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[54] **VALVE SYSTEM**
7 Claims, 4 Drawing Figs.

[52] **U.S. Cl.** **137/624.18,** 251/331, 73/23.1
[51] **Int. Cl.** **G01n 31/08,** F16k 19/00
[50] **Field of Search** 137/624.18, 624.2, 624.13, 624.15; 251/331, 61.1; 73/23, 23.1

[56] **References Cited**
UNITED STATES PATENTS

3,019,815	2/1962	Lenardon	251/331 X
2,821,434	1/1958	Hunter	137/624.13 X
3,425,446	2/1969	McNown	137/624.2 X
3,424,063	1/1969	Norwood	251/331 X

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ABSTRACT: A valve system adapted to automatically add solvents and/or reactants to a sample and a reactor by connecting multiple fluid inlets or outlets to a main flow path has an upper body with an open trough formed in the bottom surface thereof, a flexible, elastically deformable, membrane clamped between the bottom surface of the body and a lower block to close the open trough and provide a longitudinal flow path, and a plurality of ports extending into the body terminating at spaced points on its bottom surface, each port being separated from the flow path by surrounding partitions. Reciprocating actuators in the block below each port normally hold the membrane against the partitions to close the ports, and are selectively released to perit fluid flow between the flow path and various of the ports.

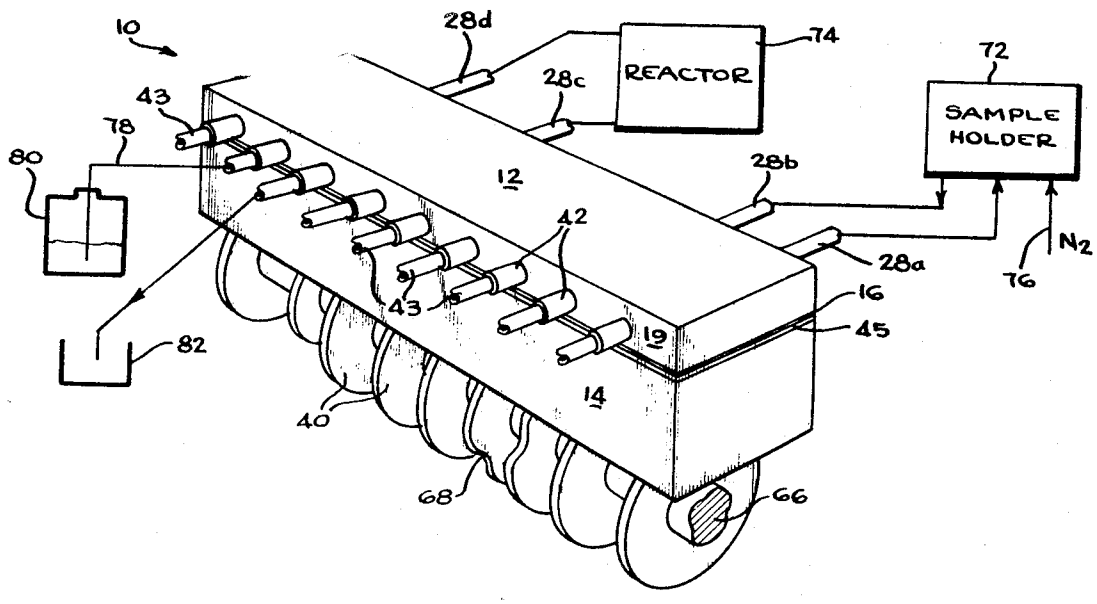


FIG.1

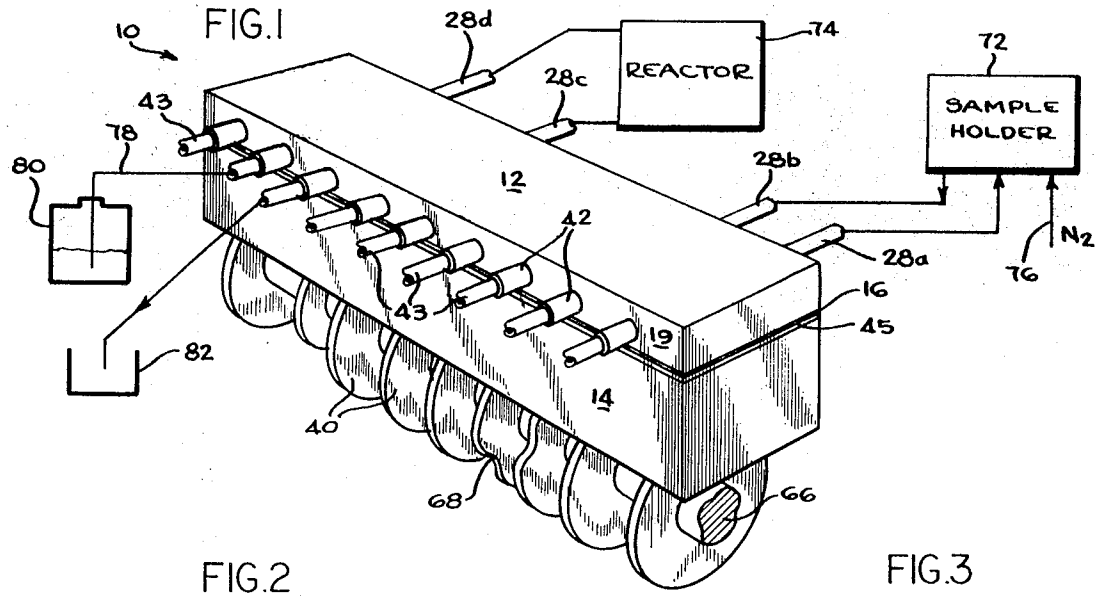


FIG.2

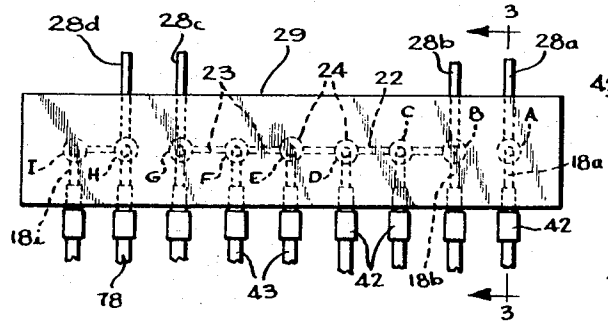


FIG.3

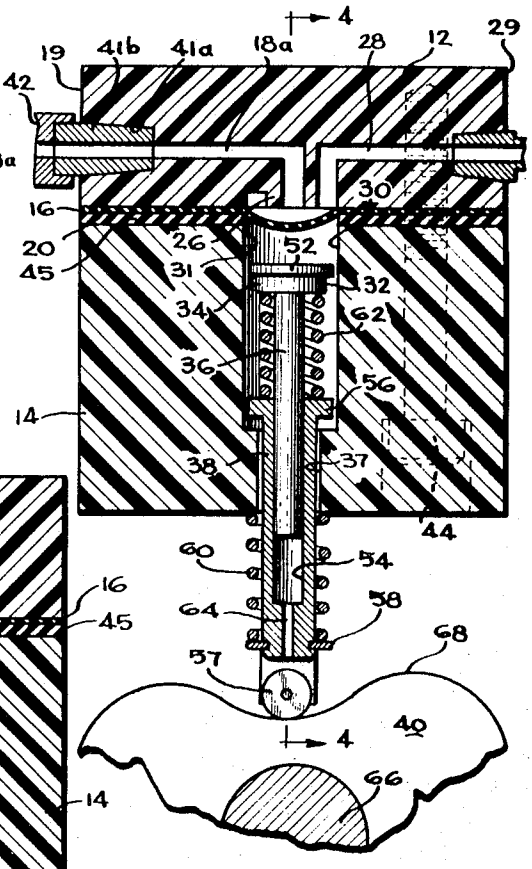
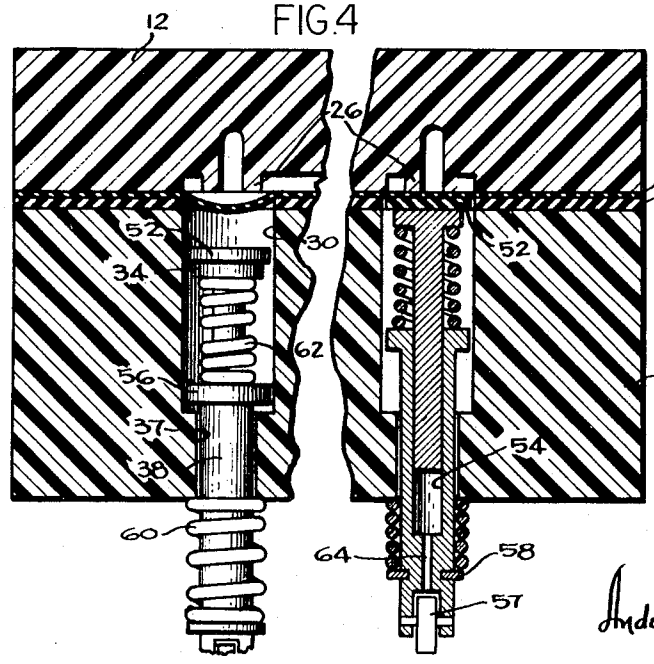


