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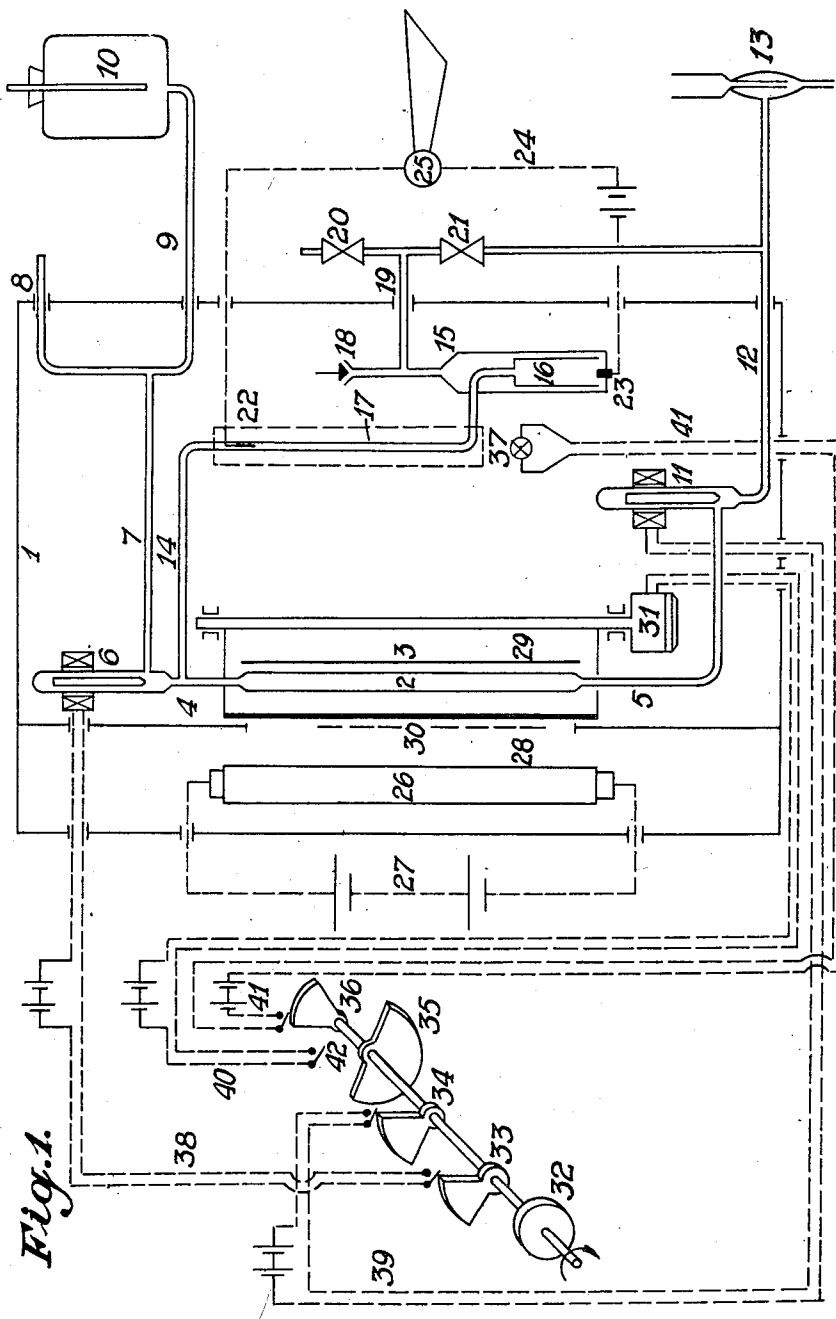
R. SCHÖBERLE ET AL

