

[54] APPARATUS FOR POWERFUL ENERGY TRANSFER TECHNIQUE

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Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 790,320, Apr. 25, 1977, Pat. No. 4,113,589, and Ser. No. 834,682, Sep. 19, 1977, Pat. No. 4,148,701.

[51] Int. Cl.<sup>2</sup> ..... B01J 1/00

[52] U.S. Cl. .... 250/527; 204/157.1 R; 330/43

[58] Field of Search ..... 204/157.1 R, 158 R; 250/DIG. 11, 527

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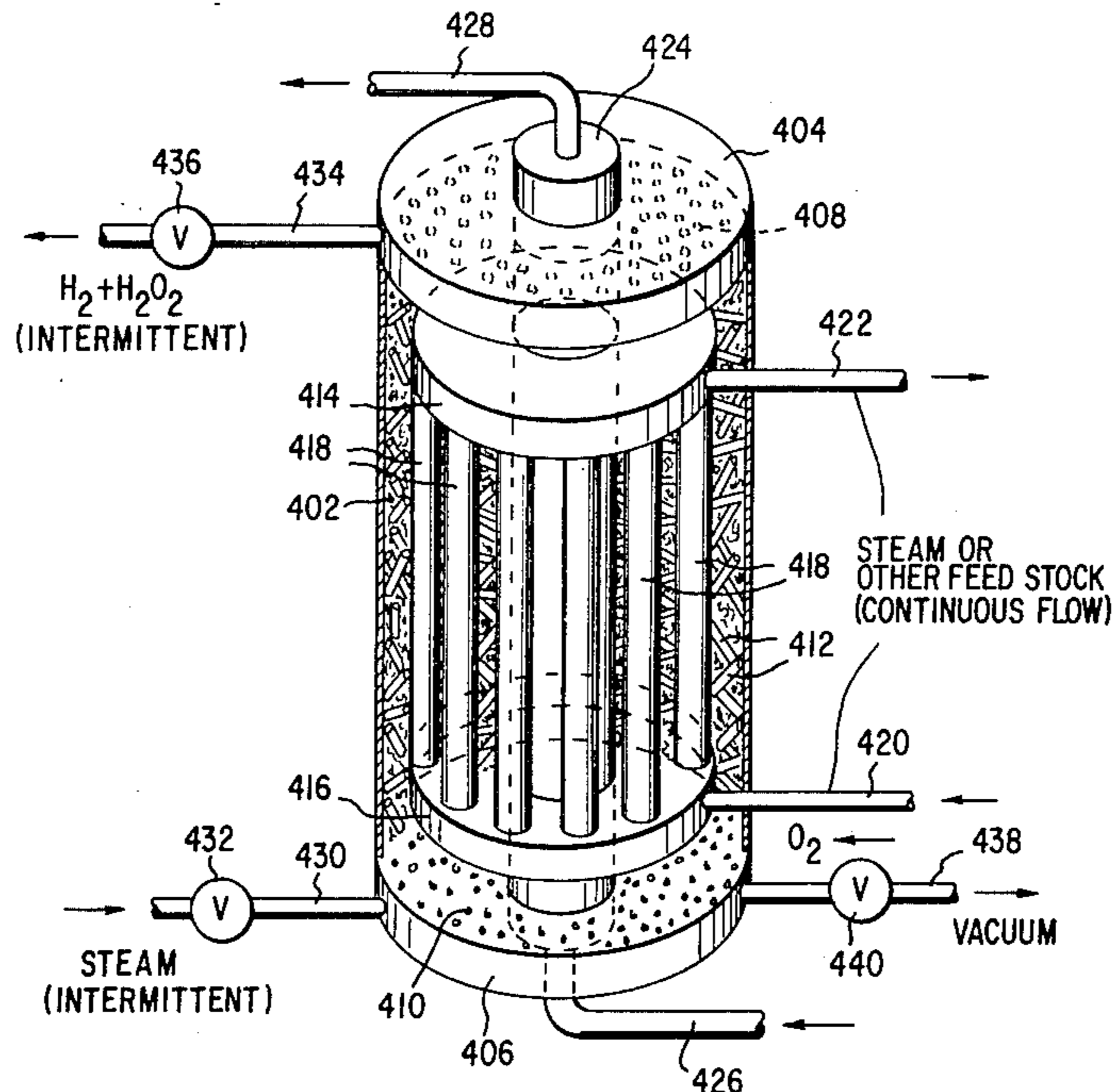
Primary Examiner—Howard S. Williams

52 Claims, 32 Drawing Figures

Attorney, Agent, or Firm—Poms, Smith, Lande & Rose

[57] ABSTRACT

In addition to the apparatus disclosed in the prior patent applications of which this application is a continuation-in-part, a reaction chamber is provided with mercury vapor quartz discharge lamps. In close proximity to the lamps are spheres, or thin continuous wires, or filaments or other physical configurations of laser-type material which produce relatively coherent radiation in a manner similar to lasers. The spheres or filaments include concentric partially reflective surfaces, and include an active material which is pumped by the efficient spectral radiation of the mercury vapor, and radiates at a frequency or frequencies matched to the absorption characteristics of the feedstock being fed through the reaction chamber. The laser-type material may be operated to produce output radiation at a harmonic, such as the second, third, fourth or higher harmonic of the basic laser radiation, and these harmonic output radiations may be enhanced by using semi-reflective coatings which reflect in the order of 70% to 90% of the radiation, particularly in the case of spheres. High energy content ultraviolet radiation may also be generated by the "beating" of radiant energy from the mercury vapor tubes and the laser-type material. Efficiency is enhanced by chain reactions which occur with the feedstock materials being fed to the reaction chamber, and these chain reactions involve the generation and regeneration of excited atoms of oxygen or other substances.



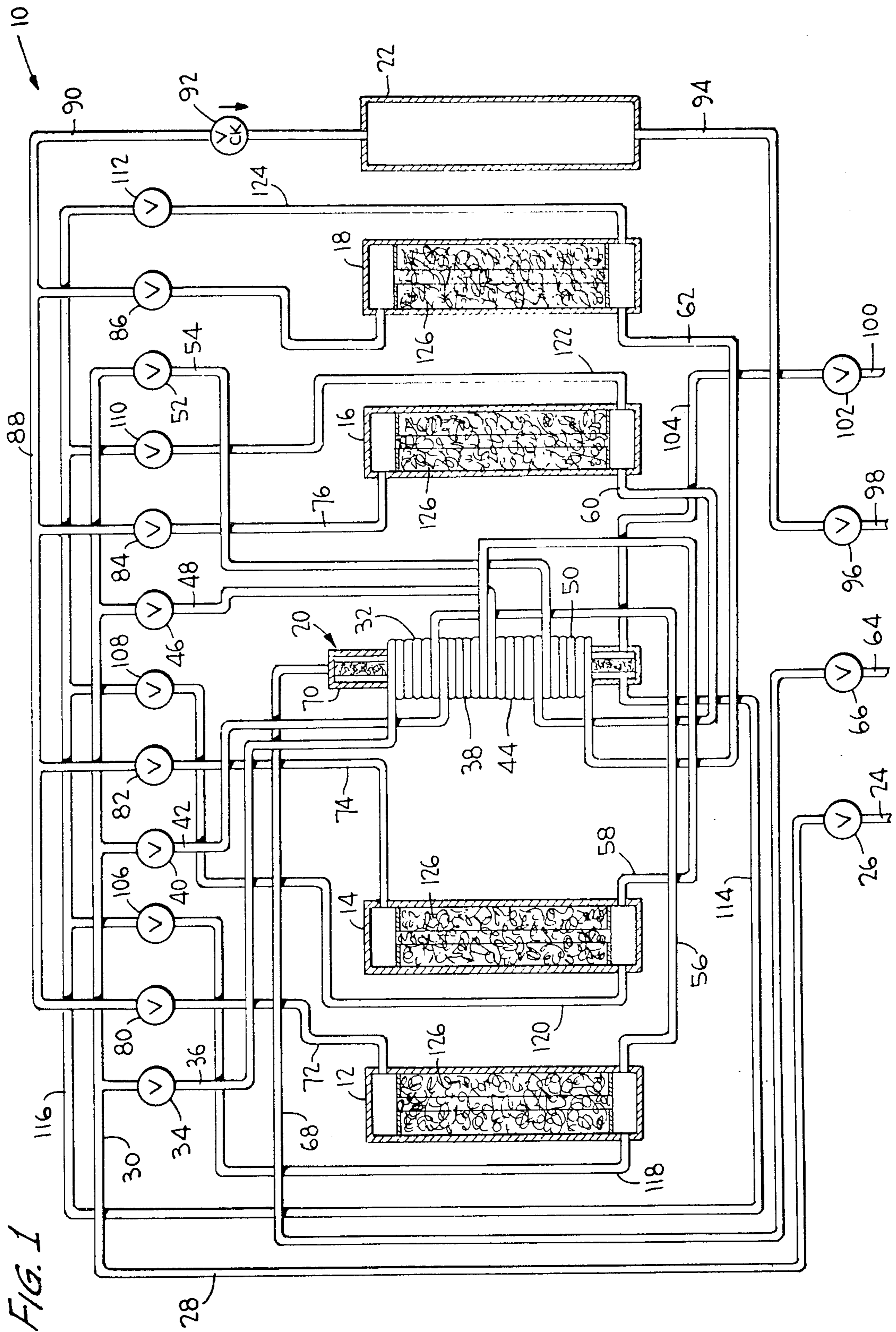


FIG. 1



FIG. 2

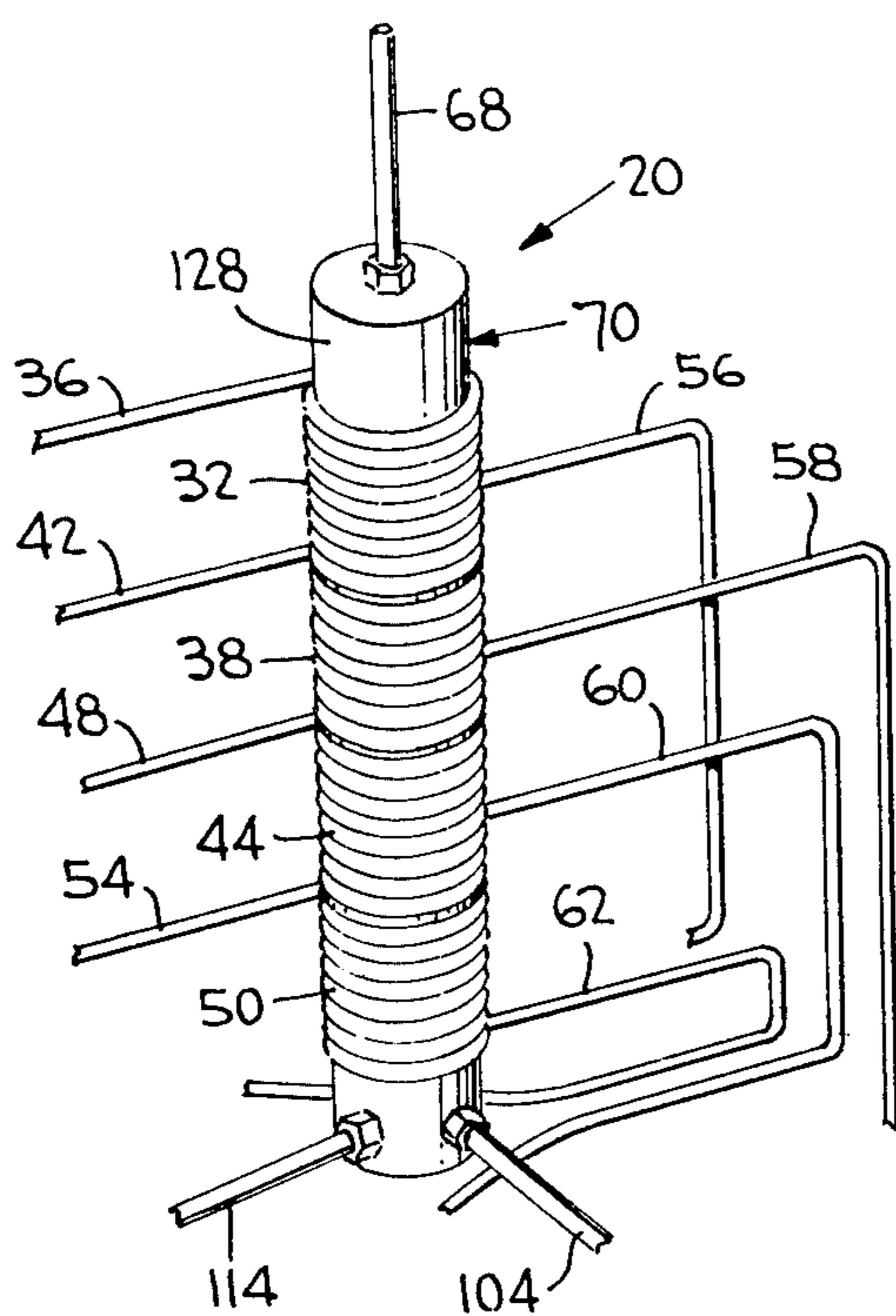
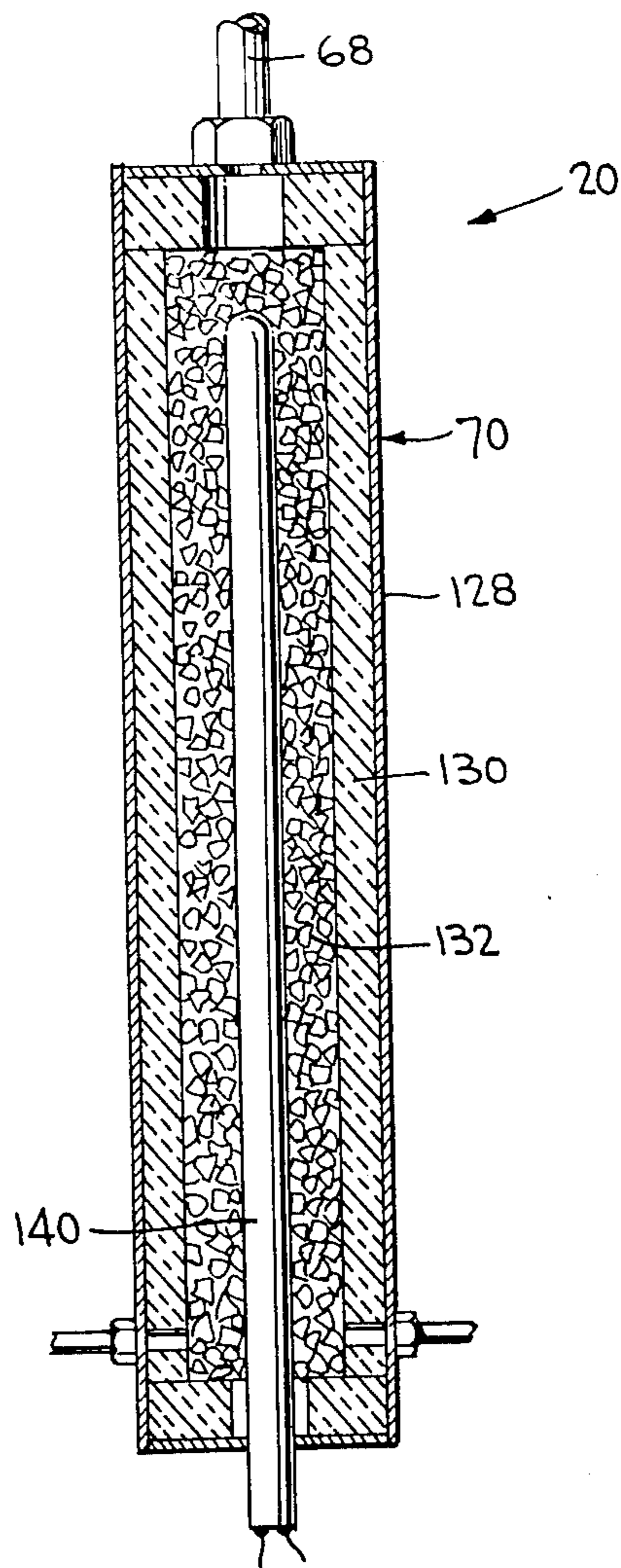


FIG. 3



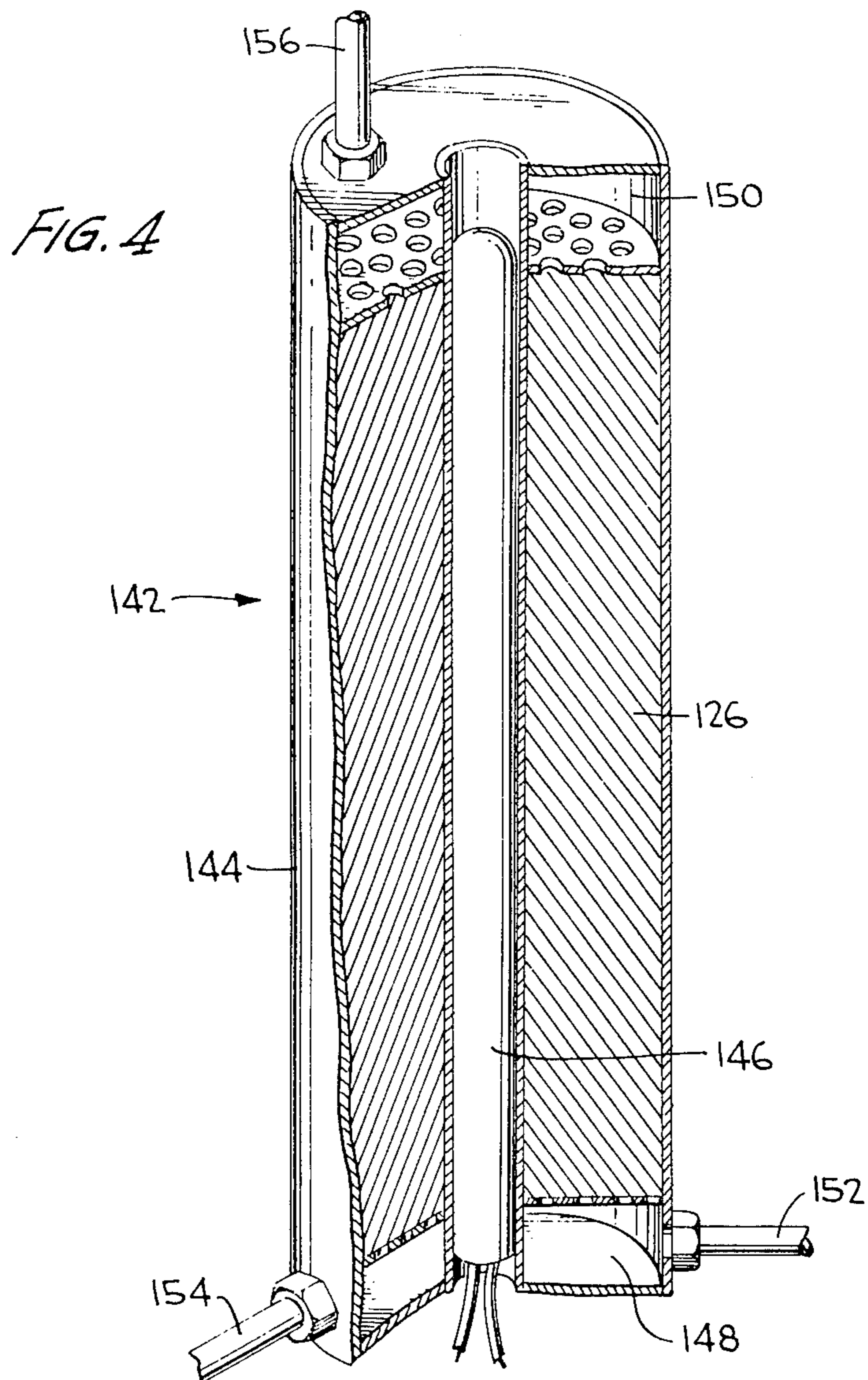
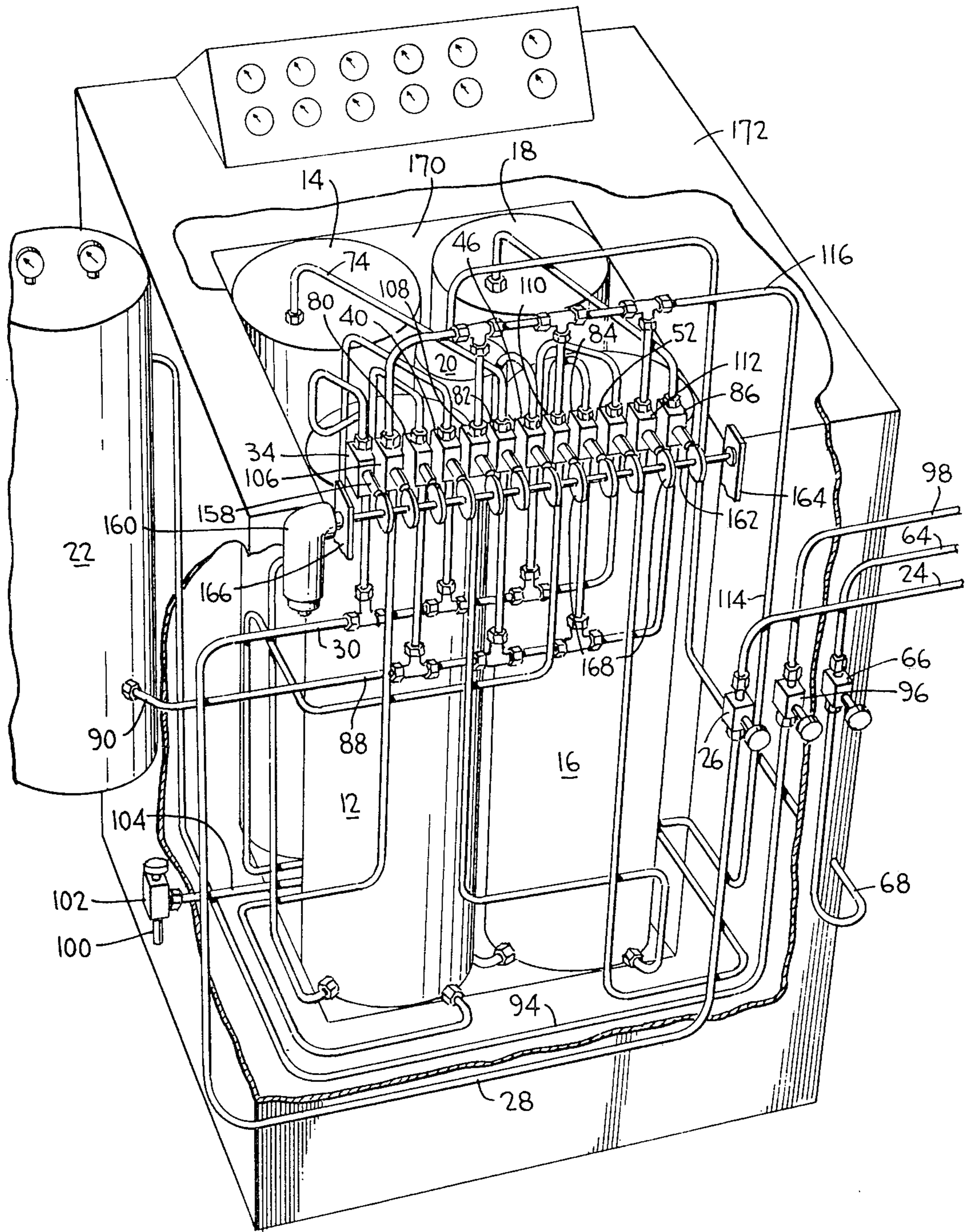
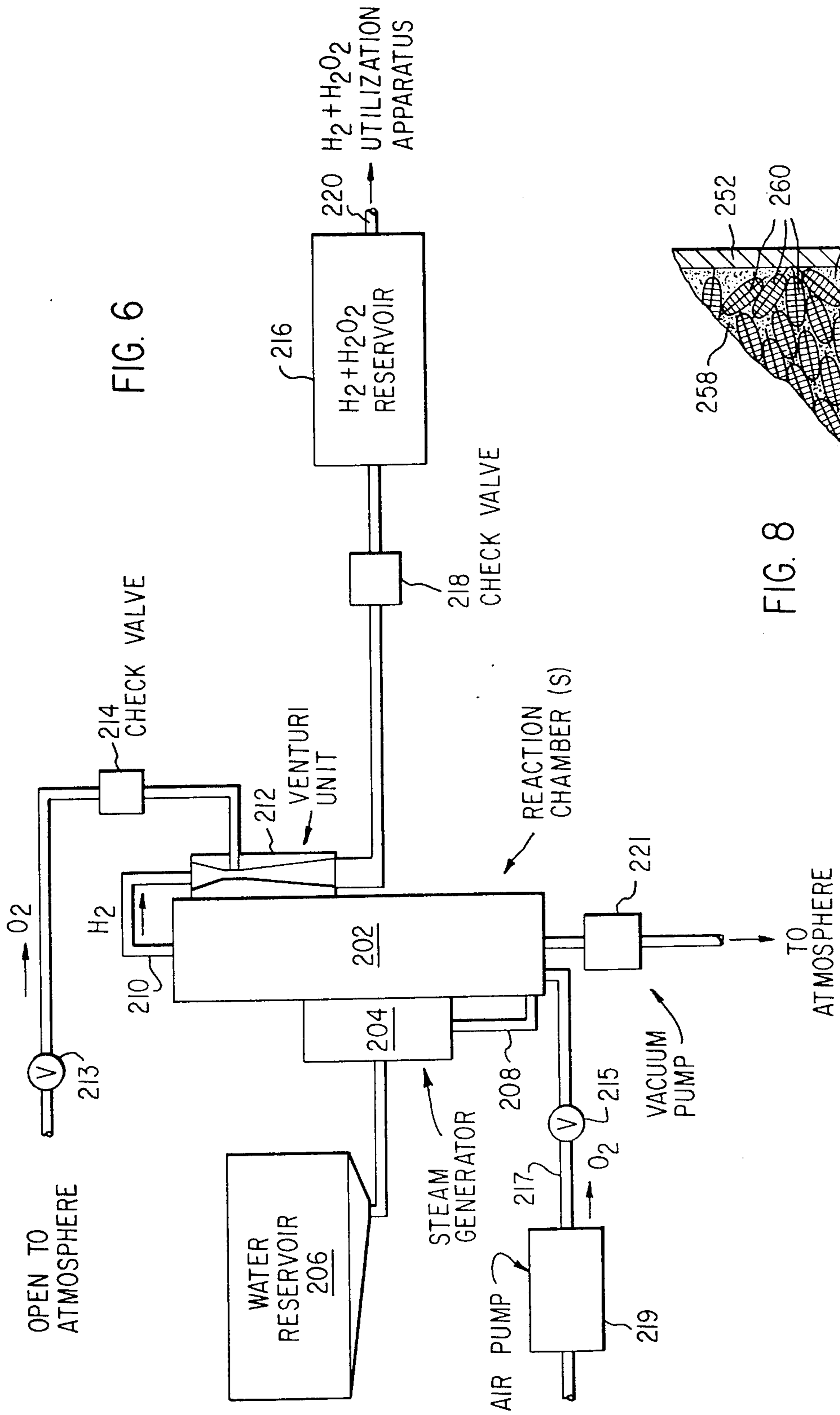


FIG. 5







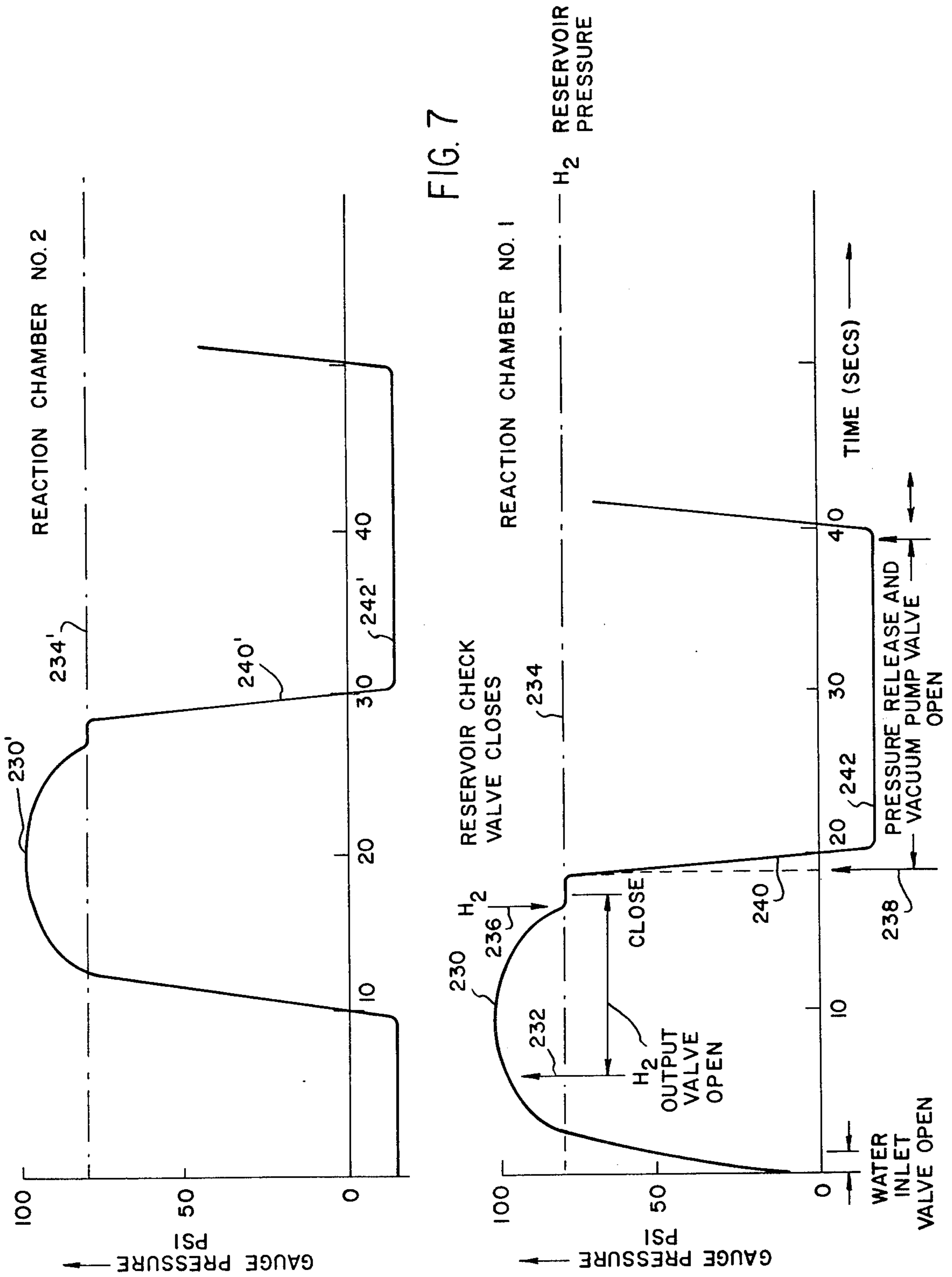


FIG. 9

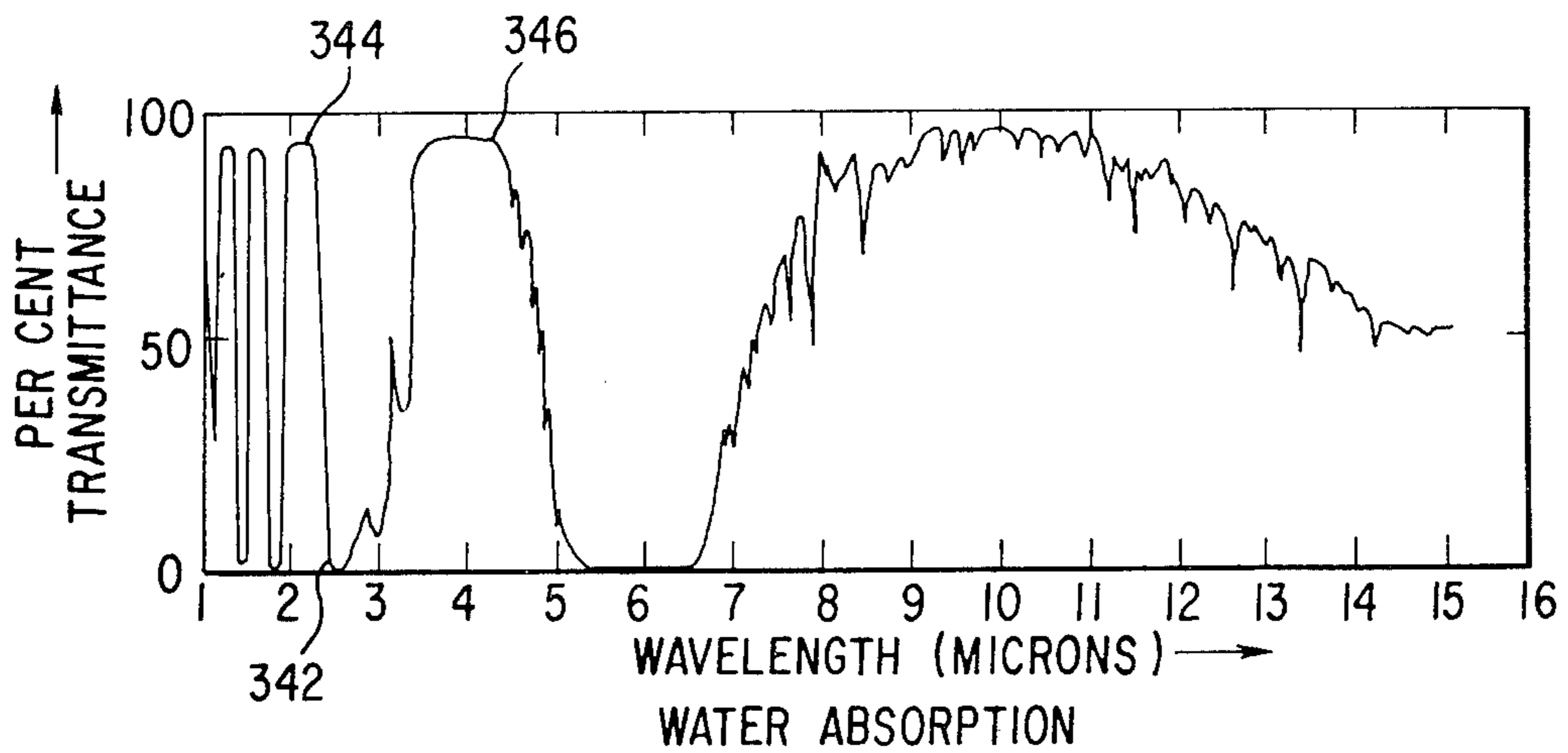
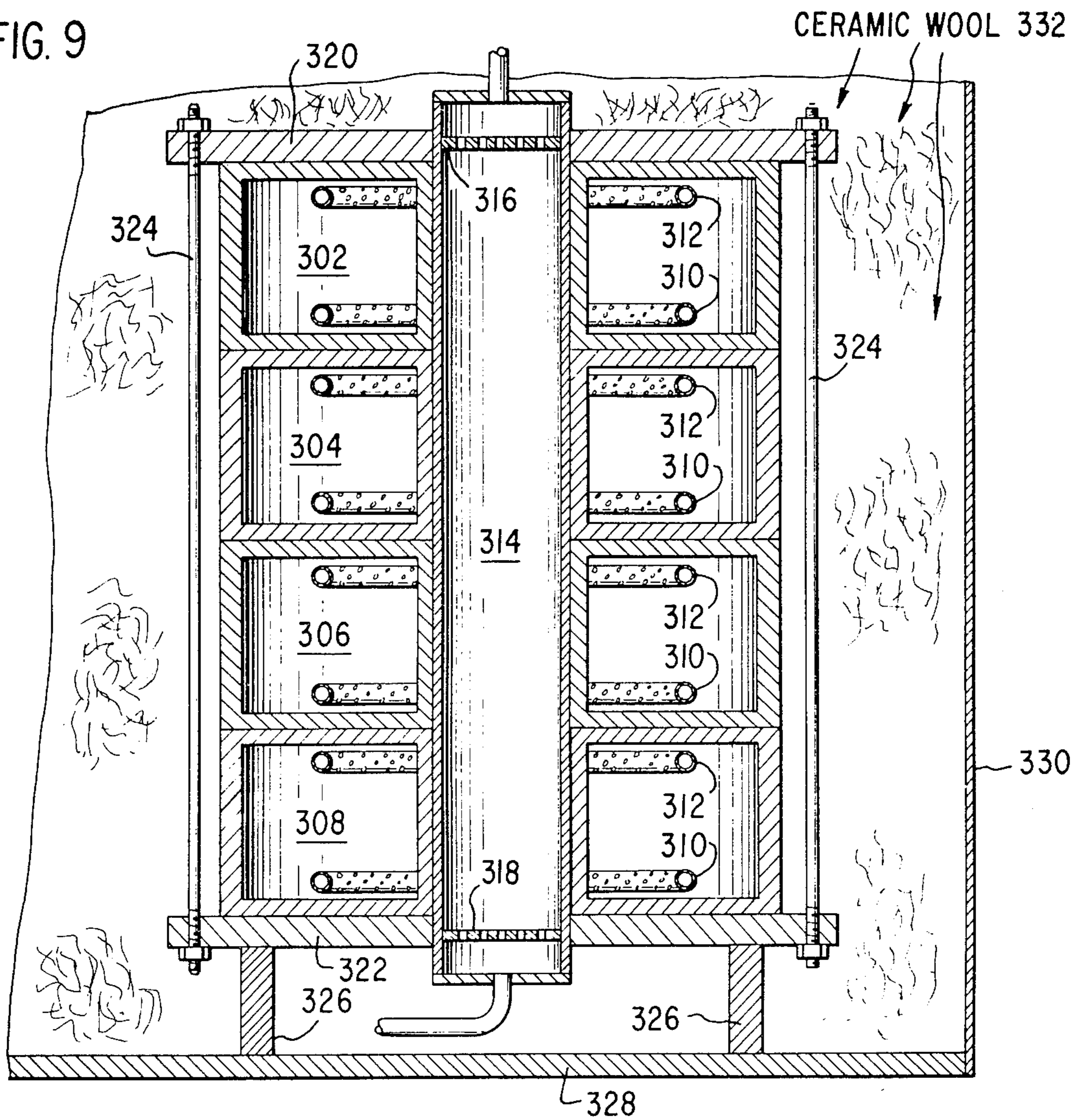


