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DETERMINATION OF THE GAS CONTENT OF LIQUID METALS

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2 Sheets-Sheet 1

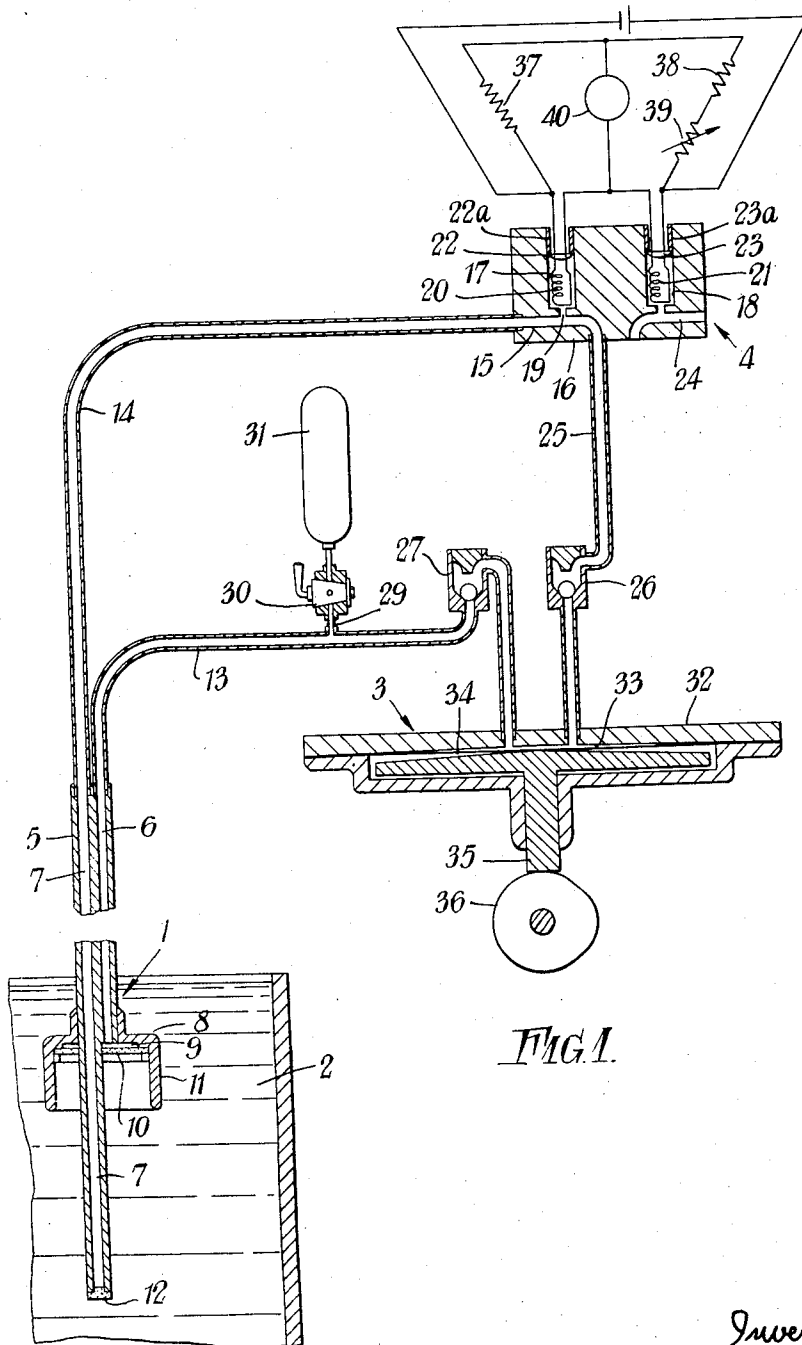


FIG. 1.