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GAS MEASURING DEVICE

Filed July 9, 1959

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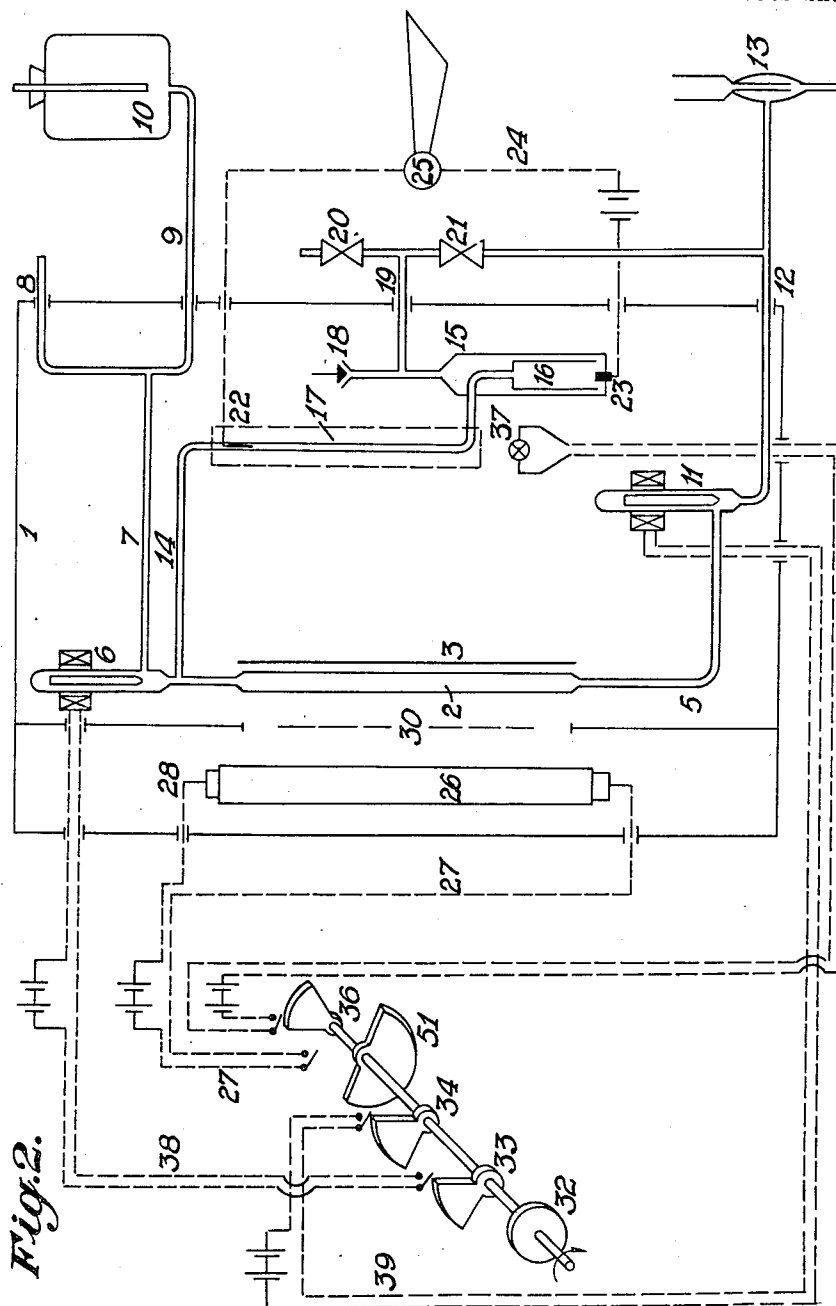
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GAS MEASURING DEVICE