FIG.4



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VALVE SYSTEM

BACKGROUND OF THE INVENTION

The present invention relates to valve systems. More particularly it is directed to a valve system for connecting multiple passages to a main flow path, which system is particularly adapted for use as a part of chemical analysis apparatus.

Chromatographic analysis, for example gas chromatography, is often used to separate and identify the various components of a sample. These samples are often originally in liquid or solid form and not sufficiently volatile to permit direct gas chromatographic analysis. It is therefore necessary that such samples undergo various preliminary chemical reactions to prepare them for the ultimate identification of their components. In such preliminary reactions, the samples may be treated with several different reactants in various sequentially performed steps.

For repetitive laboratory analyses of samples, the treatment for each sample with proper concentrations of reactants in a particular sequence is desirably automated to facilitate standardized operation with a minimum of manual intervention. Accordingly, it is desirable to have an automatic valve system which facilitates the treatment of a sample with the desired reactants in a predetermined sequence preparatory to final analysis of the sample.

It is an object of the invention to provide an improved valve system designed to handle a plurality of fluid components. It is another object of the present invention to provide a valve system adapted for the addition of reactants to a sample in predetermined amounts and in a predetermined sequence. It is a further object of the present invention to provide a valve system which permits the automatic addition of several different solvents and/or reactants to a reactor while maintaining the reagent supplies out of contact with one another.

BRIEF DESCRIPTION OF THE DRAWINGS

These and other objects of the present invention should be apparent from a reading of the following detailed description and in conjunction with the drawings wherein:

FIG. 1 is a perspective view of a valve system embodying various features of the present invention;

FIG. 2 is a top view of the valve system shown in FIG. 1,

FIG. 3 is a sectional view of the valve system taken along the line 3—3 of FIG. 2; and

FIG. 4 is a fragmentary sectional view of a valve of the present invention taken along the line 4—4 of FIG. 3.

DETAILED DESCRIPTION OF THE INVENTION

Briefly, a valve system **10** (FIG. 1) is provided including a head **12** and a block **14**, which in the illustrated embodiment are rectangular in cross section and complementary in size. A deformable membrane **16** is clamped between the head **12** and the block **14**. The head **12** contains a series of (inlet or outlet) passageways or ports **18***a* through **18***i* (FIG. 2) which extend into the valve head **12** to several of which act as inlets for various reagents, and other of which connect as outlets to collectors. As shown in FIG. 3, each of the ports **18** is a continuous passageway extending from the front surface **19** of the head **12** to the bottom surface **20** abutting the deformable membrane **16** which separates the head and the block. Individual valves A to I are formed at the end of each passageway **18** at the bottom surface **20** in cooperation with the deformable membrane **16**.

A flow path **22** (FIGS. 2 and 3) in the form of a downwardly open trough extends longitudinally along the bottom surface **20** of the head from valves B to G. The deformable membrane **16** closes the trough to form a generally closed channel serving as the flow path **22**. The illustrated flow path **22** is made up of a plurality of straight sections **23** which interconnect annular sections **24** surrounding each of the ports **18** at the spaced locations at which they emerge into the bottom surface **20**. Each port **18** is separated by a ring-shaped wall or partition **26** from the annular sections **24** of the flow path. At each end of the flow path **22**, (outlet or inlet) passageways **28** are provided which extend rearward from annular sections **24** to a rear surface **29** of the head **12**.