FIG. 10



FIG. II

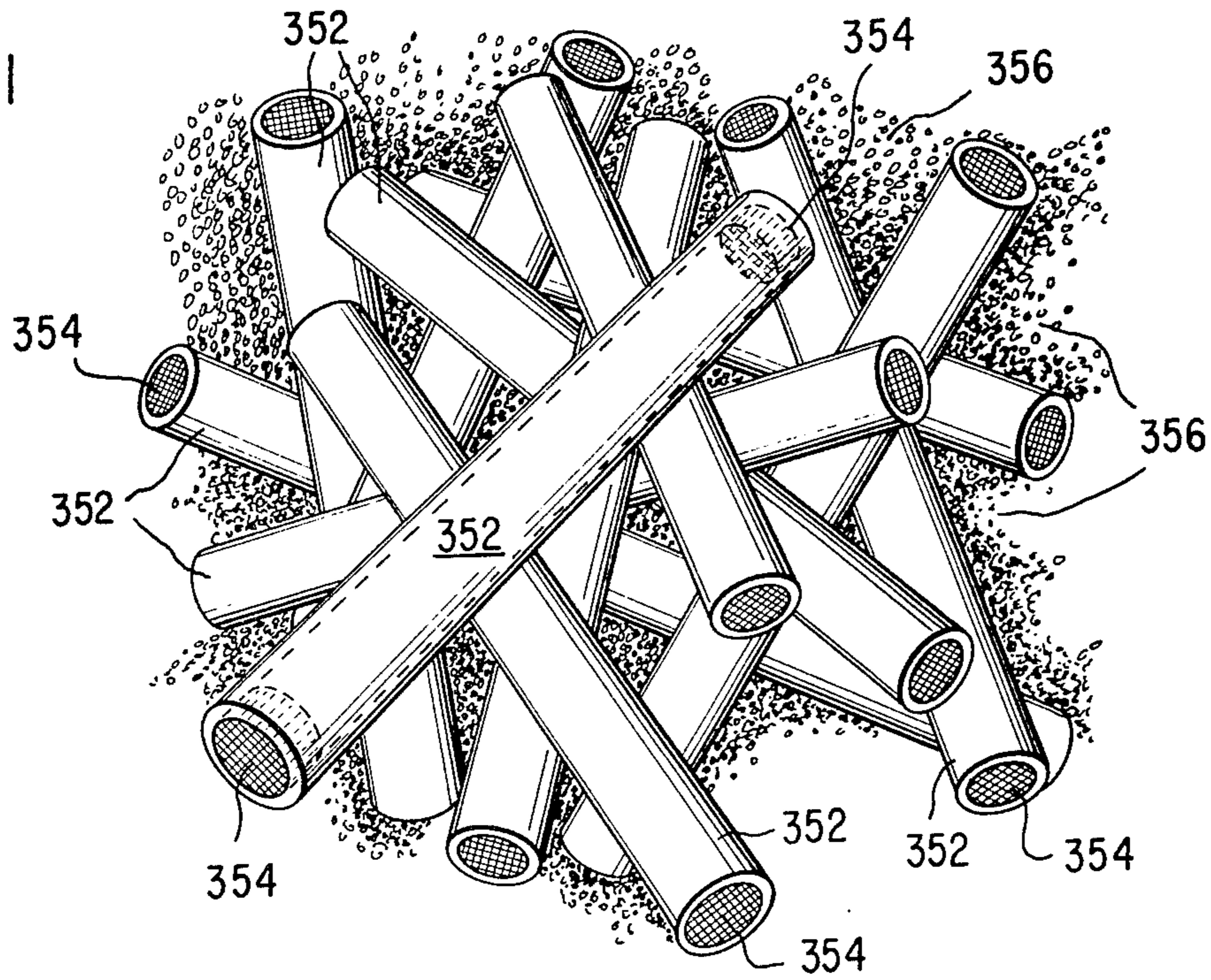
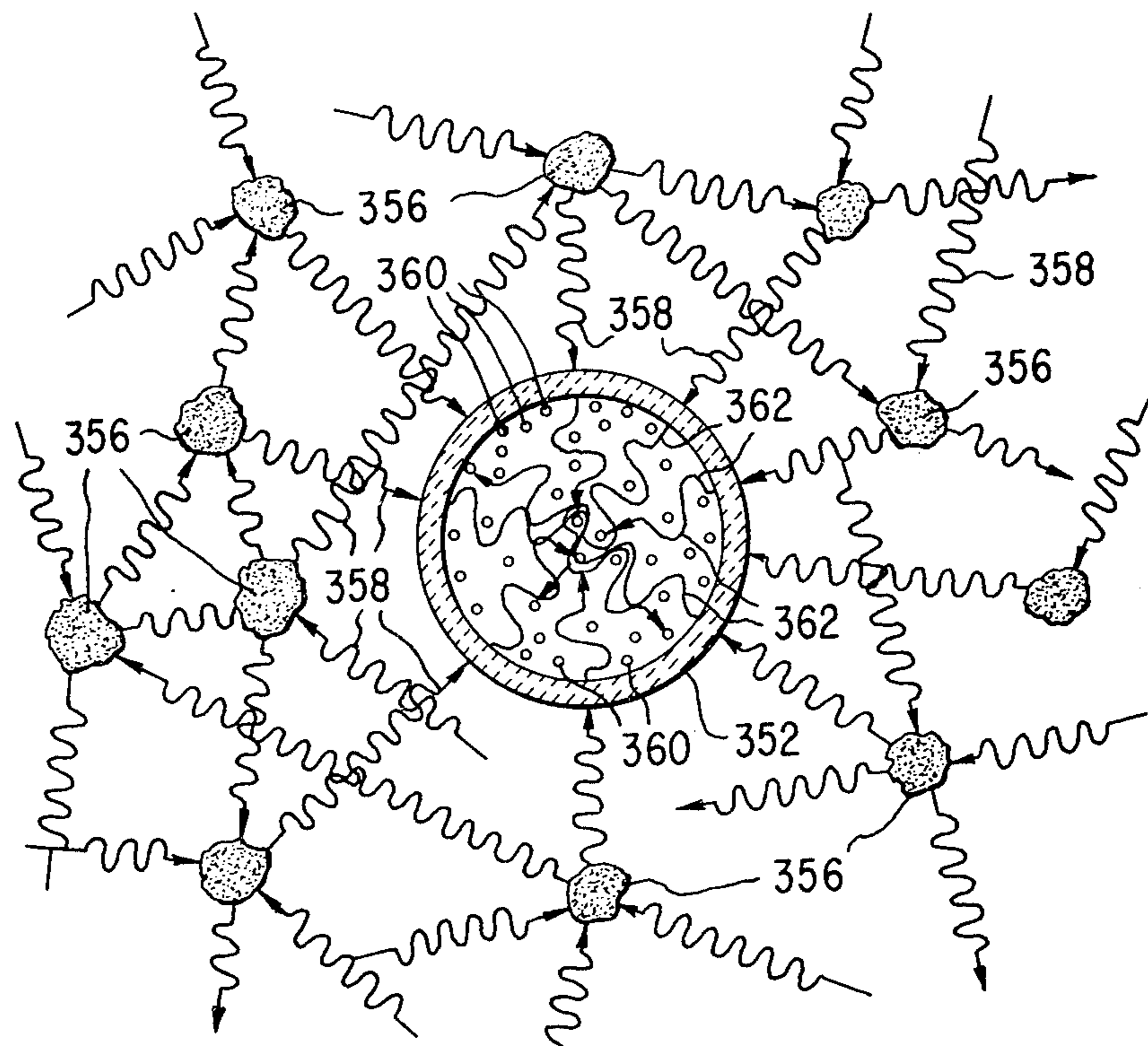


FIG. I2



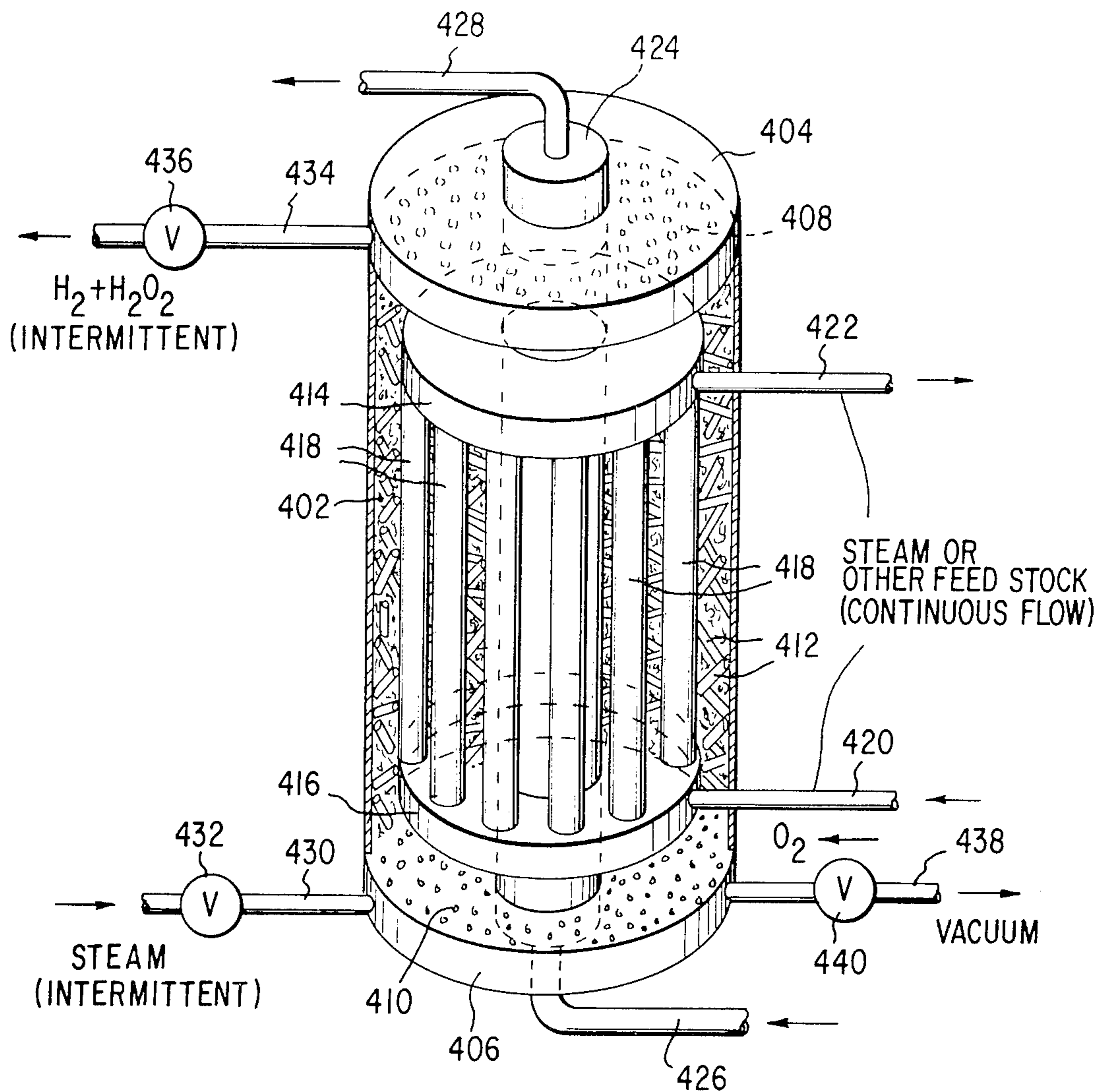


FIG. 13

FIG. 14

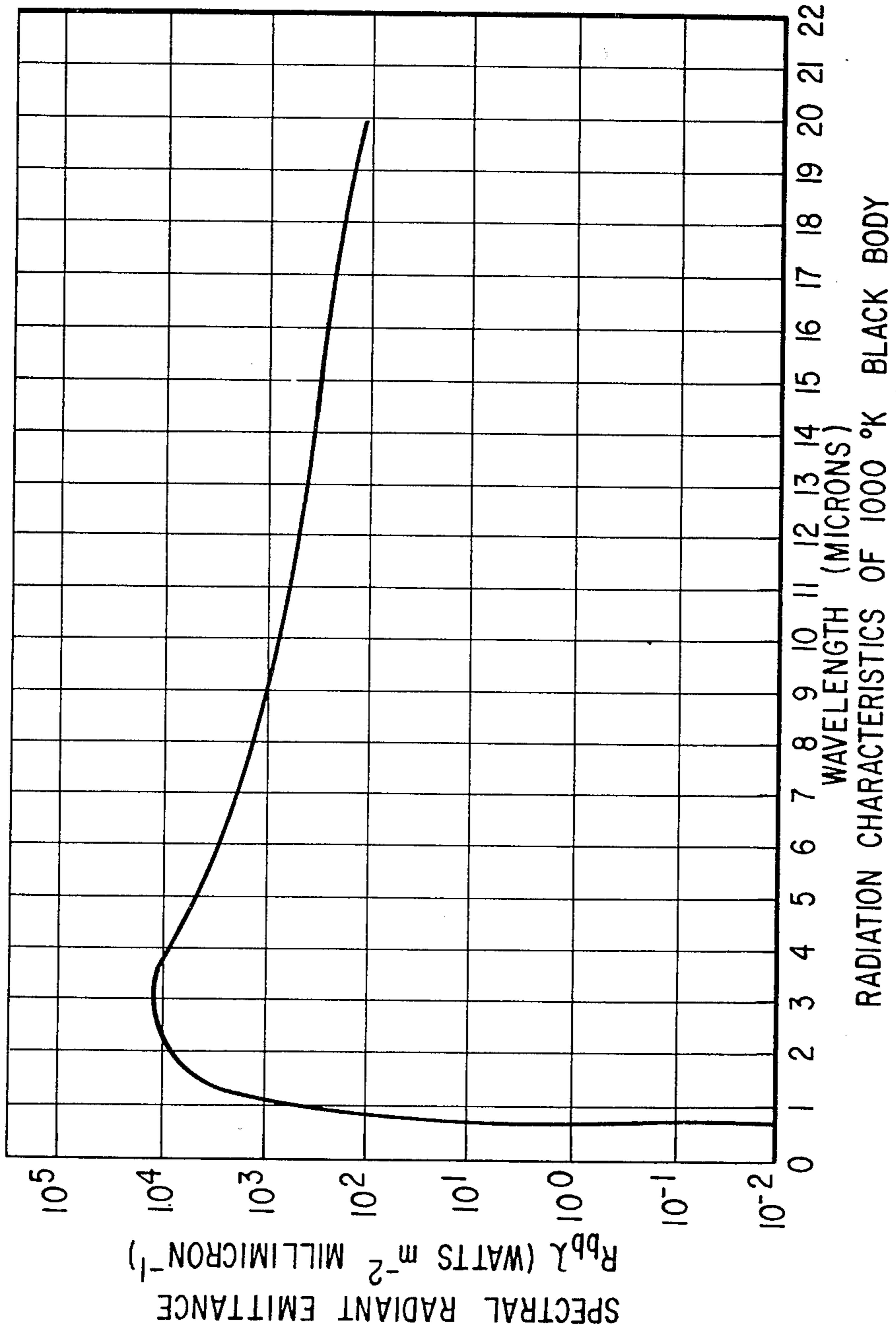
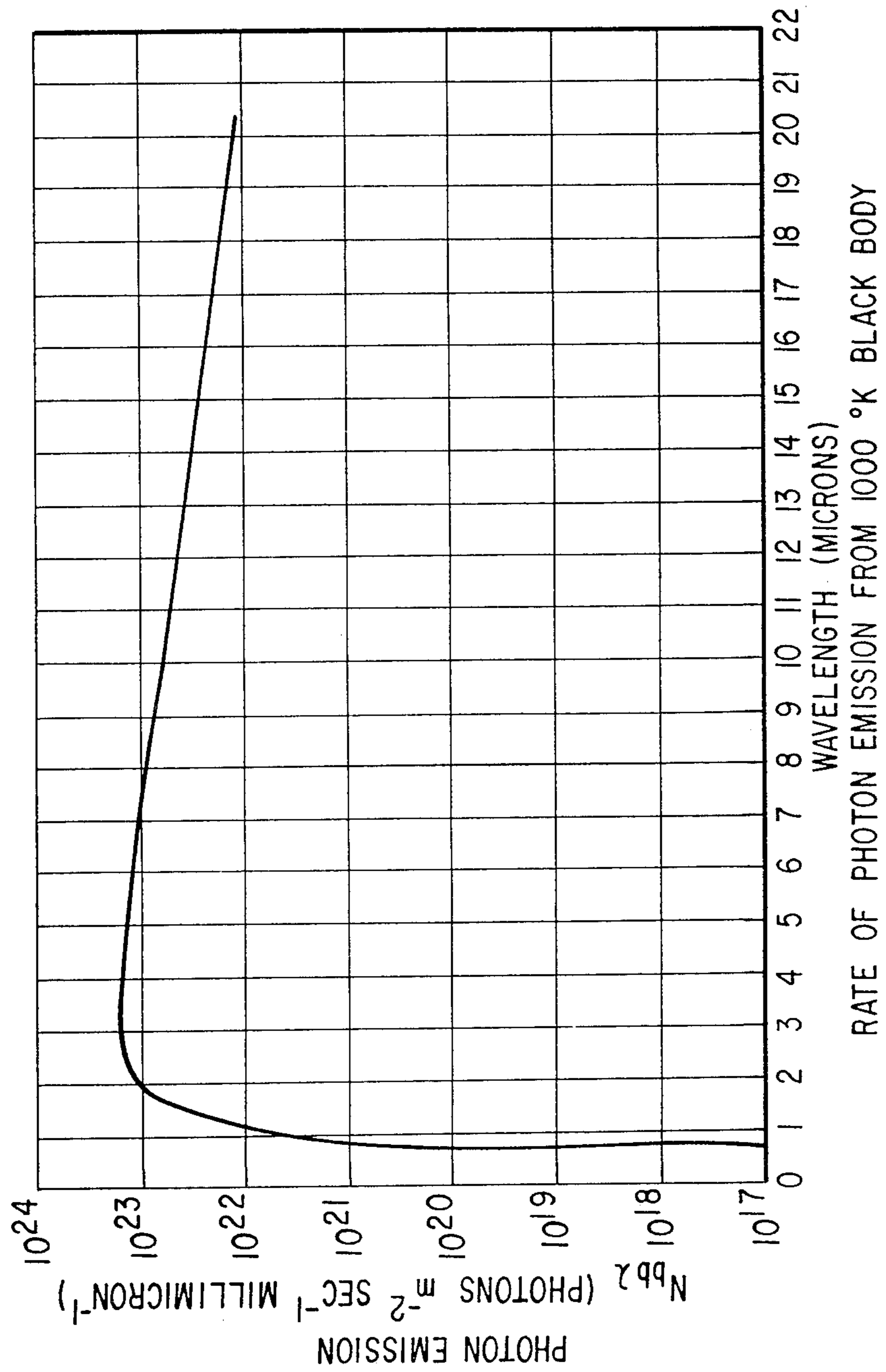




FIG. 15



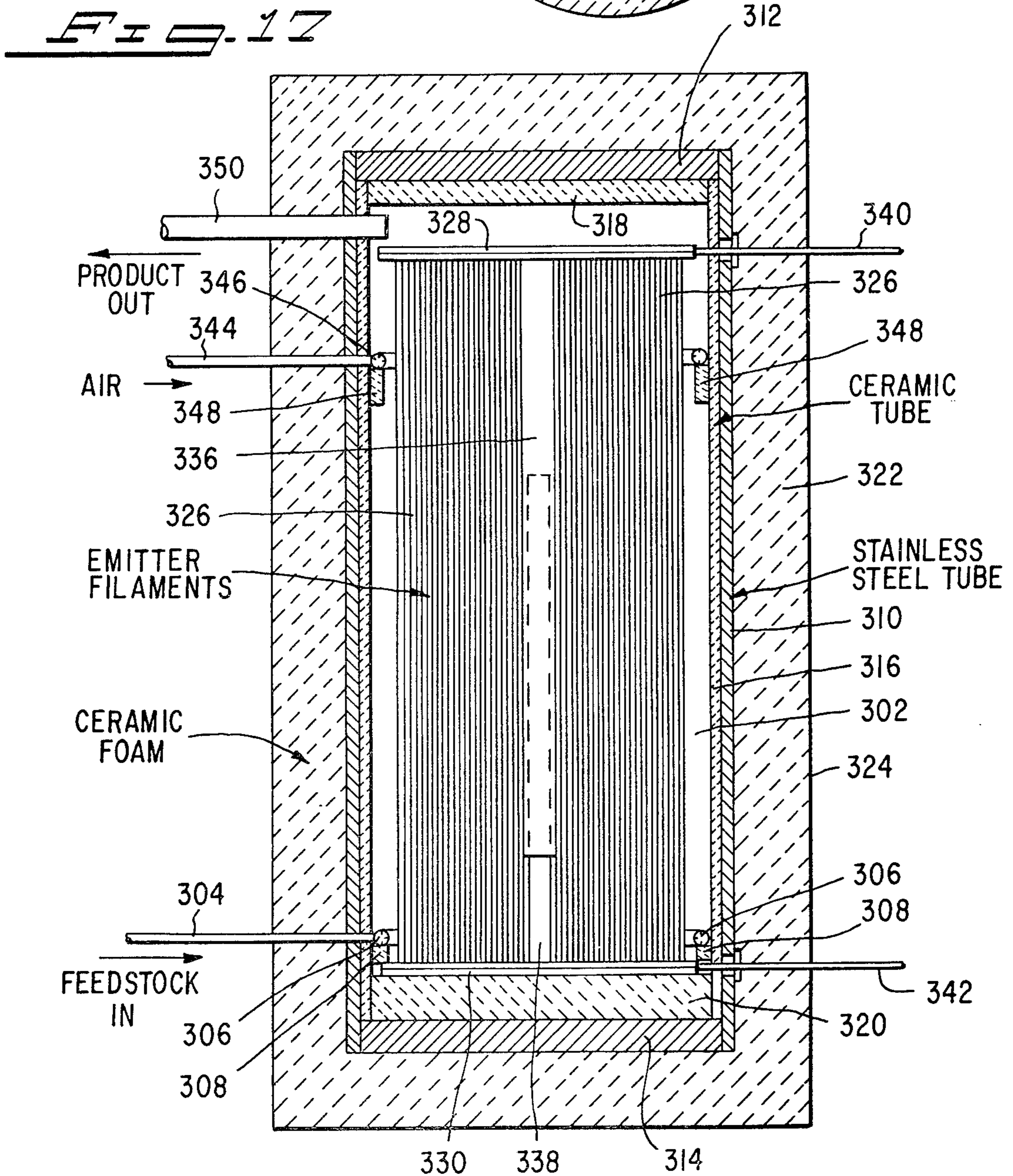
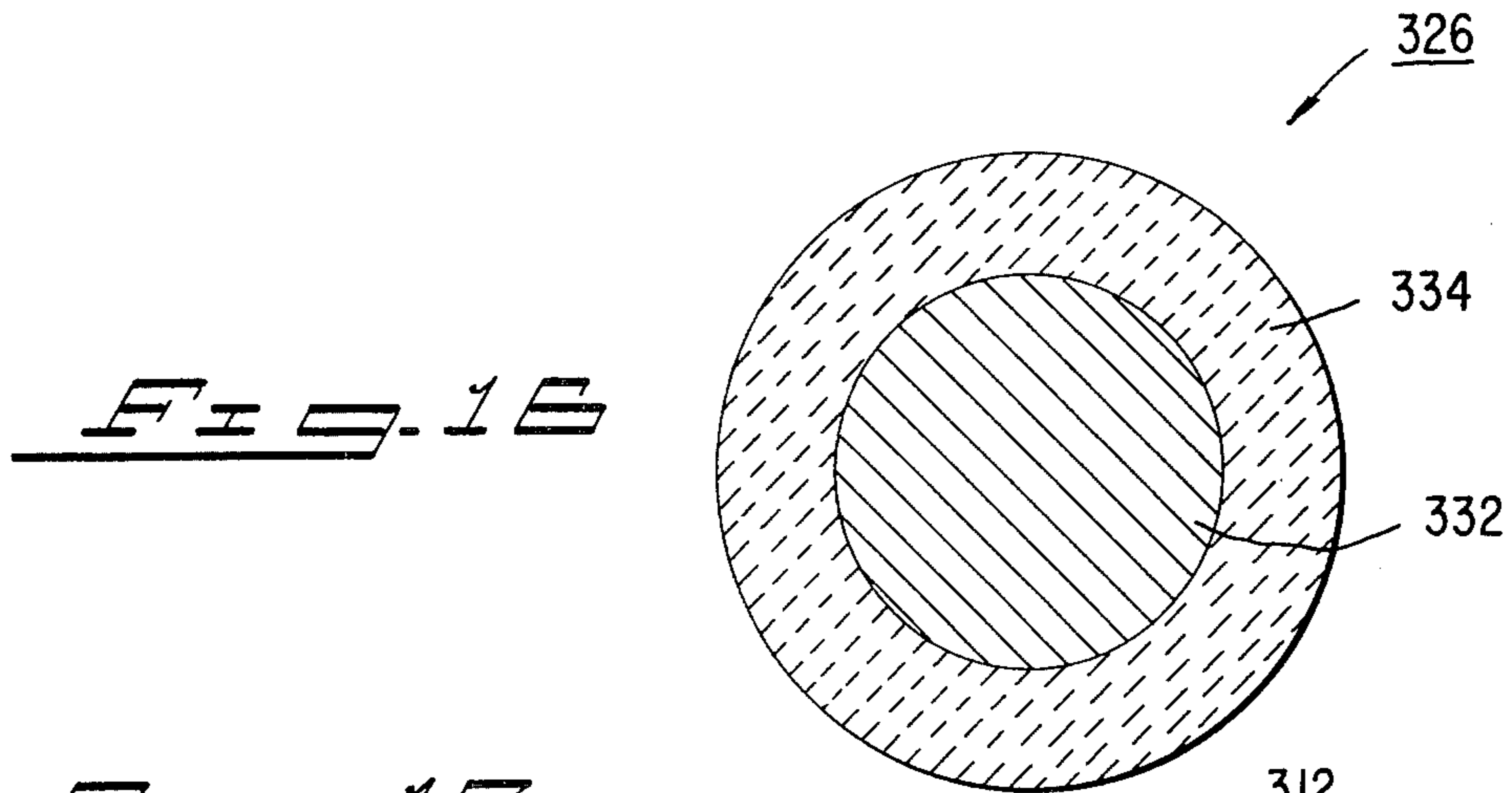


FIG. 13

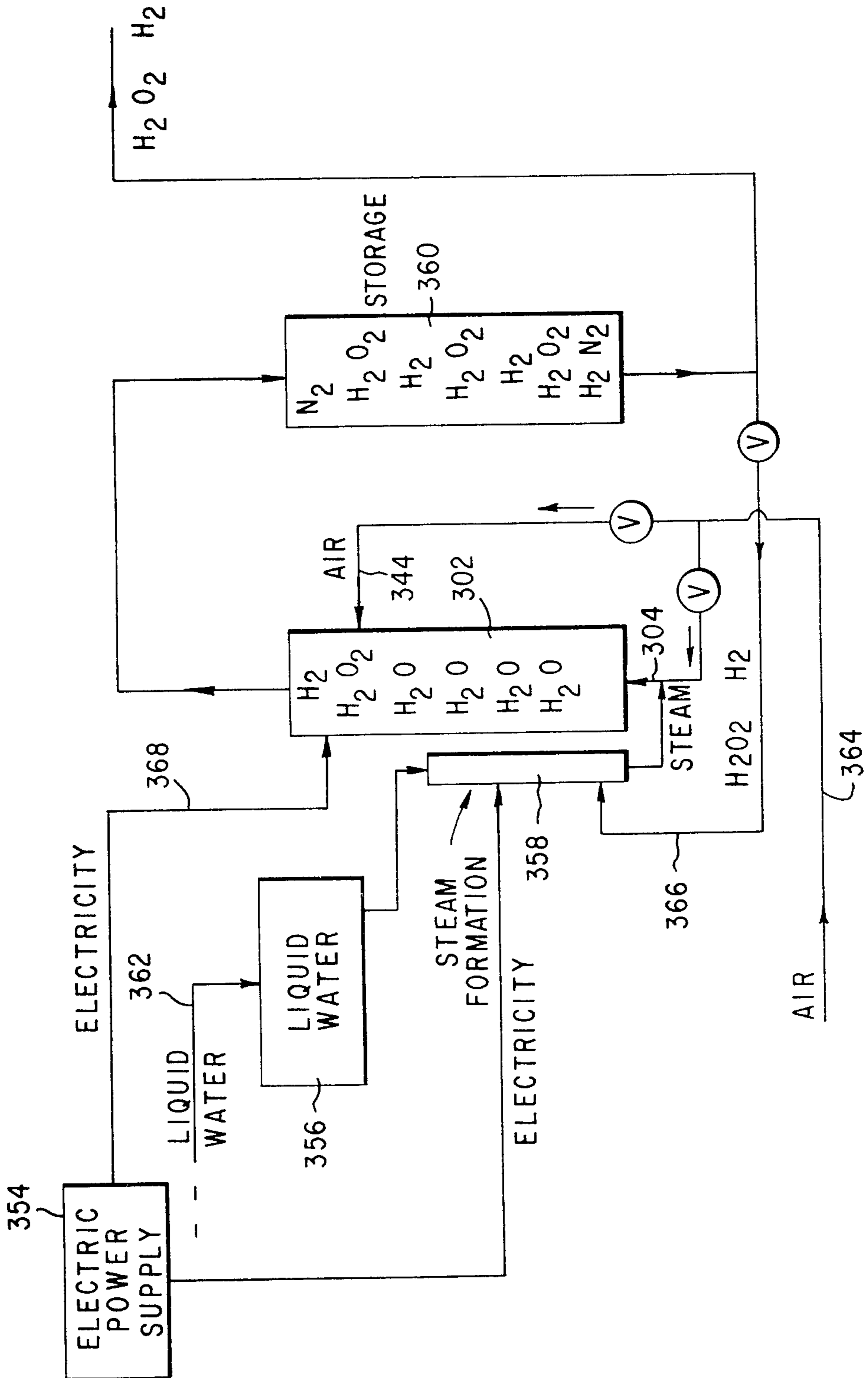
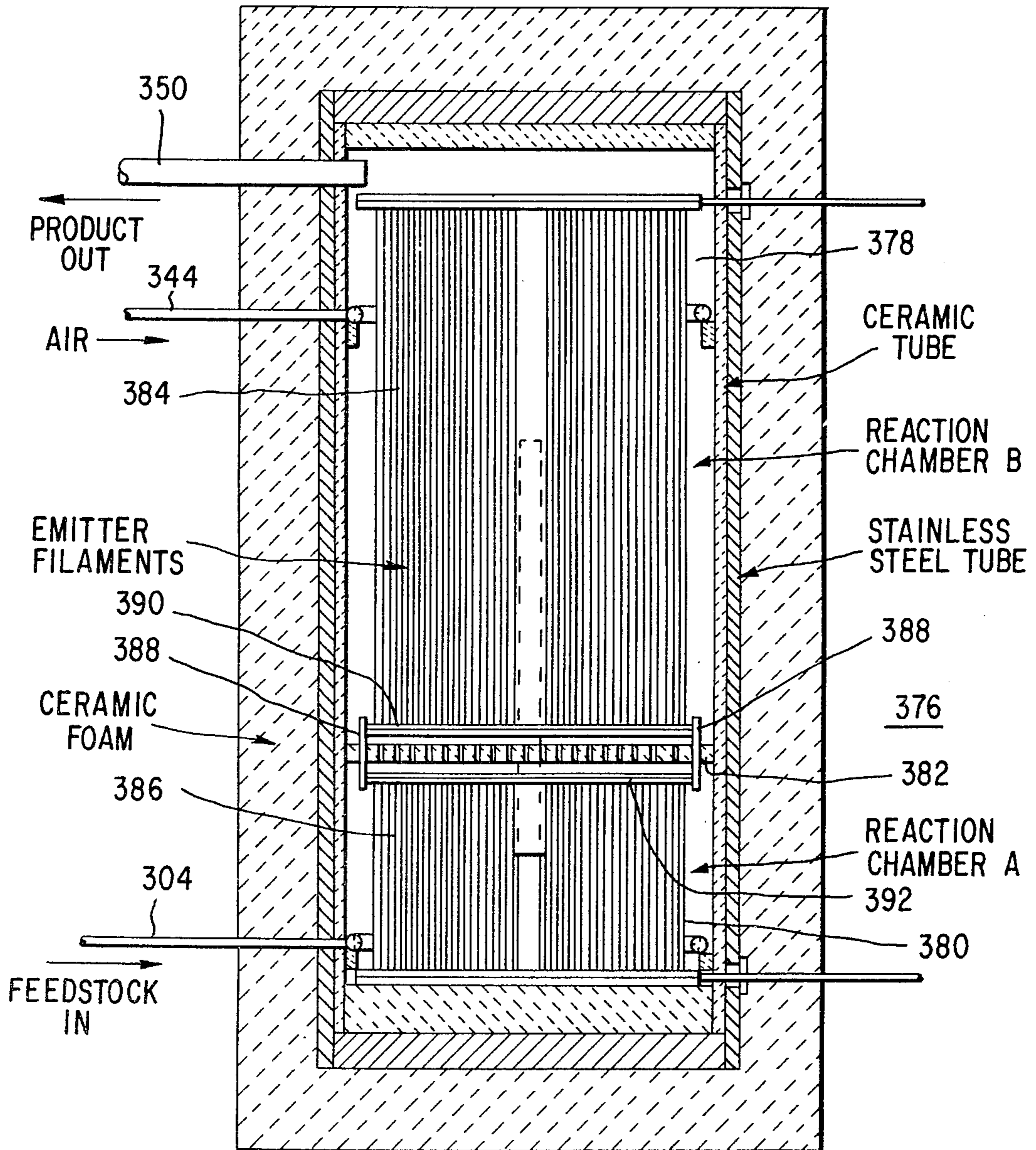




