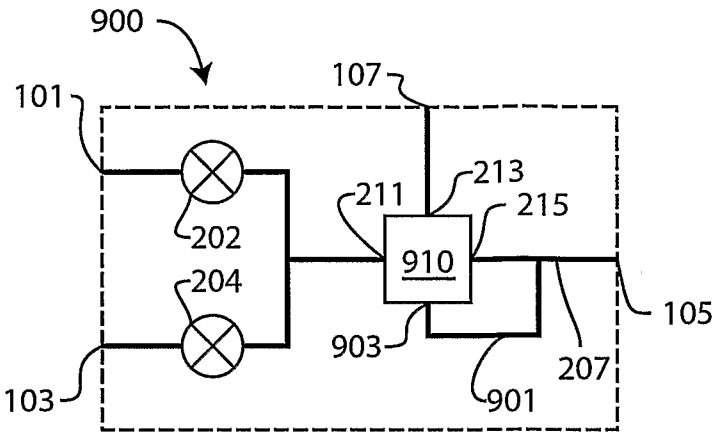


FIG. 9

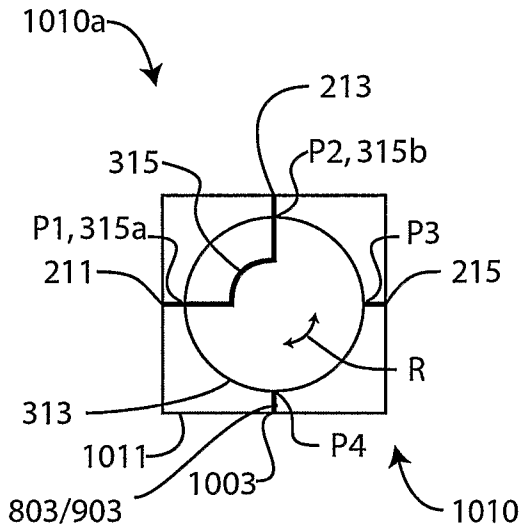


FIG. 10A

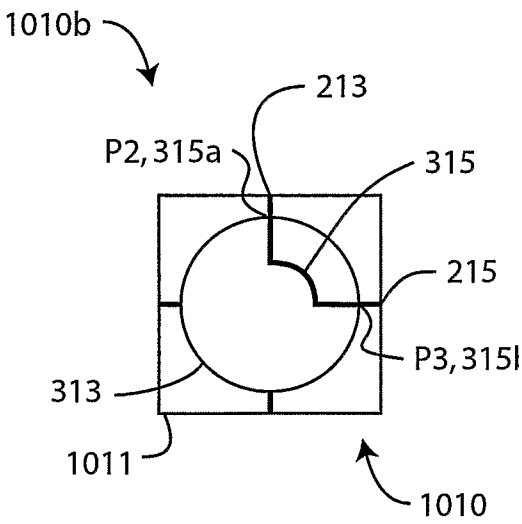


FIG. 10B

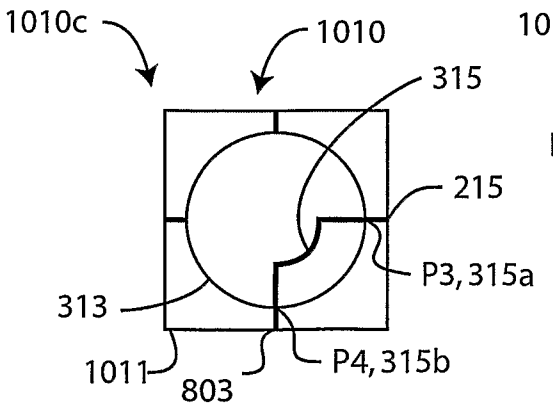


FIG. 10C

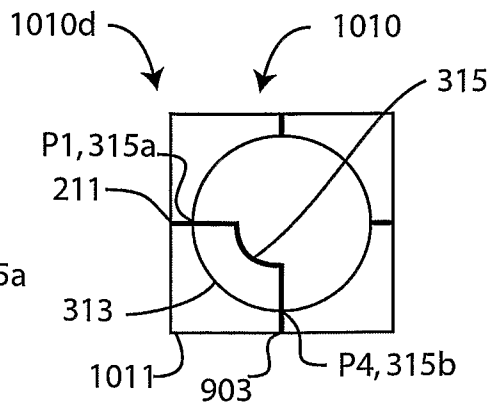


FIG. 10D

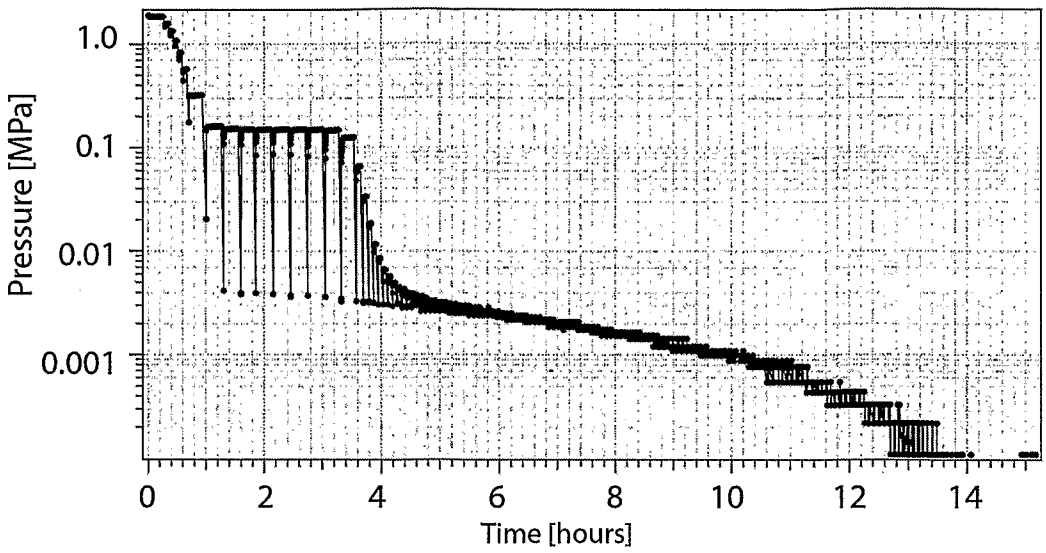

Pressure [MPa]