The membrane **16** is elastically deformable and is unsupported on its undersurface in the region of the valves as a result of cavities or cylinders **30** which are provided in the block **14** in underlying registration with each of the annular sections **24** of the flow path. Thus, the application of fluid pressure via the respective inlet passageways **18** to the upper surface of the membrane causes it to move downward away from the partition **26** to permit fluid flow between the ports **18** and the annular sections **24** of the flow path.

To maintain the valves A–I closed until it is desired to open them, plungers **32** (FIGS. 3 and 4) are provided for reciprocating movement in the vertical cylinders **30** and extend through the block **14**. Each cylinder **30** has an upper portion **31** of a diameter about the same size as the annular section **24** of the flow path. The plunger **32** in each cylinder **30** has a head **34** of a size greater than the ring-shaped partition **26** and a rod **36** which extends downwardly therefrom. The lower end of the rod **36** is received in a guide **38** which extends below the bottom surface of the block through a lower portion **37** of the cylinder **30** of reduced diameter and provides a bearing surface for the outer surface of the guide **38** which slides therein. In the illustrated embodiment, each of the nine independent valves A–I of the system contains such a guide **38**, the bottom surface of which rides along the surface of the rotating cam **40**. The shape of the individual cam **40** and the speed of its revolution determines whether a valve will be open or whether the plunger head **34** will be held in contact with the deformable membrane **16** in the latter case forcing it against the partition **26** to close the valve by preventing fluid flow between the port **18** and the longitudinal flow path **24**.

The head **12** made of a block of suitable material, such as polytrifluoromonochloroethylene (Kel-F), which is not chemically affected by exposure to the reagents employed and which has a low wettability with respect to most liquids (so there is a high angle of liquid contact with respect thereto). The head **12** is suitably formed by machining or by molding or casting.

Each of the nine ports **18***a* through **18***i* (FIG. 3) extends horizontally into the head from the front surface **19** of the valve head **12** to approximately its transverse center. At this point, the horizontal passageway ends at a vertical passageway extending downward to the bottom surface **20** where the deformable membrane **16** is located. Each of the ports **18** is of identical construction, and each port contains a tapered entrance section **41***a* (FIG. 3) of enlarged diameter which is adapted to receive a tapered plug **41***b*. Couplings **42**, which may each be provided with a calibrated orifice, are attached to the outer ends of the plugs **41***b*.

In the illustrated embodiment, liquid reagents are fed from supply lines **43** through the orifice-holding couplings **42** into individual valves A, C, E, E, F, and I. By the employment of the separate removable orifice-containing couplings **42**, careful metering and regulation of the fluid flow through each of the various ports is accomplished. The size of the particular orifice is determined by the properties, e.g. viscosity, surface tension, and/or density of the liquid which passes therethrough. Generally, a uniform pressure, for example, 1–2 p.s.i.g., of dry inert gas, upon the reagent supplies (not shown) is employed to deliver the liquids to the valves at a constant pressure head.

As stated earlier, the flow path **22** is in the form of a groove or trough formed in the bottom surface **20** of the head **12**. The deformable membrane **16** is quite thin and may be of any suitable resilient material that is chemically inert to the various reagents intended to be employed with the valve system **10**, for example polytetrafluoroethylene or special types of synthetic rubber. The valve system **10** is designed to operate at relatively low pressures, i.e., 1 to 2 p.s.i.g., and the thickness of the membrane **16** should permit deformation at such pressure differentials whenever the plunger head **34** is withdrawn

from the underside of the membrane **16**. A typical membrane **16** of polytetrafluoroethylene which may be used is of the order of 2 to 5 mils in thickness. When the plunger **32** is withdrawn from the underside of the membrane **16** (as shown in FIG. 3), it will bow downward as shown to connect the inlet port **18** and the flow path **12** in fluid communication. Such bowing occurs so long as the pressure in either the inlet port **18** or the flow path **22** is above atmospheric (discharge) pressure. The valve construction permits flow in either direction therethrough, depending upon where the higher pressure region is located.

The membrane **16** is substantially coextensive with the entire undersurface **20** of the head **12** and the block **14**. The membrane has no openings except those which permit the passage of fastening members, such as capscrews **44**, (FIG. 3), which are threaded upward into the head and clamp the membrane **16** between the block **14** and the undersurface **20** of the head **12**. The block **14** may be made of any suitable material, as all of the fluid flow passageways are in the head **12** located above the membrane.