FIG. 19



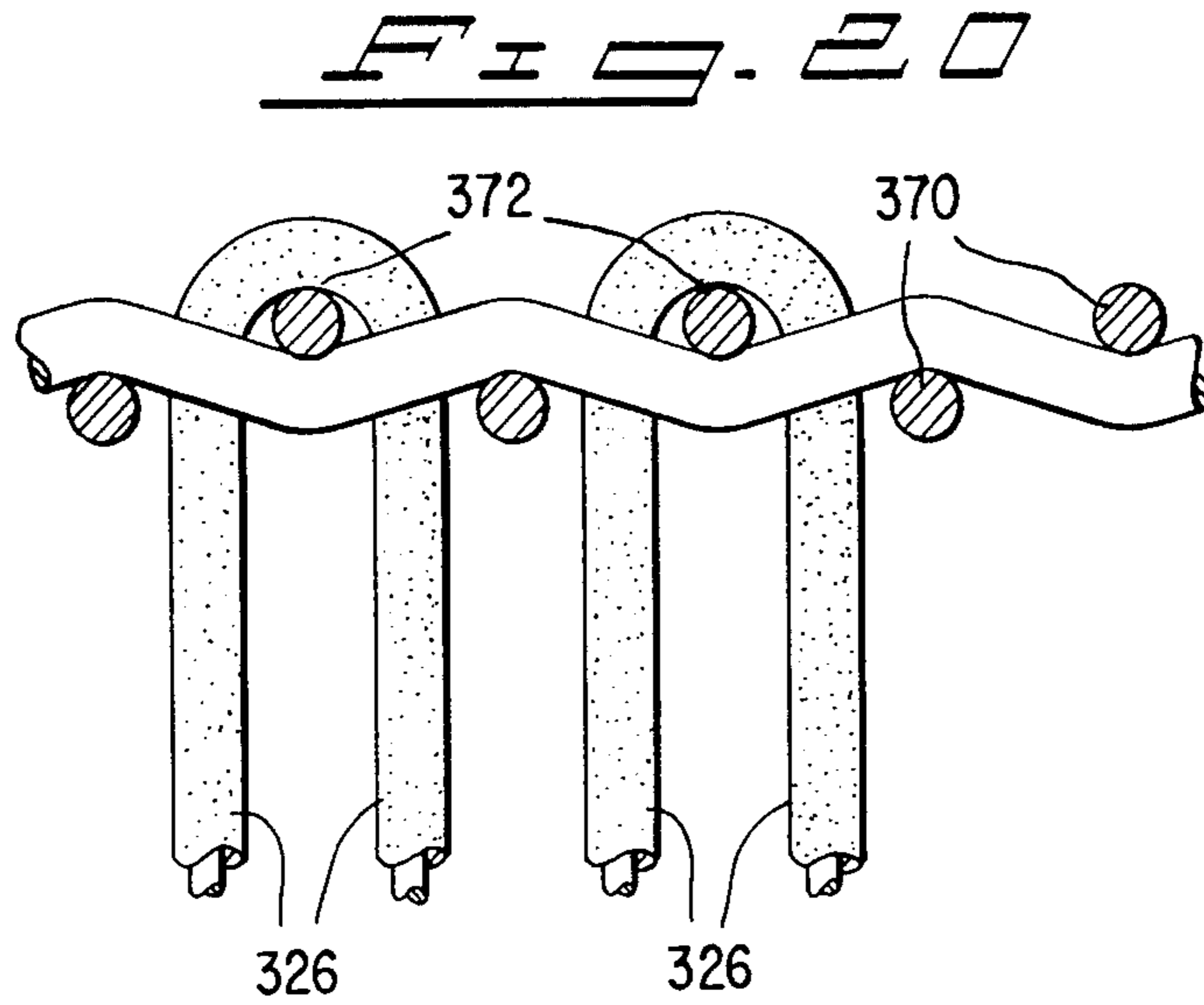


FIG. 21

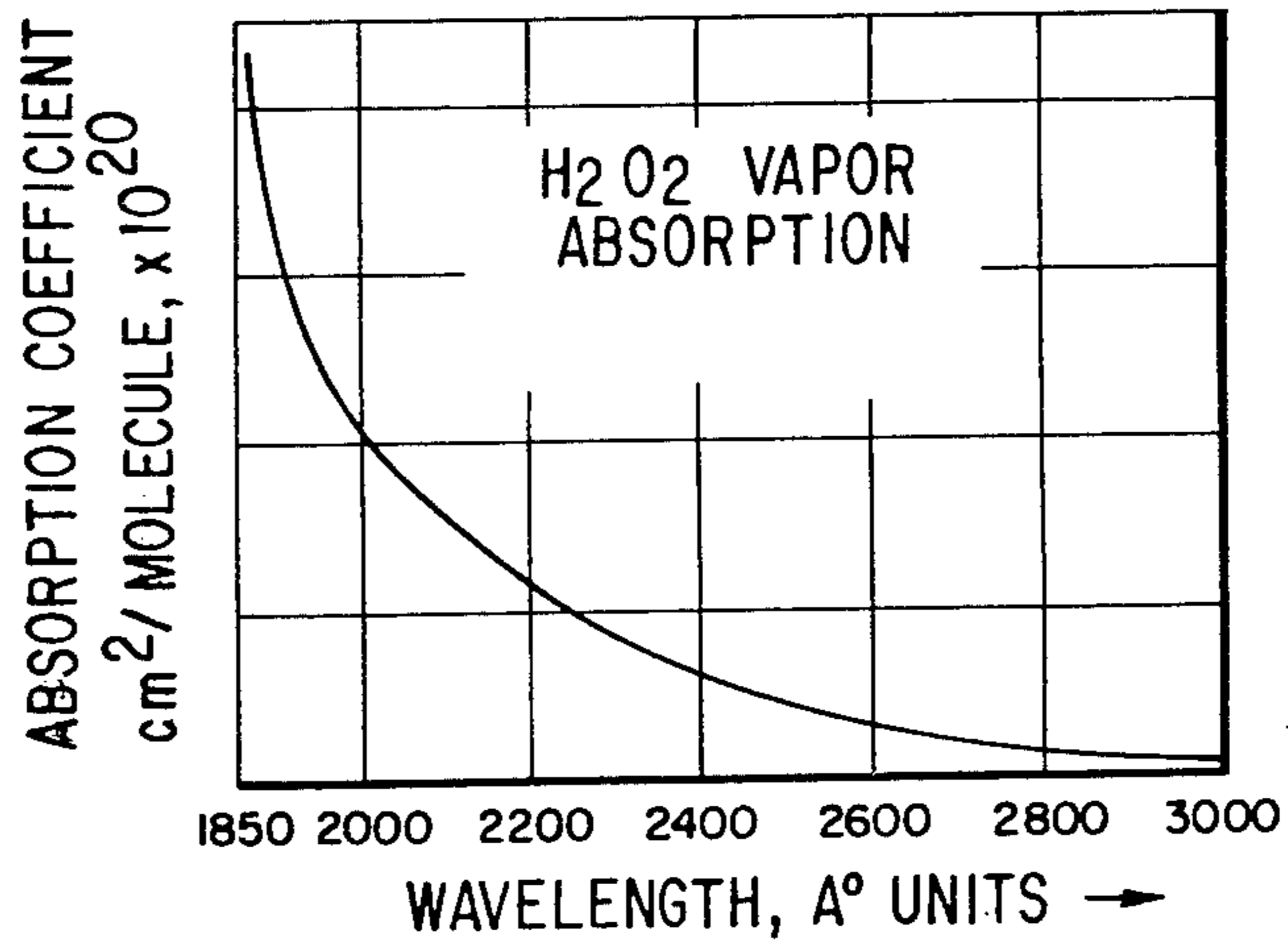


FIG. 22

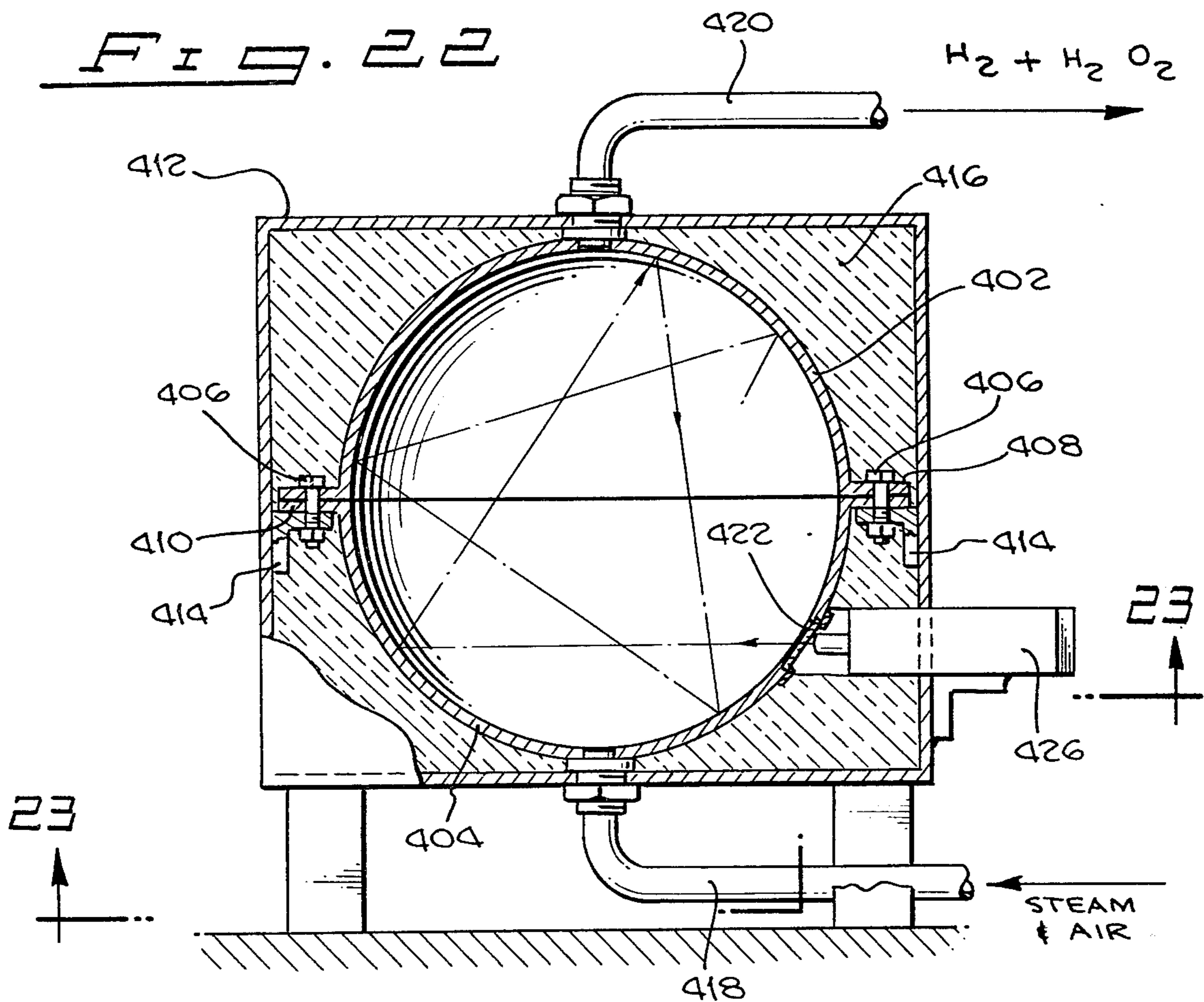


FIG. 23

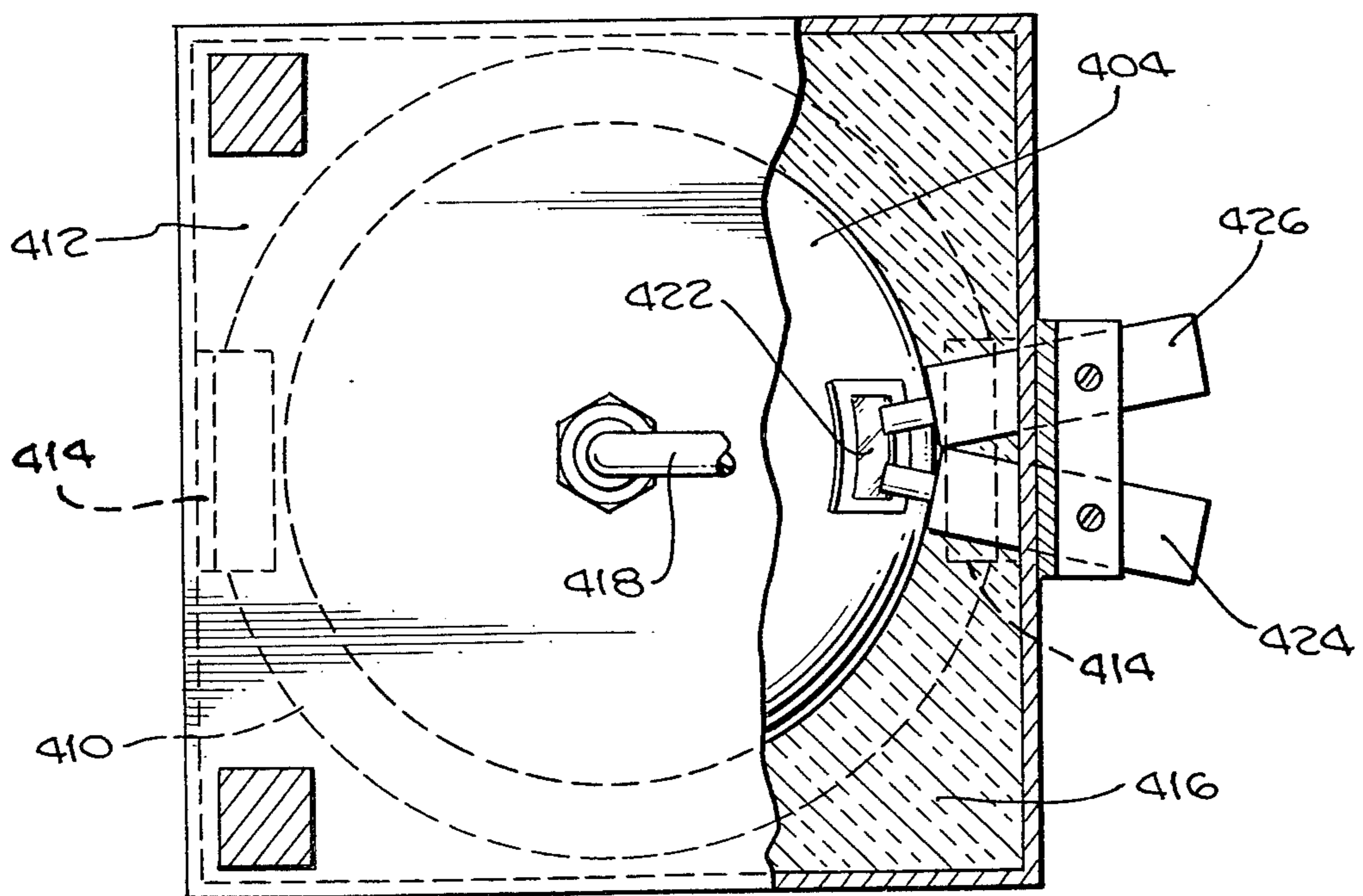




Fig. 24

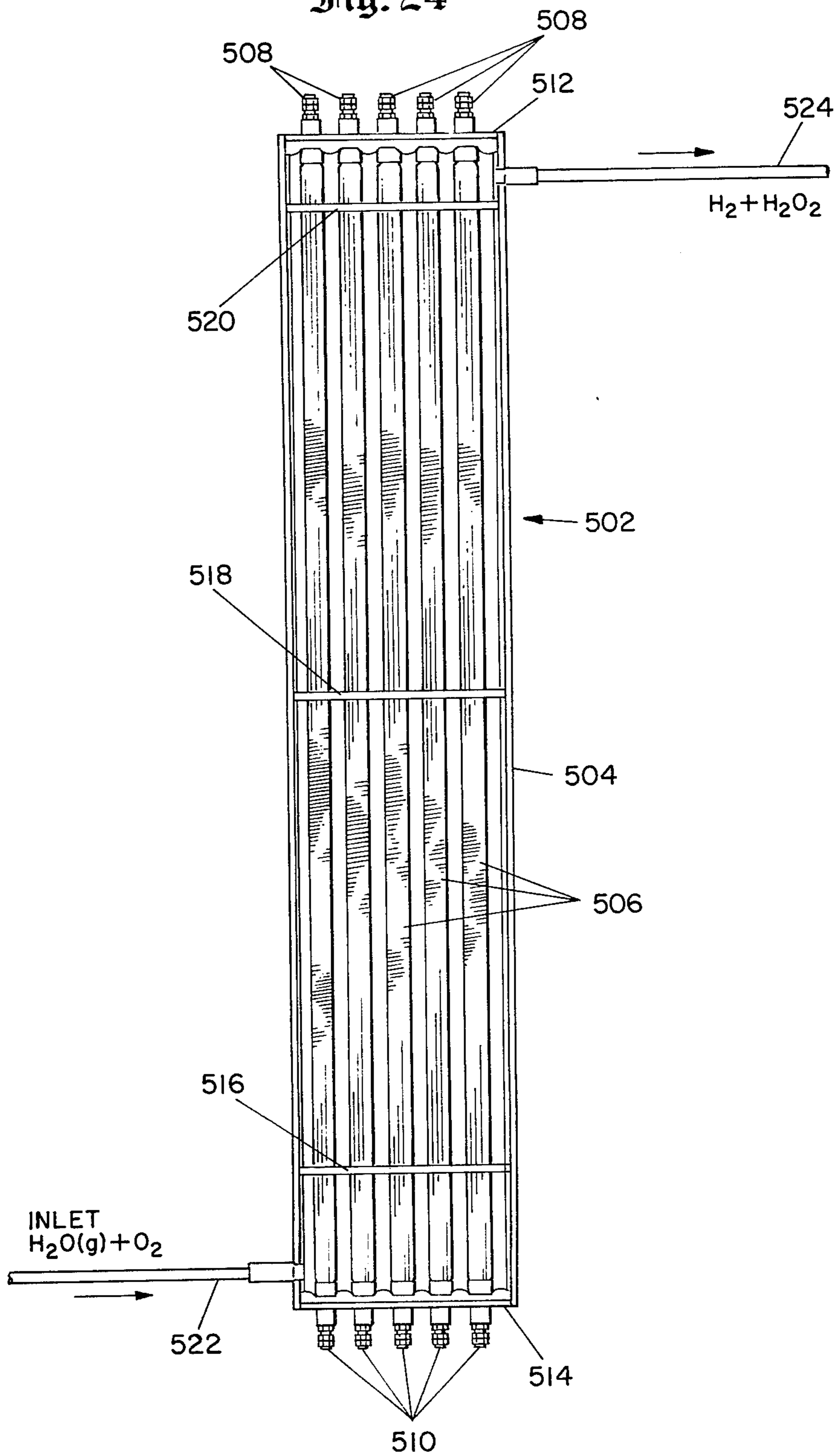


Fig. 25

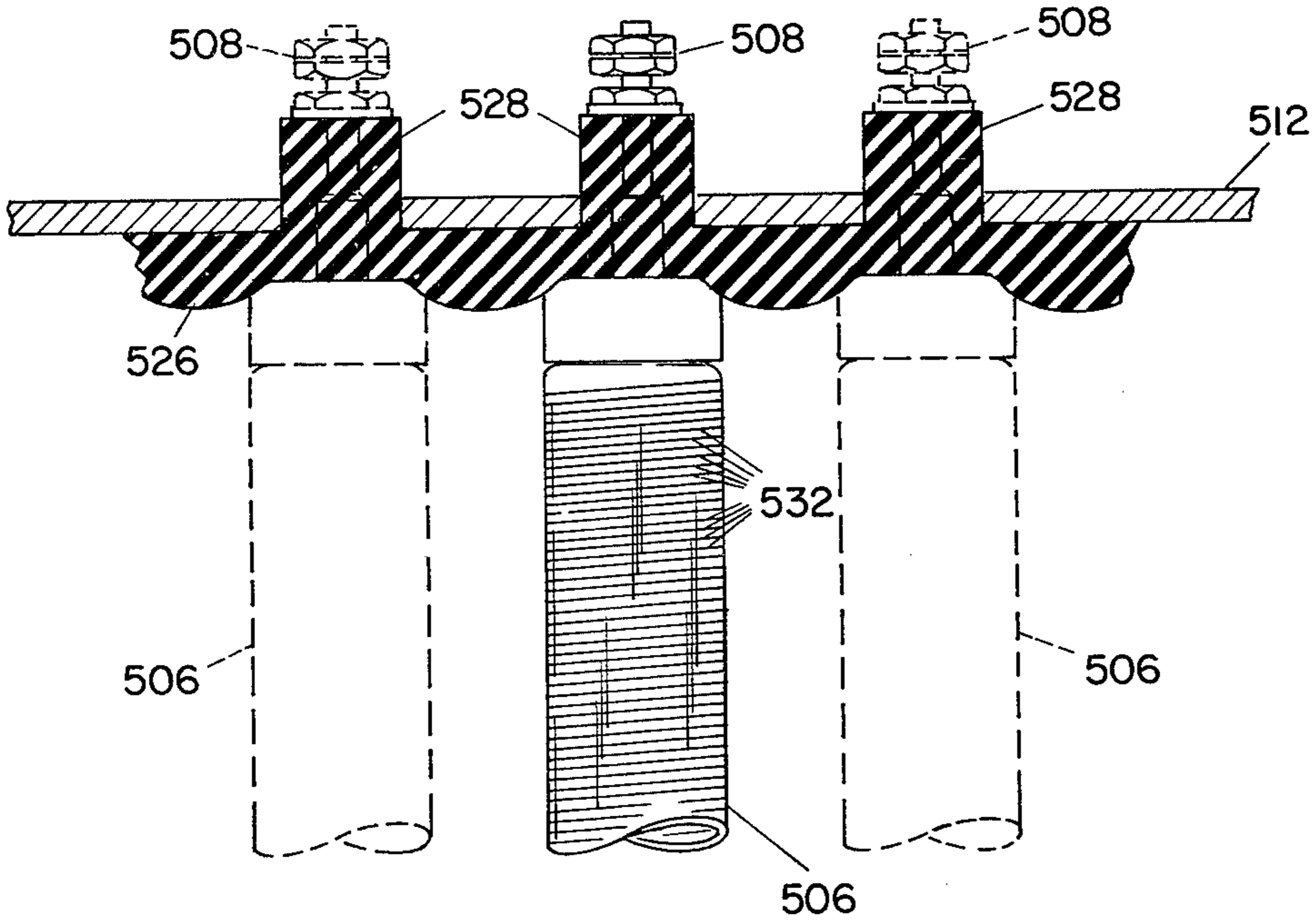


Fig. 26

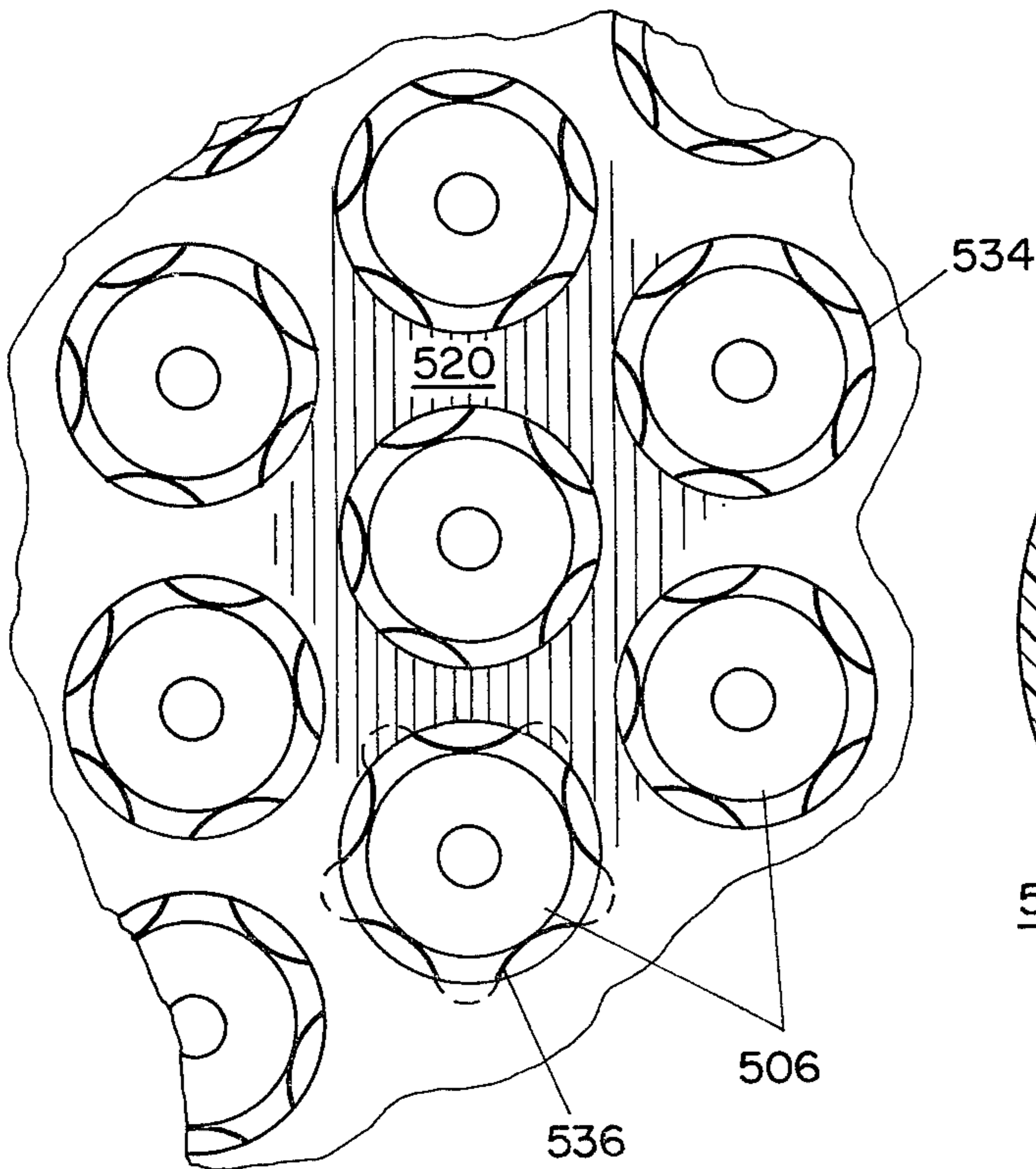


Fig. 27

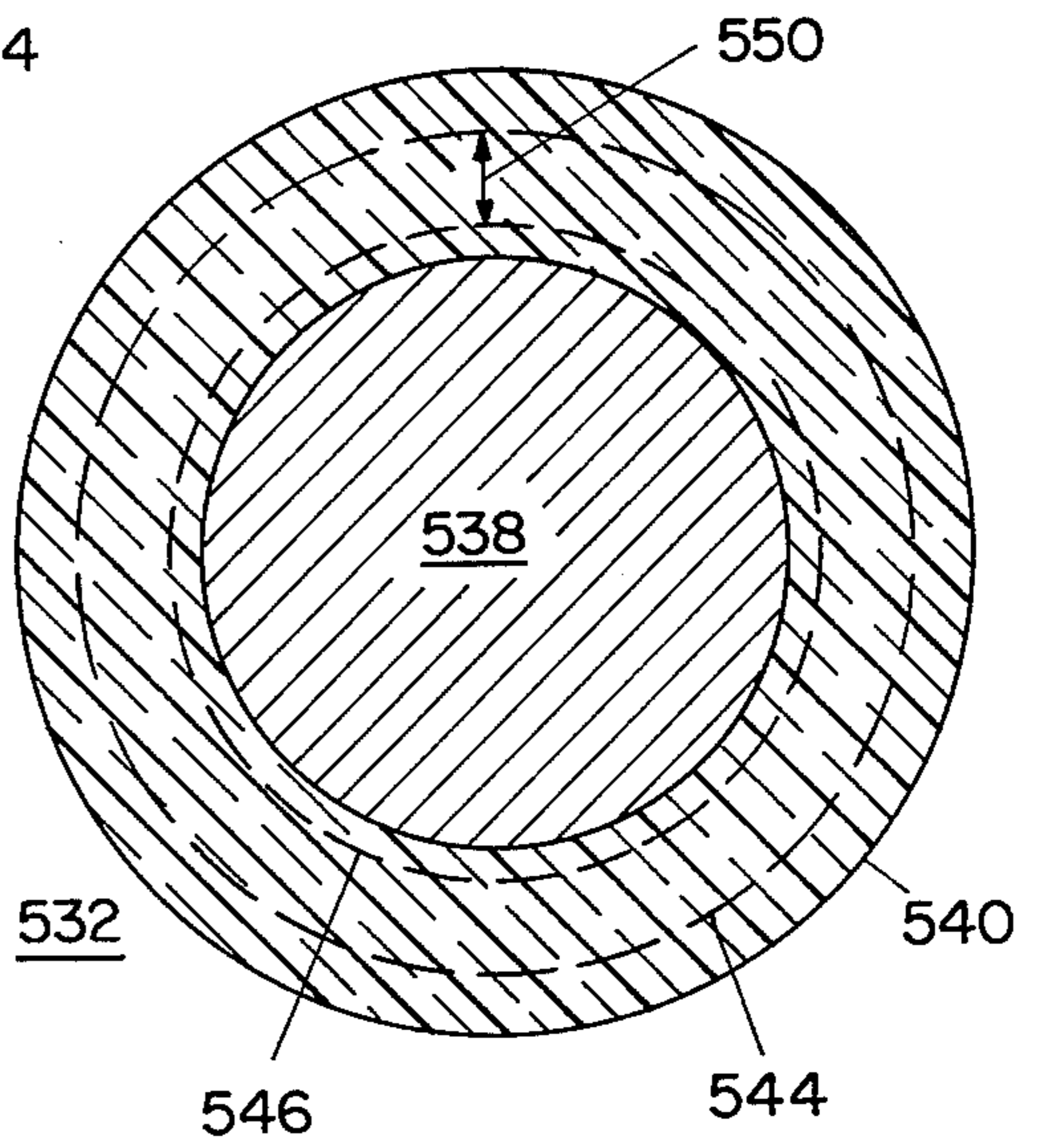


Fig. 28

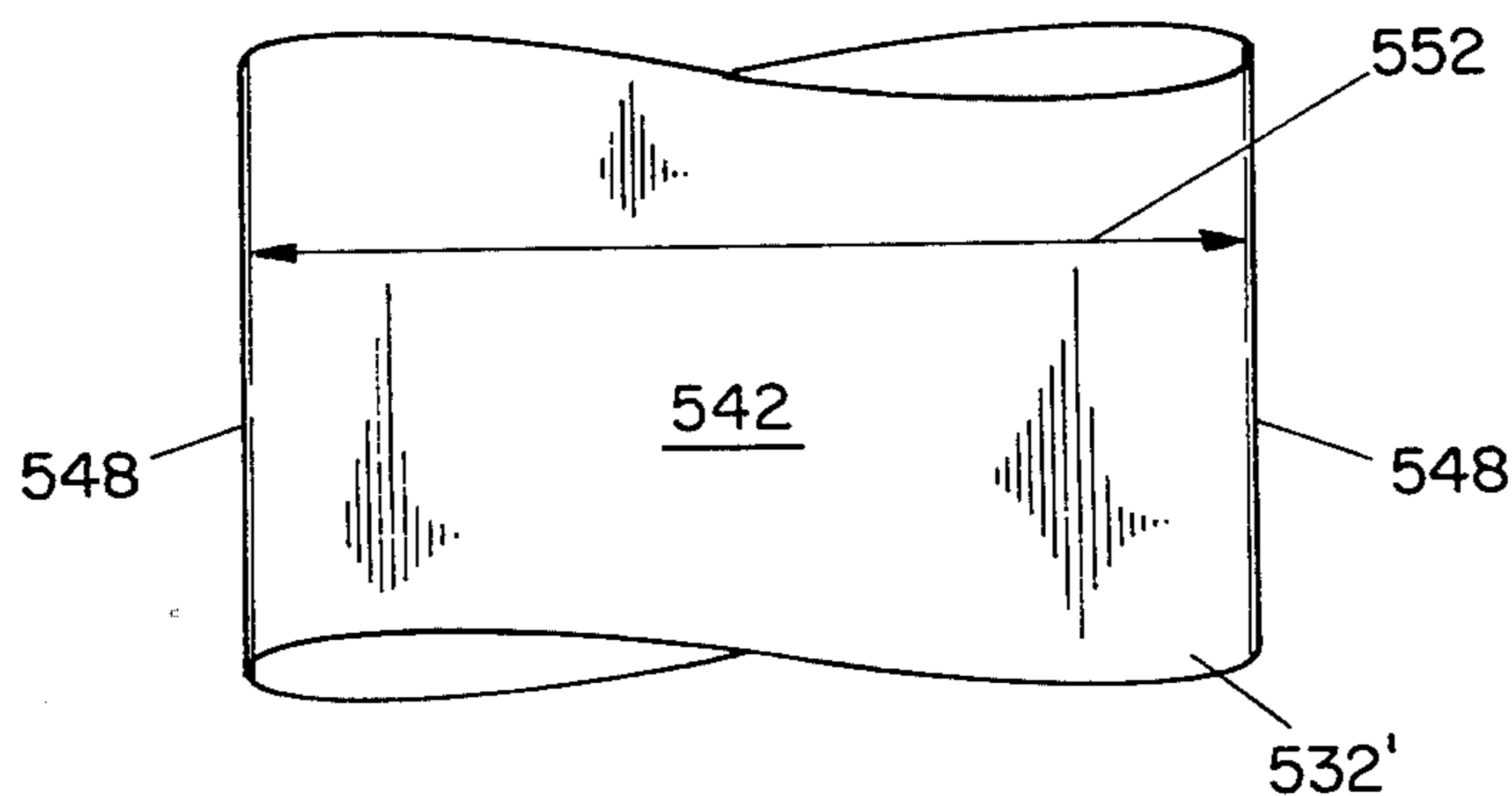


Fig. 29

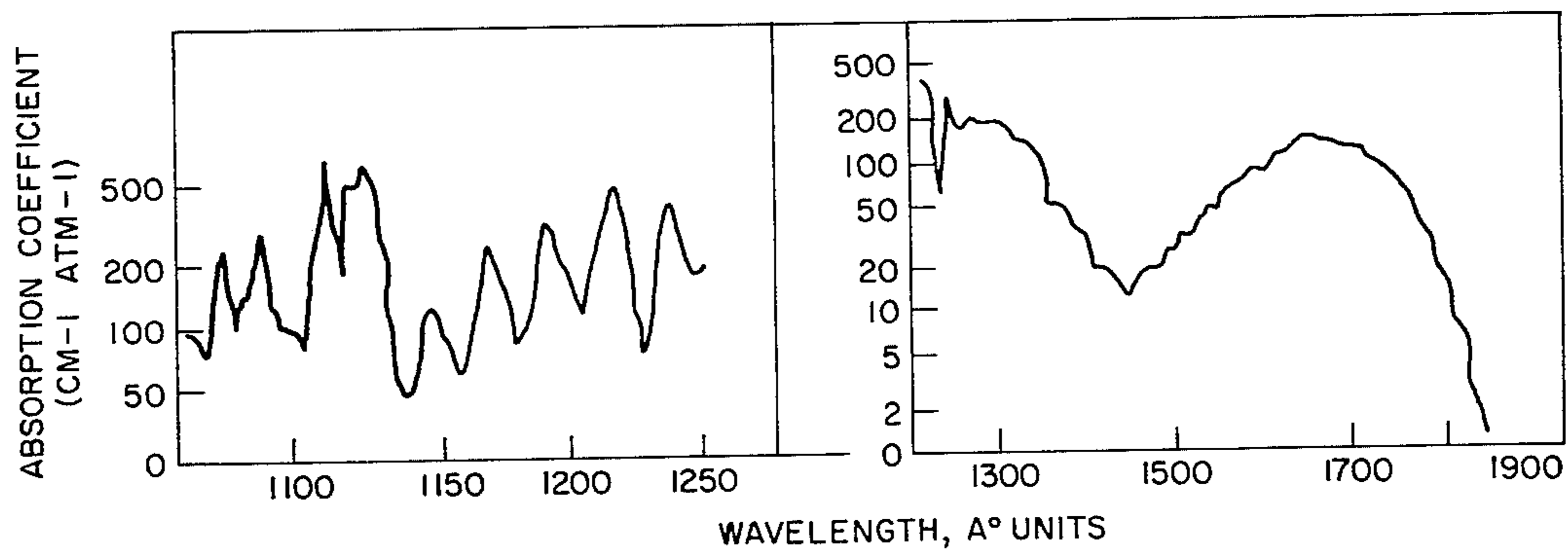
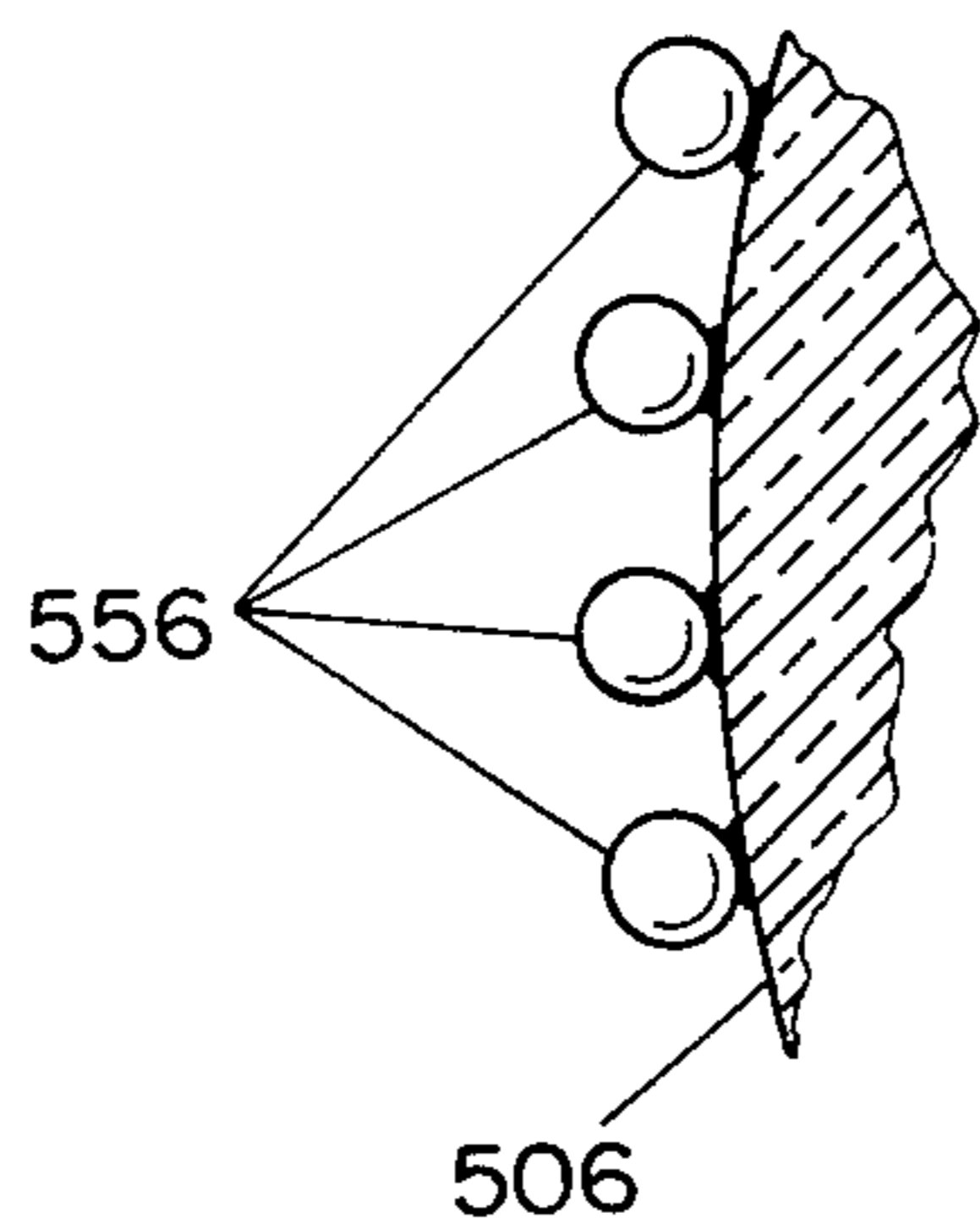
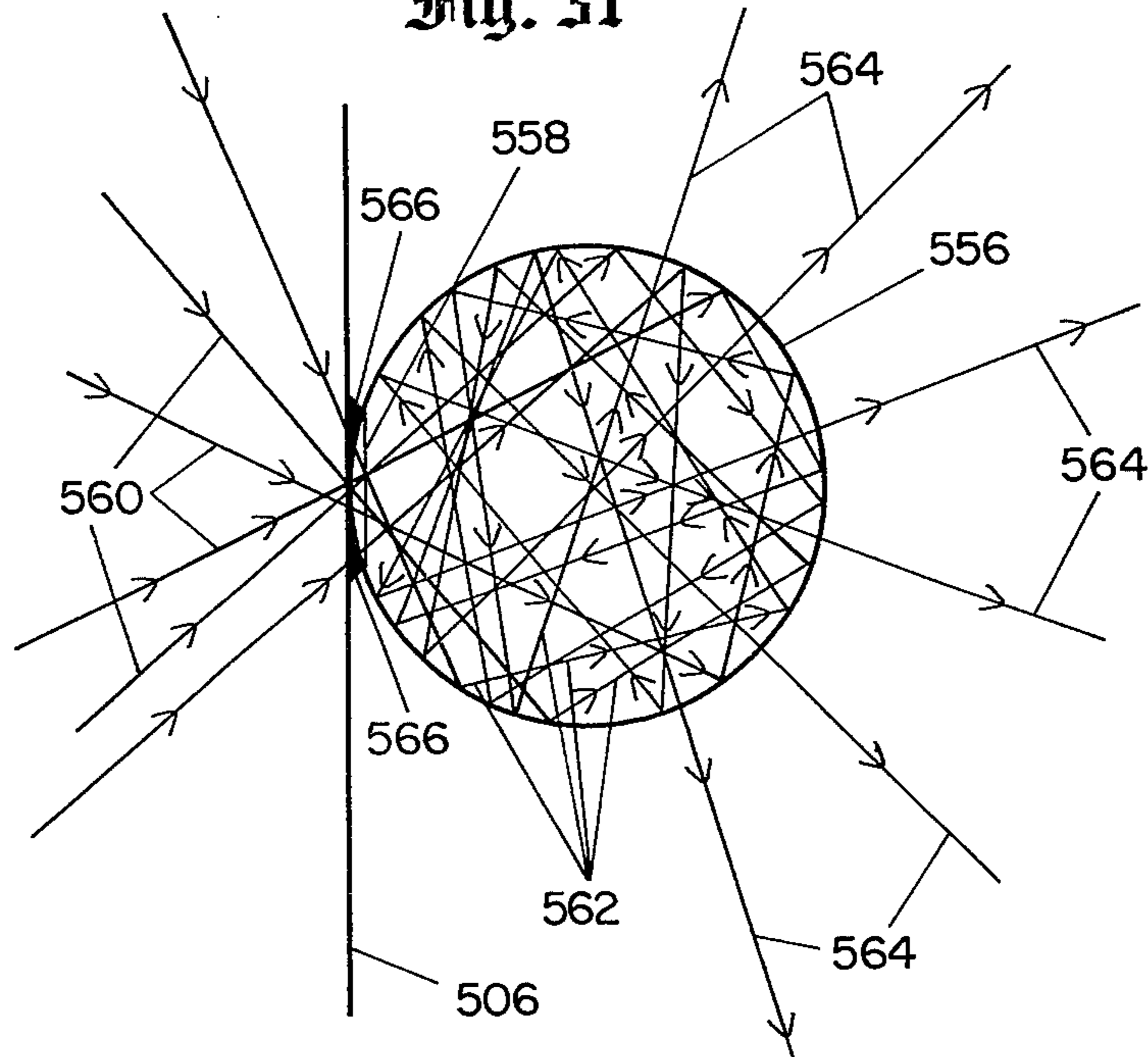


Fig. 30

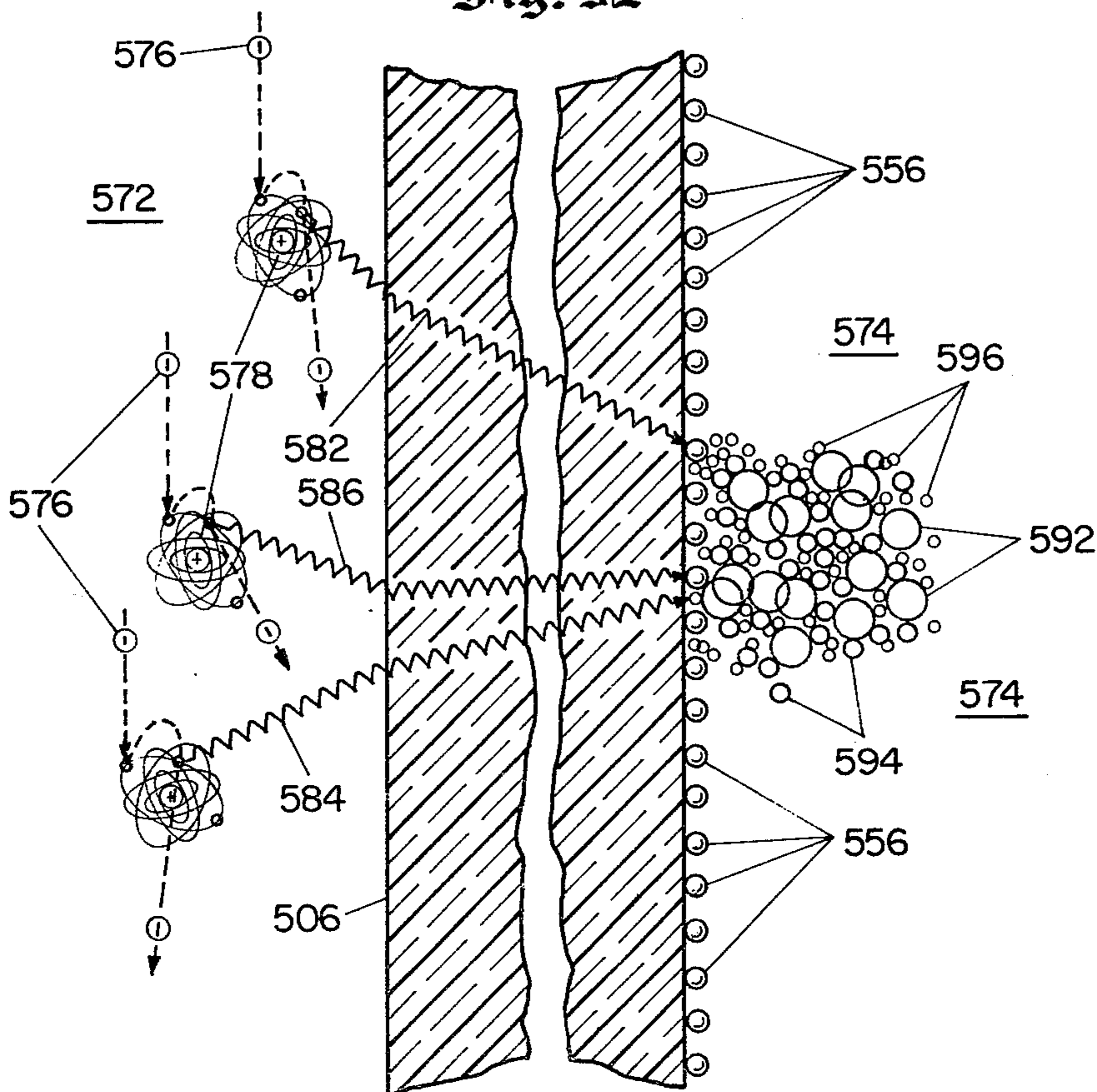




**Fig. 31**



**Fig. 32**





## APPARATUS FOR POWERFUL ENERGY TRANSFER TECHNIQUE

### REFERENCE TO RELATED PATENT APPLICATIONS

This application is a continuation-in-part of my two prior co-pending Pat. applications:

U.S. Pat. Application Ser. No. 790,320, filed Apr. 25, 1977, entitled "High Intensity Energy Transfer Technique", and these chain reactions involve the generation and regeneration of excited atoms of oxygen or other substances; and

U.S. patent Application Ser. No. 834,682, filed Sept. 19, 1977, entitled "High Efficiency Energy Transfer Technique", now U.S. Pat. No. 4,113,589, granted Sep. 12, 1978.

### FIELD OF THE INVENTION

This invention related to highly efficient photochemical techniques.

### BACKGROUND OF THE INVENTION

It has been proposed heretofore to apply coherent radiation from conventional lasers to gases to dissociate them. However, such application of laser energy is highly inefficient, and is not economically practical for commercial processes.

Accordingly, a principal object of the present invention is to practically and economically apply intense relatively coherent radiation to chemical substances to dissociate them, and initiate additional reactions.

### SUMMARY OF THE INVENTION

In accordance with one aspect of the invention, a reaction chamber is provided with a number of gas discharge tubes, and closely associated material capable of being pumped to excited states and emitting relatively coherent radiation of high intensity. Feedstock is supplied to the reaction chamber and is exposed to the radiation, which floods the reaction chamber. Further, the feedstock has absorption bands at certain frequencies, and the gas discharge and the associated laser-type material are chosen to provide intense output radiation at one or more of the absorption bands of the feedstock.

Additional gases may be supplied to the reaction chamber to react with the products formed when the basic feedstock is dissociated.

In accordance with one particular aspect of the invention the laser-type material may be in the form of filaments, wires or spheres, and may also be provided with one or more semi-transparent concentric reflecting surfaces accurately spaced to reinforce the coherent output radiation.

One particularly advantageous form of the invention involves the use of a large number of spheres of laser-type material secured to the outer surface of the gas discharge tubes. The spheres are provided with a semi-reflecting outer metallic coating, but this is not present on that portion of the spheres adjacent the gas discharge tubes to permit easy entry of the pumping radiation from the gas discharge tube. When it is desired to provide increased high frequency output radiation, by the generation of harmonics of the basic output radiation frequency of the laser type material, the reflective coating should be in the order of 70% to 90% reflecting.

In accordance with a subordinate feature of the invention, instead of normal reflecting materials such as

chromium or nickel, for example, metallic coatings may be employed which are reflective to visible and infrared frequencies but are relatively transparent to shorter wavelength ultraviolet radiation.

The use of mercury vapor gas in discharge tubes having quartz envelopes is preferred, in view of the many spectral lines of mercury vapor which are useful for pumping the laser-type material. Ruby laser material, aluminum oxide doped with chromium, may suitably be employed as the laser-type material; but other laser-type materials having different output radiation frequencies should be used as required to match the absorption bands of the feedstocks supplied to the reaction chamber.

Another feature of the invention involves the beating together of radiation at different frequencies in the presence of media discontinuities in the form of the feedstock to be irradiated, and the resultant generation of sum and difference frequencies appropriate to couple strongly with absorption bands of the feedstock material. This technique is particularly advantageous when the feedstock has absorption bands in the ultraviolet frequency spectrum.

In accordance with another specific aspect of the invention, the feedstock may be water vapor and air may also be supplied to the reaction chamber. When high intensity radiation within the ultraviolet or other absorption band of water vapor is radiated throughout the reaction chamber, the water vapor is split into hydrogen and activated oxygen atoms. These activated oxygen atoms combine with additional water vapor to form hydrogen and/or hydrogen peroxide, in additional reactions forming part of a chain reaction initiated by the basic irradiation.

In accordance with another important feature of the invention, at least two feedstocks are supplied to a reaction chamber, and the reaction chamber is flooded with radiation within at least one of the absorption bands of one of said feedstocks at an intensity level sufficient to dissociate the feedstock and the dissociation products are maintained in said reaction chamber at concentrations sufficient to create a chain reaction with the incoming feedstocks.

Another feature of the invention involves applying radiation of different frequencies to the input section as compared with the output section of the reaction chamber, to facilitate relatively complete irradiation and dissociation of the incoming feedstock and avoiding dissociation of the desired product gases. For example, in the case of water vapor as one of the feedstocks and hydrogen peroxide as one of the product gases, both water vapor and hydrogen peroxide have high absorption bands in the ultraviolet frequency spectrum; and water vapor, but not hydrogen peroxide, has absorption bands in the infrared frequency range. Accordingly, the more powerful U-V radiations may be employed in the input section of the reaction chamber, to dissociate water vapor; but in the output section where a substantial proportion of hydrogen peroxide will be present, infrared radiation may be employed to selectively dissociate the water vapor without dissociating the hydrogen peroxide. Similar considerations are of course applicable to other feedstock and product gases, taking into consideration their absorption characteristics, and relative responsiveness to radiation of different frequencies.

A feature of the invention involves the introduction of additional air into the reaction chambers to combine



with the hydrogen which is dissociated from water vapor to produce hydrogen peroxide, with the collateral advantage of supplying heat to the reaction chamber from this exothermic reaction.

Other objects, features, and advantages of the invention will become apparent from a consideration of the following detailed description, and from the accompanying drawings.

#### BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic representation of one illustrative embodiment of the system of the present invention;

FIG. 2 is a perspective view of the hydrogen burner/heating means which may be employed as part of the system;

FIG. 3 is a vertical cross-section of the hydrogen burner of FIG. 2;

FIG. 4 is a perspective view partially broken away for illustrative clarity of a reaction chamber;

FIG. 5 is a perspective view, also partially broken away, of a complete system;

FIG. 6 is a block diagram of a system illustrating certain principles of the present invention;

FIG. 7 is a pressure versus time plot for a multiple reaction chamber system;

FIG. 8 is a cross-sectional view of a portion of a reaction chamber assembly which may be employed;

FIG. 9 is a schematic diagram of the structural relationship of a plurality of reaction chambers, central burner, and enclosing insulating housing for use in a system of the present invention;

FIG. 10 is a plot of the absorption characteristics of water vapor versus wave length;

FIG. 11 is a showing of the contents of each of the reaction chambers employed in the one embodiment of the invention;

FIG. 12 is a schematic diagram indicating the generation of concentrated radiation and its application to a feedstock;

FIG. 13 shows an alternative apparatus involving the continuous flow of feedstock.

FIG. 14 is a plot of Photon Emission from a "Black Body" at 1000° K. versus Wavelength;

FIG. 15 is a plot of Radiant Emittance vs. Wavelength for a 1000° K. black body;

FIG. 16 shows a wire coated with radiation-producing material;

FIGS. 17 and 19 show reaction chambers for applying high frequency radiant energy to feedstocks;

FIG. 18 is a diagram showing the reaction chambers of FIGS. 17 and 19 included in an operative system;

FIG. 20 is a detailed showing of one arrangement for supporting the radiating wires of FIGS. 16, 17 and 19;

FIG. 21 shows the ultraviolet absorption characteristic of hydrogen peroxide, H<sub>2</sub>O<sub>2</sub>;

FIGS. 22 and 23 are side and sectional views, respectively, of a reaction chamber which is irradiated by light from two lasers of different frequencies;

FIG. 24 is a schematic view of reaction chamber containing gas discharge tubes, in accordance with the invention;

FIG. 25 is an enlarged cross-sectional view of one end of the reaction chamber of FIG. 24;

FIG. 26 is an enlarged schematic view of one of the plates which divides the reaction chamber of FIG. 24;

FIG. 27 is a cross-sectional view through one of the filaments including laser-type material which may be wrapped on the discharge tube of FIG. 24;

FIG. 28 is a schematic showing of another type of filament which may be wrapped on the gas discharge tubes of FIG. 24;

FIG. 29 includes a pair of graphs of the absorption coefficient of water vapor in the ultraviolet frequency range;

FIG. 30 is a showing of a plurality of spheres of laser-type material which may be mounted on the outer surface of the gas discharge tubes shown in FIGS. 24 and 25 of the drawings;

FIG. 31 is a schematic showing of pumping radiation applied to a laser-type material sphere mounted on the exterior surface of one of the gas discharge tubes, and the corresponding coherent output radiation from the sphere; and

FIG. 32 is a schematic showing of the generation of pumping radiation from the gas discharge tubes and its application to the laser-type spheres that are in close proximity to the feedstock and product gases in the reaction chamber.

Initially, before considering the drawings in detail, it may be noted that FIG. 1 through 23 were included in the prior co-pending patent applications, Ser. Nos. 790,320, and 834,682, of which this specification is a Continuation-in-Part. FIGS. 24 through 32 are newly added in the present specification and represent the preferred embodiments of the invention. The following description of FIGS. 1 through 23 will closely parallel that set forth in the prior patent application, Ser. No. 834,682 cited hereinabove.

#### DETAILED DESCRIPTION

Turning now to FIG. 1, the system of the present invention is generally designated by the numeral 10 and it comprises reaction chambers 12, 14, 16 and 18, heating means generally designated 20, and a hydrogen and hydrogen peroxide reservoir or accumulator 22. Water enters the system at conduit 24, passes through flow control valve 26 and conduit 28 to manifold 30. Water may then be supplied to heat exchange coil 32 through valve 34 and conduit 36, to heat exchange coil 38 through valve 40 and conduit 42, to heat exchange coil 44 through valve 46 and conduit 48, and to heat exchange coil 50 through valve 52 and conduit 54. It will be seen that conduit 36 is the inlet end of heat exchange coil 32, the outlet of heat exchange coil 32 being conduit 56 which is connected to one end of reaction chamber 12. Similarly, the outlet end of heat exchange coil 38 is conduit 58 connected to one end of reaction chamber 14, the outlet end of heat exchange coil 44 is connected to one end of reaction chamber 16 through conduit 60, and the outlet end of heat exchange coil 50 is connected to one end of reaction chamber 18 through conduit 62.