1.0
0.1
0.01
0.001
0
2
4
6
8
10
12
14
Time [hours]

FIG. 11

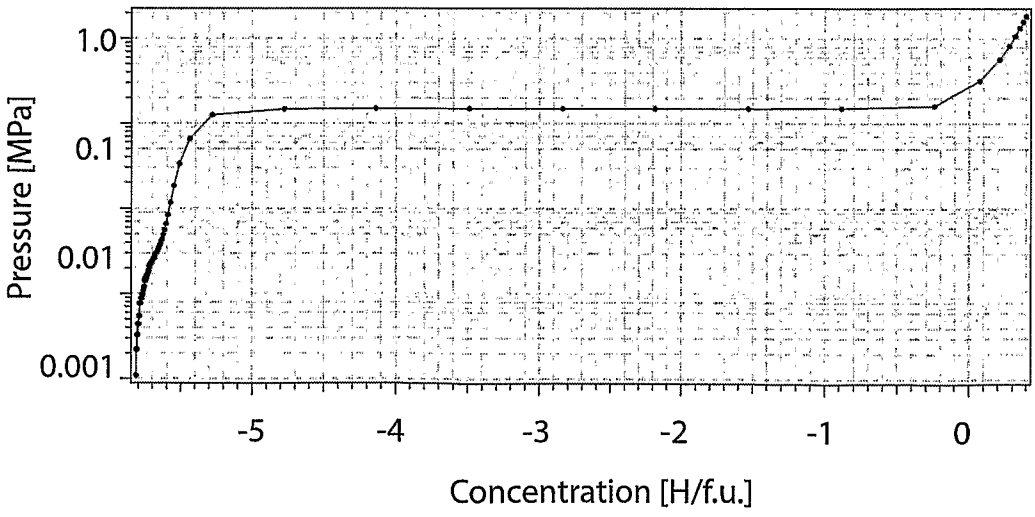

Pressure [MPa]
1.0
0.1
0.01
0.001
-5
-4
-3
-2
-1
0
Concentration [H/f.u.]

FIG. 12

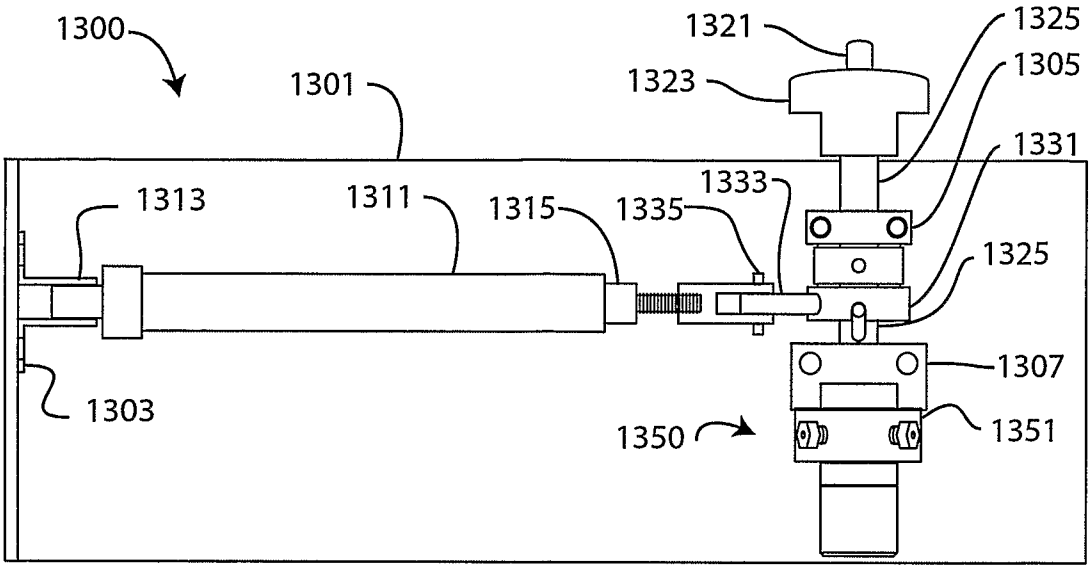

1300
1301
1321
1323
1325
1305
1331
1313
1311
1315
1335
1333
1325
1307
1303
1350
1351