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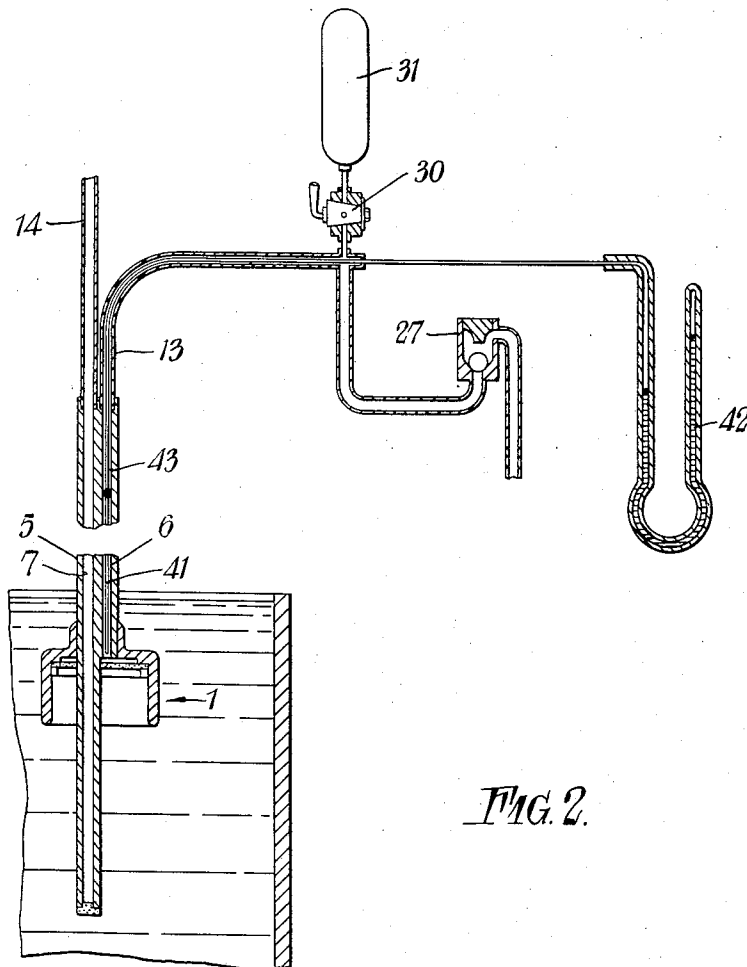


FIG. 2.

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DETERMINATION OF THE GAS CONTENT OF LIQUID METALS

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Claims priority, application Great Britain August 10, 1954

30 Claims. (Cl. 73—19)

This invention relates to improvements in the determination of the gas-content of liquid metals.

It has been proposed to measure the content of dissolved hydrogen in a molten metal by a method which comprises the steps of causing a free surface of the metal to form at a location within the body of the metal and of determining the magnitude of the equilibrium pressure of molecular hydrogen which develops at this free surface. Various forms of apparatus for carrying this method into effect have been described and although these are in general satisfactory, they have the disadvantages that a relatively long period of time (of the order of 8 minutes) is required to ensure that the end point has been reached, that the indicator employed moves comparatively slowly and that there are occasional failures to respond at all. These drawbacks appear to stem from the blanketing effect of aluminium oxide films on the transfer of hydrogen from the liquid metal to the free space created within the metal by the apparatus employed and although various methods of clearing this oxide away have been suggested they do not always guarantee success.

It is an object of the present invention to provide an improved apparatus for determining the gas-content of liquid metals which shall have a shorter response time and be more reliable in operation than the method and apparatus of the proposals referred to above.

According to one feature of the present invention an apparatus for measuring the content of hydrogen dissolved in a molten metal performs the steps of causing a free surface of the metal to form at a location within the body of metal, bringing a volume of an inert gas into contact with the metal below said free surface, circulating the gas a plurality of times through said location and a path extending externally of the body of the metal and determining the hydrogen-content of the circulated gas when it is substantially in equilibrium with the hydrogen-content of the molten metal.

The inert gas, which may be nitrogen or argon, picks up some hydrogen from the molten metal when it is first brought into contact with the latter and the hydrogen-content of the inert gas increases during each subsequent period of contact until it is in equilibrium with the hydrogen-content of the molten metal. In general, the number of contacts required between the body of inert gas and the molten metal is relatively large, e. g. about 100, before equilibrium is reached and a convenient method of securing this is to circulate a very small volume of the inert gas through a closed path which includes an internal portion in which the gas bubbles through the molten metal and an external portion in which the gas is isolated from the air. The means for determining the hydrogen-content of the circulated gas is connected into the external portion of the closed path. It may comprise a palladium thimble for separating off, in a very small subsidiary volume, the hydrogen contained in the inert gas and means, such as a manometer, for measuring the pressure developed in the subsidiary volume. The

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thimble may be arranged in the part of the apparatus which is to be dipped into the molten metal so that it will be heated to the temperature necessary to promote diffusion of the hydrogen therethrough. The preferred device for measuring or determining the hydrogen-content of the inert gas is, however, one making use of the thermal conductivity of the gas and a suitable device is a Shakespear Katharometer (see "Gas Analysis by Measurement of Thermal Conductivity"—H. A. Daynes—Cambridge University Press, 1933).