Vacuum is applied to the system, for purposes which will become apparent as the description proceeds, through conduit 64, flow control valve 66, and conduit 68 which is connected to one end of a conventional gas burner 70. It will be appreciated that heating means 20 comprises burner 70 and heat exchange coils 32, 38, 44, and 50, and their respective conduits and valves.

As will also become apparent as the description proceeds, hydrogen and hydrogen peroxide generated in the reaction chambers 12, 14, 16, and 18 passes through conduits 72, 74, 76 and 78, respectively and valves 80, 82, 84 and 86, respectively, to manifold 88. The hydrogen and/or hydrogen peroxide then passes through conduit 90 with check valve 92 to hydrogen accumulator 22 where it is then drawn off for use through con-



duit 94, flow control valve 96, and conduit 98. Conduit 100, flow control valve 102 and conduit 104 are provided to allow atmospheric air to enter the system when and if needed, as will be described more fully hereinbelow.

Before proceeding further with a description of the system, it should be distinctly understood that while the example given herein for purely illustrative purposes includes four reaction chambers, there is, in fact, no limit other than practical considerations of size and weight as to the number of reaction chambers used. In fact, the invention could be practiced with as few as one reaction chamber and as many reaction chambers as desired, there being no reason why a bank of dozens or even a hundred reaction chambers could not be used. For this reason, applicant is not limiting himself to the use of four reaction chambers except for illustrative purposes. Obviously, one skilled in the art would easily be able to include the necessary valve elements and other hardware if he were adding more reaction chambers.

With the foregoing understood, the description of the instant inventive system will proceed. The system runs at about 900° K. or 1000° K. and may be pre-heated by any well-known electrical heating means such as that described in the parent application.

Alternatively, pre-heating can be accomplished by burning hydrogen in burner 70, the hydrogen being the "tailings" left in one or more of the reaction chambers from a previous run of the system. For this pre-heating cycle, flow control valve 26 is opened to allow water to enter the system filling manifold 30. Valves 34, 40, 46 and 52 remain closed during this cycle. Valves 106, 108, 110 and 112 are opened. Vacuum is applied at conduit 64 with valve 66 opened. Thus, it will be seen that vacuum is applied via conduit 68 to burner 70. Since the other end of burner 70 is connected to conduit 114 which, in turn, is connected to manifold 116, manifold 116 is under vacuum. Then, since valves 106, 108, 110, and 112 are open, the vacuum is applied to reaction chambers 12, 14, 16 and 18, respectively, through conduits 118, 120, 122 and 124, respectively. Thus, any residual hydrogen tailings remaining in any of the reaction chambers is drawn into the inlet end of burner 70 to be burned along with any residual oxygen tailings or with atmospheric air drawn in through conduit 100 and valve 102 by the vacuum which also affects this air line. It should also be noted that in event of a "cold" start where there are no hydrogen tailings to be burned, a combustible gas, such as hydrogen, could be drawn in through conduit 100 and valve 102 to provide the initial start-up heat. The burning of hydrogen in burner 70 provides considerable heat which, by radiation and conduction is passed to the reaction chambers which are filled with reactant 126. When the system is pre-heated to a sufficiently high temperature, we are ready to proceed with the generation of hydrogen and hydrogen peroxide.

Valve 34 is opened to allow a predetermined amount of water to enter heat exchange coil 32 which is, in essence, a steam generator. The water is "flashed" to steam and delivered through conduit 56 to the inlet end of reaction chamber 12. The steam enters reaction chamber 12 containing reactant 126 to fill the total void volume and is constrained in this volume because all outlet valves are closed. The residence time, or reaction time, may be controlled from a few seconds (typically about 2 to about 3 seconds) to a rather long time (typi-

cally about 60 seconds), depending on the reactant used, the particulate size, the temperature, and the pressure. Valves 108, 110, and 112 are fully opened to allow the vacuum evacuation of all residual gases in the other reaction chambers and their respective heat exchangers and piping. It should be noted that since a predetermined amount of water was to be passed to heat exchange coil 32, valve 34 was opened for just a brief period and then closed.

Steam having entered and permeated reactant 126 in reaction chamber 12, valve 40 is then opened briefly to allow a metered amount of water into heat exchange coil 38, with the steam generated therein then passing through conduit 58 to reaction chamber 14. Valve 40 is then closed. The steam which passes into reaction chamber 14, as with the steam which had passed into reaction chamber 12, is converted into hydrogen and/or hydrogen peroxide and then held restrained in the reaction chamber for the predetermined control time. In the meantime, valve 80 is opened so that the pressure built up in reaction chamber 12 will force the hydrogen to exit through conduit 72 and valve 80 into manifold 88 and then through check valve 92 into the hydrogen accumulator 22. Valve 80 is then closed and valve 106 is opened to allow the vacuum to empty the residual hydrogen and oxygen tailings from reaction chamber 12 and pass it to burner 70 where the mixture is burned using disproportionated oxygen from reaction chambers 12, 16, and 18 along with additional atmospheric oxygen supplied through conduit 100, if necessary. It should be noted that when valve 80 was opened to pass the hydrogen and/or hydrogen peroxide out of chamber 12, and then vacuum was applied by opening valve 106, the oxidized reactant in chamber 12 disproportionated to release the bound oxygen since the temperature in the reaction chamber remained high and the pressure was lowered.

With valve 106 still open, valve 82 is also opened to allow the hydrogen and/or hydrogen peroxide generated in reaction chamber 14 to flow into the manifold 88 from which it is directed into the hydrogen reservoir 22. In the meantime, valve 46 had briefly opened to allow a metered amount of water into heat exchange coil 44 and then the steam formed in heat exchange coil 44 passes to the inlet end of reaction chamber 16. At this point, valve 84 is still closed. Valves 106 and 112 are still open to allow vacuum to exhaust chambers 12 and 18.

Valve 82 then closes and valve 108 opens along with valves 106 and 112 which are also open. Thus, hydrogen and/or hydrogen peroxide and oxygen tailings are being conveyed through valve 108 to burner 70 for combustion with the combustion gases being exhausted through conduit 68.

Then, valve 84 is opened to pass the hydrogen and/or hydrogen peroxide from reaction chamber 16 to manifold 88. Valves 106 and 108 are opened to allow vacuum to exhaust the respective chambers 12 and 14 while valve 52 has been allowed to briefly open to pass a metered amount of water to heat exchange coil 50 with the steam being formed then passing to reaction chamber 18. The steam in reaction chamber 18 reacts with reactant 126 to form hydrogen and/or hydrogen peroxide which is restrained since valve 86 is still closed. Valves 106, 108 and 110 are all open so that the other reaction chambers are being exhausted.

Valve 88 is then opened to relieve the pressure on reaction chamber 18 and allow the hydrogen and/or hydrogen peroxide to pass to manifold 88. At this point,



the whole cycle starts again and valve 14 is briefly opened to allow a metered amount of water to pass to heat exchange coil 32, valve 86 is closed, and valve 112 is opened. The whole cycle then repeats.

While the system of the invention is shown schematically, it will be readily understood by one skilled in the art that it can be easily constructed. The valves are all of a mechanical type which are cam operated so that a precise timed sequence of events can be carried out in a predetermined manner, the timing of the opening and closing of the valves being controlled by the size, shape, configuration and speed at which the cams are moving.

The following "steps" are identifiable in the total reaction cycle involving gases and solids:

- (1) Supply of the water vapor (steam) in the direction of flow.
- (2) Diffusion of this steam into contact with the particulates of manganese oxides or to the reacting interface which may be on the surface, or inside the particulate, depending on the oxidation level of that particular particulate in the gradient (overall).
- (3) Interface reaction (intrinsic rate), including sequestering of oxygen and the release of the gaseous product  $H_2$ .
- (4) Diffusion of product from the interface.
- (5) Removal of product,  $H_2$ , in the direction of flow.
- (6) Concurrently with Steps 2-5, the water vapor is also being directly dissociated by photon action, producing both  $H_2$  and  $H_2O_2$ , as described in detail below.
- (7) Diffusion of combined oxygen from the interior of the reactant to the interface, and then away from the reactant in the direction of flow of the  $H_2$  and  $O_2$  residual tailings.
- (8) Combustion of the  $H_2$  and  $O_2$  tailings in the centrally located burner.
- (9) Removal of products of combustion from the burner in its separate direction of flow.

The instant process is a process in which a relatively small amount of heat-energy input, (in the form of pre-heat for the reactant) provides conditions for the reactant to effect changes of state, during which a gaseous chemical molecule is completely dissociated into its separate gaseous atoms by two distinct phenomena. In the course of one of these phenomena, the solid reactant concurrently effects a "change of state" by means of an exothermic transformation from one oxidation product level to another oxidation product level; and in the course of the second phenomena, to be described in detail below, the  $H_2O$  molecules are directly dissociated by photon energy, forming  $H_2$  and also  $H_2O_2$ , hydrogen peroxide.

It should also be noted that pressure changes play an important part in the system. Specifically, the reactant is heated to a temperature well above the dissociation temperature for oxygen from the metallic oxide of higher oxidation number at room temperature. This temperature for  $MnO_2$  is given in handbooks as  $535^\circ C.$ , and at atmospheric pressure this  $MnO_2$  will dissociate to  $Mn_2O_3$  at temperatures above  $535^\circ C.$  Accordingly, it is desired to operate at temperatures well above  $535^\circ C.$  such as  $600^\circ C.$  to  $950^\circ C.$  In addition, during the hydrogen formation portion of the cycle, the pressure must be well above atmospheric so that the oxygen will be absorbed by the  $Mn_2O_3$  (the oxide of lower oxidation number), with a pressure of about at least 75 psi or 100 psi being preferred, and preferably between 100 psi and 150 psi to as high as 200 psi or more. In addition, during the oxygen disproportionation phase, the free oxygen and

other gases are removed from the vicinity of the reactant, preferably by a reduction in pressure to less than atmospheric, with about one-tenth atmosphere being successfully employed. As can be appreciated, by using temperatures and pressures well above and below critical levels during the two phases of the cycle, increased speeds of operation may be obtained.