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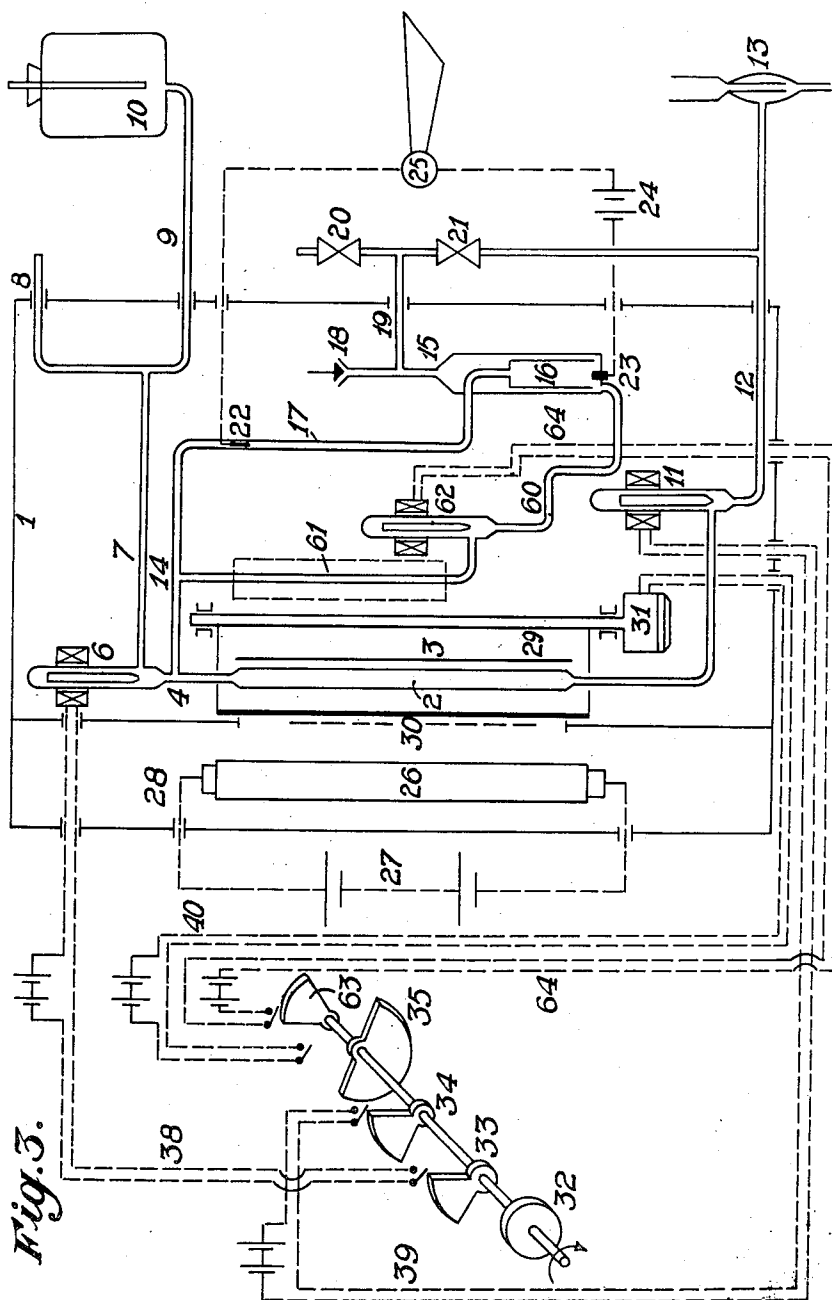
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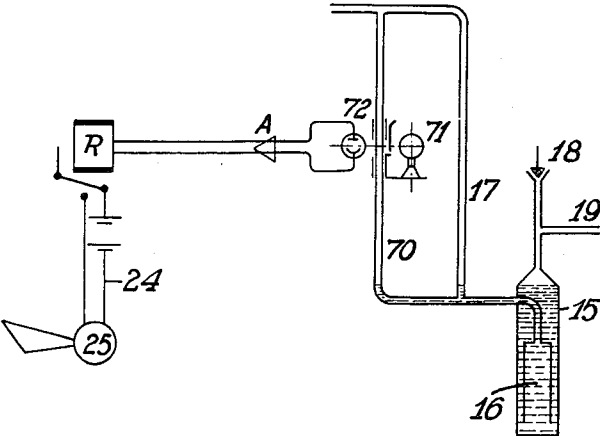
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Fig. 4.