In order that the invention may be clearly understood, some embodiments thereof will now be described by way of example reference being made to the accompanying drawings in which:

Fig. 1 is a sectional view of one embodiment thereof, and

Fig. 2 shows a modification.

The apparatus comprises, as essential parts, an immersion head indicated generally at 1 by means of which the insert gas is to be brought into direct contact with the molten metal 2 below the surface thereof; a pump indicated generally at 3 by means of which the gas is to be circulated to and from the immersion head 1; and means indicated generally at 4 for measuring the concentration of hydrogen in the gas as it circulates externally of the molten metal.

The total volume of the inert gas which is to be employed in an actual determination must be very small and it has been found that a volume of 1 to 2 cc. (at standard temperature and pressure) is suitable.

A suitable material from which to construct the immersion head 1 must be one which is (1) not attacked by the molten metal concerned, (2) impermeable to gas, (3) stable to hydrogen at the temperature of the molten metal, even after exposure to air at elevated temperatures, (4) mechanically robust, and (5) resistant to thermal shock. Although dense ceramic materials, e. g. of alumina, are capable of use under experimental conditions, they are not suitable for routine use in production work and it has been found that a material which fulfills all requirements is stainless steel (e. g. of the 18-8 Cr-Ni type) coated with a vitreous enamel and, preferably, protected with a refractory wash which adheres firmly to the enamel.

In the present example, illustrated in Fig. 1 the immersion head comprises a vertical twin bore tube 5 the bores being indicated at 6 and 7 which over the lower part of its length is partially cut away so that it only comprises the single bore 7 in this part. A small hood 8 is secured on the lower end of the twin-bore portion of the tube 5 so that the shorter bore 6 opens into the upper part 9 of the hood-space, this part being separated from the lower part of the space by a partition or diaphragm 10 of porous ceramic material which prevents entry of molten metal into the bore. The longer bore 7 which extends below the skirt 11 of the hood 8 by, for example, about 1"—1.5", is plugged at its lower end with porous ceramic material 12 for the same purpose. The hood 8 may have an internal diameter of about 0.8" and a depth of about 0.4", while the bores 6 and 7 in the tube 5 may be about 0.04" in diameter.

The head 1 when for use with molten aluminium, is constructed from the material referred to above, namely 18-8 heat-resisting stainless steel enamelled with, for example, a vitreous enamel known by the trade name "Solaramic 5210/3.0" and coated with a refractory material which reacts with the enamel at the temperature of molten aluminium and becomes firmly adherent thereto.

The upper ends of the twin bores 6 and 7 in the immersion head 1 are each connected by a suitable small-bore tube 13 and 14 respectively (internal diameter

preferably not more than 0.04") to the remainder of the apparatus which is suitably housed somewhat remote from the head 1 so that immersion of the latter in molten metal 2 cannot harm the rest of the equipment. The tube 14 connected to the bore 7 of the head leads into one end of a small bore passage 15 formed through a copper block 16 adjacent to the cell 17 of one of two substantially identical cells 17 and 18 formed therein, this first or measuring cell 17 communicating with the passage 15 through a further such passage 19. Each cell 17 and 18 has supported therein a fine platinum wire spiral indicated at 20 and 21 respectively which is insulated from the block 16 and connected at its ends to lead-out wires passing through a gas-tight seal of glass 22 and 23 respectively or the like which seals the lower end of a copper cylinder 22a and 22b respectively secured in a gas-tight manner in the copper-block 16 to close the ends of the cells 17 and 18 respectively. The volume of each cell 17 and 18 may be about 0.5 cc. and the second or comparator cell 18 is in free communication with a small-bore passage 24 formed through the block 16 but in free communication at its ends with the atmosphere.