Reference is now made to FIGS. 2 and 3 wherein the heating means 20 is shown in more detail. Heating means 20, as already discussed, comprises burner 70 and heat exchange coils 32, 38, 44, and 50. Burner 70 comprises casing 128 made of any suitable metallic material lined with a porous fire brick insulation 130 which is carved or otherwise formed to fit casing 128 and has an axial hollow core running longitudinally through most of its length. The hollow core is, in turn, filled with a suitable surface catalyst 132 for "burning" hydrogen and oxygen to form steam. Through the center of heating means 30 is a conventional electrical resistance heating element 140 which is used, when necessary, for pre-heating the system for a cold start. At the lower end of heating means 20 as in the drawings, are atmospheric air inlet 104 and residual tailings inlet 114. At the upper end is exhaust line 68.

The next sub-system under consideration is the reaction chambers 12, 14, 16 and 18. For an understanding of the construction of the reaction chambers, attention is directed to FIG. 4 where a single reaction chamber designated generally as 142 is shown. Reaction chamber 142 comprises an outer casing 144 made of any suitable material such as  $\frac{3}{8}$ " thick stainless steel or as discussed in the aforementioned co-pending application. It is filled with reactant 126 as discussed above and as shown and described below in connection with FIGS. 8, 11 and 12. Passing axially through the reactant is a conventional electrical resistance heating element 146, this heater being essentially the same as heater 140 in FIG. 22. This may be used for pre-heat in a cold start. As already discussed, however, the exact means used for pre-heating the system is not critical to the invention and any means well-known in the art for accomplishing this end may be used. The reactant 126, including sensitizer and host materials, is placed in casing 144 leaving a space at each end, these spaces being designated in FIG. 23 as 148 and 150. Spaces 148 and 150 essentially serve the function of surge tanks, manifolds, or the like. Steam inlet 152 and vacuum inlet 154 are provided at one end of reaction chamber 142 and hydrogen outlet 156 is provided at the other end. Steam inlet 152 corresponds to conduit 56, for instance, vacuum outlet 154 corresponds to conduit 118, for instance, and hydrogen outlet 156 corresponds to conduit 72, for instance, in FIG. 1.

Turning now to FIG. 5, the preferred configuration of the apparatus is shown along with the sub-system which includes the valves and driving mechanism for the same as well as the "plumbing". It will be seen that the valves which are described above are arrayed in a single line. The valves are of a conventional type which are operated by pushing or releasing a plunger designated, for convenience of illustration, as 158 in conjunction with valve 34. It will be appreciated that while the description of the valves refers to valve 34 and plunger 158 for exemplary purposes, each of the valves operates in the same manner. A variable speed motor 160 turns a drive shaft 162 which is journaled in mounting plates 164 and 166. Fixedly mounted on drive shaft 162 are cams 168, with one cam corresponding to each of the valves and mounted on drive shaft 162 in such a way as



to cooperate with plunger 158 of each valve. Thus, as motor 160 turns drive shaft 162 and, in turn, cams 168, the valves are opened and closed in a manner which is predetermined by the positioning of cams 168. This, of course, will be readily understood by one skilled in the art.

Referring further to FIG. 5, it will be seen that the reaction chambers are set vertically in an enclosure that is square in cross-section and are shown in the drawing with reaction chamber 12 in the front left-hand corner, reaction chamber 14 in the rear left-hand corner, reaction chamber 16 in the front right-hand corner, and reaction chamber 18 in the rear right-hand corner. Heating means 20 is disposed in the center. The enclosure or, more specifically, inner enclosure 170 is preferably made of magnesium oxide packed in a stainless steel container. This material was chosen because it distributes heat evenly throughout the volume of the enclosure 170. Surrounding inner enclosure 170 is outer enclosure 172 which is made of any suitable material such as stainless steel and filled with a high quality insulation such as alumina fibers. It will be appreciated by one skilled in the art that any high quality, high temperature, insulating material may be used.

Returning to a consideration of the drawings, FIG. 6 is a block schematic drawing showing in a central position the reaction chamber or chambers 202 and an immediately associated steam generator 204. A reservoir of water 206 supplies water to the steam generator 204, which may be of any of the types described in connection with earlier figures of the drawings. In this connection, it may be noted that all of the arrangements shown in FIG. 6 are applicable to the hydrogen generation apparatus shown hereinabove in the present specification.

Steam or water vapor is supplied to the reaction chamber or chambers 202 through line 208 which may of course be internally connected between the immediately adjacent and thermally connected units 202 and 204. Hydrogen from reaction chamber or chambers 202 may be routed through output line 210 to the venturi tube combining unit 212 which is also in intimate heat-conducting relationship with reaction chamber 202 and the steam generator 204. As mentioned above, in connection with manganese oxide the temperature of the entire assembly, including the venturi unit 212, may be in the order of 600° to 950° C.

Hydrogen peroxide may be formed in either of two ways, and the proportion of hydrogen peroxide to hydrogen gas may be controlled by valves 213 and 215. Initially, considering the formation of H<sub>2</sub>O<sub>2</sub> within the reactor chambers, by photon action, valving 215 would be opened while steam is present in the reaction chambers and while the H<sub>2</sub> gas is being drawn off, and oxygen at high pressure, corresponding to the pressure of the reaction chamber is admitted to chambers 202 via conduit 217 from pump 219.

Now considering the subsequent formation of H<sub>2</sub>O<sub>2</sub>, valve 215 would be permanently closed, and valve 213 would be open. When hydrogen starts to flow rapidly through the Venturi unit 212 the check valve 214 will open and oxygen will be combined with hydrogen to form hydrogen peroxide. The Venturi unit 212 is in intimate heat conducting relationship with reaction chamber 202 and during the preheat period, absorbs heat from the reaction chamber. Later, during operation, the combination of hydrogen with oxygen is an exothermic reaction as set forth quantitatively in equa-

tion form hereinbelow, and supplies heat to the system. The hydrogen and hydrogen peroxide is stored in reservoir 216, which is maintained at a relatively high pressure level by the check valve 218 which prevents loss of hydrogen back toward the reaction chamber 202 between the intermittent withdrawing of hydrogen from the reaction chamber 202. Hydrogen and hydrogen peroxide may be withdrawn as needed from the reservoir 216 through an output line 220. By closing both valve 213 and valving 215, the amount of hydrogen peroxide which is generated is severely limited, and the bulk of the output will be hydrogen, rather than H<sub>2</sub>O<sub>2</sub>.

Vacuum pump 221 may be employed to speed up separation of oxygen, hydrogen tailings, and other residual gases from the reactant during dissociation or disproportionation.

With regard to the block diagram of FIG. 6, it is to be understood that the components shown in this figure may be employed in connection with any system described hereinabove in the present specification. Specifically, the various input and output control valves have been, for the most part, omitted from FIG. 6 for purposes of simplicity. Similarly, the precise physical arrangement, with the units 202, 204 and 212, for example, being in intimate heat-conducting relationship with each other, and insulated from the atmosphere, is not shown in FIG. 6, but may be in accordance with disclosures of other units disclosed in the present specification.

FIG. 7 shows a typical pressure versus time cycle for a system in accordance with the present invention using manganese oxide as the reactant, and four reaction chambers. This is, for example, of the type described hereinabove in connection with FIGS. 1 through 5 of the drawings.

The pressure is "gauge" pressure in pounds per square inch (psi). With this pressure scale, atmospheric pressure is of course indicated by zero.

Considering the cycles shown in FIG. 7 from an overall standpoint, the complete cycle for each reaction chamber including both breaking up the water vapor and dissociating the oxygen from the reactant may be 40 seconds. However, the cycles of the reaction chambers are evenly staggered in operation, by 10 seconds in the example so that hydrogen is generated on a substantially continuous basis. In FIG. 7 the pressure cycle for reaction chamber No. 1 is shown in the lower characteristic, and the pressure cycle for reaction chamber No. 2 is shown in the upper characteristic. The pressure versus time characteristics for reaction chambers Nos. 3 and 4 are substantially the same as those of chambers No. 1 and 2, but are displaced by additional 10 second intervals.

Now, referring specifically to the lower characteristic 230 in FIG. 7, the cycle starts with the opening of the water inlet valve for a couple of seconds at the beginning of the cycle. Steam is promptly generated and fills the first reaction chamber. At about 6 seconds, the hydrogen outlet output valve is opened as indicated by arrow 232. Hydrogen and/or H<sub>2</sub>O<sub>2</sub> continues to flow until about 16 or 17 seconds of the cycle, when the hydrogen pressure drops to the hydrogen reservoir pressure, indicated as equal to 80 pounds by the dash dot line 234 in FIG. 7. The closure of the hydrogen reservoir check valve 218, as shown in FIG. 6, is indicated by the arrow 236 in FIG. 7. Soon after the closure of check valve 236 the pressure release and vacuum pump valve is opened, as indicated by arrow 238 and



the pressure drops along characteristic 240 to the negative pressure of about one-tenth of an atmosphere indicated by line 242. During the interval from about 20 seconds to 40 seconds the disproportionation phase takes place. Then at approximately 40 seconds the water inlet valve is opened again, and the cycle repeats.

The upper characteristic in FIG. 7 shows the same cycle for reaction chamber No. 2 as described above for reaction chamber No. 1. In the upper characteristic the same reference numerals are employed, but primes are employed in place of the unprimed numbers used in connection with the lower plot of FIG. 7.

FIG. 8 is a fragmentary view of a portion of a reaction chamber such as that shown in FIGS. 1 and 4 described hereinabove. In FIG. 8 the outer cylindrical wall 252 may for example be made of one-quarter or three-eighths inch stainless steel.

Referring more specifically to FIG. 8, in order to expose the manganese oxide powder fully to the space within reaction chamber 258, this chamber is filled with a large number of hollow stainless steel screen elements which may be formed by taking small strips of stainless steel and folding them over upon themselves and welding or otherwise securing them together to form a hollow enclosed space. The chamber 258 is initially filled with these stainless steel, hollow mesh cells 260. Then a large quantity of manganese oxide is poured into the reaction chambers and is shaken down in among the stainless steel mesh cells to completely fill the entire chamber 258. In FIG. 8 a number of these stainless steel mesh cells designated 560 are shown, and the manganese oxide powder 262 between the cells is also indicated. It is to be understood, of course, that other techniques may be employed for exposing the reactant to the space within the reaction chamber, but the foregoing system has proved eminently satisfactory in at least one 4-reaction chamber apparatus which has been successfully operated.

In addition, the host and sensitizer material may be included in the fabrication of the wire mesh cells 260. With water vapor within these wire mesh cells, this feedstock is fully exposed to the intense radiation from the sensitizer.

FIG. 9 shows an improved structural arrangement of the reaction chambers in which the four reaction chambers 302, 304, 306 and 308 are donut-shaped and are stacked up on top of one another in intimate heat conducting and transferring relationship. Each of the four reaction chambers is provided with two manifolds 310 and 312 to supply gases to the reaction chambers and to remove gases therefrom. These input and output manifolds serve the same functions as the spaces 148 and 150 at the top and bottom of the cylindrical reaction chambers as shown in FIG. 4, for example.

Each of the reaction chambers 302, 304, 306, and 308 contain reactant, such as manganese oxide, and voids created by wire mesh cells as described above, or other structure which will be described below, with which the sensitizer and host materials are associated.

A burner 314 extends through the central opening of all of the four donut-shaped reaction chambers. The burner 314 has the general configuration shown in FIG. 3, but is provided with upper and lower apertured plates 316 and 318 for ease in applying the hydrogen and oxygen to the burner and for ease of withdrawing the burned gaseous products from the unit. Although the details of the burner 314 are not shown, it includes the

refractory lining and the granular refractory material such as is shown at 130 and 132, respectively, in FIG. 3.

The unit of FIG. 9 is also provided with heavy upper and lower plates 320 and 322, which are bolted together with a series of bolts 324 spaced around the periphery of the plates 320 and 322. With this arrangement the reaction chambers 302, 304, 306, and 308 are rigidly together in intimate heat conducting relationship, and can withstand very high pressures even at very high temperatures without deformation of the reaction chambers.

The reaction chamber assembly is mounted on any suitable insulating support as indicated by the blocks 326. A lower metal base 328 and lighter gauge stainless steel metal sidewalls 330 are also provided. High temperature heat insulating ceramic wool encloses the reaction chamber assembly and reduces heat radiation to very low levels. The ceramic wool is indicated by reference numeral 332 in FIG. 9. In passing, it may be noted that the use of flat donut-shaped reaction chambers provides a geometry which is superior to the set of five cylinders shown in FIG. 5, in that the reaction chambers are in more intimate heat conducting association with one another and with the central burner, than in the arrangement of FIG. 5.

Apart from the physical arrangement of the four reaction chambers and the central burner, the "plumbing" and mode of operation of the system as described in connection with FIGS. 1 through 8, remains unchanged.

A more detailed consideration of the absorption characteristic of water vapor and other possible feedstocks, and the matching of the host and sensitizer materials to the feedstock absorption characteristic will now be undertaken.

In FIG. 10 the relative transmittance and absorption of water vapor at different wavelengths is shown. By way of example, note that at wavelengths of about 2.5 to 2.6 microns, the curve which represents transmittance has a dip designated 342 in FIG. 10. This is in contrast to the peaks 344 and 346 which are centered just above 2 microns, and in the vicinity of 4 microns, respectively. A combined host material and sensitizer which will provide intense coherent radiation in the vicinity of 2.5 and 2.6 microns, and which absorbs energy in the vicinity of 1.2 to 1.3 microns, will be employed as one set of materials for concentrating energy and applying it to water vapor. The particular host material and sensitizer which provides this wavelength of absorbing heat energy and radiating energy is calcium fluoride  $\text{CaF}_2$  as the host material, and uranium-3 as the sensitizer.

Before considering FIGS. 11 and 12 some background relative to the phenomena which are taking place will now be included.

Initially, it may be noted that the theory of Masers and Lasers of course forms a background for the present invention. The word "LASER" is an acronym which stands for the Light Amplification by the Stimulated Emission of Radiation. Although related to some extent to Maser and Laser theory, the present invention does not involve the intense collimated beams of energy characteristic of Masers and Lasers; and of course, Masers and Lasers do not derive their energy from a heat reservoir made up of a body of material at elevated temperatures.



## Types of Radiation

There are two separate processes by which a material can become a generator (or producer) of radiation energy after absorbing suitable quantities of primary energy. In the first process the absorbed energy is converted (degraded) into a low-quantum-energy heat that diffuses through the material which then emits radiation called thermal radiation.

In the second process an appreciable part of the absorbed energy is temporarily localized as relatively high-quantum-energy excitation of atoms or small groups of atoms which then emit radiation called luminescence radiation.

Specifically, "luminescence" is a process whereby matter generates nonthermal radiation which is characteristic of the materials involved and not the temperatures. Sometimes, however, the radiation as generated is also called "luminescence". It is in fact luminescence only when the radiated energy is in excess of the thermal radiation produced by heat.

Thermal radiation from solids is generally a broad continuous spectrum of radiation, especially infrared, which is emitted in increasing amount as the temperature of the solid is increased.

The quality and quantity of thermal radiation depend almost exclusively on the temperature rather than the nature of the emitting solid material. Broadly and objectively speaking, luminescence describes emission of radiation (of subatomic origin) in excess of thermal radiation; that is, luminescence yields photon emission in excess of the photon emission produced entirely by thermal agitation.

Luminescence is generally excited by primary photons or charged material particles having individual energies ranging from about 2 eV to over  $10^6$  eV and affords emitted photons with energies in excess of 1 eV. When luminescence is excited by energy liberated during chemical reactions, the liberated energy per emitting atom or molecule usually exceeds 1 eV. These excitation energies are hundreds to millions of times greater than the energies of individual phonons in solids. A single phonon can increase the energy of an electron or atom in a solid by at most a few hundredths of an electron volt, whereas the individual primary particles normally used to excite luminescence can provide energy increases up to the total amount of energy carried by the primary particle (except for rest-mass energy), that is, tens to millions of electron volts.

In order to obtain barely visible emissions of thermal radiation from a solid, the temperature of the solid must be raised above  $900^\circ$  K. to obtain an appreciable probability of getting 1.7 eV (or greater) electronic excitations by the cumulative action of phonons.

The thermal radiations from real solids cannot exceed the emission which would be obtained from a perfect black body at the given temperature and frequency. Most solids emit somewhat less thermal radiation than the maximum which is expressed by:

$$P_{84} = [\pi h \nu^3 C^{-3} (E^{h\nu/kT} - 1)^{-1}] \text{erg cm}^{-2} \text{sec}^{-1} \quad (50)$$

The peak wavelength  $\lambda_{pk}$  of the broad emission band of black body radiation is inversely proportional to T, according to WIEN'S displacement equation.

$$\lambda_{pk} = 0.29T^{-1} \text{cm} = 2.7 \times 10^7 T^{-1} \text{A} \quad (51)$$

The TOTAL THERMAL EMISSIVE POWER  $P_T$  of a perfect black body increases as  $T^4$ , according to the STEFAN-BOLTZMANN LAW:

$$P_T = 2.5k^4 T^4 / 15C^2 h^3 = 5.7 \times 10^{-5} T^4 \text{ erg cm}^{-2} \text{sec}^{-1} \quad (52)$$

At room temperature (about  $200^\circ$  K.),  $\lambda_{pk}$  is in the far infrared at 97,000 A, and  $P_T$  is only  $4.6 \times 10^5 \text{ erg cm}^{-2} \text{sec}^{-1}$ , so that there is not an appreciable amount of radiation in the VISIBLE region between 4000 and 7000 A.

At the temperature of an incandescent lamp filament (about  $2800^\circ$  K.),  $\lambda_{pk}$  is about 10,000 A, and  $P_T$  is  $3.5 \times 10^9 \text{ erg cm}^{-2} \text{sec}^{-1}$ , so that there is an appreciable emission in the visible part of the spectrum. In the temperature range between about  $700^\circ$  and  $1000^\circ$  K. there is an overlapping of feeble luminescence and feeble incandescence.

The present invention involves temperatures from a lower limit of about  $900^\circ$  to  $1000^\circ$  Kelvin or about  $600^\circ$  to  $700^\circ$  Centigrade and ranges upward from these temperatures with the upper limit controlled only by the strengths of the materials utilized (1) as the reactant or host/sensitizer, (2) for the reaction chamber, and (3) for the tanks, tubing, etc.

## THE HASER CONCEPT

The Maser/Laser type of acronym may also be applied to another system termed "Haser", an acronym for "Heat Amplification by Stimulated Emission of Radiation." As will be developed below, however, the term "Amplification" is not used in the sense of increasing signal strength, but in the sense of amplifying the effectiveness of heat energy.

The Haser application depends not as much on coherence or monochromaticity per se, but rather on the unprecedented energy per unit area. This radiated energy is a by-product of the coherence of the radiation, and can be many orders of magnitude greater in energy than normal incoherent thermal radiation. To understand why this is possible, it is necessary to review briefly a few of the basic differences between the incoherent radiation produced by an ordinary bright source and the coherent light (radiation) produced by a laser or maser.

In a conventional source the atoms of a solid (or a gas) are agitated either thermally or electrically to higher energy states. When these atoms return spontaneously to their lower levels, they radiate some of their excess energy as light. Since each atom behaves independently at this state, its emission is at a random time and in a random direction with a random polarization.

It follows that the light radiated in a single direction in the complex sum of all the light from the individual atoms. The phases of any two atoms will tend to cancel their radiation in some directions and enhance it in others. The total energy of the source will on the average be radiated uniformly in all accessible directions, and the amount of energy observed in a given direction will be proportional to the solid angle subtended by the observing device. In the Haser interior the observing device is either a water-vapor molecule (or other feedstock) or another particulate of reactant.

The maximum total energy that can be radiated by a given source depends on two factors: the surface area of the source and the maximum temperature to which the source has been heated. Therefore, in practice, the only way to increase the power output from an ordinary



source beyond the limitations imposed by the source material is to increase the surface area of the source.

Power output, however, is only half the solution. Concentrated power is much more important than power itself. A 40-watt fluorescent lamp, for example, produces more light than a 40-watt incandescent lamp, but the fluorescent lamp is not nearly as effective as the incandescent light source for a spotlight.

Now, in a laser or maser, the energy is also emitted when atoms drop from a higher energy level to a lower one; however, in this case the atoms are triggered and emit radiation (to a large percentage) in unison. In the case of the Haser, the atoms are triggered to emit radiation in unison by phonon/photon waves within the unit cavity or cell interior. Enough of the energy previously generated is retained within the mass of particulates to maintain emission in a compatible phase, polarization and direction. This phonon wave interacts with the excited atoms and causes them (to a large degree) to emit their excess energy in phase with the stimulating wave before they have a chance to do it randomly.

As a result, the Haser generates a good percentage of its radiated energy so that it travels in synchronism with the standing phonon waves, therefore concentrating the energy emitted as photons.

In effect, the radiated photons from the Haser particulates are all relatively concentrated, monochromatic, and therefore, relatively coherent energy sources. This results in an excellent energy density even though the photons are traveling in practically an infinite number of directions, due to the fact that the particulate sources number in hundreds of millions. The photons moving from particulate to particulate impact and are absorbed by other particulates. Then, this STORAGE, BUILD-UP, AND RELEASE of the "phase and amplitude of radiated energy," combined with the fine particulate geometry of the Haser power (energy) source, which provides surface area to emit photons in extremes, allows a "maximum efficiency utilization" of the radiated energy within the Haser cavity.

The act of controlling the spectral emissions to most effectively dissociate (for example) water vapor, by sensitizing the host compound properly is another very important point. The monochromatic waves may become distorted in passing through substances, so that harmonic waves are generated at two or more times their original frequency.

Infrared wavelengths may be converted into visible light, and visible light into ultraviolet waves.

This new system utilizes fine (small) particulates of solids comprised of oxides which are predetermined by design within which some of the host atoms are replaced by other frequency sensitive atoms also predetermined by design, which, provide stimulated absorption and emission at predetermined wavelengths.

An ohmic (or other) pre-heat provides to the heat reservoir mass the original energy to liberate a massive volume of photons at the frequency range which will activate the sensitive atoms included in the host compound; the fine multi-faceted particulates absorb the photons which normally proceed as phonons through the particulate to generate and provide large numbers of cavity resonances which stimulates emission with each internal excursion; therefore, again, the gain by this regenerative amplifier when driven by the thermal noise fluctuations from the cavity walls, can be significant.

In the case of the HASER, the principle emissions of radiation designed and produced to dissociate the chemical product may be emitted from the woven wire mesh cavity balls or cells 260 (FIG. 8) that fill the entire Haser cavity.

The "preheat" energy can be electrical and inserted (through resistance heaters) into the internal cavity or the heaters may also be external to the cavity and heat the mass by conduction and radiation through solids.

Also, the "preheat" energy may be inserted by combusting suitable fuels such as hydrogen, hydrogen peroxide, alcohol, and other hydrocarbons, directly in the internal cavity of the unit or within a "center-core" burning unit as is designed into the unit of FIG. 9, for example.

As the reactive mass reaches temperature levels which excite the molecules and atoms to a radiating level of energy, phonons and photons evolve which distribute the thermal energy within the mass. Incidentally, relative to the use of the terms "photon" and "phonon", when a photon traveling through space impinges on a solid, the resultant wave in the solid is termed a "phonon".

The ability of 'atoms' to store energy has to do with the electrons within the individual atoms. The electrons exist as a cloud of negative charge around the positively charged nucleus. Each election occupies a state of energy and angular momentum that cannot be occupied by any other election.

Therefore, the electrons tend to fill stable shells surrounding the nucleus.

The electrons of the outermost shell are the ones most easily affected by outside forces because of their accessibility. These outer electrons can be moved to higher energy states, but they always tend to return to their lowest energy state: the ground state. Electrons at certain levels decay (fall to a lower state) more easily than electrons at other levels.

Each excited electronic state of the atom has a characteristic lifetime that indicates the average time it takes an electron to fall to a lower level and therefore radiate a photon. Most excited states have lifetimes of about  $10^{-8}$  second.

There are some excited states or levels in all atoms in which the electron cannot decay easily by giving up a photon. Such atoms must therefore wait for other means of giving up their energy, such as colliding with other atoms or with the walls of the system. Electrons in this state of energy tend to stay there for relatively long periods of time (0.001 second or more), and are referred to as being in metastable states. This is an important part of the storing of energy, which can then be retrieved in the excitation process by stimulation.

the normal radiative decay from a higher electronic state to a lower one is termed spontaneous emission. As discussed earlier, processes exist that can force an atomic electron to a higher state or stimulate it to jump to a lower state. An example of forcing, as discussed earlier, is provided when a photon collides with an atom and excites the outer electron to a higher level, which can happen when the energy or wavelength of the photon corresponds exactly to the difference in energy between the state the electron is in and some higher possible state. This process is known as absorption because the photon (energy) is actually absorbed by the atom and all the photon's energy goes into raising the electron to a higher state.



Similarly, as discussed earlier, the stimulated electron can move to a lower level, provided that such a level exists and that the difference between the two levels corresponds to the energy of the incoming photon exactly. The energy given up by the electron in jumping to a lower state goes into creating an additional photon with the same characteristics as the colliding photon.

A large number of atoms can provide an increase in the radiated energy at the desired frequency or energy level, if the population of electrons in the excited states of the atoms is suitably arranged. Consider two excited levels of a system of identical atoms with the electrons divided between the upper and lower levels. If a radiated photon having a wavelength corresponding to the difference in energy between the two levels is allowed to pass through the system medium, it will be amplified if there are more atoms with electrons in the upper state and absorbed if there are more atoms with electrons in the lower state. The condition of having more atoms in the upper state is called a "population inversion" (because it goes against the normal processes of nature, which tend to keep more electrons at lower energies than at higher energies).

The search for new Haser "systems" is therefore not easy, because one is working against the natural tendencies of the electrons.

Another important consideration is the actual 'lifetimes' of the ion energy levels of the impurity atoms involved in the population inversion. The upper level of a two-level system with a population inversion radiates energy corresponding exactly to the difference between the two levels.

The electrons that have thus yielded energy by radiation, end up at the lower level. If they remained there, the situation would result wherein there would be more atoms at the lower level than at the upper level, and as discussed earlier, there would be absorption instead of gain. For continuous operation, one must find impurity atoms with combinations of levels such that the lower level has a short lifetime and the upper level is preferentially populated. This necessity rules out the ion ground state as a possible Haser level, since all ion ground states are metastable. The pair (or more) of ion energy levels which will provide amplification must be energetically above the ground state but still below the metastable states.

Although the original gas laser utilized electrical excitation of electronic transitions, later versions use vibrational transitions in molecules such as carbon dioxide, and the excitation mechanism may involve electrical or chemical excitation, or the burning of fuel. In the chemical laser, atomic species such as hydrogen and fluorine can be reacted to produce molecules in an excited vibrational state which in turn yields amplification or oscillation.

An entirely new excitation process was announced by Garry in 1970. In this, the gas dynamic laser, an appropriate fuel is burned to produce carbon dioxide and nitrogen at high temperature and pressure. When released through a nozzle into the optical resonator region, the gas cools rapidly in terms of its kinetic or translational energy, but the population of the vibrational energy levels of the carbon dioxide molecules becomes inverted since the lower level of the laser transition relaxes more rapidly. In addition, the vibrationally excited nitrogen molecules are in near resonance with the upper laser state of the carbon dioxide and transfer energy with high efficiency to maintain the

inversion. This type of 'laser' has produced continuous powers as high as 60 kw.

The HASER phenomenon as utilized in the present invention, actually uses a thermochemical excitation mechanism. The original preheat energy prepares the reactant material within the reaction chamber by bringing the material to photon emitting temperatures.

When water vapor is introduced into the chamber of FIGS. 1 and 8, for example, the excited billions of photons emitted and traveling between particulates, strikes the sensitized "Cvities" with a barrage of photons designed to provide frequency, amplitude, and steric factor impact adequate to dissociate the H<sub>2</sub>O molecules. On dissociation, the 2H<sub>2</sub>, and O<sub>2</sub> molecules are vibrating at very high temperatures and pressures which are compatible with recombining these molecules through the "activated complex" mechanism into their (high temperature) preferential H<sub>2</sub>O + H<sub>2</sub> molecules, which incidentally evolves more than 33 KCal/mole heat energy. As the steam enters and traverses the cavity, an amount of the steam (depending upon the design of the contents of the reactor chamber and the relative amount of reactant, manganese oxide or other similar metal oxide, and the host/sensitizer material), combines with the reactant, which raises the oxidation level through the process of oxidation; and this of course, evolves heat energy (because this is an exothermic reaction), which, broadcasts more photons of energy throughout the cavity interior, to react with the sensitizers and activators; and this in turn creates massive amounts of new photons of energy to dissociate the H<sub>2</sub>O vapor and maintain the reaction temperatures within the host materials.

#### HASER CAVITIES

Referring again to FIG. 8, the cavities 260 can be fabricated of very fine mesh woven wire, which is cut into small sections, stamped, folded, and the outer edges of the wire mesh are secured together to form a hollow cell. The wire, of a diameter approximately equal to 0.002 inch, is made up of the elements, compounds, and a metal carrier (inert to the process), and is initially woven and formed into the cells as described above. It is then transformed into the desired host and sensitizer materials through oxidation in an atmospherically controlled furnace or kiln.

#### CERAMIC HASER TUBES

Instead of the wire mesh cells 260 as shown in FIG. 8, the preferred form of Haser cavity is shown in FIG. 11 in which a large number of ceramic tubes 352 are present. These tubes are preferably extruded from mullite, which is a common clay having the approximate chemical structure of 2Al<sub>2</sub>O<sub>3</sub> · SiO<sub>2</sub> with a range to 3Al<sub>2</sub>O<sub>3</sub> · 2SiO<sub>2</sub>. Suitable quantities of host and sensitizer materials, as described below, are added to, and thoroughly mixed with the mullite prior to extrusion. Subsequent to extrusion the tubes are fired in a suitable kiln or furnace. The tubes may suitably have a diameter of about ¼ inch or ½ inch and be from 1 to 12 inches in length. The sidewalls may suitably be from 1/32 to 1/16 of an inch in thickness, but none of the foregoing dimensions are critical. After firing, the tubes 352 are provided with filters 354 in both ends. The filters may be of any suitable structure, for example, several layers of metal gauze, to prevent the intrusion of the reactant 356 which may, for example, be manganese oxide. In prac-



tice the ceramic tubes 352 with their associated filters 354 may be initially placed in one of the reaction chambers such as reaction chamber 302, 304, 306, and 308 of FIG. 9, or the chambers 126 of FIG. 1; and then powdered metallic manganese or manganese oxide may be poured in and the entire unit vibrated until the manganese oxide 356 as shown in FIG. 11 fills all the space around the ceramic tubes 352. With this arrangement, of course, the water vapor is present within all of the ceramic tubes 352; heat is provided by the manganese oxide 356; and radiation from the host/sensitizer combination forming part of the ceramic walls 352 radiates intense coherent energy in one or more of the absorption bands of water vapor; and this intense radiation serves to dissociate the hydrogen and oxygen atoms making up the water vapor molecule.

The foregoing action is shown diagrammatically in FIG. 12 in which the tube 352 is shown centrally located and the surrounding particles of manganese oxide 356 are shown radiating broad spectrum thermal radiation 358 in all directions including into the ceramic tube 352. The water vapor particles 360 shown as small circles within the tube 352 may be directly impacted by the coherent radiation 362 which is emitted by the host/sensitizer combination included in the walls of ceramic tubes 352. It may be noted, that for convenience in illustration, the manganese oxide particles are shown spaced apart in FIG. 12; however, in practice they would be filling all of the space within the reaction chambers which is not filled with the ceramic tubes 352.

#### HOST/SENSITIZERS FOR WATER VAPOR FEEDSTOCK

In the tabulation which will be set forth below, suitable host materials and sensitizers for applying radiation to water vapor will be set forth. In this tabulation the chemical symbols for the elements will be employed, and the host material will be listed first followed by the sensitizer material. In each case the absorption band for the host material will initially be given and then the emission wavelength of the sensitizer will be set forth. Following the tabulation, the absorption characteristic of water vapor as shown in FIG. 10 will be reviewed and the relationship of the emission lines of the sensitizers to the absorption bands of the water vapor will be discussed.

(a) $\text{CaWO}_4 : \text{Nd}^{3+}$	Where
Absorption = 0.74 microns-0.76 microns	Ca,(Calcium)
Emission = 1.065 microns	W,(Tungsten)
	Nd,(Neodymium)
(b) $\text{CaWO}_4 : \text{Nd}^{3+}$	(Same)
Absorption = 0.87 microns-0.89 microns	
Emission = 1.3372 microns	
(c) $\text{Y}_3\text{Al}_5\text{O}_{12} : \text{Er}^{3+}$	Where
Absorption = 0.46 microns-0.47 microns	Y,(Yttrium)
Emission = 1.6602 microns	Al,(Aluminum)
	Er,(Erbium)
(d) $\text{Y}_3\text{Al}_5\text{O}_{12} : \text{Er}^{3+}$	(Same)
Absorption = 0.52 microns-0.54 microns	
(e) $\text{CaF}_2 : \text{U}^{3+}$	Where
Absorption = 1.2 = microns-1.3 microns	Ca,(Calcium)
Emission = 2.5111 microns-2.613 microns	F(Fluorine)
	U(Uranium)

In the foregoing tabulation it may be noted that there are only three separate combinations of host and sensitizer materials which are being employed. More specifically, the combination of calcium tungstate and neodymium produce output radiations both at 1.065 mi-

crons and also at 1.3372 microns as set forth in examples (a) and (b). It may be noted that the absorption wavelengths for the two output emissions differ correspondingly. The combination tabulated in examples (c) and 8d) set forth above include yttrium aluminum oxide as the host material and erbium as the sensitizer. In this case, the emitted radiation for both (c) and (d) is at 1.6602 microns; however, the absorption for the two examples is at different frequencies. The final example (e) using calcium fluoride as the host material and uranium-3 as the sensitizer was mentioned above

With regard to the matching of the emitted radiation from the sensitizers with the absorption bands shown in FIG. 10 for water vapor as a feedstock, the high absorption band for water vapor extending from about 2.4 microns to about 3.1 microns is well located to receive emitted energy in the 2.5 microns to 2.6 micron wavelength region from example (e) tabulated above. With regard to examples (a) through (d), a cursory review of the emission wavelengths and the corresponding moderately sharp absorption bands between 1 and 2 microns would indicate that there is not necessarily an exact correspondence. However, it has been determined that there is a certain amount of broadening of the radiation and of the absorption characteristics which occurs at high temperatures; accordingly, with the basic location of the emission lines and the absorption points as indicated in the above table and in FIG. 10, the practical result is good coupling from the emitted radiation to the water vapor molecules at the 1,000 °Kelvin temperature at which the system is operative.