Because of its thinness, the membrane **16** does not provide a reliable seal, and a separate resilient gasket **45** (FIGS. 3 and 4) is preferably employed, which is substantially thicker than the membrane **16**. The resilient gasket **45** cushions and protects the membrane **16** and avoids the creation of stresses at locations adjacent the cylinder openings **30** where it would otherwise be tightly clamped between two rigid surfaces. The gasket **45** has circular openings which register with each of the cylinders **30** and permit the deformation of the membrance thereinto.

As previously indicated, the illustrated block **14** is provided with nine cylinders **30**, wherein plungers **32** are located, below each partition. The plunger **32** in each cylinder **30** selectively seals the respective port **18** in a positive manner by forcing the membrane **16** upward against the partition **26**. In the illustrated embodiment, each plunger head **34** is circular, having a flat upper surface upon which a resilient pad **52** of rubber or other suitable material is mounted to engage the membrane **16**. The resilient pad **52** avoids damage to the thin membrane **16** which might result from repeated cycling of the plunger **32** into and out of contact with the membrane. The guide **38** has a central bore **54** into which the plunger rod **36** is slidingly accepted. The guide **38** in turn is slidingly received in the lower portion **37** of the cylinder **30** and is provided with a circular flange **56** at its upper extremity that prevents its removal downward from the cylinder.

Near the bottom of the guide **38** (FIGS. 3 and 4) (which carries a wheel **57** that rides along the peripheral edge of the cam **40**), a groove is provided to receive a retaining or snapring **58**. A coil spring **60** is provided between the retaining ring **58** and the undersurface of the block **14** to bias the guide **38** downward. When the location of the cam **40** allows the guide **38** to move downward, the plunger **32** follows as a result of gravity and the sliding friction between the outer surface of the rod **36** and the bore **54** of the guide. To interconnect the plunger **32** and the guide **38**, a second coil spring **62** is located surrounding the rod **36** between the upper surface of the flange **56** on the guide and the undersurface of the piston head **34**. In order to permit free movement of the rod **36** within the central bore **54** of the guide, a small air vent **64** is located in the bottom of the guide **38**. The provision of the spring **62** cushions the closing of each valve and determines the force with which each plunger **32** contacts the thin membrane **16**.

As mentioned earlier, the plunger assembly of each of the nine valves is actuated by means of cams **40** which are mounted on a common shaft **66** positioned therebelow. The radius of each cam **40** is sufficient at at least one location about its periphery to force the guide **38** upward a sufficient distance to cause the resilient pad **52** on the piston head **34** to press the membrane **16** against the partition and close the respective valve. Each cam **40** is relieved to provide one or more cutouts **68** which are of varying size and permit the downward displacement of the guide **38** and plunger **32**, thus establishing the desired sequence of valve openings. For purpose of illustration, one cutout **68** is shown on the cam **40** in FIG. 3.

When the guide **38** is forced upward by the cam **40**, the coil spring **60** surrounding the guide **38** is compressed, and the flange **56** at the upper end of the guide moves upward. The coil spring **62** surrounding the rod **36** in turn elevates the plunger head **34** and the pad **52** until it contacts the membrane **16** and presses it against the partition **26** and closing the valve. Some compression of the coil spring **62** occurs which cushions the closing of the valve. Thus, the strength of the spring **62** determines the force with which the valve is held closed. The valve remains closed until the cam **40** rotates to position a cutout **68** below the cylinder **30**, to permit the lower coil spring **60** to withdraw the guide **38** and the plunger **32** which follows the guide downward. The valve then remains open for the desired length of time which is determined by the speed of rotation of the shaft **66** and the cutout area of the cam **40**.

EXEMPLARY USE

The operation of the valve system **10** may be better understood in connection with an illustrative process wherein the valve system may be utilized. In this respect, reference is made to copending U.S. Pat. application Ser. No. 750,235, filed Aug. 5, 1968, in the names of Milton Winitz and Jack Graff, entitled "Amino Acid Analysis," or to Analytical Chemistry, 34, No. 11, 1414 (Oct. 1962). This copending application describes a process for analyzing a biological sample to quantitatively determine the amounts of amino acids therein.