FIG. 13

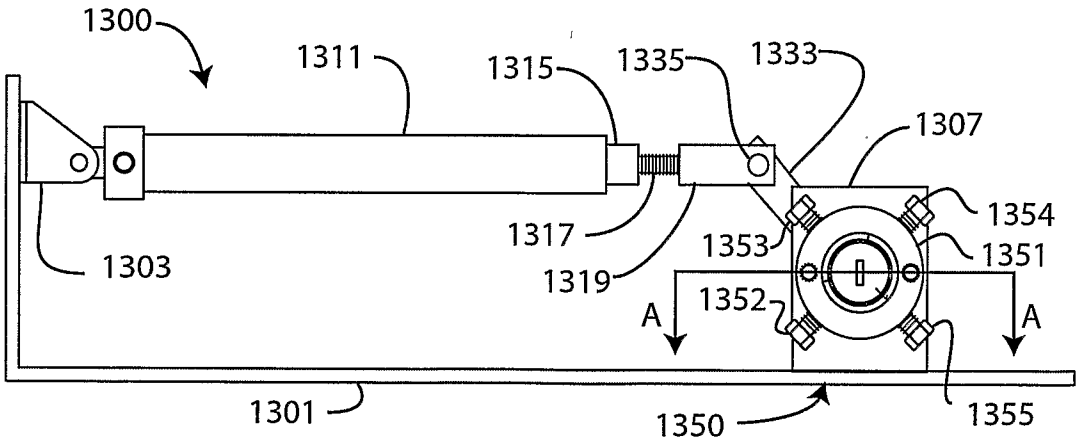

1300
1311
1315
1335
1333
1307
1354
1317
1353
1351
1319
1352
A
A
1303
1301
1350
1355

FIG. 14

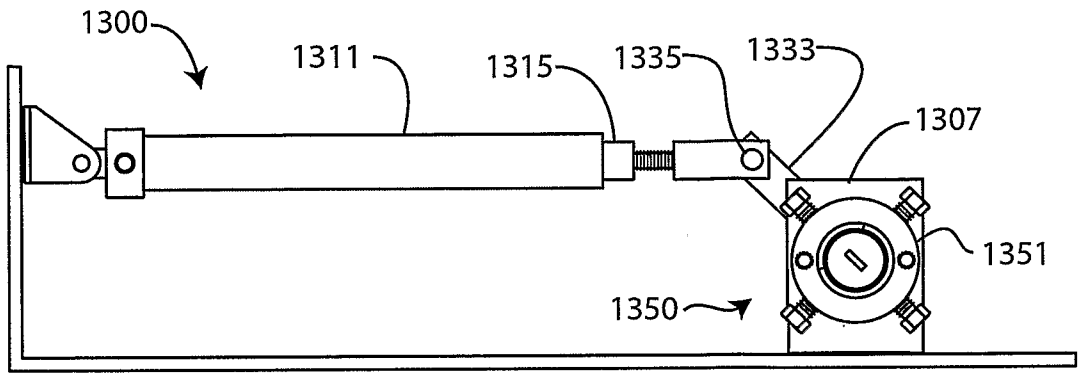


FIG. 15A

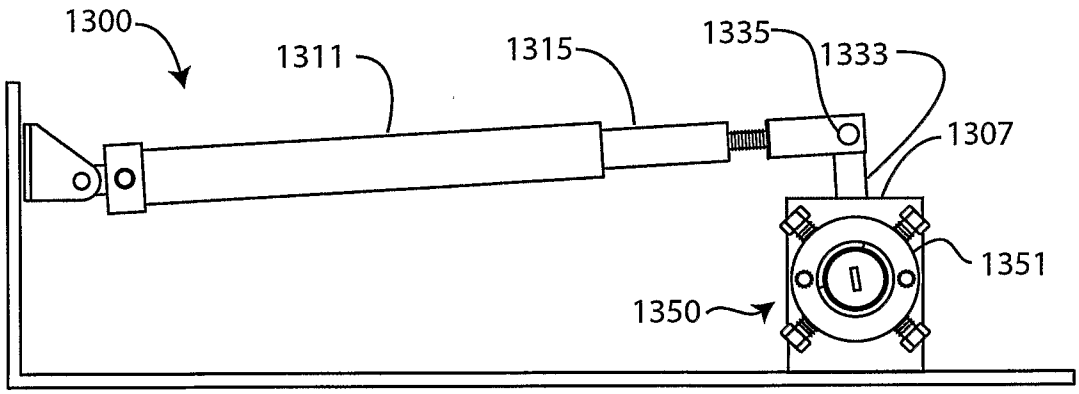


FIG. 15B

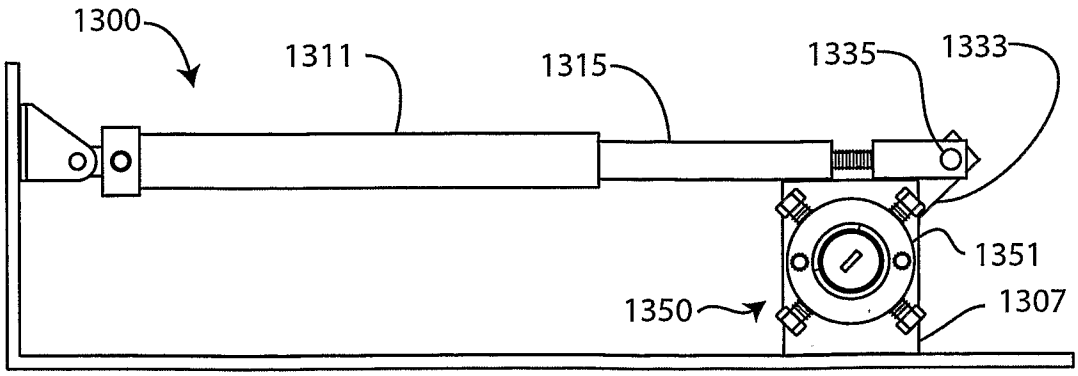


FIG. 15C