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GAS MEASURING DEVICE

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6 Claims. (Cl. 23-255)

The present invention concerns an apparatus for measuring the constituents of reactive gaseous mixtures and simultaneously indicating that the explosive limit of the said mixtures has been reached; it concerns particularly an automatic device for the determination of hydrogen in chlorine, for example in the chlorine which comes from the electrolysis of aqueous solutions of chlorides of alkali metals in cells with mobile mercury cathodes. It is of particular interest for controlling the good working of electrolytic cells.

It is known that in electrolytic cells having a mobile mercury cathode, hydrogen can fortuitously be formed at the surface of the cathode by local decomposition of the alkali metal amalgam. The formation of hydrogen brings about not only a lowering of the yield of the electrolysis but the mixture of this gas with the gas liberated at the anodes can also rapidly become explosive. It is therefore of interest to arrange means which permit the measurement of the hydrogen in the chlorine and thus to detect any abnormal working of the electrolytic cell.

It is known that a reaction between two gases can be brought about by burning one in the other, for example, before the content of one of the constituents has reached such proportions as to render the mixture explosive. Continuous measuring methods have already been proposed for gaseous mixtures based on absorption, upon combination or upon combustion of the gases. However the devices based on these processes are relatively complicated, costly and difficult to maintain.

In Belgian Patent No. 509,023 the applicant has described a process and apparatus for the detection of gaseous explosive mixtures based on the principle known as such, consisting of periodically causing photochemical combination of the gases and making use of the physical conditions which result from that combination, that is to say by causing the variation in resulting pressure to act upon a manometric device which at a given value of the variation, brings about the closing of an electrical circuit to activate an indicating relay. Although this device is able to forestall abnormal working of the electrolytic cell it cannot however indicate with precision the amount of hydrogen in the chlorine and thus permit the continuous observation of the working of the electrolytic cells.

The object of the present invention is an improved automatic apparatus for determining with precision the amount of hydrogen in the chlorine and to indicate with respect to this amount as to whether the mixtures of the two gases have reached a predetermined limit, well below the limit of explosion.

The apparatus according to the invention comprises in combination: (a) a reaction chamber permeable to actinic radiation, provided with a feeding system for a gaseous mixture to be analysed, an exhaust system for the resulting products of the reaction and a system creating a depression in the apparatus, (b) a manometric system comprising a manometric liquid which conducts electricity and which may be coloured, a reading device which may also be capable of recording and an indicator device arranged in an electrical circuit, (c) a system for periodic illumination of the reaction chamber by means of an actinic light and (d) controllers for disengaging

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the sequence of operations automatically achieved in the device.

The apparatus which forms the object of the present invention is simple economical and strong. In contrast to previously proposed apparatus, it does not need previous purification and drying of the gaseous mixture to be analysed. The working principle of the apparatus consists in bringing about the combination of hydrogen and chlorine by irradiation by means of actinic light, the determination being based upon the volume contraction due to the absorption of hydrogen chloride formed during the combination of chlorine and hydrogen. It must be understood that this combination could be brought about by other means, for instance by means of an electric spark.

A predetermined volume of chlorine is taken containing hydrogen and possibly other gases inert with respect to chlorine. The combination of chlorine and hydrogen is then brought about. The hydrogen chloride formed is then absorbed in water or in a salt solution, saturated with chlorine. At the end, the contraction of volume resulting from the absorption of the hydrogen chloride is measured.

Water can be used as solvent because of the weak solubility of chlorine and the great solubility of hydrogen chloride which is immediately absorbed, so much so that the presence of droplets of water or of a thin layer of water on the wall of the reaction chamber is enough to absorb it completely. The solubility of the chlorine in the water can be still further reduced by dissolving a salt in it, the presence of this salt not influencing in any appreciable manner the absorption of the hydrogen chloride.

The apparatus forming the object of the invention will be described in the following with reference to FIGURES 1, 2, 3 and 4 of the accompanying drawing which represents various embodiments of the invention. It must be understood that the invention is in no way limited by these drawings and that it is capable of variations without departing from its scope.