To facilitate treatment of a biological sample according to the teaching of this copending application, a sample holder **72** (FIG. 1) is connected between lines **28***a* and **28***b*. A reactor **74** wherein the programmed reaction takes place is connected between lines **28***c* and **28***d*. The biological sample, which may for example be human blood (containing a mixture of nonvolatile amino acids), is first pretreated using cationic exchange resins and then eluted from the resins, using a suitable liquid such as acidified n-propanol. The eluted sample which contains the amino acids is then transferred manually to the sample holder.

The automatic programming of the device then takes place with the shaft **66** being driven by a suitable motor (not shown) at the desired rate of rotation, e.g., 1 revolution an hour, causing the cams **40** to actuate the individual valves A to I at the desired sequences. When the process is actuated, a slow constant flow of dry inert gas, for example nitrogen, is fed to the sample holder **72** through the line **76** and carries the sample through the line **28***b* to the valve B. The cams **40** are arranged so that the valves A and B open generally in unison, and additional solvent for the sample is supplied to the sample holder **72** through the valve A. The carrier gas entering through the line **76** moves the sample and solvent to the valve B. For convenience in making connection, the construction of the valve B is reserved with respect to the valve A (as seen in FIG. 2), and the line **28***b* connects to the center of the valve B whereas the port **18***b* connects the annular section **24**.

To facilitate movement along the flow path **22** toward the reactor **74**, an ancillary flow of dry nitrogen is fed through the port **18***b* throughout the operation of the device. This nitrogen flow assists travel along the flow path into the reactor **74** during the time allotted.

At the end of the flow path **22**, the sample passes out the line **28***c* and into the reactor **74** for conversion to volatile amino acid derivatives preparatory to gas-liquid chromatography. Here, a liquid gas separation takes place, and the gas flows through the line **28***d* and out the valve H, which is open throughout most of the process, to a line **78** leading to a waste container **80**. While the valves A and B are open, the carrier gas flows through the sample holder **72** to assure that the sample holder is completely cleared of sample and solvent.

After the sample has been transferred to the reactor **74**, different reagents are supplied sequentially by systematically opening the valves C, D, E and F. The reagents sequentially: (1) dry the sample by azeotropic distillation, (2) esterify the amino acids, (3) again dry by azeotropic distillation, (4) acetylate to form a volatile derivative, and (5) again dry. In carrying out the process described in the copending patent application, a mixture of n-propanol and benzene (as azeotroping agent) is supplied through valve c, and anhydrous n-propanol-HC1 (esterification agent) is supplied through valve D. Acetic anhydride (acetylating agent) is supplied through valve E, and pyridine (to neutralize the (HC1) is supplied through valve F. It takes the cams **40** about 60 minutes to make one complete revolution, and during this time various of the valves open and close more than once.

As previously indicated, the valve H remains open until the reaction is complete and then closes. When the valve H closes, the valves G and I open. The valve I leads to an open top collector **82**. A source of dry nitrogen gas and a suitable solvent, such as ethyl acetate, is connected to valve I. Accordingly, the ethyl acetate is carried in a line **28***d* into the reactor **74**, where it dissolves the sample, and flows out of the bottom of the reactor through line **28***c* leading to the flow path **22**. Because the valve G is open and because the supply of carrier gas continues into the port **18***b*, preventing flow of the liquid from the reactor along the flow path **22**, the liquid leaving the reactor passes out the valve G through the port **18***g* to the open top collector **82**.

In an operation such as this, it is important that metered amounts of liquid be fed to the reactor **74** throughout the individual process steps. Metering of the liquids is carried out by the amount of time the individual valves are open and by the size of the individual orifices disposed in the receptive couplings **42** connected between supply of reagent and the port leading to the valve. A relatively constant gas pressure, for example 1 to 2 p.s.i.g., is maintained on all of the reagent supplies, and it is this gas pressure which causes the flow of liquid whenever the valves A, C, D, E or F are opened. Thus, based upon this constant driving pressure, the desired amount of flow is established by choosing the proper size orifice relative to the amount of time that the valve will be open. For a different reaction or when a liquid of different physical properties is employed, a desired timed flow can be achieved simply by changing the orifice size, within certain limits.