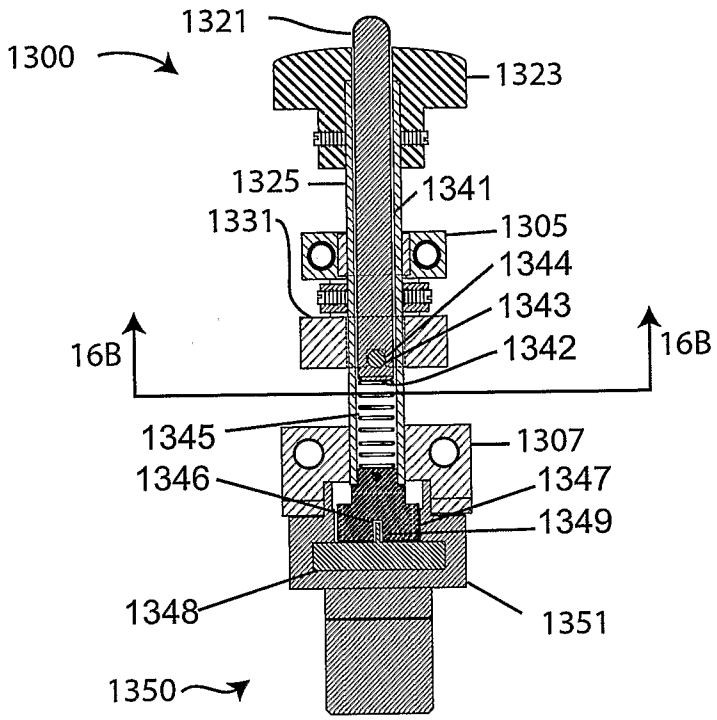


FIG. 16A

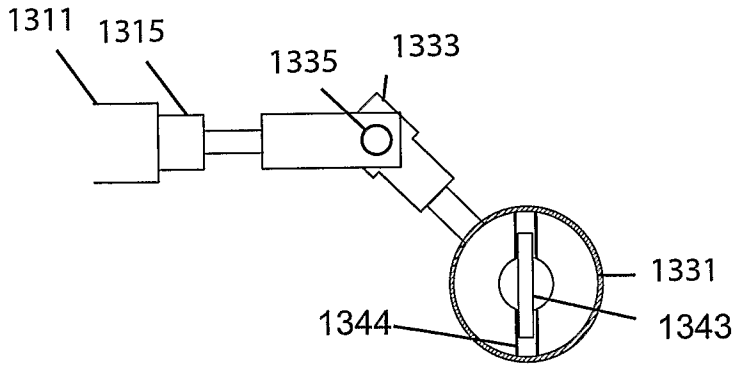


FIG. 16B

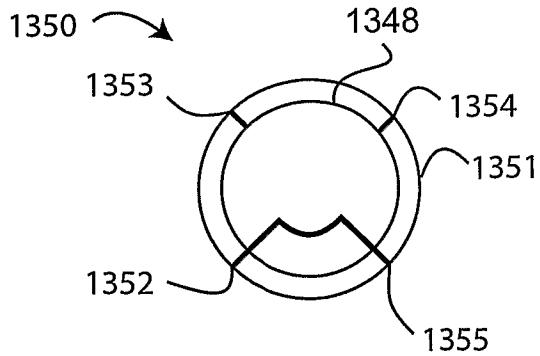


FIG. 16C

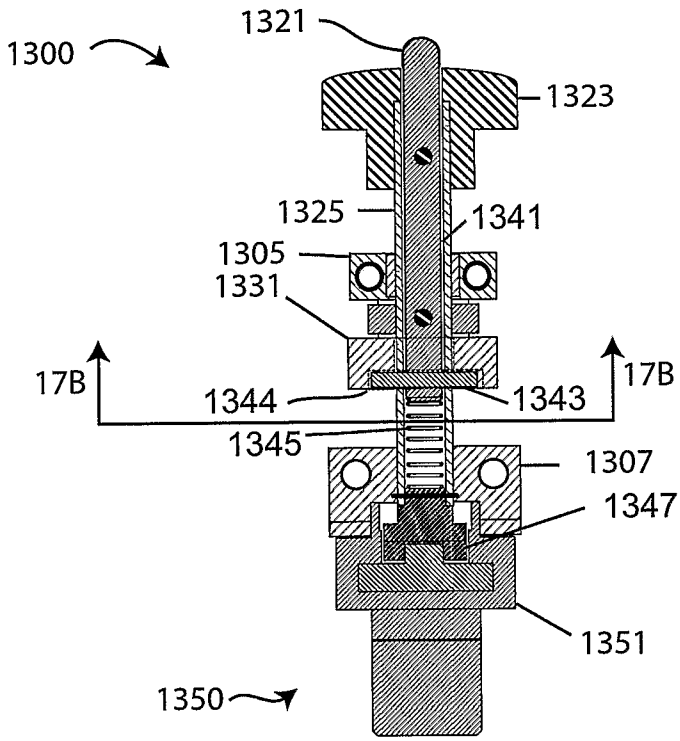


FIG. 17A

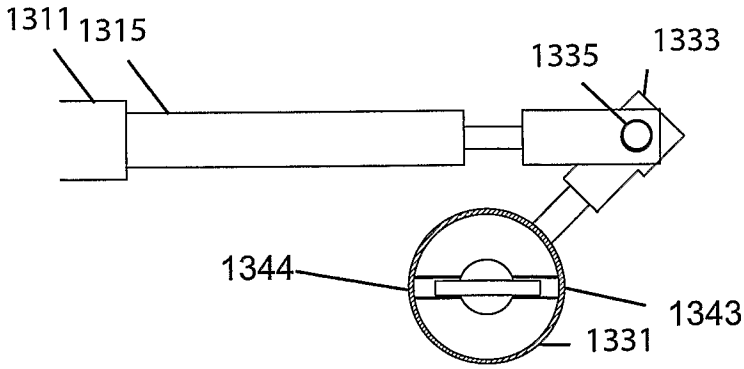


FIG. 17B

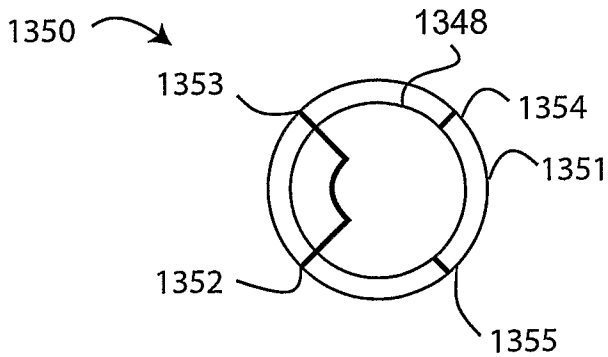