The other end of the small-bore passage 15 associated with the measuring cell 17 is connected by another fine-bore tube 25 through a ball-type outlet valve 26 to the pump 3 which has an extremely small swept volume, the inlet valve 27 of this pump 3 being arranged to control the passage of gas to the pump the fine-bore tube 13 leading to the upper end of the shorter bore 6 in the immersion head 1. The last-mentioned tube 13 has a branch connection 29 through which an inert gas may be supplied, under the control of a cock 30, from a source such as a small cylinder of the compressed gas 31. The cock 30 is such that when closed the gas-filled volume on the circuit side thereof is extremely small.

A convenient form of pump 3 comprises a steel disc 32 having the connections from the inlet and outlet valves 27 and 26 arranged to open into the deepest part of a shallow concavity 33 machined in its underside and over which is secured, in a gas-tight manner, a thin steel diaphragm 34. Means is provided for periodically depressing the central portion of the diaphragm 34 into the concavity 33 and releasing it, for example a plunger 35 operated by a cam 36 which is rotatable by means of a crank-handle (not shown). The volume of the pump chamber may be 0.5 cc.

The two platinum spirals 20 and 21 are connected electrically into a normal Wheatstone bridge arrangement with two fixed resistances 37 and 38 having a low temperature coefficient, and a potential difference of, say, 1.8 volts is established across the bridge. Under these conditions a current of about 120 milliamperes is passed through each filament 20 and 21. The bridge is initially balanced by adjustment of a subsidiary resistance 39, the total resistance in each arm being of the order of 16 ohms. Should the inert gas, in this example, nitrogen, in the measuring cell 17 become richer in hydrogen, the filament or spiral 20 in this cell will be cooled relative to that in the comparator cell 18 and its resistance will be lowered to unbalance the bridge. The most convenient method of measurement is to determine the out-of-balance potential across the bridge by means of a millivoltmeter 40 or potentiometer. If the former is used it is preferably an instrument with a high electrical resistance (say, 50 ohms) in order that damping of the bridge may be avoided.

In the operation of the apparatus, nitrogen is admitted to the gas circulation circuit and when the measuring cell 17 is filled with the gas, the supply of current to the bridge is established and the bridge balanced.

The cock 30 is opened so that nitrogen will flow through both bores 6 and 7 of the immersion head (the inlet and outlet valves 27 and 26 being so arranged that they are both opened by the pressure of the gas) and issue

as a steady stream from both the hood 8 and the lower end of the bore 7 of the twin-bore tube 5. The head 1 is immersed in the molten metal 2 with the gas still flowing and after a few seconds the cock 30 is closed and the operation of the pump 3 commenced. Conveniently, the rate of operation is such that the total volume of nitrogen in the circuit is circulated about once every second and, under these conditions, the equilibrium concentration of hydrogen is built up in about 1½ minutes.

Where an inert gas other than nitrogen is employed, the comparator cell 18 must be maintained full of this gas at atmospheric pressure during the measuring operations.

The example described with reference to Fig. 1 may be modified as shown in Fig. 2 by replacing the means described for measuring the hydrogen content of the inert gas with means for measuring the pressure of the hydrogen in the inert gas. This means may comprise a thimble 41 of a material, e. g. palladium, which is pervious to hydrogen, but is impervious to the inert gas, the thimble 41 being disposed with clearance within the lower end of the bore 6 of the measuring head 5 and having its interior connected to a pressure sensitive device, e. g. a manometer 42. The annular space 43 between the thimble 41 and the wall of the head 1 defining the bore 6 is connected to the cock 30 and to the inlet valve 27 of the previous example and the fine bore tube 14 is connected directly to the tube 25 leading to the outlet valve 26 (the copper block 16 being omitted). The thimble 41 is heated by the molten metal 2 to the temperature necessary to promote diffusion of hydrogen therethrough.

The operation of the modified apparatus will be readily understood from the foregoing example.

It will be understood that the apparatus described is capable of modification in various ways. For example, other types of valves may be employed in the pump construction in place of the ball valves referred to and the pump elements may be constructed from non-corrodible materials such as Phosphor-bronze.

The bores 6 and 7 in the tube 5 may, if desired, be of the same length in which case the lower end of the bore 6 would be sealed and a passage would be provided in the wall of the tube 5 to place the bore 6 in connection with the upper part 9 of the hood-space.

What I claim is:

1. Apparatus for determining the gas-content of liquid metals, comprising an immersion head adapted to be immersed within the body of liquid metal, said immersion head including means for bringing a volume of inert gas into contact with the liquid metal in an area adjacent said head and within the body of liquid metal, means providing a path connected with said head for flow of the gas externally of said immersion head, means for circulating the gas a plurality of times through said immersion head and said liquid metal and through said path, and means for determining the hydrogen-content of the circulated gas.