In the drawings, FIG. 1 is a diagrammatic representation of an apparatus assembly embodying features of the present invention;

FIG. 2 is a similar view of another embodiment of the invention;

FIG. 3 is a similar view of a still further embodiment of the invention; and

FIG. 4 is a partial view showing a further embodiment of the indicator system which forms part of the apparatus shown in FIGS. 1, 2 and 3.

In FIGURE 1, the apparatus, constituted in a cover 1, comprises a reaction chamber 2 made of material permeable to actinic radiation and provided with a reflector 3. The reaction chamber is itself equipped with inlet tube 4 for the gaseous mixture to be analysed and outlet tube 5 for the products resulting from the reaction. The inlet tube 4 is provided with an electromagnetic inlet valve 6 which connects tube 4 with the feed tube 7 for chlorine and chlorine water or the salt solution saturated in chlorine. The chlorine coming, for example, from the receiver of an electrolytic cell, is led by means of tube 8 connected to the said receiver—not shown—while the chlorine water contained in the receiver 10 is fed by means of tube 9. Tubes 8 and 9 are connected with tube 7.

The outlet tube 5 is likewise provided with an electromagnetic valve 11 and communicates with tube 12 in relation with the jet 13 which serves to maintain a constant depression in the apparatus and thus, to draw through the chlorine coming from the receiver. The depression is maintained constant by means of a manostat—not shown.

The manometric system of measurement is connected

to the reaction chamber 2 by means of tube 14 which opens into the inlet tube 4. It comprises the receiver 15 in which there is disposed bell 16 connected to the reading system 17. The reading system 17 is placed in front of an opening arranged in the cover 1, it is represented as dotted line in the figure. Filling of the manometric system with manometric liquid which conducts electricity, is carried out through 18. For degassing the manometric liquid there are provided the tube 19 and the gate valve 21 working in connection with the jet. The gate valve 20 puts the manometer into communication with the atmosphere. The manometric device is further provided with electrodes 22 and 23, and an electric circuit 24 and an audible indicator 25 arranged in this circuit. The electrode 23 is continuously submerged in the manometric liquid while the electrode 22 is only in contact therewith if the amount of hydrogen in the chloride attains the concentration corresponding to the predetermined limit well below the explosive limit.

The source of actinic light is the lamp 26, fed by the electric circuit 27. It is arranged in an enclosure 28 in relationship to the reaction chamber 2. An opening 30 is arranged in the cover, facing the lamp.

In front of this opening in the interior of the cover 1, a shutter 29 is arranged which is moved around the reaction chamber by an electromagnet rotating against a resilient spring 31. This movable shutter serves to cut out the light, the lamp 26 remaining constantly alight.

The various operations carried out in the apparatus are controlled by means of contacts. These take the form of a sector of which the angle varies according to the time for which contact is to be made and are staggered in space around a common axis 42 at an angle corresponding to a predetermined sequence of operations. The axis 42 is driven by a synchronous motor 32 provided with a reducing gear, not shown, rotating at a predetermined constant speed.

Contacts 33 and 34 act respectively on electromagnetic inlet valve 6 and outlet valve 11 by means of the electric circuits 38 and 39. Contact 35 acts by means of circuit 40 on the electromagnet 31 operating the shutter 29. Contact 36 acts on the luminous pilot lamp 37 by means of circuit 41. This pilot lamp indicates the moment when the measurement is to be made visual.

The apparatus functions as follows. It is convenient to observe that in the description of this functioning the times are all counted from zero.

The lamp 26 is lit, the jet 13 is set going and the synchronous motor 32 turns at such a speed that the axis 42 which carries the various contacts makes one complete rotation in 180 seconds.