FIG. 17C

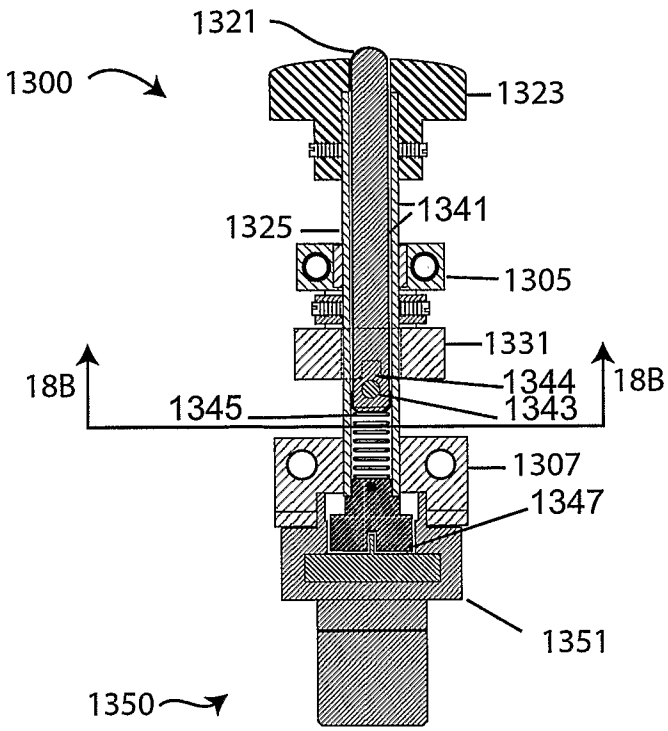


FIG. 18A

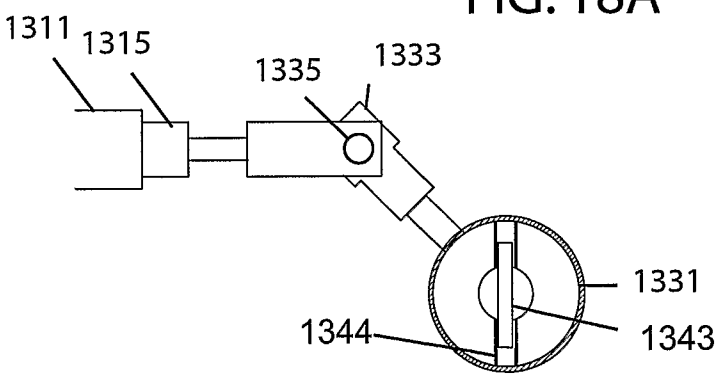


FIG. 18B

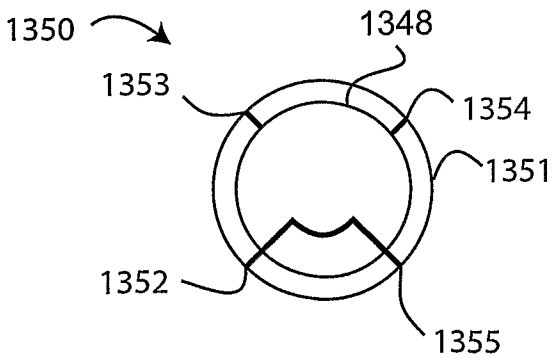


FIG. 18C

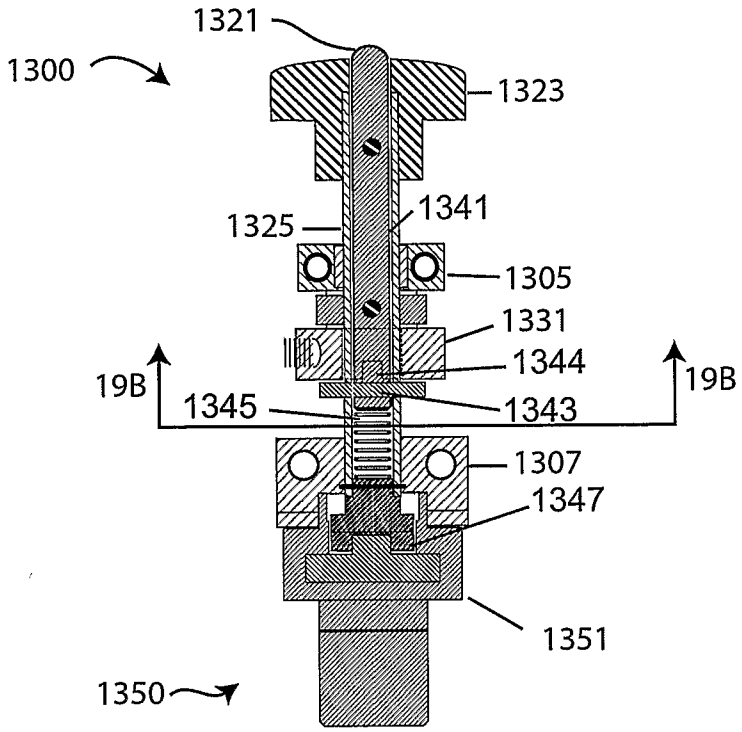


FIG. 19A

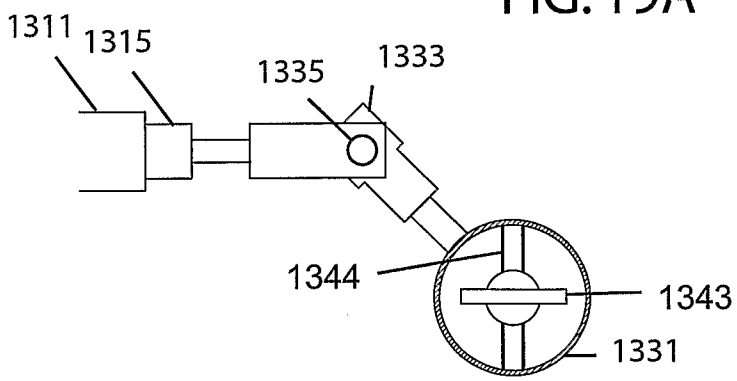


FIG. 19B

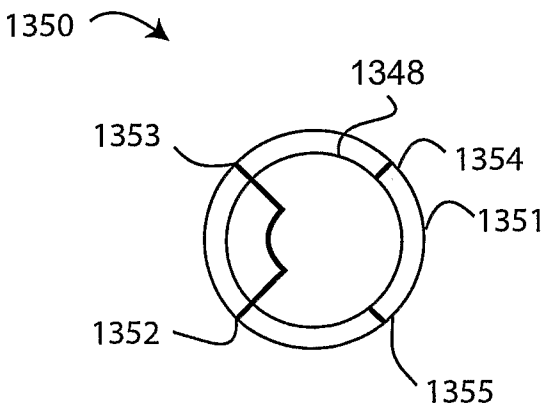