With regard to the relative quantities of the host and sensitizer material in the mullite, the quantity of host material should be approximately 25 to 1,000 times greater than the amount of associated sensitizer material. A ratio is approximately 0.5% of sensitizer of the amount of host material is the general order of magnitude which should be employed. In addition, the quantity of each particular category of host and sensitizer material such as those set forth in the tabulation of combinations (a) through (e) set forth above, should be proportioned to the absorption bands of the feedstock which is being irradiated. Thus, in the particular example under consideration, where the host/sensitizer combination (e) using calcium fluoride and uranium-3, is matched to a broad absorption band of water vapor, a larger quantity of this host/sensitizer combination should be employed as compared with combination (a), (b) and combination (c), (d). Thus, in the making of the ceramic tubes, the material which is being prepared might include approximately 88% by weight of mullite, 8% by weight of the host/sensitizer combination (e), and 2% by weight of each of host/sensitizer combinations (a), (b) and (c), (d). Similarly, in the event that the wire mesh is employed, the host sensitizer/sensitizer combinations may be added in the same proportions to stainless steel wire and the combination material drawn into wires and formed into mesh. Alternatively, after the preparation of the stainless steel wire cells, mullite together with the host sensitizer combinations could be applied in several bands in the plastic state around the stainless steel wire mesh cells, and then fired, to produce the desired result. This result, as mentioned above, involves the provision of spaces throughout a body of material constituting a heat reservoir, and locating host/sensitizer combinations around the boundaries of these spaces or voids in the material.



The chemical formula for mullite was given above, and it is again noted that mullite includes aluminum oxide  $\text{Al}_2\text{O}_3$  and silicon dioxide  $\text{SiO}_2$  in certain proportions noted above. In order to enhance the "HASER" action and increase the energization of the host/sensitizer combinations (a) through (e) set forth above, a material such as chromium, which acts as a sensitizer in cooperation with the aluminum oxide in mullite which acts as the host material. The chromium-aluminum oxide, sensitizer-host combination produces strong output radiation at a number of wavelengths, including output radiation centered at 0.6934 microns, when the  $\text{Al}_2\text{O}_3$  is absorbing energy at 0.5 microns. The radiation centered at 0.6934 is broadened at the high operating conditions so that the radiation extends from 0.6 or 0.65 to 0.75 or 0.8 microns, thus providing supplemental input energy to example (a) set forth hereinabove, which involves absorption at about 0.74 to 0.76 microns. The  $\text{Al}_2\text{O}_3/\text{Cr}$  combination may also directly apply energy to the feedstock when the output radiation is of the proper frequency and may also pump other host/sensitizer combinations. When chromium is used it will be present in quantities in the order of five per cent by weight or less of the mullite employed as the basic material of the tubes 352 as shown in FIGS. 11 and 12.

#### MATERIAL REQUIREMENTS

The primary requirements for potential solid-state Maser/Haser materials are, first, that the composition should fluoresce with a suitably high intensity at elevated temperatures by means of thermal energy alone and, second, that the matrix should be transparent or has no absorption transition at the operation frequency; it should also be chemically stable and have no caustic characteristic.

Preferably, the terminal level of the Haser transition of the active ion should be far enough above the ground state so that three or four-level operation is possible and at elevated temperatures.

The lifetime of the metastable level from which the Haser transition originates should be, insofar as possible, equal to the lifetime for spontaneous emission with no constraints imposed by competitive dissipation to the matrix. In four-level operation of the lifetime of the terminal level of the transition must be smaller than that of the metastable level; otherwise, a suitable excess population in the upper level cannot be maintained.

This condition is generally obtained when the terminal level lies in the phonon absorption region, preferably between 6000 and 19,000  $\text{cm}^{-1}$ . In addition, it is helpful for the excited active ion to be unable to absorb photons corresponding in energy to the Haser transition. Where such absorption into a higher level or band is possible, the photon/phonon flux in the particulate cavity is reduced and the metastable level depleted.

For best coherence the active ions should occupy equivalent positions in the host structure, so that there will not be a multiplicity of spectra. When these ions are in completely unique sites, the emission spectrum has the minimum detail and line width consistent with the site symmetry, the crystal field, and the active-ion concentration. In general, the higher the site symmetry the more degenerate the electronic states of the active ion. Therefore, fewer distinct transitions should be observed in fluorescence and, on the average, each emission transition should fluoresce a greater portion of the absorbed energy. However, there are also fewer distinct absorption transitions, and certain emission transitions may be

favored in a low-symmetry environment. As long as the emission transitions are few in number, the low symmetry environment may prove to be advantageous by virtue of a broader absorption coverage.

Different classes of active ions seldom find optimum environments in the same host structure. Different activator ions are best accommodated in oxides or fluorides, where the cations of the matrix are approximately equal in size to the activator.  $\text{Al}_2\text{O}_3$ ,  $\text{MgO}$ ,  $\text{MgF}_2$ , and  $\text{ZnF}_2$  are typical matrices for transition-metal ions,  $\text{CaF}_2$  is particularly useful for divalent rare-earth ions, and  $\text{CaWO}_4$ ,  $\text{LaF}_3$ , and  $\text{Y}_2\text{O}_3$  are best suited for trivalent rare-earth ions for lasers.  $\text{Y}_3\text{Al}_5\text{O}_{12}$  can readily accommodate both trivalent rare-earth ions and trivalent 3d transition-metal ions. Certain crystals have conveniently disposed matrix absorption bands and these can be used to absorb pumped radiation over a broad spectrum.

The excitation may be subsequently transferred to trivalent rare-earth ions contained in the matrix and therefore, greatly enhance the overall efficiency of fluorescence. It probable is essential to move into the visible region, to obtain continuous operation for molybdates or niobates.

In comparison, materials which have their matrix absorption edges well above the excitation range but absorb strongly as a result of the active ions having strong absorption bands of their own, together with narrow emission lines, can afford very favorable pumping conditions.

Ions such as,  $\text{Cr}^{3+}$ , Chromium, and  $\text{Dy}^{2+}$ , Dysprosium offer this advantage.

The past decade has provided rapid extension of spectral measurements and theoretical analysis, such that the properties of most of the divalent and trivalent activator species are well understood. The interest in solid-state masers and lasers, has motivated the preparation of various crystals containing divalent rare-earth ion species and the extensive study of their infrared characteristics. Parallel studies of the infrared properties of the transition-metal ions and trivalent rare-earth ions have been equally productive.

The selection of materials for Hasers which will operate in the infrared region depends on the disposition of the vibrational bands in the matrices. Because vibrational levels may drain an electronic state, they should not be too close below the metastable level, or the latter should lie below the vibrational levels in energy.

Suitable coupled pairs which provide a mutual cross relaxation can also be used advantageously to minimize loss of efficiency due to fluorescence from levels lying higher than the metastable level of interest and loss to the phonon spectrum. It is also desirable to increase the efficiencies of masers that terminate on phonon levels. This mechanism of operation offers the possibility of a maser that can be tuned over a broad range of frequencies.

#### PREFERRED LATTICES

Oxygen-dominated compounds are those in which oxygen is a major chemical constituent of the host lattice. They may be classified according to their chemical composition into four groups.

The first group, comprising the simplest compounds, has the generic formula  $\text{M}_x\text{O}_y$ , representative numbers being the alkaline earth oxides and  $\text{Al}_2\text{O}_3$ ,  $\text{Y}_2\text{O}_3$ , and  $\text{ThO}_2$ , with  $\text{Cr}^{3+}$ ,  $\text{Mn}^{2+}$ , and the rare earths as common activators. Other compounds included in the ge-



neric formula are CuO, and ZnS and the other II-VI wide-band-gap compounds.

The second and largest group are the binary oxides,  $M_xA_yO_z$ , where M is any element of Group II, A or B, and Period 2 to 6, and A is Ti, Zr, V, Nb, Mo, B, Al, Si, Ge, P, As, Sb, or S.

In many cases  $x=4y$ , the oxygens nearly tetrahedrally arranged around the multivalent atom, A.

The common activators are  $Mn^{2+}$ ,  $Mn^{4+}$ ,  $Ag^+$ ,  $Sn^{2+}$ ,  $Tl^+$ ,  $Pb^{2+}$ , and the rare earths. Included in this group also are the well-known self-activated compounds comprised of tungstates and molybdates, which are commonly called scheelites (although some do not have the scheelite structure). These require no activating impurity, because the energy transitions take place within the anion, although impurity-activated luminescence is also observed.

Of the impurity-activated members of the binary oxides, the borates, phosphates and silicates are the most numerous.

Ternary systems,  $M_xA_yB_zO_w$ , constitute the third category. M and A and B are the elements listed in the binary systems plus the alkali metals.

The most common activators, other than the rare earths, are those listed with the binary oxides. There are a few ternary compounds not containing tungsten or molybdenum which are believed to be self-activated.

There are many other oxygen-containing inorganic luminescent solids, including a large number of rare-earth salts and impurity-activated nitrites, carbonates, etc. The work on the latter is largely incomplete. The work on the rare-earth salts constitutes a well-studied separate discipline (Dieckmann et al, 1961).

Considering the small number of possible combinations of simple oxides and activators, it is surprising that new prospects in this group continue to be found. New compounds, however, consisting of oxides of antimony, germanium, thorium, calcium, strontium, yttrium, and gadolinium with various activators have been developed over the last few years.

The valence of manganese in phosphors or compounds is interesting because of its use as an activator in many lattices. Kroger (1948) showed that the broad structureless red or green emission spectra of manganese-activated compounds is generally due to  $Mn^{2+}$ , whereas the red narrow-banded emission is due to  $Mn^{4+}$ .

### SUMMARY

In the same way that the spectroscopy of atoms provided basic information on atomic structure, careful study of controlled luminescence of solids provide information on band structures and energy levels of impurities and imperfections. In some cases, the spectra of impurities yield, through the application of crystal field theory, information on the symmetry and strength of the crystal field at the impurity site. The absorption or excitation spectra involve electronic states of the system with equilibrium nuclear coordinates characteristic of the ground state; luminescent emission spectra involves electronic states with the equilibrium nuclear coordinates of the emitting state.

Additionally, detailed theoretical knowledge of band structure and of impurities and imperfections obtained from semiconductor and photoconductor research provides understanding of the luminescence of these materials.

Luminescence is generally investigated as a steady-state phenomenon, wherein the compound interacts with the excitation source and emits radiated energy continuously. The thermodynamic parameters of the compound remain time independent at every point in the system, despite the occurrence of excitation, emission, and dissipative processes.

Irreversible thermodynamics is concerned with just such open systems, which interact with their environment in a stationary way.

It is a principle of irreversible thermodynamics that the entropy production is positive in every macroscopic region of the system undergoing irreversible processes.

Macroscopic regions refer to regions large enough for microscopic fluctuations to exist but small enough for approximate equilibrium to exist within each region. We are especially interested in the more complex excitation mechanisms involving energy transfer between different macroscopic regions not in equilibrium with each other.

### LIGHT ABSORPTION AND COLOR

An electromagnetic radiation, (such as radiowave, light, and X-ray) can be characterized by its particular wavelength,  $LAMBDA$ ,  $\lambda$  (measured in cm or  $\text{\AA}$ ), or by its wave number,  $\nu$ ,  $\nu$  (the reciprocal of the wavelength),  $\nu=1/\lambda$ , commonly expressed in reciprocal centimeters,  $cm^{-1}$ .

Each unit of radiation (a photon) corresponds to a quantum of radiant energy,  $E$ , which is directly proportional to the wave number,  $\nu$ . Since chemical calculations are founded on a mole basis, in discussing the relationship between radiant energy and chemical processes (responsive activators and hosts) it is convenient to express radiant energy in kcal/mole of photons. We can do so with this accepted relationship: the radiant energy in 1 mole of photons, with  $\nu=350\text{ cm}^{-1}$ , is equal to 1 kcal.

Therefore, we can obtain the energy (expressed in kcal/mole) for photons of a given wave number simply by multiplying the value of  $\nu$  expressed in  $cm^{-1}$  by the conversion factor

$$\frac{1 \text{ kcal/mole of photons}}{350 \text{ cm}^{-1}}$$

For example, the energy of light photons with  $\nu=20,000\text{ cm}^{-1}$  is:

$$\text{energy} = 20,000 \times \frac{1 \text{ kcal/mole of photons}}{350 \text{ cm}^{-1}} = 57.1 \text{ Kcal/mole of photons}$$

and the energy of a single photon of  $\nu=20,000\text{ cm}^{-1}$  is:

$$\text{energy 1 photon} = \frac{57.1 \text{ kcal/mole of ph.}}{6.02 \times 10^{23} \text{ photons/mole of ph.}} = 9.48 \times 10^{-23} \text{ Kcal/photon.}$$

The wave number, and the energy, of electromagnetic radiations varies within an extremely wide range— $\nu=10^{14}\text{ cm}^{-1}$  for the  $\gamma$ -rays emitted in nuclear reactions to  $\nu=10^{-6}\text{ cm}^{-1}$  for radiowaves. In between these two extremes, there is a continuum of radiations of intermediate wave numbers—the “visible region”,



which extends approximately from  $27,000\text{ cm}^{-1}$  to  $13,500\text{ cm}^{-1}$ .

In general, when white light strikes a substance, part of the light is absorbed and part is transmitted (if the substance is transparent) or part is reflected (if the substance is opaque). A substance may absorb preferentially the light photons of one (or more) region(s) of the spectrum, so that the transmitted light or the reflected light is relatively richer in the radiations of the remaining regions.

The combined effect of these remaining radiations is observed as a particular color (when it is in the visible spectrum)

For example, a substance that, when exposed to white light, absorbs almost all photons in the entire yellow-to-violet region (say from  $17,000$  to  $27,000\text{ cm}^{-1}$ ) will "appear red", because only the radiations in the red region of the spectrum ( $13,500$  to about  $17,000\text{ cm}^{-1}$ ), which are not absorbed, remain to be observed.

Similarly, a substance that "appears yellow" absorbs photons of both the green-to-violet region (from  $19,000\text{ cm}^{-1}$  to  $27,000\text{ cm}^{-1}$ ) and the red region (from  $13,500$  to  $16,000\text{ cm}^{-1}$ ) of the visible spectrum.

Since light (radiation) is energy, the absorption of radiation is absorption of energy; it is well known, that, if a substance absorbs light, the corresponding absorbed energy may be used to promote certain atoms, ions, or molecules of a substance from "ground-state" to an "excited state". For example, an atom, ion, or molecule which absorbs a photon of a given wave number takes on a 'quantum' of energy that may serve to promote one electron from a lower energy orbital to a higher (available) energy orbital. In general, different electronic transitions involve the absorption of different quanta of energy.

#### HASER DESIGN CONSIDERATIONS

Some of the factors which are involved in the design of Haser apparatus include the following:

- (a) Thermally isolated chamber.
- (b) Sensitizers-activators responsive to input heat-energy frequencies.
- (c) Design amounts of "impurity" sensitizers required.
- (d) Design the host solid while considering the following:

- (1.) Lattice Vibrations
  - (1.1) Geometry of crystalline solids.
  - (1.2) Crystal lattice and reciprocal lattice. p1 (1.3) Brillouin zone and g-space.
  - (1.4) Lattice vibrations of an infinite crystal with one atom per unit cell.
  - (1.5) Lattice vibrations of a finite crystal with one atoms per unit cell.
  - (1.6) Lattice vibrations of a crystal with more than one atom per unit cell.
- (2.) Thermodynamics of Phonons
  - (2.1) Density matrix of an ensemble
  - (2.2) Internal energy of a phonon gas.
  - (2.3) Einstein and Debye approximations of the density of (A) phonon states.
  - (2.4) Phonons and photons: similarities and differences.
- (3.) Ion-Photon Interaction: Absorption and Emission of Radiation
  - (3.1) Ion-radiation interaction.

- (3.2) Expansion of the interaction hamiltonia Different types of radiation.
- (3.3) Density of final states
- (3.4) Transition probability per unit time.
- (3.5) Dipole radiation.
- (3.6) Selection rules for radiative transiting
- (3.7) Selection rules for transitions between eigenstates of angular momentum.
- (3.8) Selection rules for atomic systems.
- (3.9) Electric dipole radiation.
- (3.10) Magnetic dipole radiation.
- (3.11) Electric quadrupole radiation.
- (3.12) Selection rules for ions in crystals.
- (3.13) Intensities of radiative transitions
- (4.) Ion-Vibration Interaction: Radiationless Processes, Thermal Shift, and Broadening of Sharp Spectral Lines
  - (4.1) Ion-vibration interaction.
  - (4.2) Radiationless processes in a crystal absorption and emission of a phonon.
  - (4.3) Raman processes.
  - (4.4) Orbach processes.
  - (4.5) Multiphonon processes.
  - (4.6) Line broadening mechanisms
  - (4.7) Probability densities and superposition of probability densities: Voigt profile
  - (4.8) Thermal broadening of sharp lines.
  - (4.9) Raman scattering of phonons
- (5.) Vibrational-Electronic Interaction
  - (5.1) Ion-vibration interaction in molecular complexes.
  - (5.2) Vibronic spectra of molecular complexes
  - (5.3) Vibronic lines in absorption.
  - (5.4) Selection rules for vibronic processes.
  - (5.5) Space groups and lattice vibrations.
  - (5.6) Normal modes of vibrations in crystals.
  - (5.7) Lattice absorption in perfect crystals.
  - (5.8) Phonon activation due to impurity ions in crystals.
  - (5.9) Selection rules for vibronic transitions due to magnetic impurities in crystals.

#### SPECIFIC EXAMPLES

Some underlying principles involved in the selection of Haser systems have been set out hereinabove and a preferred embodiment has been described which involves water vapor as a feedstock and the generation of hydrogen and/or hydrogen peroxide. It is to be understood that the Haser concept is not limited to the specific embodiment described herein but has more general applicability in the conversion of broad spectrum heat energy or radiation to particular frequencies which lie within the absorption band or bands of any selected feedstock.

The feedstock may be gaseous or liquid or even a slurry, and may be brought into proximity with the heat reservoir and associated host and sensitizer material in any desired and practical manner. The heat in the heat reservoir may be generated in any suitable manner including the use of the exothermic reactor for generating hydrogen and hydrogen peroxide and/or the combustion of the hydrogen and hydrogen peroxide.

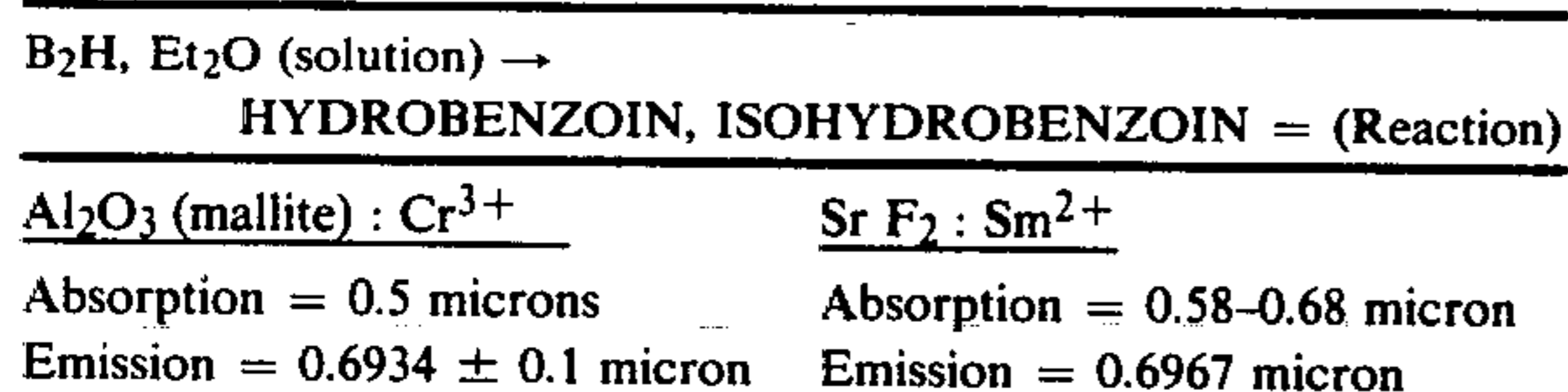
The feedstock may for example be directed through the heat reservoir by a pipe suitable coiled to provide for adequate exposure to the radiation. The pipe may be transparent to the radiation being applied to the feedstock; or alternatively, the pipe may be made of material



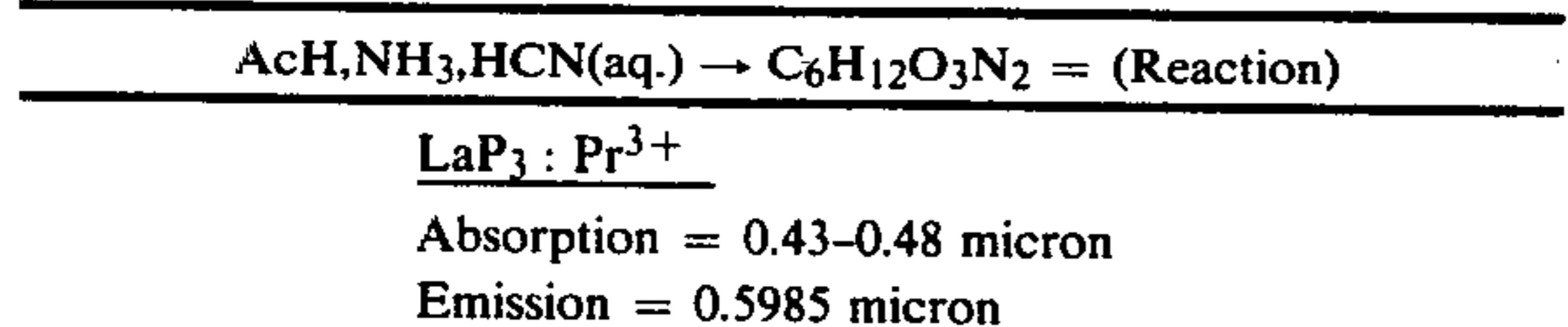
containing the specially selected host and sensitizer material.

In the following examples, a number of reactions are set forth and these are followed by an identification of a host and sensitizer material which will concentrate the broader spectrum heat energy to one of the absorption bands of the feedstock. Incidentally, in the following examples, in addition to the standard symbols for the elements, the following abbreviations are used: Et for ethyl, C<sub>2</sub>H<sub>5</sub>; Ph for phenyl, C<sub>6</sub>H<sub>5</sub>; Pr for propyl, C<sub>3</sub>H<sub>7</sub>; and Bu for butyl, C<sub>4</sub>H<sub>9</sub>. In addition to the host and sensitizers shown in each of the following examples, Al<sub>2</sub>O<sub>3</sub> in mullite and Cr +3 may advantageously be used (absorption at 0.5 microns; emission centered at 0.6934 microns). As noted above, the mullite may conveniently be employed to physically support the host and sensitizer materials. The actual examples follow:

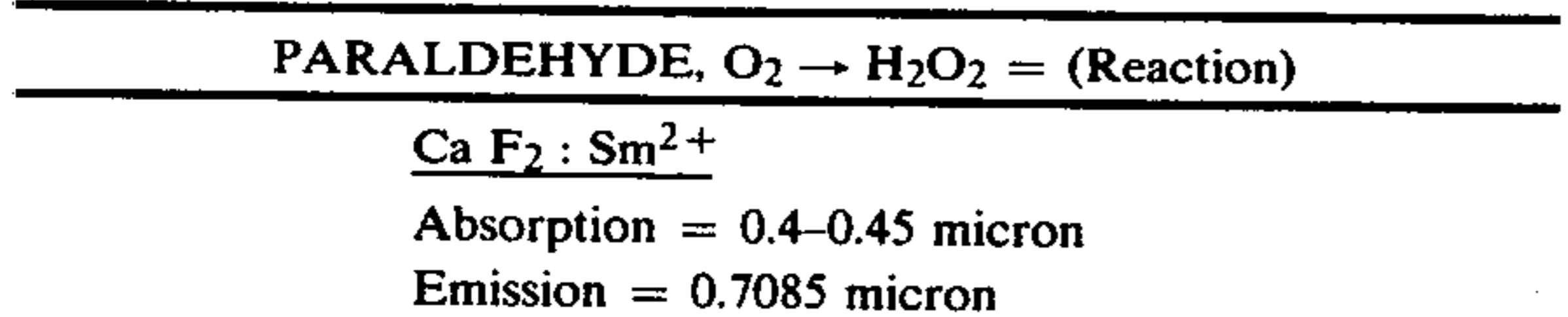
#### Example No. 1



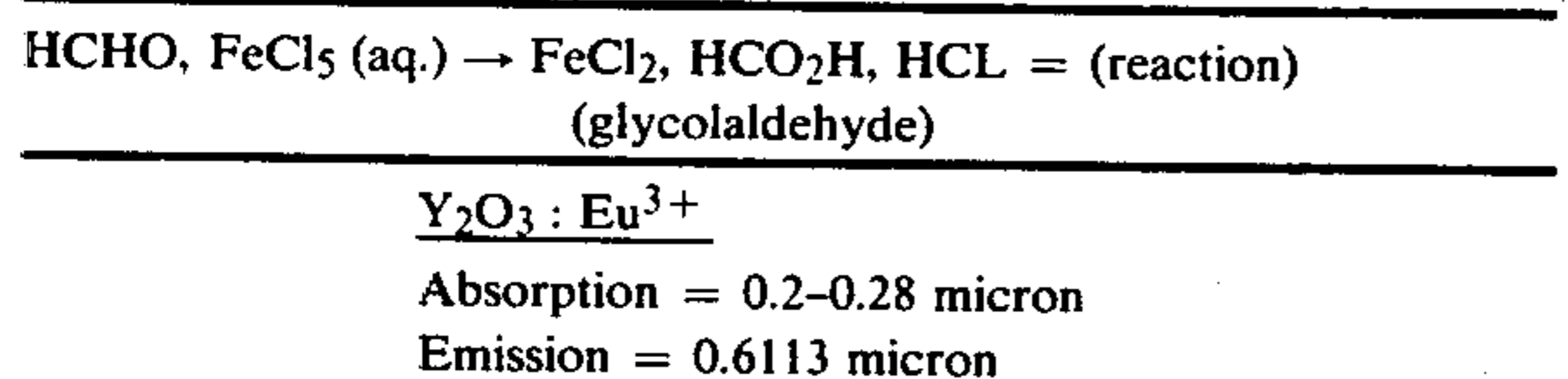
#### Example No. 2



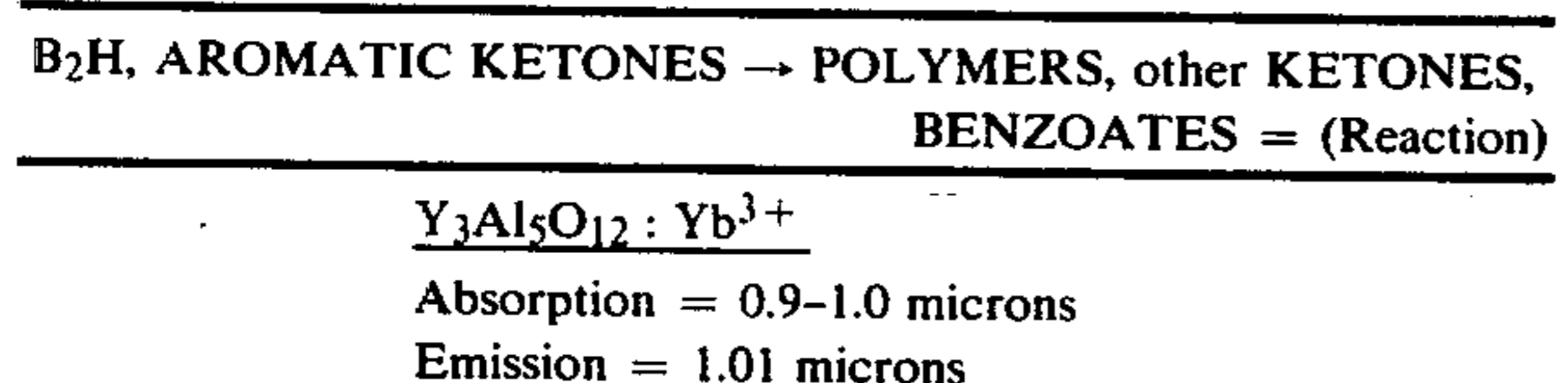
#### Example No. 3



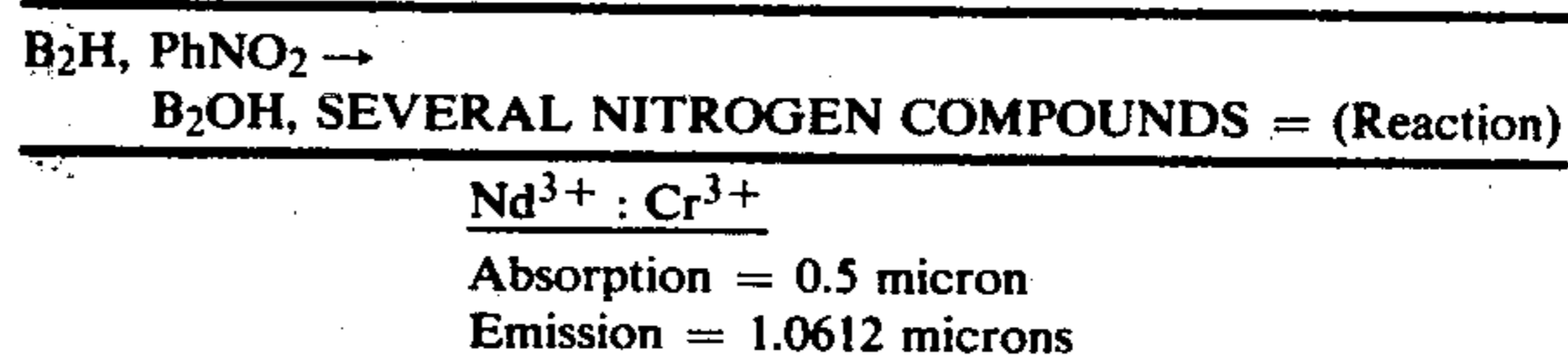
#### Example No. 4



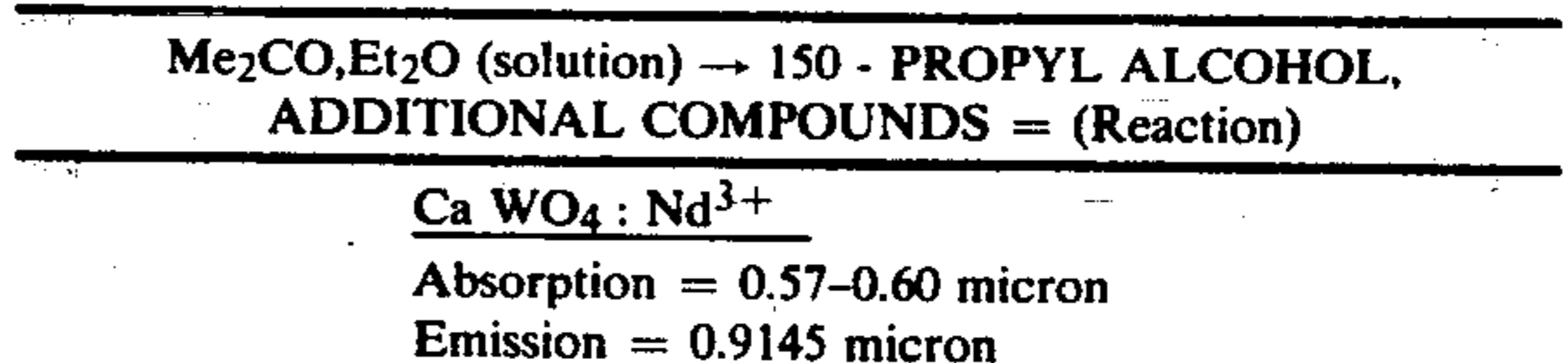
#### Example No. 5



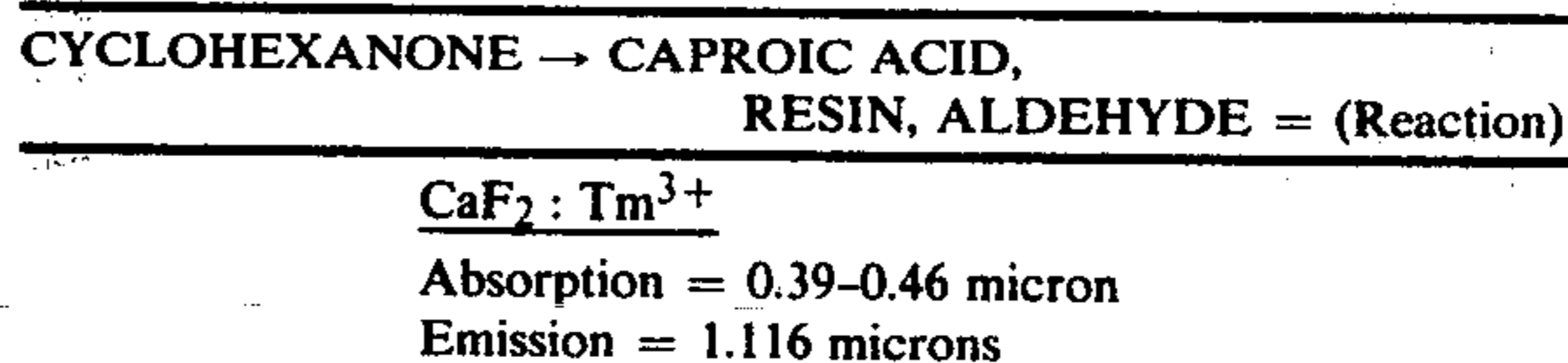
#### Example No. 6



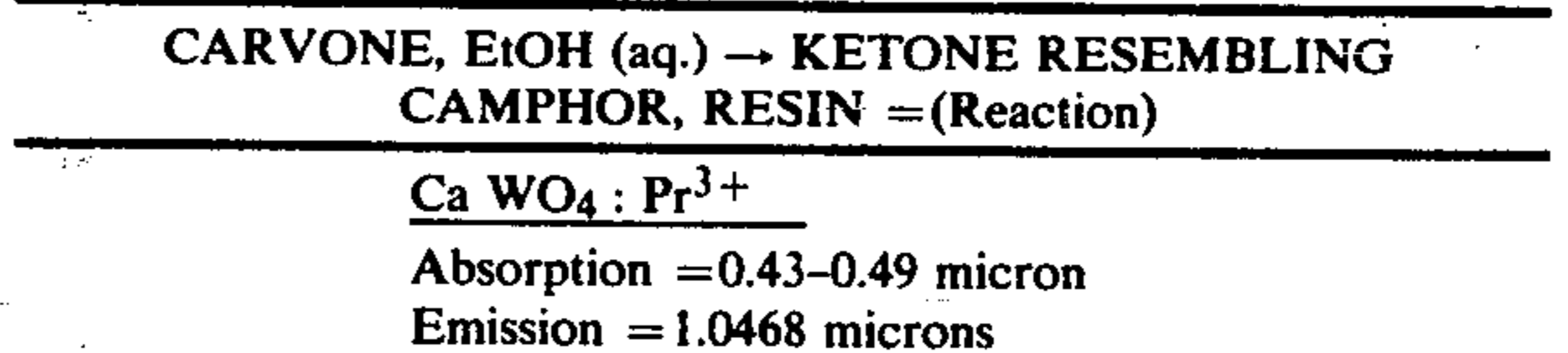
#### Example No. 7



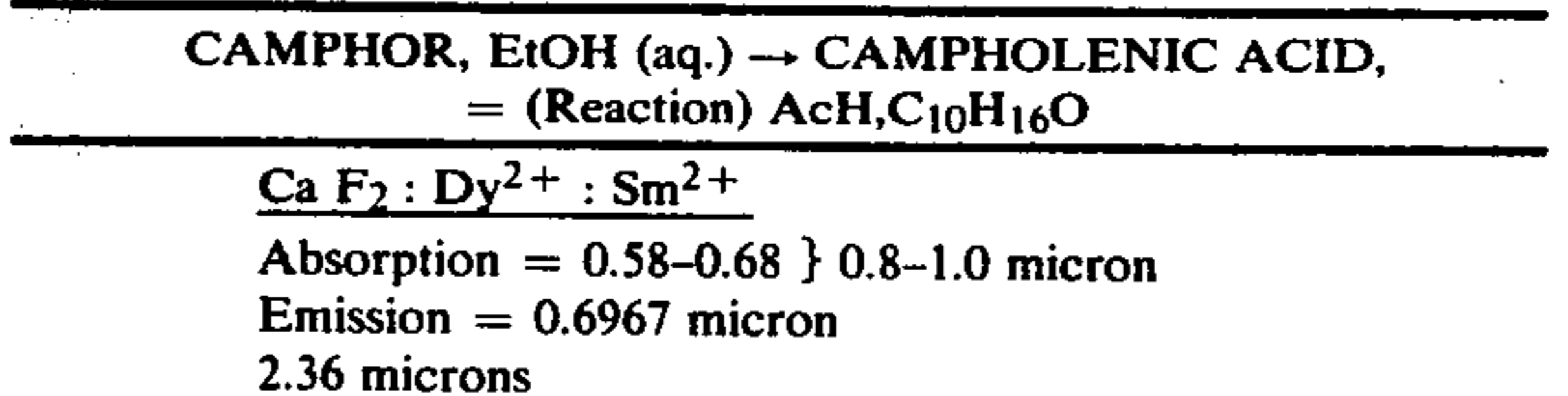
#### Example No.8



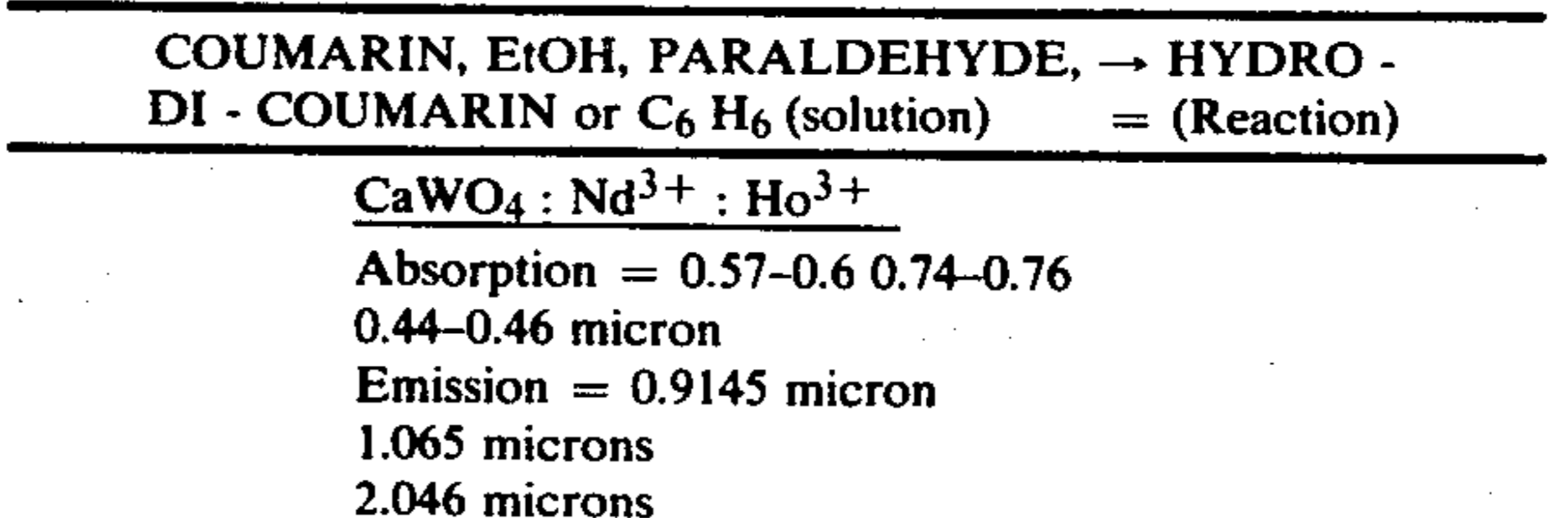
#### Example No. 9



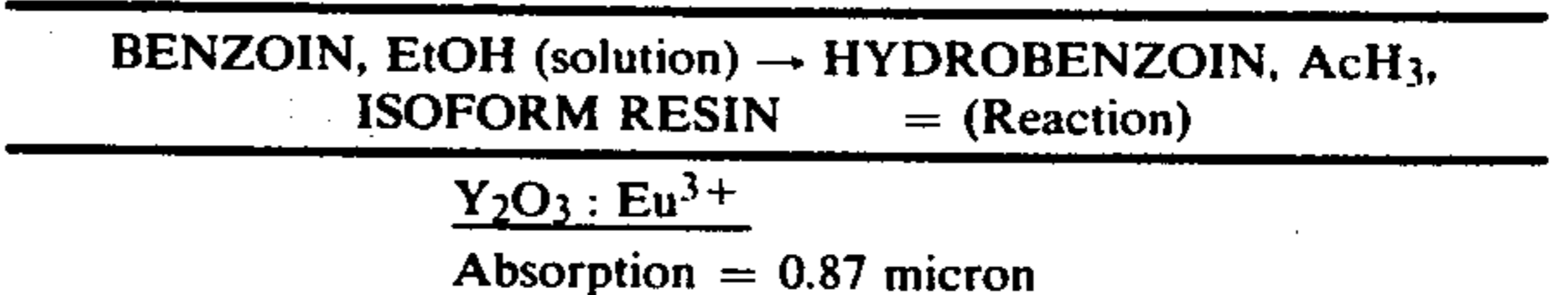
#### Example No. 10



#### Example No. 11



#### Example No. 12





-continued

BENZON, EtOH (solution) → HYDROBENZON, AcH <sub>3</sub> , ISOFORM RESIN = (Reaction)
Emission = 0.6113 micron

## Example No. 13

QUINONE, Et <sub>2</sub> O (solution) → HYDROQUINONE, RESINS = (Reaction)
Same Host/Sensitizer; Absorption; and Emission as Nos. 1, 3 and 4

## Example No. 14

THYMOQUINONE, Et <sub>2</sub> O (solution) → POLYMER (POLYTHYMOQUINONE) = (Reaction)
Same Host/Sensitizer; Absorption; and Emission as Nos. 1 and 3

## Example No. 15

4 - Me QUINOLINE → RESIN, ALKALI SOLUBLE PRODUCT = (Reaction)
Same Host/Sensitizer; Absorption; and Emission as Nos. 5, 6, and 8

FIG. 13 is a schematic showing of an apparatus for a continuously processing feed stock such as the materials disclosed in the foregoing examples, or steam, of course. In FIG. 13 the reaction chamber 402 is provided with upper and lower manifold chambers 404 and 406 which are separated from the main portion of the reaction chamber 402 by apertured plates 408 and 410. Within the reaction chamber 402 are a large number of the ceramic tubes 412 such as those shown in FIG. 11. All of the space within chamber 402 apart from that occupied by the tubes 354 is filled with a reactant such as manganese oxide or other reactants disclosed elsewhere in the present case and in my prior co-pending specification cited above.

A heat or radiation exchanger including upper and lower manifold structures 414 and 416 as well as the interconnecting tubes or pipes 418 exposes the feed stock, which is applied through input tube 420 and brought out through tube 422, to the high temperatures and radiation present within the main reaction chamber 402.

At the center of the apparatus shown in FIG. 13 is a burner 424 to which a lower inlet pipe 426 and an upper outlet pipe 428 are connected. This central burner unit may be of the type shown in FIG. 9 of the drawings and as described hereinabove. The entire reaction chamber 402 shown in FIG. 13 is fully insulated and mounted as shown in FIG. 9, and equipped with suitable automatic valving of the type described above in connection with other embodiments of the invention.

In operation, steam is initially supplied to the reaction chamber 402 through inlet line 430 when valve 432 is opened. Of course prior to this initial step, the reaction chamber 402 has been preheated to a temperature in the order of 1000° Kelvin, and the steam is supplied under high pressure. Hydrogen is then displaced by the action of the reactant, and the host/sensitizer materials in-

cluded in tubes 412, as described above. Hydrogen H<sub>2</sub> and hydrogen peroxide H<sub>2</sub>O<sub>2</sub> are drawn off through the upper manifold 404 and the connecting line 434 through valve 436. During the hydrogen displacement phase of the cycle, additional oxygen may be supplied through line 438 via valve 440. The additional oxygen promotes the formation of hydrogen peroxide, which is, with the hydrogen, drawn off through line 434.

The overall cycle of reaction chamber 402 may be substantially as indicated by one of the two plots shown in FIG. 7. Accordingly with the steam valve 432 and the valve 436 to the hydrogen storage tank both closed, the vacuum may be applied to the reaction chamber 402 so that disproportionation of the oxygen from the reactant takes place.

While the hydrogen displacement at high pressure and the oxygen disproportionation phase of the cycle at low pressure is occurring in the main reaction chamber 402, the feed stock may be continuously passed through the heat and radiation exchanger 414, 416, 418, at a suitable rate to maintain the desired high temperature and high level of radiation of the feedstock. Incidentally the tubes 418 interconnecting the upper chamber 414 and the lower chamber 416 may be made of mullite including the host/sensitizer materials mentioned in the various examples given above. Similarly the manifolds 414 and 416 may be made of such materials. Alternatively the elements 414, 416, and 418, may be made of metal, such as stainless steel, to which suitable quantities of host/sensitizer materials have been added in order to give the desired intimate irradiation action with regard to the feed stock.

Instead of using a single reaction chamber as shown in FIG. 13, a heat and irradiation exchange unit could be employed with a multiple reaction chamber apparatus such as that shown in FIG. 9. When used with a multiple reaction chamber arrangement such as that shown in FIG. 9, of course the heat exchange elements must make sealing engagement with the walls of the individual reaction chambers which will be at different pressures during different portions of the individual staggered cycles in the different reaction chambers.

It may be noted that, in accordance with disclosures in my prior co-pending patent application cited above, and teachings found elsewhere in the present specification, the hydrogen and H<sub>2</sub>O<sub>2</sub> "tailings", obtained as a vacuum is being drawn on line 438, and such output hydrogen and/or hydrogen peroxide from line 434 as may be desired, may be applied through line 426 to the central burner 424. This may serve the purpose of supplying additional heat to the entire unit to permit more rapid flow of feed stock through lines 420 and 422 without loss of temperature in reaction chamber 402.

## ENERGY BALANCE

In my prior co-pending patent application an "Energy Balance" section was included. In the present specification, a portion of the prior analysis will be set forth, and a more thorough energy analysis involving the new material in this application will be included.

In view of the fact that the apparatus of the present type and as disclosed in my prior application are exothermic on a net basis and also produces hydrogen or hydrogen peroxide which can be burned, there have been some suggestions that certain so-called Laws of Thermodynamics are being violated. This is of course



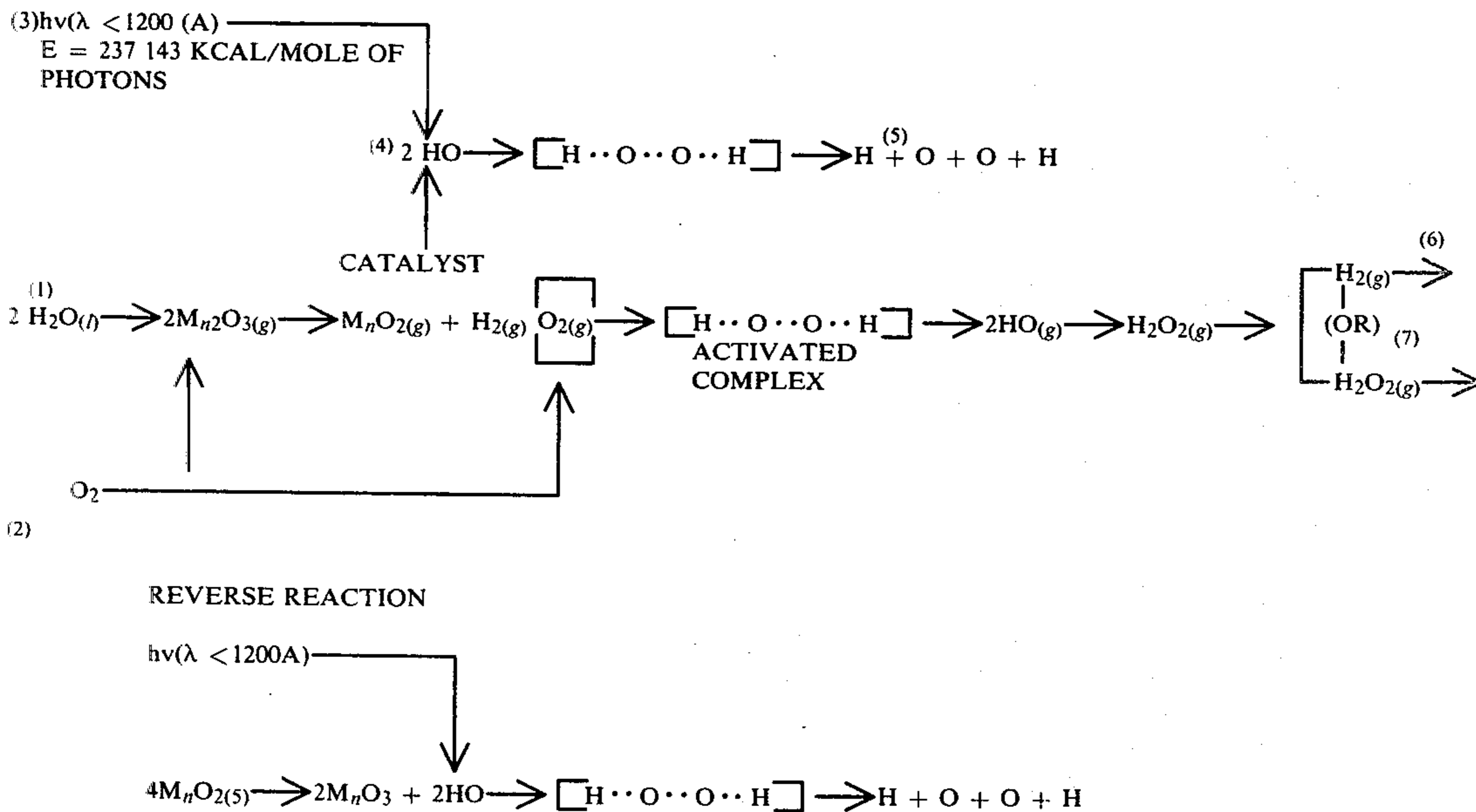
not the case, as will be developed by the Energy Balance analysis set forth below.

From an overall standpoint, the present system may be viewed as providing an energy balance and not violating any "Laws of Thermodynamics" as a result of the low energy content gaseous products which are released in the course of the process. These low energy gaseous products may include HO and HO<sub>2</sub>, which are less well known gaseous products. When these gaseous products are released into the atmosphere, it is believed that they absorb high frequency radiations, and eventually change state to become hydrogen gas, oxygen gas, water vapor, atomic hydrogen and atomic oxygen. In one sense, therefore, the present systems may be considered to utilize solar energy.

The stoichiometric reactions set forth below represent one of several modes of operation which may obtain in implementations of the present invention.

The foregoing equations may be analyzed from two different standpoints. Incidentally, it may be noted that the "2HO" designated (4) in the upper equation is actually evolved in the disproportionation phase. In addition, a portion of the hydrogen gas H<sub>2</sub> from (6) in the upper equation is an input in the lower equation which combines with the disproportionated oxygen to form HO. Also, of course, the incident photons are applied in the atmosphere, and not in the apparatus per se. It should also be noted that the O<sub>2</sub> input designated (2) is essentially optional and may involve the venturi unit 212 or inlet 217, of FIG. 6, whereby additional O<sub>2</sub> is supplied to generate H<sub>2</sub>O<sub>2</sub>, as noted above.

STOICHIOMETRIC REACTION (ONE OF SEVERAL MODES)



Now, the upper equation will be analyzed from a potential energy standpoint:

POTENTIAL ENERGY IN:		
K. Cal		
(1)	2 H <sub>2</sub> O	141.2
(2)	O <sub>2</sub> + H <sub>2</sub>	43.2
(3)	h v	237.143
		<b>= 421.543 K. Cal.</b>

60  $\Delta G: \Delta H - T\Delta S = -28.76 - (+51.57)$   
 $\Delta G: = -80.33 \text{ Kcal/Mol-Egn}$

Reverse Reaction

65  $\Delta H^{\circ}_{form}: 4(-126.7) \text{ (in)} 2(-228.6) \quad -43.2$   
 $S^{\circ}_{form}: 4(+12.7) \text{ (in)} 2(+26.4) \quad +43.89$   
 $\Delta H^{\circ}_{react}: -500.4 - (-506.8) = +6.40 \text{ Kcal/Mol-Egn}$   
 $\Delta S^{\circ}_{react}: +96.69 - (+50.8) = +45.89 \text{ Cal/Mol-Egn} \times \text{Deg.}$   
 $T\Delta S: 1000 \text{ degrees} \times (+45.89) = +45.89 \text{ Kcal/Mol-Egn}$   
 $\Delta G: \Delta H - T\Delta S = +6.40 - (+45.89)$   
 $\Delta G = -39.49 \text{ Kcal/Mol-Egn}$

POTENTIAL ENERGY OUT:

K. Cal		
(4)	2HO	43.2
(5)	H+O+O+H	223.96
(6)	H <sub>2</sub> , or	63.479
(7)	H <sub>2</sub> O <sub>2</sub>	114.262
		<b>= 330.639 K. Cal. (H<sub>2</sub> Out)</b>
		<b>or</b>
		<b>381.422 K. Cal (H<sub>2</sub>O<sub>2</sub> Out)</b>

Efficiency (H<sub>2</sub> Out) = 0.78  
 Efficiency (H<sub>2</sub>O<sub>2</sub> Out) = 0.90

Actually, there is often a combination of H<sub>2</sub> and H<sub>2</sub>O resulting in an intermediate efficiency.

Now, from a Gibbs Free Energy (G) Analysis standpoint involving Enthalpy (Heat, H), Entropy (S), and temperature T, the following analysis obtains:

In the following analyses, the enthalpies and entropies of the starting reactants are subtracted from the enthalpies and entropies, respectively, associated with products. The letters "in" have been associated with the initial values relating to the starting products.

Oxygen Sequestering Reaction

(Upper Equation designated "Stoichiometric Reaction")

$\Delta H^{\circ}_{form}: 2(-70.6) \text{ (in)} 2(-228.6) \text{ (in)} 4(-126.7) \quad -43.2$   
 $\Delta S^{\circ}_{form}: 2(+45.11) \text{ (in)} 2(+26.4) \text{ (in)} 4(+12.7) \quad +43.89$   
 $\Delta H^{\circ}_{react}: -627.16 - (-598.4) = -28.76 \text{ Kcal/Mol-Egn}$   
 $\Delta S^{\circ}_{react}: +194.59 - (+143.02) = +51.57 \text{ Cal/Mol-Egn} \times \text{Deg.}$   
 $T\Delta S: \frac{1000 \text{ degrees} \times (+51.57)}{1000} = +51.57 \text{ Kcal/Mol-Egn}$



-continued

Complete Cycle

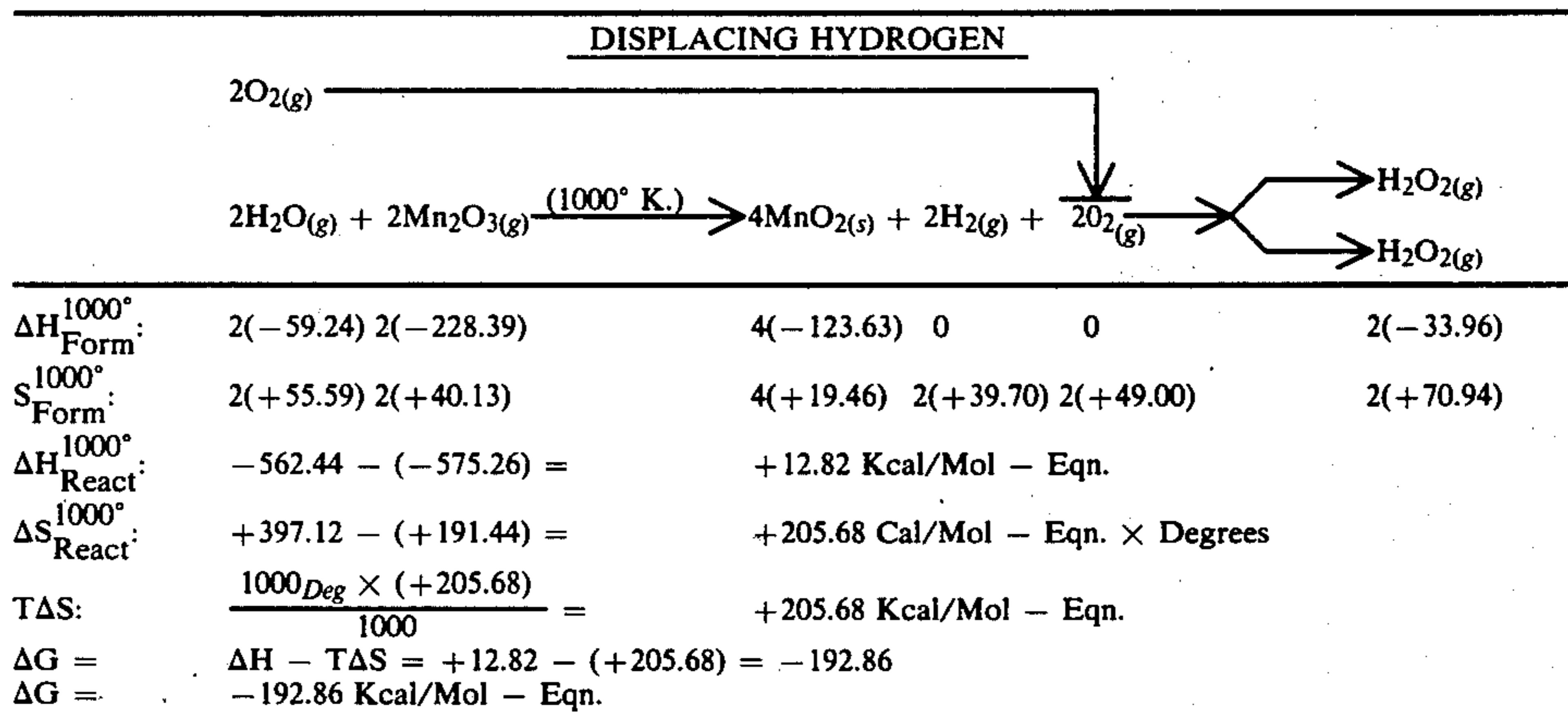
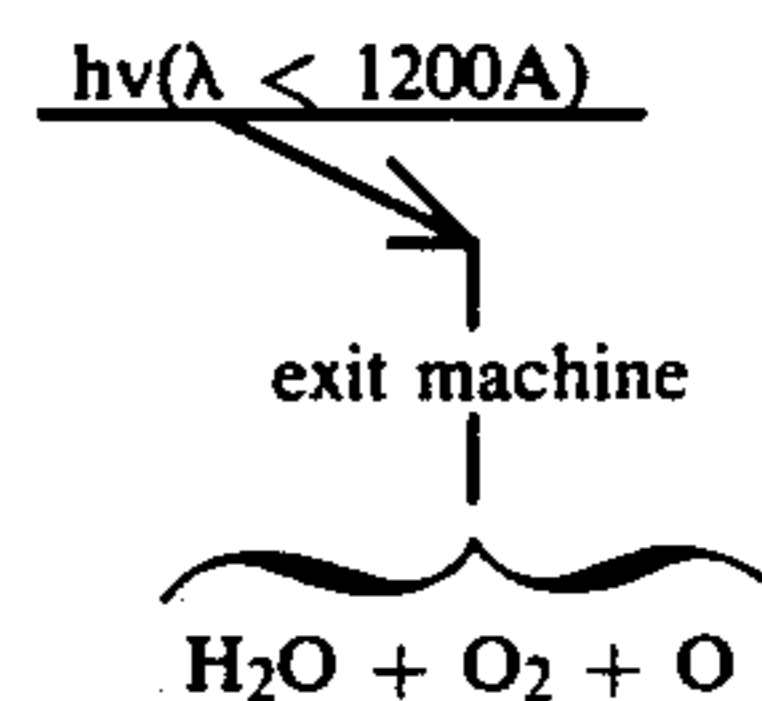
$$\Delta H = -28.76 + (+6.40) = -22.36 \text{ Kcal/Mol-Eqn}$$

$$\Delta S = +51.57 + (+45.89) = +97.46 \text{ Kcal/Mol-Eqn}$$

From the foregoing analysis, it may be noted that the heat or enthalpy for the hydrogen generation portion of the cycle is equal to  $-28.76 \text{ K Cal/Mol-Eqn}$ , which means that the reaction is exothermic. For the "Reverse Reaction" or the oxygen disproportionation part of the cycle, the heat or enthalpy figure is  $+6.40 \text{ K. Cal/Mol-}$

mode emphasizes the production of hydrogen peroxide,  $\text{H}_2\text{O}_2$ , and carries over its use in the disproportionation part of the cycle. It may also be noted that the first mode and second mode presentations are not precisely comparable as  $\text{H}_2\text{O}_{(e)}$  is assumed as an input for the first mode, and  $\text{H}_2\text{O}_{(g)}$  is assumed as an input for the second mode as set forth below. As indicated by the negative value of the enthalpy for the two reactions of the second mode, it is also exothermic on an overall basis.

The equations for (1) hydrogen displacement and (2) oxygen disproportionation, are set forth below, together with their associated Enthalpy (H), Entropy (S) and Gibbs Free Energy functions.

OXYGEN DISPROPORTIONATION

$\Delta H_{\text{Form}}^{1000^\circ \text{ K.}}$ :	4(-123.63)	2(-228.39)	-59.24 0 0
$S_{\text{Form}}^{1000^\circ \text{ K.}}$ :	4(+19.46)	2(+40.13)	+55.59 +55.3 +42.83
$\Delta H_{\text{React}}^{1000^\circ \text{ K.}}$ :	$-516.02 - (-494.52) = -21.50$	$\text{Kcal/Mol} - \text{Eqn.}$	
$\Delta S_{\text{React}}^{1000^\circ \text{ K.}}$ :	$+233.98 - (+77.84) = +156.14$	$\text{Cal/Mol} - \text{Eqn.} \times \text{Degrees}$	
TAS:	$\frac{1000 \text{ Deg} \times (+156.14)}{1000} = +156.14$	$\text{Kcal/Mol/Eqn.}$	
$\Delta G =$	$\Delta H - T\Delta S = -21.50 - (+156.14) = -177.64 \text{ Kcal/Mol} - \text{Eqn.}$		
$\Delta H =$	$+12.82 + (-21.50) = -8.68 \text{ Kcal/Mol-Eqn.}$		
$\Delta S =$	$+205.68 + (156.14) = +361.82 \text{ Kcal/Mol-Eqn.}$		

Eqn. This means that the disproportionation part of the cycle is endothermic, but that the heat required is much less than that generated in the other portion of the cycle. With thoroughly insulated equipment the heat generated during the exothermic portion of the cycle, in the same or other adjacent reaction chambers, is more than sufficient to provide the heat needed during the disproportionation part of the cycle. It may also be noted that the positive entropy value for the "Reverse Reaction", or the disproportionation cycle, indicates that this reaction will go forward spontaneously.

ENERGY BALANCE—SECOND MODE

Another pair of (1) Displacement of Hydrogen and (2) Disproportionation reactions appears below, together with a classical Gibbs Free Energy Analysis. Also included are the text citations for the entropy and enthalpy values used in the analysis. The following

The values for Enthalpy (H) and Entropy (S) used in the foregoing analyses are all taken from published texts as follows:

1.  $\text{MnO}_2$  Enthalpy (H)  $900^\circ \text{ K.} = 123.63$   
 $\text{MnO}_2$  Entropy (S)  $900^\circ \text{ K.} = 19.46$
2.  $\text{Mn}_2\text{O}_3$  Enthalpy (H)  $1000^\circ \text{ K.} = -228.39$   
 $\text{Mn}_2\text{O}_3$  Entropy (S)  $1000^\circ \text{ K.} = 40.13$

Selected values of Chemical Thermodynamic Properties, by F. D. Rossini et al, and U. S. Government National Bureau of Standards Accession No. 6500390, N.B.S. Circular No. 500, dated Feb. 1952, pages 122 ( $\text{MnO}_2$ ) and 123 ( $\text{Mn}_2\text{O}_3$ )



3. H<sub>2</sub> Entropy (S) 1000° K. = 39.70  
 Thermodynamic Properties of the Elements Published November 1956, American Chemical Society, 1155 Sixteenth Street, N.W., Washington 6, D. C.  
 4. H<sub>2</sub> Enthalpy (H) 1000° K. = 0 (By Definition)  
 5. O<sub>2</sub> Enthalpy (H) 1000° K. = 0 (By Definition)  
 6. O<sub>2</sub> Entropy (S) 1000° K. = 49.0

7. H<sub>2</sub>O Enthalpy (H) 1000° K. = 59.24  
 H<sub>2</sub>O Entropy (S) 1000° K. = 55.59  
 "Thermodynamic Properties of Minerals and Related Substances . . ."—Geological Survey Bulletin 1259 Washington, D. C., U.S. Dept. of the Interior, 1968, p. 114.

8. OH Enthalpy (H) 1000° K. = 9.13  
 9. H<sub>2</sub>O<sub>2</sub> Enthalpy (H) 1000° K. = -33.46  
 10. OH Entropy (S) 1000° K. = 52.49  
 11. H<sub>2</sub>O<sub>2</sub> Entropy (S) 1000° K. = 70.94  
 12. H<sub>2</sub>O Entropy (S) 1000° K. = 55.59  
 TRC Tables, Selected Values of Properties of Chemical Compounds, Thermodynamics Research Center, Texas A&M University; Table 2 I T for items 9-12 above; Table 2 I W for items 7 and 8 above.

From the negative value of -8Kcal/Mol-Eqn. of the enthalpy (heat) of the entire reaction, including both displacing hydrogen from water vapor and disproportionating oxygen from the reactant, it is clear that the process is exothermic, in addition to generating hydrogen and/or hydrogen peroxide. And this surprising result, in one or the other or a combination of the modes described in the foregoing equations has been confirmed by the operation of prototypes using manganese oxide as the reactant.

Set forth below is a further analysis involving the photon dissociation of H<sub>2</sub>O, and an examination of the energy "borrowed from nature" and "returned to nature", or to the environment. In connection with the following analyses, it may be noted that the energy for photon dissociation of the H<sub>2</sub>O is obtained from the heat reservoir of hot reactant which is of course main-

$$(1.130859375 \times 10^9) \times (3.64 \times 10^{14})$$

Photons =  $4.116.328.125 \times 10^{23}$  (second)  
 C. Assuming a continuum of 15 seconds

$$15.0 \times (4.116328125 \times 10^{23})$$

Photons in 15.0 Seconds =  $6.174492188 \times 10^{24}$

D. Since there are  $6.02 \times 10^{23}$  photons in 1. mole (of photons)

$$\frac{6.174492188 \times 10^{24}}{6.02 \times 10^{23}}$$

Energy (15 sec.) = 10.256632 moles photons  
 E. Converting to Kilocalories

$$10.256632 \times 26.48$$

Energy = 271.60 Kilocalories (average)  
 F. Energy Required to Dissociate (1) Mole H<sub>2</sub>O(g)

$$1 \text{ Mole} = 59.24 \text{ Kcal}$$

$$\frac{271.6}{59.24} = 4.58 \text{ Moles H}_2\text{O(g)}$$

G.

(1) Dissociation by Reactant	2.00 Moles H <sub>2</sub> O(g)
(2) Dissociation by Radiant Energy	4.58 Moles H <sub>2</sub> O(g)
Total 6.58 Moles H <sub>2</sub> O(g)	

H. 6.58 Moles H<sub>2</sub>O(g) = 5.22 cu. ft. H<sub>2</sub>O<sub>2</sub>(g)

I.

1. cu. ft. H<sub>2</sub>O<sub>2</sub>(g) = 318 BTU  
 5.22 (cu. ft.) × 318 (BTU) = 1660.00 BTU  
 15.0 seconds = 1.660.00 (BTU) = 418.49 Kcal (Potential)

J. Energy Required to Operate Unit for 15.0 Seconds

(1) Dissociating 6.58 Moles Liquid Water at 70.6 Kcal/Mole	=	389.8
(2) Sensible Heat Lost in Gases and Cooling Water	=	22.4
(3) Radiated Heat Losses (all surfaces)	=	5.29
(4) Vacuum PUMP (1.0 H.P.)	=	0.27
(5) Water Pressure Pump (1.0 H.P.)	=	0.27
(6) Cooling Fan (Electronic Controls) (0.3 H.P.)	=	0.10
(7) Cam-Motor and DC Controls (0.3 H.P.)	=	0.10
(8) Digital Readouts Power (0.1 H.P.)	=	0.03
(9) Compressed Air (0.5 H.P.)	=	0.14
(10) Compressed Hydrogen (0.5 H.P.)	=	0.14
TOTAL		418.5

tained at an elevated temperature by the net exothermic nature of the hydrogen displacement and oxygen disproportionation cycle. When mention is made of the combustion of H<sub>2</sub>O<sub>2</sub> in the following analysis, this combustion is in the course of performing useful work such as driving an engine, or the like, apart from the reaction chamber as described herein.