At zero time, the contact 36 leaves circuit 41 and the luminous pilot lamp 37 is extinguished. At the 2nd second, the contacts 33 and 34 respectively close the circuits 38 and 39 and this brings about the opening of the electromagnetic valves 6 and 11. On account of the constant depression created in the apparatus by the jet 13 for equal periods, equal volumes of chlorine are introduced into the reaction chamber 2. The chlorine carries with it a small quantity of chlorine water required for dissolving the hydrogen chloride formed by the reaction. While the electromagnetic valves 6 and 11 are open—the circuits 38 and 39 being closed—the reaction chamber is swept by chlorine and thus cleaned. At the 30th second, the contact 33, leaving the circuit 38, brings about the closing of the valve 6. At the 33rd second, the contact 34 leaves the circuit 39 which is re-opened and thus brings about the closing of the valve 11. In the reaction chamber 2, a predetermined constant volume of gas to be analysed is enclosed, the constant pressure in the chamber read from the manometer (tube 17) at this instant is the initial pressure and it is in relation to this pressure that the final measurement of the amount of hydrogen in chlorine will be effected. At the 35th second, the contact 35 closes the circuit 40 which acts on the electromagnet fitted with

spring 31, and the shutter 29 uncovers the opening 30, the gaseous mixture in the reaction chamber 2 being thus subjected to the action of the actinic rays issued from the lamp 26. The combination of chlorine and hydrogen takes place immediately, and since this reaction is exothermic, the manometric liquid is first driven back from the tube 17 towards the receiver 15, the bell 16 serving as a hydraulic guard. After a certain time which is comparatively short, the temperature returns to its initial value and the manometric liquid rises again in the tube 17 to a height—superior to the height corresponding to the initial pressure—in relation to the contraction of volume due to the absorption of hydrogen chloride formed, that is to say in relation to the amount of hydrogen in chlorine. A simple preliminary calibration of the tube 17 permits to connect the reading of the pressure variation to this amount.

At the 123rd second, the contact 35 leaves the circuit 40 and the electromagnet 31 is no longer under tension; by the action of its spring, it moves the shutter 29 back before the opening 30. At the 150th second, when the temperature in the reaction chamber 2 has returned to its initial value, the contact 36 closes, the circuit 41, the luminous pilot lamp 37 lights up and the pressure variation indicated by the manometric system is then read. After 180 seconds, the initial state is re-established and the various operations start again.

The tube 17 has previously been calibrated; the electrode 22 is placed in this tube at a height corresponding to an amount of hydrogen in the chlorine corresponding to the predetermined limit. When this amount is reached, the conductive manometric liquid rising in the tube 17 contacts the said electrode and this closes the circuit 24, the audible indicator thus being activated.

It is also possible to use other systems of indication and measurement. FIG. 4 shows, for example, an indicator system operated by means of photo-electric cell. According to this figure, the manometric system comprises, in addition to the reading tube 17 described above, an "indicator" tube 70 on which the indicator system is arranged at a height corresponding to the amount of hydrogen corresponding to the predetermined limit. This indicator system comprises a luminous source 71, the rays of which are focussed on the photo-electric tube 72. The photo-electric current is amplified by the amplifier A and actuates the relays R which open the circuit 24 of the indicator 25 when the photo-electric tube is illuminated. When using such a system, a strongly coloured manometric liquid is employed. When the amount of hydrogen in the chlorine reaches the predetermined limit, following the combination of the two gases and the contraction of volume due to the absorption of hydrogen chloride formed, the manometric liquid rises in the tubes 17 and 70 and, in the latter, intercepts the luminous rays issued by the lamp 71; the photo-electric tube is thus considerably less illuminated and, since the relay R is no longer under tension, the circuit 24 is closed and the audible indicator 25 actuated.

Instead of a visual reading device, it is also possible to arrange in the tube 17 any automatic recording system known as such, and to record continuously the functioning of the electrolytic cells.

The apparatus according to the invention may comprise numerous variations. Thus, FIG. 2 illustrates an apparatus which is similar to that of FIG. 1, but in which the means of periodic illumination of the chamber 2 are not represented by a shutter interposed between the reaction chamber 2 and the lamp 26, but by the periodic operation of the lamp 26. For this purpose, the contact 35 of FIG. 1 is replaced by an identical contact 51 which closes the circuit 27 of the lamp at the very instant when the contact 35 closes the circuit 40 acting on the electromagnet 31. Consequently, the lamp 26 is illuminated for a period extending from the 35th to the 123rd second after the start of the operations, and the gaseous mixture

in the reaction chamber is subjected to the action of the actinic rays.