FIG. 19C

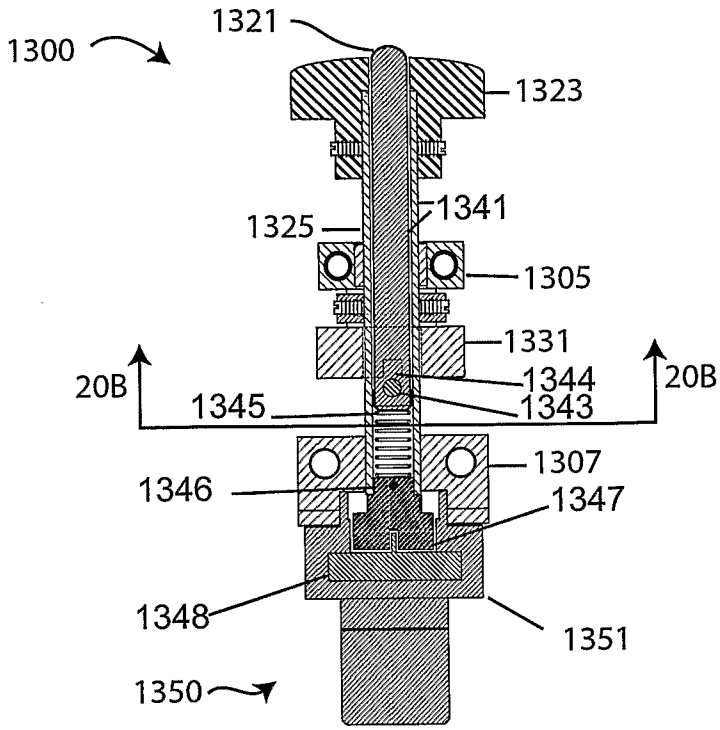


FIG. 20A

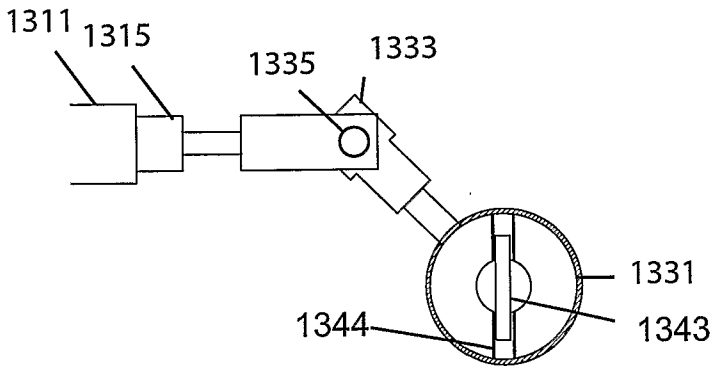


FIG. 20B

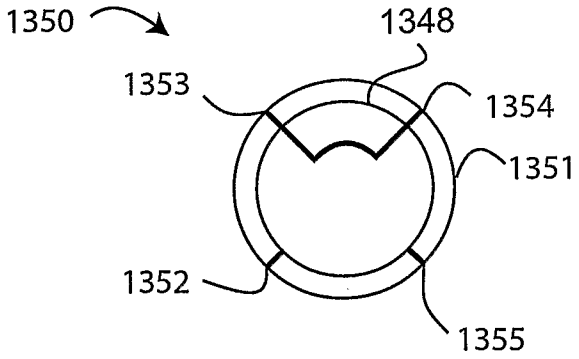


FIG. 20C

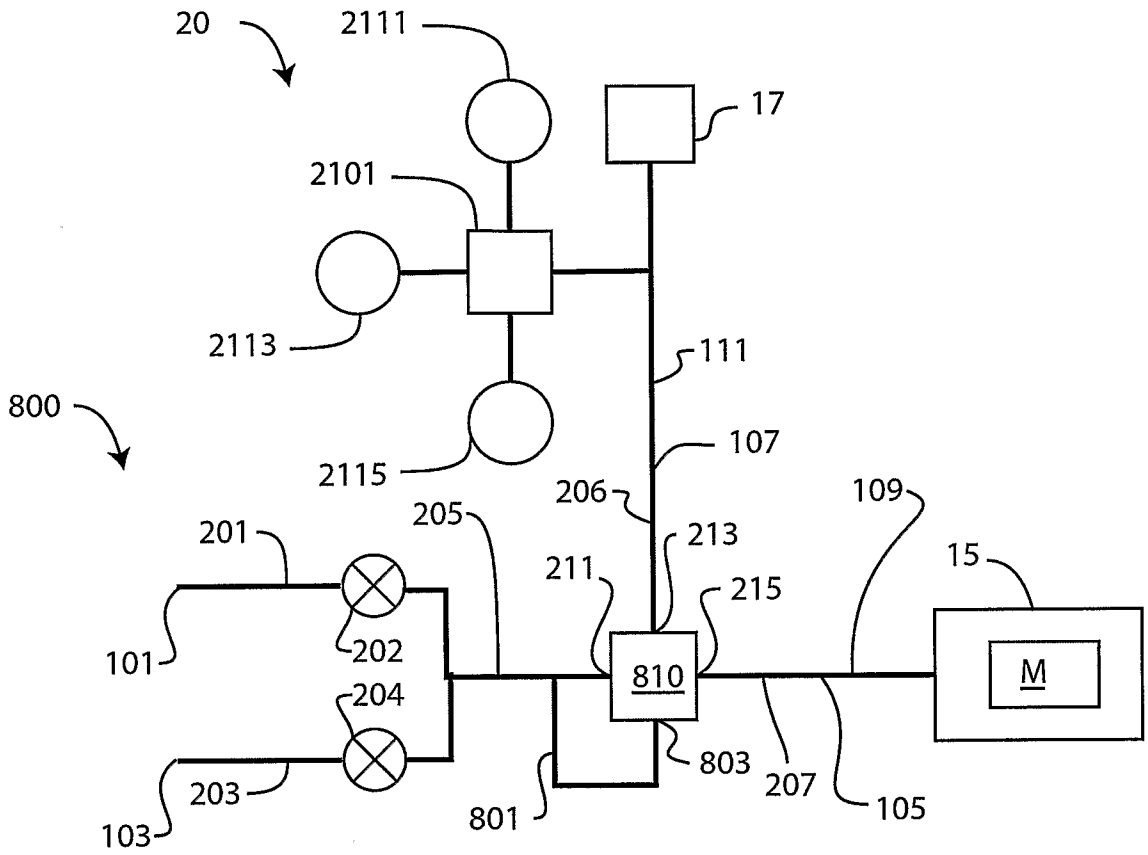

20
2111
17
2101
2113
111
800
2115
107
206
109
205
213
201
211
15
215
101
202