2. Apparatus according to claim 1 wherein the immersion head comprises a hollow body adapted to be at least partly immersed in the liquid metal and having at least a part of its walls composed of a material which is pervious to hydrogen and to the inert gas but impervious to the molten metal.

3. Apparatus according to claim 1 wherein the immersion head comprises a hollow body adapted to be at least partly immersed in the liquid metal and having at least a part of its walls composed of a porous ceramic material which is pervious to hydrogen and to the inert gas but impervious to the liquid metal.

4. Apparatus for determining the gas-content of liquid metals, comprising an immersion head adapted to be immersed within the body of liquid metal, said immersion head including means for bringing a volume of inert gas into contact with the liquid metal below the surface

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thereof, and a closed path for flow of said inert gas, said path including an internal portion in which the gas bubbles through the liquid metal and an external portion in which the gas is isolated from the air, means for circulating the gas through said path and means for determining the hydrogen-content of the circulated gas.

5. Apparatus according to claim 4 wherein the volume of the external portion of the closed path is of the order of 1 to 2 cc.

6. Apparatus according to claim 4 wherein the means for determining the hydrogen-content of the circulated gas is connected to the external portion of the closed path.

7. Apparatus according to claim 4 wherein the means for determining the hydrogen-content of the circulated gas comprises means for separating off, in a very small subsidiary volume, the hydrogen contained in the inert gas and means for measuring the pressure developed in the subsidiary volume.

8. Apparatus according to claim 4 wherein the means for determining the hydrogen-content of the circulated gas comprises a vessel for separating off, in a very small subsidiary volume, the hydrogen contained in the inert gas, and said vessel has at least a part of its wall composed of a material which is pervious to hydrogen and impervious to the inert gas, and means for measuring the pressure developed in the subsidiary volume.

9. Apparatus according to claim 4 wherein the means for determining the hydrogen-content of the circulated gas comprises a vessel for separating off, in a very small subsidiary volume, the hydrogen contained in the inert gas, and said vessel has at least a part of its wall composed of palladium, and means for measuring the pressure developed in the subsidiary volume.

10. Apparatus according to claim 4 wherein the means for determining the hydrogen-content of the circulated gas is connected to the external portion of the closed path and measures the thermal conductivity of the gas.

11. Apparatus according to claim 4 wherein the means for determining the hydrogen-content of the circulated gas is connected to the external portion of the closed path and comprises an electrical resistance wire having a high temperature coefficient of electrical resistance and means for measuring the electrical resistance of the wire.

12. Apparatus according to claim 4 wherein the means for determining the hydrogen-content of the circulated gas is connected to the external portion of the closed path and comprises an electrical resistance wire having a high temperature coefficient of electrical resistance and electrical resistance measuring means comprising an electrical bridge network having the electrical resistance wire connected in one arm thereof.

13. Apparatus according to claim 4 wherein the circulating means comprises a pump having a chamber connected in the external portion of the closed path.

14. Apparatus according to claim 4 wherein the circulating means comprises a pump having a chamber connected in the external portion of the closed path, and two valves are connected in the external portion of the closed path one on each side of the pump chamber, one of said valves being arranged to close and the other to open on the pumping stroke of the pump whereby the gas is circulated in one direction only in said closed path.

15. Apparatus in accordance with claim 4 wherein a supply of inert gas is connected to the external portion of said closed path.

16. Apparatus according to claim 4, wherein the circulating means comprises a pump having a chamber connected in the external portion of the closed path and two valves are connected in the external portion of the closed path and a supply of inert gas is connected to the external portion of the closed path, the valves being positioned on the same side of the supply of inert gas and being opened by the pressure of said gas flowing from the supply thereof.

17. Apparatus for determining the gas-content of liquid

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metals, comprising an immersion head adapted to be immersed within the body of liquid metal, said immersion head including a pair of open ended tubes, a hood fixed to said tubes, a partition of porous ceramic material mounted within said hood and separating the hood space into an upper area and a lower area to prevent entry of liquid metal into said upper area, one of said tubes opening into said upper area and the other tube opening into the liquid metal and the open end of said other tube being plugged with a ceramic material to prevent entry of liquid metal into the tube, said tubes being connected with a closed circulatory path for bringing an inert gas thereto for flow therethrough and through the liquid metal, means for circulating said gas through said path and tubes and means for determining the hydrogen-content of the circulated gas.