Another variation of the apparatus is shown in FIG. 3. This apparatus is identical with the one of FIG. 1, except for the manometric system. Reading is effected on a separate apparatus represented by the tubes 60 and 61 which communicate with the receiver 15 and the tube 14 respectively. The tube 61 is fitted with an electromagnetic valve 62 actuated by means of the circuit 64 and the contact 63—identical with the contact 36 of FIG. 1. The indicator system is represented as in FIG. 1 by the electrode 22, arranged in the tube 17 thus becoming the "indicator" tube, and the electrode 23, the circuit 24 and the audible indicator 25.

In this apparatus the consecutive operations during the first 150 seconds are identical with those carried out in the apparatus of FIG. 1. At the 150th second, the temperature in the reaction chamber 2 having been then returned to its initial value, the contact 63 closes the circuit 64 and actuates the electromagnetic valve 62 bringing the reading tube 61 in contact with the manometric system. The manometric liquid arranges itself in the tube 61 at the height corresponding to the amount of hydrogen in chlorine. After 180 seconds, the initial state is re-established, the contact 63 leaves the circuit 64 and the valve 62 closes itself. The manometric liquid in the tube 61 remains therefore at the height corresponding to the amount of hydrogen in chlorine. By means of such an apparatus, the consecutive measurements can be compared, since the height of the manometric liquid in the tube 61, isolated from the manometric system by the valve 62, remains constant by the whole period of operations from time 0 to time 150 seconds and corresponds to the amount of hydrogen in chlorine measured during the preceding operation.

We claim:

1. An apparatus for measuring the constituents of a gaseous mixture which comprises, in combination, a reaction chamber permeable to actinic radiation, inlet means for supplying the gaseous mixture to be analyzed to said chamber, first valve means in said inlet means, outlet means for removing the products of the reaction from said reaction chamber, second valve means in said outlet means, means for inducing a predetermined vacuum in said reaction chamber, a manometric assembly in fluid communicating relationship with said reaction chamber, said manometric assembly including a manometric liquid which is a conductor of electricity, a reading unit and an indicator unit in an electrical circuit adapted to be closed by said manometric liquid to indicate a predetermined limit of concentration of a gas in said gaseous mixture,

means for effecting periodic illumination of the reaction chamber by said actinic light, and automatic control means for selectively operating said first valve means, said second valve means, and said means for effecting periodic illumination of said reaction chamber, said manometric assembly comprising a receiver provided with a feed tube and means for degassing the manometric liquid, a bell submerged in said receiver and fitted with a reading tube connected with the reaction chamber, and said indicator unit comprising an electrode constantly submerged in the manometric liquid, an electrode disposed in the reading tube at a height corresponding to an amount of gas corresponding to said predetermined limit well below the explosive limit, and an audible indicator in said circuit which operates when said electric circuit is closed.

2. Apparatus as defined in claim 1, wherein said first valve is an electromagnetic valve and said inlet means comprises a feed tube provided with said electromagnetic valve, and a feed tube for the gas mixture adapted to be connected to a source of said mixture.

3. Apparatus as defined in claim 1, wherein said second valve is an electromagnetic valve.

4. Apparatus as defined in claim 1, wherein said means for effecting periodical illumination of the reaction chamber comprises a source of actinic radiation constantly under tension, and a shutter interposed between said source and the reaction chamber, and means to rotate said shutter periodically.

5. Apparatus as defined in claim 1, wherein said means for effecting periodic illumination of the reaction chamber comprises a source of actinic radiation and means for periodically placing said source under tension.

6. Apparatus as defined in claim 1, wherein said automatic control means comprise contacts in the form of sectors having an angle corresponding to the duration of desired action on electric circuits to control the actuation of the apparatus, said contacts being disposed around a common axis, and a synchronous motor to drive said contacts at a predetermined speed so that a pre-established sequence of operations may be carried out.

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