810
M
204
803
203
207
105
801
103

FIG. 21

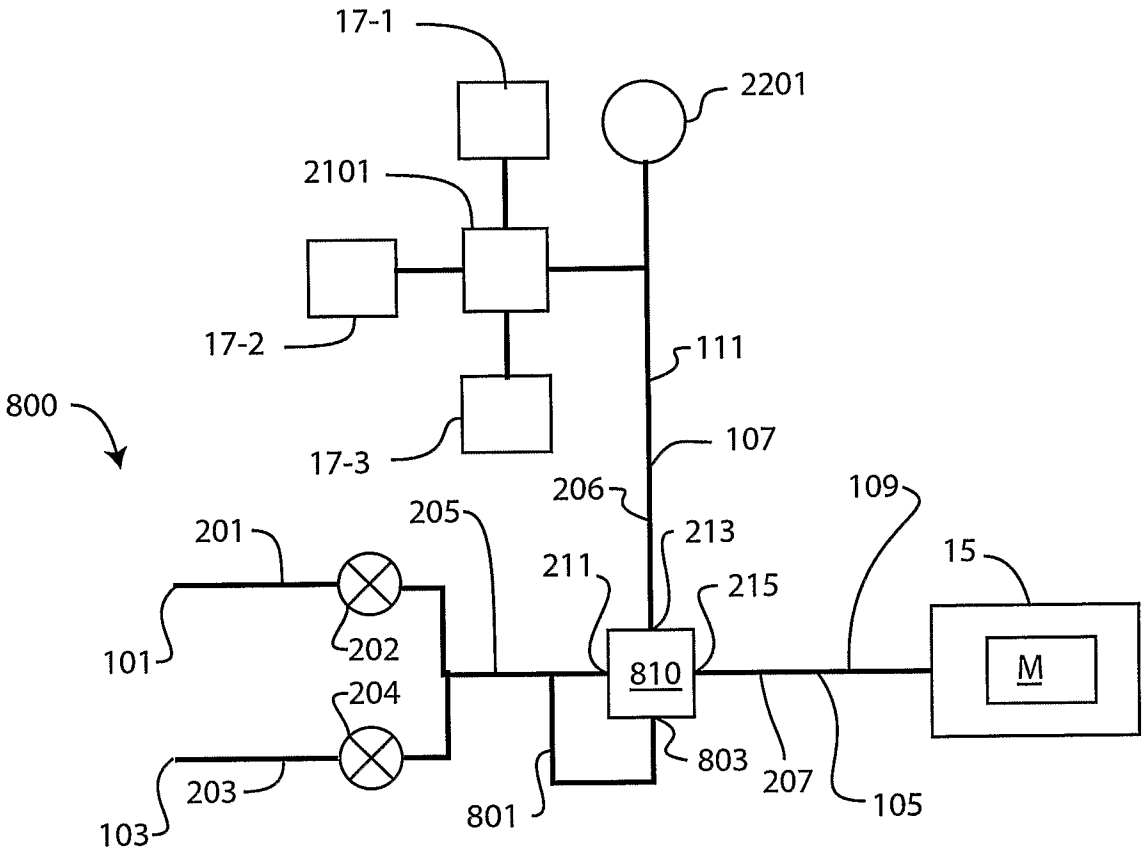

17-1
2201
2101
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17-3
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M
803
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203
801
103

FIG. 22