18. Apparatus for determining the gas-content of liquid metals, comprising an immersion head adapted to be inserted in the liquid metal, said immersion head including a pair of open ended tubes, one of said tubes being longer than the other of said tubes, a hood fixed to said tubes, a partition of porous ceramic material mounted within said hood and separating the hood space into an upper area and a lower area to prevent entry of liquid metal into said upper area, the shorter of said tubes opening into said upper area and the longer of said tubes extending and opening into the liquid metal and the open end of said longer tube being plugged with a ceramic material to prevent entry of liquid metal into said tube, said tubes being connected with a closed circulatory path for bringing an inert gas thereto for flow therethrough and through the liquid metal, means for circulating said gas through said path and tubes and means for determining the hydrogen-content of the circulated gas.

19. Apparatus according to claim 18 wherein said hood provides a skirt and the longer tube extends into the liquid metal below said skirt.

20. Apparatus according to claim 18 wherein said hood provides a skirt and the longer tube extends into the liquid metal below the skirt a distance of about 1"-1.5", the hood having an internal diameter of approximately 0.8" and a depth of about 0.4" and the internal diameters of the tubes are about 0.04".

21. Apparatus according to claim 18 wherein the immersion head is constructed from 18-8 heat-resisting stainless steel.

22. Apparatus according to claim 18 wherein the immersion head is constructed from 18-8 heat-resisting stainless steel enamelled with a vitreous enamel.

23. Apparatus according to claim 18 wherein the immersion head is constructed from 18-8 heat-resisting stainless steel enamelled with a vitreous enamel and the enamel is coated with a refractory material which reacts with enamel at the temperature of the liquid metal and becomes firmly adherent thereto.

24. Apparatus for determining the gas-content of liquid metals, comprising an immersion head adapted to be immersed within the body of liquid metal, said immersion head including a pair of open ended tubes, one of said tubes being longer than the other of said tubes, a hood fixed to said tubes, a partition of porous ceramic material mounted within said hood and separating the hood space into an upper area and a lower area to prevent entry of liquid metal into said upper area, the shorter of said tubes opening into said upper area and the longer of said tubes extending and opening into the liquid metal and the open end of said longer tube being plugged with a porous ceramic material to prevent the entry of liquid metal thereto, said tubes being connected with a closed circulatory path including a pump having a pump chamber for circulating an inert gas a plurality of times through said path, said tubes and the liquid metal, the shorter tube being connected at its other end to the pump chamber by way of a first valve which is arranged to close on the pumping stroke of the pump, and a cell

for measuring the hydrogen-content of the gas, and a second valve, the pump chamber being connected by way of the second valve which is arranged to open on the pumping stroke of the pump with the cell, and the cell being connected to the other end of the longer tube. 5

25. Apparatus according to claim 24 wherein a supply of inert gas is connectible into the closed circulatory path which is connected to the other end of the shorter tube and said two valves are caused to open by the pressure of the inert gas when it is connected into the closed circulatory path. 10

26. Apparatus according to claim 24 wherein said pump comprises a steel disc formed with a concavity on one side and having an inlet connected to said first valve and opening into the concavity and having an outlet connected to said second valve and opening into the concavity, and a thin steel diaphragm secured in a gas-tight manner over the concavity, the space between the diaphragm and the face of the disc defining the concavity constituting the pump chamber and the central portion of the diaphragm being arranged to be periodically depressed into the cavity, and means for depressing the central portion of the diaphragm into the concavity. 15 20

27. Apparatus according to claim 24 wherein the volume of the pump chamber is of the order of 0.5 cc. 25

28. Apparatus according to claim 24 wherein a plati-

num wire spiral is mounted in the cell and is connected in one arm of a bridge network.

29. Apparatus according to claim 24 wherein the volume of the measuring cell is of the order of 0.5 cc.

30. Apparatus according to claim 24 wherein a platinum wire spiral is mounted in the cell and is connected in one arm of a bridge network and a comparator cell is provided which is substantially identical with the aforementioned cell, a platinum wire spiral being mounted in said comparator cell and connected in another arm of said bridge network.

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