Although the invention has been illustrated with respect to a particular arrangement of a flow path and interconnected valves, it will be understood that many variances are possible using the basic valve system to provide automatic, timed, sequential flow of liquids for use in chemical processes, particularly preliminary to anaylsis.

The arrangement of the individual valves located generally interior of the annular sections **24** of a longitudinal flow path provides an arrangement wherein there is essentially zero dead space at the valves wherein reagents might accumulate and influence subsequent steps, as for example by interreacting with another reagent being supplied for a subsequent step. The constant purge flow of carrier gas throughout the longitudinal flow path **22** during the operation assures the transportation of the liquids injected into the system through the individual valves (particularly when the head **12** is made of a material having the low wettability of Kel-F). This serves as a positive prevention of any undesirable accumulation in the flow path. Likewise, provision of orifices in couplings **42** which can be substituted to change the size thereof affords flexibility in establishing precise metered amounts of liquid being fed to the reactor during any single step, and it also affords adaptation of the overall system to other liquids having different physical properties.

Other modifications as would be apparent to one skilled in the art may be made to the illustrated valve system without departing from the scope of the invention which is defined in the appended claims. Various of the features of the invention are set forth in the following claims.

What is claimed is:

1. A valve system comprising a body, open through means formed in one surface of said body, a membrane positioned against said one surface of said body and acting as one wall of said trough means to provide a closed flow path, a plurality of ports extending into said body and terminating at spaced points on said one surface adjacent to said flow path, partition means separating each of said ports from said flow path at said spaced points, said membrane being elastically deformable in response to fluid pressure to move away from said partition means and allow fluid communication between said ports and said flow path, a plurality of movable means for contacting an opposite surface of said membrane and holding it in contact with each said partition means to close each said port from said flow path, actuator means engaging each said movable means for selectively opening and closing each of said ports to permit fluid flow between said flow path and any selected ports, said membrane being clamped between said body and a block, said block including a series of cylinders located in registration with each of said partition means, said movable means for closing said ports constituting plungers which are reciprocatingly mounted in said cylinders, and said plungers containing separate parts which are slidably interconnected with resilient spring means for transferring force to the part which bears against said membrane to force it in contact with said partition means.

2. A valve system in accordance with claim **1** wherein one end of said flow path connects to a reactor, and wherein a separate valve in said valve system which is opened and closed by said membrane connects to said reactor and to a waste.

3. A valve system in accordance with claim **2** wherein s source of carrier gas is connected to the end of said flow path opposite to said one end to supply gas through said flow path to said reactor.

4. A valve system in accordance with claim **3** wherein means for introducing a sample is connected to said opposite end of said flow path through one of said ports.

5. In a valve system for predetermined addition of reactants selectively to a sample in a reactor, said valve system being adapted to be connected to a sample source, a plurality of reactant sources and reactor means, the combination comprising,

a valve body having trough means defining a closed flow path,

a plurality of ports extending into said path and terminating adjacent to said flow path,

valve means separating each of said ports from the flow path,

means connecting said sample source to one of said ports adjacent one end of the flow path,

means connecting respective ones of said reactant sources to intermediate ones of said ports,

means for selectively opening and closing said valve means for each of said ports to permit flow between the selected port and said flow path, and

means for establishing a constant purge flow of carrier gas through the flow path from said sample holder end to the reactor end thereof so that said sample and reactants when introduced into the flow path upon opening of their respective valves are moved completely out of the flow path into said reactor.

6. A valve system as claimed in claim **5** wherein said trough means is formed in one surface of said body and said valve means comprises a membrane positioned against said one surface of the body acting as one wall of said trough means to provide the closed flow path, partition means separating each of said ports from said flow path, said membrane being elastically deformable in response to fluid pressure to move away from said partition means and allow fluid communication between said ports and said flow path, a plurality of movable means for contacting an opposite surface of said membrane and holding it in contact with each of said partition means to close each said ports from said flow path.

7. A valve system as claimed in claim **6** wherein said membrane is clamped between said body and a block, said block

including a series of cylinders located in registration with each of said partition means, said movable means for closing said ports constituting plungers which are reciprocatingly mounted in said cylinders, means for biasing said plungers in a direction away from said partition means, and rotatable cam means for moving said plungers to open and close said ports in a predetermined selective manner during rotation of said cam means.