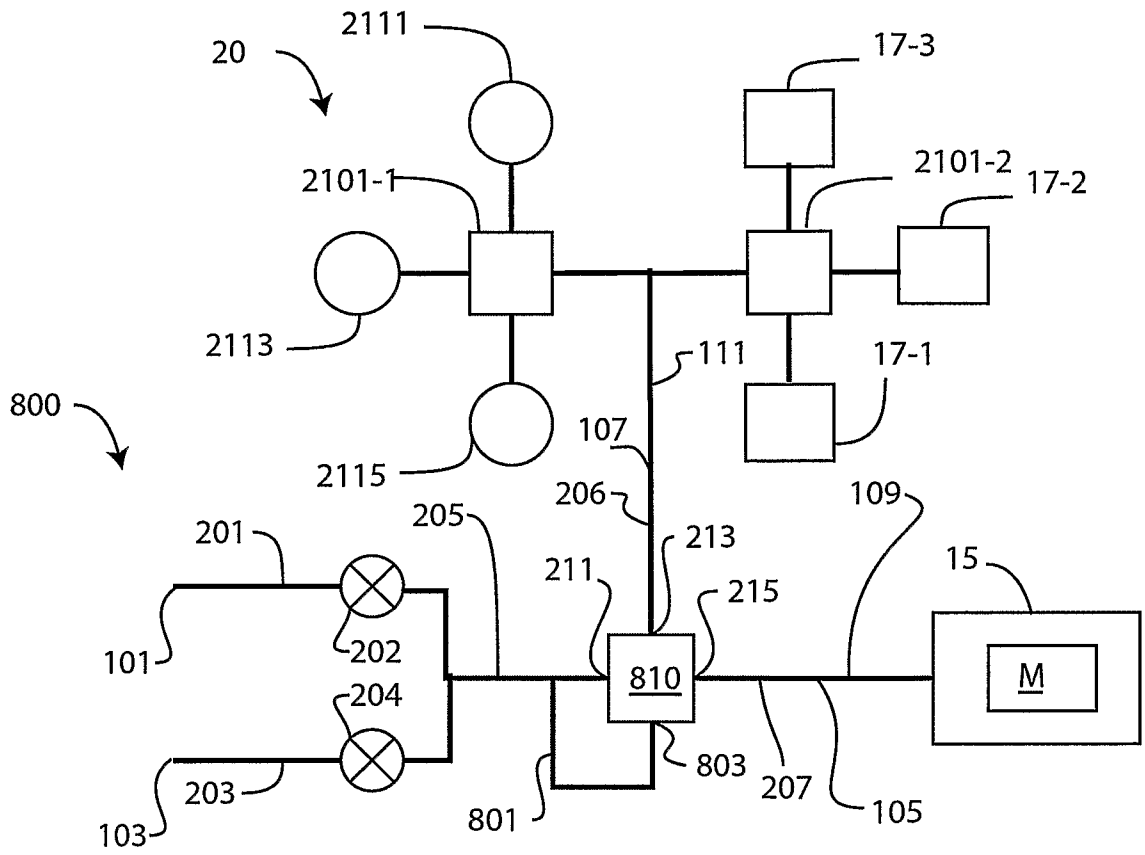

2111
20
17-3
2101-1
2101-2
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17-1
800
107
2115
206
109
205
213
201
211
215
15
101
202
810
M
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207
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801
105
103

FIG. 23