#### PHOTON DISSOCIATION OF H<sub>2</sub>O(g)

A. Average number of <(0.008)> particulates in 539.0 Cu. in. reaction chamber.

$$= 1.130859375 \times 10^9$$

B. Assuming radiated energy frequency averages <F> =  $3.64 \times 10^{14}$  (second)

K. Energy Balance = Output Minus Input

$$418.5 - 418.5 = 0$$

BORROWED FROM NATURE		
(during 15.0 sec. period)		
A. Energy		Kcal
1. 658 Moles H <sub>2</sub> O(l) × 70.6 Kcal/Mol	=	389.8
2. Peripheral Equipment (15.0 sec.)	=	28.69
(Kcal) TOTAL	=	418.5



## RETURNED TO NATURE

A.	Potential Energy
B.	Combustion of 5.22 cu. ft., $H_2O_2 \times 318$ BTU/cu.ft.
	= 1660.00 BTU
	= 418.5 Kilocalories
	Required Energy (from J) 418.5 Kcal
	- Energy from Combustion, 418.5 Kcal = 0

In closing, reference is again made to my copending patent application Ser. No 768,808, filed Feb. 15, 1977, in which more detail is presented relative to the temperatures, pressures, and other reactions which may be used. As noted in the prior specification, the temperature of operation should be above the dissociation temperature for oxygen for the reactant being employed at atmospheric pressure. Advantageous high speed results have been achieved with the reactant in the pyroplastic state of incipient fusion. Concerning pressures, the pressure during dissociation should be at least as low as atmospheric pressure, and preferably a vacuum should be applied to reduce the pressure to a fraction of atmospheric. The vacuum may be applied to draw the tailings through the burner to extract additional heat from the tailings. During the hydrogen displacement portion of the cycle the pressure should be well above atmospheric to facilitate sequestering of the oxygen by the reactant. Successful results may be achieved with reactants such as MnO with gauge pressures of about 100 to 130 or 150 and up to 500 pounds per square inch. Even higher pressures may be employed. Concerning the active reactant, as mentioned in my prior copending specification, it preferably includes at least one metal having a plurality of valence states. It should also have an oxide which will, when subjected to water vapor at elevated temperature and/or pressure, and preferably both, combine with the oxygen and displace the hydrogen in gaseous form exothermically. The reactant also preferably has the property of disproportionation or dissociation to release the combined oxygen when the temperature is raised or preferably when the pressure is reduced, and when the evolved oxygen is separated from the reactant. Advantageously, the heat required in the disproportionation part of the cycle is significantly less than that generated in the exothermic portion of the cycle when the reactant combines with the oxygen in the steam and releases hydrogen, so the entire cycle is exothermic. Also, the reactant should be susceptible of remaining in the pyroplastic state of incipient fusion during the change in state from one oxidation level to another, and back again, under the described conditions.

Some of the metals and oxides thereof which fulfill the foregoing requirements include (1) antimony, (2) cesium, (3) barium, (4) iron, (5) manganese, (6) chromium, (7) iridium, (8) nickel, and (9) thallium. Other metals which have multiple valence states are known, but most of these have practical problems which preclude their use. Thus, for example, mercury has too low a melting point, and its oxides are unstable. In the case of other metals having multiple valence states, their oxides may be poisonous, they may be caustic or are not available in practical or commercially available quantities. Other metals having multiple valence states have oxides which will not readily disproportionate. Combinations of reactants satisfying the requirements indicated above may be employed in the form of alloys,

eutetics, and with other materials to obtain desired temperature and mechanical properties.

FIGS. 14 and 15 are particularly useful in analyzing the apparatus of the present invention from a radiation standpoint. FIG. 14 shows spectral radiant emittance, or power in watts radiated at various wavelengths from a "black body" having a temperature of 1000° Kelvin, while FIG. 15 is a similar plot showing photon emission, or the number of photons emitted at various wavelengths. The FIG. 14 plot drops off more rapidly than that of FIG. 15 because shorter wavelength photons are more energetic and have higher power. In accordance with known principles, the energy is directly proportional to the frequency and inversely proportional to the wavelength. It may also be noted that, in the plots of FIGS. 14 and 15 the visible range is from about 0.4 to 0.7 microns. Accordingly for the temperature of 1000° Kelvin (about 727° Centigrade and about 1341° Fahrenheit), which is plotted in FIGS. 14 and 15, the radiation peaks in the spectrum at wavelengths somewhat longer and at frequencies slightly lower than the visible band.

FIGS. 16, 17, and 18 show a system for applying radiant energy to a feedstock. In FIG. 17 the feedstock is applied to reaction chamber 302 by inlet tube 304 which is connected to manifold 306. Manifold 306 is supported by insulating ceramic material 308 which may either be in the form of a ring or a series of supporting blocks.

The reaction chamber has an outer cylindrical stainless steel wall 310 secured to upper and lower stainless steel end plates 312 and 314. The chamber 302 is provided with a cylindrical ceramic liner 316 and upper and lower inner ceramic end plates 318 and 320. Suitable insulation 322 such as ceramic foam and an outer casing 324 are also provided.

A series of coated wires 326 extend for most of the length of the chamber 302 between upper and lower electrically conducting support members 328 and 330. As shown in FIG. 16, the wires 326 are made up of an inner wire 332 of conducting or resistive material and an outer coating 334 of ceramic material of radiation emitting material of one or more of the types previously described.

The upper and lower wire supporting members 328 and 330 may be held apart by the elongated ceramic member, and the metal rod 338 which extends into the lower hollow end of ceramic member 336. The coated wires 326 are heated up by the application of electricity to power input conductors 340 and 342 to a temperature in the order of 1000° Kelvin. This causes a certain amount of thermal expansion in the wires, and by using a suitable metal rod 338 which has a slightly higher coefficient of thermal expansion, the wires 326 may be maintained in operative positions relative to each other.

In the case of a process involving steam as the feedstock and where it is desired to have hydrogen gas and  $H_2O_2$  as the output product, air may be supplied either through input tube or pipe 304 and/or through separate input 344 to the apertured ring shaped manifold 346 which is held in position by supports 348. Output product is drawn off through pipe 350.

In practice, and as indicated in the block diagram of FIG. 18, air may be supplied to the reaction chamber 302 either through input 304 along with the input feedstock such as steam, or through input 344 at the upper zone of the reaction chamber. When the air is supplied through input 344, toward the upper end of 302, it com-



bines with the previously-formed hydrogen, resulting from dissociation of the water vapor, to form  $H_2O_2$ .

Other blocks shown in FIG. 18 include a source of electrical power 354, a supply of liquid water at 356, a steam formation unit 358, and a storage container 360 for fuel gas such as gaseous hydrogen  $H_2$  and hydrogen peroxide  $H_2O_2$ . The supply line for water is indicated at 362, and that for air at line 364.

As indicated by line 366, a portion of the fuel gas which is formed may be fed back to the steam formation unit 358 to increase the temperature of the water vapor being supplied to reaction chamber 302. After the unit is in operation for a short period of time, the steam is supplied to the reaction chamber 302 at a temperature well above the intended operating temperature of reaction chamber 302 so that little or no electricity need be supplied from the source 354. Thus, for example, with steam being supplied at between  $1100^\circ$  and  $1200^\circ$  Kelvin, the temperature of  $1000^\circ$  Kelvin desired within the reaction chamber 302 may be sustained with the supply of very little or no electricity over line 368.

With reference to FIG. 20, the coated wires 326 are shown supported by a screen 370 which may be made of any suitable high temperature resistant conducting material. The wires 326 are woven in and out of the surface of the screen 370 to form the array as shown in FIG. 17. It may be noted that the frame or support members 328

More specifically, before going into the example in detail, it may be noted that various units are used in the present specification in reference to the wavelength of the radiations which are employed. For reference purposes and for ease in converting various units, it may be noted that the visible range extends from about 4000 Angstrom units to 7000 Angstrom units, with an Angstrom unit being equal to  $10^{-8}$  centimeters. Expressed in microns this visible range corresponds to wavelengths from 0.4 to 0.7 microns, with a micron being equal to  $10^{-4}$  centimeters. Similarly, when millimicrons are employed to measure wavelength, they correspond to  $10^{-7}$  centimeters, and the visible spectrum range is from 400 to 700 millimicrons.

It may also be noted, in converting frequency to wavelength and vice versa that the frequency of light is equal to 3 times  $10^{10}$  cms. per sec. and that the product of frequency and wavelength is equal to the velocity of light. Accordingly, using this simple expression that the product of the frequency times the wavelength is equal to the velocity of light, easy conversion may be made from frequency to wavelength, and vice versa. For convenience, reference is also made to Table I which indicates the location of the visible light band relative to the infrared and ultraviolet frequency bands, in addition to the remainder of the electromagnetic radiation spectrum.

TABLE I

TABLE I-2 The Wavelength Frequency, and Energy of Typical Electromagnetic Radiation				
Approximate Description	Typical Wavelength, A	Frequency, cycles/sec	Wave Number, $cm^{-1}$	Energy, kcal/cinsein
Radio wave	$1.00 \times 10^{13}$ (1000 m)	$3.00 \times 10^5$ (300 kc)	$1.00 \times 10^{-5}$	0.000000286
Short-wave radio wave	$1.00 \times 10^{11}$ (10 m)	$3.00 \times 10^7$ (30 Mc)	$1.00 \times 10^{-2}$	0.00000286
Microwave	$1.00 \times 10^8$ (1 cm)	$3.00 \times 10^{10}$	1.00	0.00286
Far infrared	$1.00 \times 10^5$ (10 $\mu$ )	$3.00 \times 10^{13}$	$1.00 \times 10^3$	2.86
Near infrared	$1.00 \times 10^4$ (1 $\mu$ )	$3.00 \times 10^{14}$	$1.00 \times 10^4$	28.6
Visible light				
Red	$7.00 \times 10^3$ (700 m $\mu$ )	$4.28 \times 10^{14}$	$1.43 \times 10^4$	40.8
Orange	$6.20 \times 10^3$	$4.84 \times 10^{14}$	$1.61 \times 10^4$	46.1
Yellow	$5.80 \times 10^3$	$5.17 \times 10^{14}$	$1.72 \times 10^4$	49.3
Green	$5.30 \times 10^3$	$5.66 \times 10^{14}$	$1.89 \times 10^4$	53.9
Blue	$4.70 \times 10^3$	$6.38 \times 10^{14}$	$2.13 \times 10^4$	60.8
Violet	$4.20 \times 10^3$	$7.14 \times 10^{14}$	$2.38 \times 10^4$	68.1
Near ultraviolet	$3.00 \times 10^3$	$1.00 \times 10^{15}$	$3.33 \times 10^1$	953
Far ultraviolet	$2.00 \times 10^3$	$1.50 \times 10^{15}$	$5.00 \times 10^4$	142.9
Schumann ultraviolet	$1.50 \times 10^3$	$2.00 \times 10^{15}$	$6.67 \times 10^4$	190.6
Long X-ray	$3.00 \times 10^2$	$1.00 \times 10^{16}$	$3.33 \times 10^5$	953.0
Short X-ray	1.00	$3.00 \times 10^{18}$	$1.00 \times 10^5$	285,910
Gamma ray	$1.00 \times 10^{-2}$	$3.00 \times 10^{20}$	$1.00 \times 10^{10}$	28,591,000

Photo-chemistry region

Radiation chemistry region

and 330 of FIG. 17 are shown as being formed of two parts. These two parts are open frame members which clamp the screen 370 as shown in FIG. 20 and support it. If desired or if the conductivity of the particular coating employed in the system is relatively low, the coated wires 326 may be scraped bare and welded contacts made at points such as those indicated at 372 in FIG. 20 to make better conductive engagement with the screen 370 by which electricity is initially supplied to these wires. It is also noted that, instead of using the screen as shown in FIG. 20, the supporting structures 328 or 330 may be simple perforated plates with the coated wires 326 threaded through them.

Now, considering one specific example, the wires 326 of FIG. 17 may be coated with the host and sensitizer materials set forth in examples Nos. 1 and 2 of the 15 examples set forth hereinabove in the present specification.

With the foregoing background, reference is again made to examples Nos. 1 and 2 of the 15 numbered examples set forth earlier in the present specification. It may be noted that the emission, for Example No. 1 was approximately 0.69 microns corresponding to a frequency of approximately  $4.34 \times 10^{14}$  cycles per second. This corresponds to a red color in the visible spectrum. Example No. 2 provides a yellow output light with a wavelength of approximately 0.59 microns corresponding to a frequency of approximately 5.08 times  $10^{14}$  cycles per second. Incidentally, another yellow line is produced by the materials of Example 12, with a wavelength of 0.61 micron, corresponding roughly to 4.91 times  $10^{14}$  cycles per second.

Referring back to FIG. 17, one-half of the wires extending from support 328 to support 330 are coated with material providing red output radiation such as specified in Example No. 1 referred to above, and one-



half of the wires are coated with material providing a yellow output radiation. These wires are threaded through the supports 328 and 330 so as to be interspersed with one another so that the yellow and red output radiation wires are not grouped together but are entirely interspersed with one another.

When feedstock is supplied to the reaction chamber 302, the radiation will be directed from the wires to the medium and the radiation of different frequencies will impinge upon the discontinuities provided by the feedstock vapors and will beat with one another and will be converted into sum and difference frequencies. More specifically, considering examples Nos. 1 and 2, the frequency for the red radiation of Example 1 was approximately  $4.34 \times 10^{14}$  cycles per second, and the frequency for Example No. 2 was approximately  $5.084 \times 10^{14}$  cycles per second. One frequency which will be formed as these radiations impinge on the feedstock will be the sum frequency equal to approximately  $9.42 \times 10^{14}$  cycles per second. This corresponds to a wavelength of about 0.32 microns, in the near ultraviolet frequency spectrum. Water vapor has a number of absorption peaks in the near ultraviolet frequency spectrum and these peaks are broadened by the elevated temperature present at  $1000^\circ$  Kelvin at which the reaction chamber 302 is operated. Accordingly, in addition to the dissociation action produced by the direct radiation at the red and yellow frequency bands, the powerful ultraviolet radiations will have a strong dissociative effect on the water vapor being transmitted through the reaction chamber 302. Incidentally, the energetic nature of the radiations in the near ultraviolet may be noted from the far right-hand column in Table No. I in which the radiation in the near ultraviolet is shown to have an energy level in the order of double that in the red and yellow regions of the visible spectrum.

Attention is also directed to the plot of FIG. 21 showing the absorption characteristic for hydrogen peroxide  $H_2O_2$  which is being formed in the radiation chamber 302. More specifically, it may be seen that the absorption coefficient increases rapidly from the near ultraviolet range of 3000 Angstroms, or about 0.3 microns, to the far ultraviolet range toward the left of FIG. 21. Accordingly, with near ultraviolet radiation being employed in the chamber of FIG. 17 (reaction chamber 302) to dissociate water vapor, it may be noted that the desired product gas  $H_2O_2$  will be little affected and will be essentially transparent to this near ultraviolet radiation and will thus remain in its  $H_2O_2$  chemical state, after it is formed, without adverse effect from the near ultraviolet radiation.

FIG. 19 shows an alternative reaction chamber 376 which is divided into an upper section 378 and a lower section 380. Dividing these two sections of the chamber is a perforated ceramic plate 382. In addition, two different sets of coated wires 384 in the upper section and 386 in the lower section, are provided. These two sets of wires are electrically interconnected by the links 388 which extend through the ceramic plate 382 and join the lower support 390 for the upper set of wires 384 to the upper support 392 for the lower set of wires 386. Apart from being divided into two chambers with two sets of different coated wires in the upper and lower portions 378 and 380 of the reaction chamber 376, the chamber of FIG. 19 is generally similar in configuration to that of FIG. 17.

With regard to the nature of the coatings on the wires 384 and 386, the upper wires 384 are coated as described

above in connection with FIG. 17 to produce ultraviolet radiation.

The lower set of wires 386, however, are coated to provide strong output radiation in the infrared radiation spectrum, as disclosed hereinabove in connection with examples A, B, and C. Accordingly, the arrangement of FIG. 19 is organized to provide powerful radiation in portion 380 which will impinge vigorously on the feedstock and provide an initial very substantial dissociative effect on the water vapor. Then, in the upper portion 378 of the reaction chamber the dissociation of the water vapor is continued, but at a frequency in the near ultraviolet range which is clearly at a frequency spectrum with respect to the hydrogen peroxide,  $H_2O_2$ , product gas which will not adversely affect or dissociate it. The combined effect of the two stage radiation chamber with different radiation frequencies being employed in each of the two chambers, is such as to maximize the production of the desired output gas.

Of course, in connection with FIGS. 16 through 21, two specific examples of reaction chamber arrangements employing radiation to produce desired product gases have been set forth. It is to be understood that through the examination of the spectral absorption characteristics of the feedstocks and products, and by suitably providing radiation within the reaction chamber matched to the characteristics of the feedstock and the product, many other similar combinations may be developed by those skilled in the art.

It is also particularly to be noted that through the use of coated wires, the amount of initial heat input required to raise the reaction chamber to operating temperature conditions, is greatly reduced.

For completeness, one set of dimensions for the wires 326, 384 and 386 will now be given. The overall diameter of the coated wires may be 0.00257 inch, and the diameter of the inner metal wire is 0.00157 inch with the coating being about 0.0005 inch thick, adding about one-thousandth of an inch to the diameter. The inner metal wires may, for example, be made of tungsten or other metal having a relatively high melting point and adequate strength at  $1,000^\circ$  Kelvin.

FIGS. 22 and 23 show an alternative arrangement for applying high frequency radiation to feedstock supplied to a reaction chamber. In FIG. 22 the reaction chamber per se is made up of two hemispheres 402 and 404 which are secured together by bolts 406 which extend through the mating flanges 408 and 410 of the hemispheres 402 and 404. An outer sheet metal housing 412 is provided to enclose the unit and to support the various enclosed elements of the system. Thus, for example, the hemispheres 402 and 404 are supported from brackets 414 secured to the housing 412. Between the reaction chamber 402, 404 and the housing 412 is suitable insulation for 416 of the ceramic foam insulation type.

Feedstock is supplied to the reaction chamber 402, 404 through input pipe 418, and product gases are withdrawn from the reaction chamber through pipe 420.

Input radiation is supplied to the reaction chamber 402, 404 through the window 422 which may, for example, be made of high temperature resistant quartz glass.

FIG. 23 is taken along line 23—23 of FIG. 22. Shown to advantage in FIG. 23 are the two lasers 424 and 426 which direct coherent radiation of different colors through the window 422 into the reaction chamber 402, 404 which has a highly polished interior surface. One of the lasers 424, 426 is a ruby laser with output radiation in the red spectral region, while the other laser is an



yttrium aluminum garnet, or Yag laser with output radiation in the green frequency band. These lasers are directed at an acute angle through the window 422 so that the radiation of the two lasers beat to produce a higher frequency in the ultraviolet spectrum, as discussed and developed hereinabove in connection with the radiation from the wires of FIGS. 17 and 19. Accordingly, the feedstock supplied to the reaction chamber through the pipe 418 will be irradiated not only with the red and green direct laser illumination, but also by the beat frequencies which arise when the red and green radiation impinge on the discontinuities provided by the feedstock materials supplied to the chamber.

It may also be noted that in all of the embodiments described herein, where additional oxygen is supplied, and hydrogen peroxide, or  $H_2O_2$ , is formed, this reaction is exothermic and supplies heat to the reaction chamber. This factor is useful in increasing the efficiency of the processes, and contributes to the self-sustaining nature of the processes, as discussed above.

On a general basis, the processes described herein provide a mechanism for the transformation of low grade thermal radiation into specific coupled modes of intense monochromatic radiation providing new higher frequencies and shorter wavelengths with considerably increased power.

The energy change is accomplished through the creation of controlled spatial harmonics beating together while passing through media discontinuities within a non-linear medium. The effect is much like a parametric amplifier which controls the disposition of the electromagnetic energy conveyed by the waves. On a comprehensive basis, the transformation of the broad black body radiation into specific monochromatic frequencies of high energy which are matched to the absorption bands of the feedstock and to the transmission bands of the product, make for process efficiencies which are extremely high.

With regard to the operating temperatures and pressures for the apparatus of FIGS. 16 through 19, and that of FIGS. 22 and 23, the temperatures and pressures are less critical than for the embodiments disclosed earlier in the present case. In general, in order to provide radiation in the desired spectral range the apparatus of FIGS. 16 through 19 should be operated at a temperature in the order of 1000° Kelvin; however, other temperatures may be employed which produce adequate radiation at the desired frequencies, and a departure of 100° or 200° above or below 1000° K. would be operative, it is expected, with radiation drop off toward the lower end of this temperature range and possible materials failure problems toward the upper end of the range. Concerning the embodiment of FIGS. 22 and 23, a lower temperature such as 250° F., above the boiling point for water at the pressure which is employed, would be adequate.

Concerning pressures, somewhat lower pressures are adequate, as compared with the embodiments involving the use of metallic oxides, and no change in pressure is needed. For the embodiments of FIGS. 22 and 23, a gauge pressure of 3 or 4 pounds would be adequate, although higher pressures of up to several hundred pounds, for example, could be employed where higher fuel gas reservoir pressures are desired. Similar pressure considerations are applicable to the apparatus of FIGS. 16 through 20.

The apparatus of FIGS. 1 through 23, described hereinabove, were also described in the co-pending patent

applications of which the present patent application is a continuation-in-part. New FIGS. 24 through 32 will now be described.

FIG. 24 represents an alternative form of reaction chamber which may be employed in a system substantially conforming to FIG. 18 of the present drawings. More particularly, the reaction chamber 502 of FIG. 24 could be employed as the reaction chamber 302 of FIG. 18.

Referring more particularly to FIG. 24, it includes an outer cylindrical shell 504 which may, for example, have a stainless steel interior surface, and contains a substantial number of closely spaced mercury vapor lamps 506 having quartz envelopes. The mercury vapor discharge tubes 506 may, for example, be cold cathode tubes and have electrical terminals 508 at one end of the chamber, and 510, at the lower end of the reaction chamber 502. The mercury vapor discharge tubes 506 may be supported by the upper and lower aluminum plates 512 and 514.

Apertured transverse plates 516, 518 and 520 extend transversely across the reaction chamber 502, and plate 518 may serve much the same function as the transverse baffle 382 in FIG. 19. Feedstock is applied to reaction chamber 502 through inlet 522 at the bottom of the reaction chamber, and the output products from reaction chamber 502 are carried off through tube 524. The space below baffle 516 serves as an input manifold, while that above baffle 520 serves as an output manifold. In accordance with the reaction which is to be undertaken, the radiation in the input portion of the reaction chamber 502, between baffle plates 516 and 518, may be of a somewhat different frequency of radiation, than that in the output irradiation portion of the reaction chamber 502 between baffle plates 518 and 520. The design factors going into the irradiation and to specific frequencies in the input and output sections of the reaction chamber were discussed hereinabove in connection with the embodiment of FIG. 19. Similar considerations, of course, apply here.

The physical mounting arrangements and electrical connections for each mercury vapor tube may be provided as indicated in FIG. 25. More particularly, as shown in FIG. 25, the mercury arc lamps 506 are provided with conducting terminals 508 which are silver soldered to the existing pins extending from the ends of commercially available mercury arc lamps. A thick silicone rubber sheet 526 is provided to support, cushion and locate the ends of the mercury arc lamps 506. In addition, the silicone rubber heavy wall tubes 528 enclose the electrical terminals 508 and insulate them from the aluminum conducting end plate 512. The sheet 526 and tubes 528 may be either integral or separate, with the tubes ending even with the lower surface of plate 512.

Helically wrapped around the outer cylindrical surface of the mercury arc tubes 506 are filaments 532 which are formed of laser-type material. The laser-type material included in the filaments 532 may be of the host and sensitizer type as discussed hereinabove, or they may be of ruby laser-type material, if desired.

The mercury arc tubes 506 extend through clearance holes in the plates 516, 518 and 520. As indicated in FIG. 26, the plate 520 is provided with holes 534 which are of slightly larger diameter than the outer diameter of the tubes 506. If desired, the tubes may be firmly supported as indicated in FIG. 25 at both ends of the reaction chamber and merely pass freely through the



plates such as plate 520 of FIG. 26. Alternatively, each of the apertures in plate 520 may be grooved to receive a lamp retaining spring which will provide additional support and location to each of the mercury vapor lamps. These lamp retaining springs 536 are shown schematically in FIG. 26.

The filaments 532 and 532' of FIGS. 27 and 28, respectively, may include a central metal filament 538 which may be of resistive material as disclosed hereinabove in connection with FIG. 16 of the drawings, or the filaments may be made up entirely of laser-type material, as indicated in FIG. 28. The central metal filaments 538 may be employed to ohmically heat the filaments to an elevated temperature to produce the desired output radiation as discussed above in connection with the embodiments of FIGS. 17 and 19, for example. Under these operating conditions, electricity would be applied both to the individual filaments to heat them to the proper temperature, and also across the terminals 508 and 510 of the mercury gas discharge tubes to appropriately energize them.

The laser-type materials for use in the coating 540 of FIG. 27 or as the entire filament in FIG. 28 may be of any of the host-sensitizer types as discussed hereinabove in connection with other embodiments of the invention. Alternatively, other known laser materials such as suitably doped aluminum oxide, used in the ruby laser, may be employed. Other known laser materials may also be used.

To enhance laser action, the filaments 532 or 532' of FIGS. 27 and 28, respectively, may be provided with one or more semi-transparent, or partially reflective layers 544 and 546 (see FIG. 27), or 548 constituting an outer peripheral partially transparent metallic coating on the outer surface of filament 532', in FIG. 28. The semi-transparent surfaces 544, 546, and 548 may be made by depositing a thin layer of chromium or other good reflecting material on the filament 532 or 532' as they are being formed. The distance between substantially perpendicular surface areas of the semi-transparent layers 544 and 546, for example, along the line segment 550, should be an integral multiple of half wavelengths, in order to maximize lasing effect and to produce essentially coherent output radiation. Similarly, the diametral distance 552 in FIG. 28 should be an integral number of half wavelengths at the desired output radiation frequency.

Concerning the radiation within the reaction chamber, it is a function of the output radiation both of the mercury arc lamps 506, and also the radiation produced by the filaments 532 and/or 532'. With media discontinuities within the reaction chamber caused by the presence of feedstock within the reaction chamber, the different frequencies which are generated will "beat" with one another and produce sum and difference frequencies. Thus, for example, if ruby laser-type material is employed as the laser-type material as indicated by the reference numerals 540 and 542 in FIGS. 27 and 28, respectively, the radiation wavelength is approximately  $7.0 \times 10^3$  Angstrom units. The output radiation from the mercury arc lamps includes a prominent spectral line at  $2.537 \times 10^3$  Angstrom units, and a very broad emissions band which peaks at about  $3.0 \times 10^4$  Angstrom units. When these radiations impinge on the media discontinuities provided by water vapor feedstock, for example, the resultant sum frequency has a wavelength of approximately  $1.752 \times 10^3$  Angstrom units, in the ultraviolet frequency spectrum. This high frequency ultraviolet

radiation is within the U. V. absorption band of water vapor as shown in FIG. 29 of the drawings. Accordingly, by way of example, this combination of frequencies may usefully be employed in the input section of the chamber of FIG. 24 between the baffles 516 and 518. This is particularly useful in this area in view of the high energy content of the  $1.7 \times 10^3$  Angstrom unit ultraviolet radiation, and the low concentration of hydrogen peroxide in the input section of the reaction chamber. As noted in FIG. 21,  $H_2O_2$  has a relatively high absorption coefficient for  $1.7 \times 10^3$  Angstrom radiation, and it is preferred that far ultraviolet radiation of this type not be used in the output section of the reaction chamber 502, between baffle plates 518 and 520, where high concentrations of  $H_2O_2$  are present, for most efficient use of the radiated energy. On the other hand, in this output region, it would be preferable to have irradiation of the water vapor at lower frequencies and longer wavelengths, to couple to selected water vapor absorption bands that are present at longer wavelengths as shown in FIG. 10 of the drawings, thereby avoiding absorption of the radiation by hydrogen peroxide. Suitable materials for producing such radiation are disclosed hereinabove in Examples (a) through (e) in the section of this specification entitled "Host/Sensitizers for Water Vapor Feedstock". Similarly, other design controlled radiation systems may be developed for both the input sections and the output sections of the reaction chamber 502 to smoothly facilitate the desired dissociation and recombination chemical reactions.

FIGS. 30, 31, and 32 of the drawings show an important embodiment of the invention in which spheres are employed in proximity to the outer surface of the gas discharge tubes, instead of the filaments shown hereinabove. Specifically, as shown in FIG. 30, the outer surface of all of the quartz mercury vapor tubes 506 are provided with a large number of spheres 556. These spheres may be formed of any of the laser type materials, or the host-sensitizer materials discussed hereinabove, and they are preferably coated with a semitransparent metallic coating to facilitate the radiation of substantially coherent radiation. With regard to dimensions, the quartz tubes 506 may be in the order of  $\frac{3}{4}$  inch in diameter; the spheres 556 may be in the order of 0.002 to 0.004 inches in diameter, and the semireflecting coatings are preferably spaced apart along a diametral line by an integral number of half wavelengths at the output radiation frequency of the laser type material. The spheres 556 may be secured in proximity to the outer surface of the tubes 506 in any desired manner, preferably by the use of glass frit, fired when the spheres are firmly held against the quartz envelope by a suitable high temperature wrapping. The spheres may occupy in the order of 50% of the area of the tube, or a greater or lesser area depending on the scheduled relative radiation from the mercury vapor lamps and the laser spheres, which is desired for the reaction being undertaken.

As more clearly shown in the diagram of FIG. 31, the reflective coating extends over most of the outer surface of sphere 556 but stops at line 558. With the reflective coating not present where sphere 556 engages the outer surface of gas discharge tube 506, the pumping radiation from the mercury gas discharge, indicated by rays 560, has easy access to the laser material within sphere 556, by passing through the transparent glass frit 566.



In the diagram of FIG. 31, the pumping radiation 560 serves to raise the atoms in the laser-type material to the excited state; and the rays 562 represent the coherent radiation characteristic of laser materials, which is generated as atoms drop from the excited state to lower energy levels triggered by arriving radiation from other transitions within the sphere. The reflecting coating on the outer surface of sphere 556 is preferably in the order of 70% to 90% reflecting and only 30% to 10% transmissive in order to enhance the generation of harmonic radiation. Accordingly, the output radiation as indicated by the rays 564 may have a significant energy content which is at a frequency which is a multiple of the basic output frequency of the laser material in sphere 556.

For example, with the ruby laser having a fundamental radiation wavelength of just under 7,000 Angstrom units, the fourth harmonic would have a wavelength of about 1,750 Angstrom units, in the far ultraviolet.

Background texts relating to this subject matter include "Photochemistry of Gases", by William Albert Noyes, Jr. and Philip Albert Leighton, published in 1941 by Reinhold Publishing Company; "Combustion, Flames and Explosions of Gases", published by Academic Press, Inc., 1961, by Lewis and Von Elbe; and "Photochemistry", by Calvert and Pitts, published by Wiley, in 1966.

One form of chain reaction which is diagramed below involves the absorption by molecule A by radiation such as light, and its dissociation into identical fragments. The secondary reactions involve a chain which may be stopped at low pressures by the removal of the carriers at the walls, and at high pressures by a homogeneous recombination involving a third body or reactant. The overall reaction produced by the chain is  $A + B \rightarrow 2C$ . Various examples are to be found among "halogenation" and "hydrogen-oxygen" reactions. The mechanism is as follows:

	PRIMARY:	(1) $A + hv \rightarrow D_1 + D_1$
CHAIN BREAKING	CHAIN:	(2) $D_1 + B \rightarrow C + D_2$
		(3) $D_2 + A \rightarrow C + D_1$
	LOW-PRESSURE	(4) $D_1 + S \rightarrow \frac{1}{2}A + \dots$
	(SURFACES)	(5) $D_2 + S \rightarrow X + \dots$
	HIGH-PRESSURE	(6) $D_1 + D_1 + M \rightarrow A + M$
		(7) $D_2 + D_2 + M \rightarrow Y + M$

Incidentally, as shown in FIG. 31, the transparent glass frit 566 is shown securing the spheres 556 onto the quartz envelopes 506. With suitably transmissive material being selected for the frit 566, and with the semi-reflective coating stopping at line 558, the mercury vapor radiation from within the discharge tubes readily passes into the spheres 556.

In the diagram of FIG. 32 the quartz envelope 506 separates the gas discharge region 572 from the reaction chamber region 574. In the gas discharge region 572, electrons 576 are shown moving at high velocities downward, and the heavy ionized mercury molecules 578 are drifting upwardly. Collisions cause the radiation of energy from the mercury vapor, and the complex atomic structure of mercury produces radiation at a large number of spectral lines. The resultant radiation is shown schematically at 582, 584, and 586.

Within the reaction chamber region 574 are shown water vapor molecules 592, oxygen molecules 594 and hydrogen molecules 596, with the showings being in the form of circles of progressively reduced size. It is also interesting to note that some of the radiation from the ionized mercury vapor provides pumping energy to spheres 556, and some of the radiation passes directly into the radiation chamber region 574.

### CHAIN REACTIONS

The apparatus of the present invention are particularly well suited for the implementation of chain reactions. This is particularly true of the reaction chambers shown in FIGS. 19 and 24, in which different frequencies of radiation may be applied to incoming feedstocks as compared with feedstocks during the subsequent portion of the chain reactions.

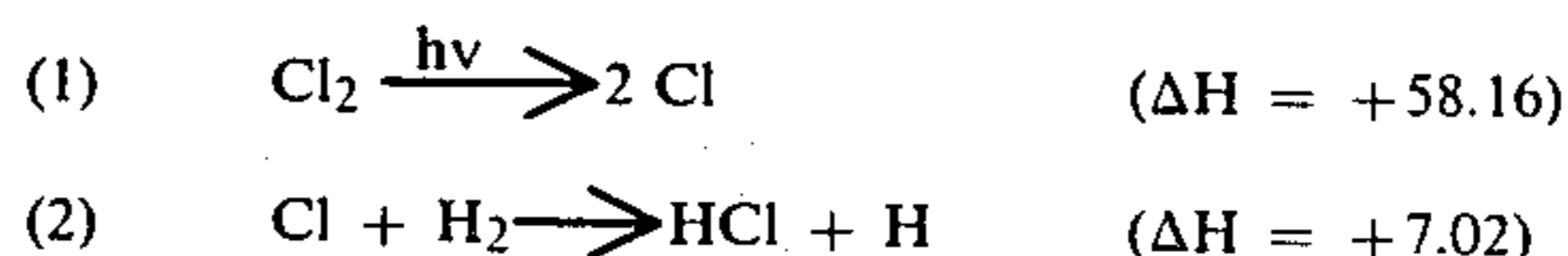
In considering the mechanisms involved in photochemical kinetics, it is important to recognize that most complete photochemical reactions may be divided into three somewhat overlapping stages: (1) The initial act of absorption of radiant energy, (2) the primary process, and (3) secondary reactions.

Concerning radiated energy effects, when a molecule or a polyatomic ion is irradiated by electromagnetic energy of a wavelength appropriate to couple with the molecule or ion, this radiation may be absorbed, and the energy of the molecule or polyatomic ion may be increased; the molecule or ion may be excited rotationally, vibrationally, or electronically, or one or more of the covalent bonds that hold the molecule together may be broken. This bond-breaking gives rise to the formation of atoms, or groups of atoms, which have one "unpaired" electron each and are called "free radicals".

Accordingly, the absorption of radiated energy by a molecule may cause it to decompose into fragments or free radicals, which are extremely more reactive than the original molecule. When this is the case, the sequence of reaction steps leading to the final products involves these free radicals (even though they may exist only temporarily in the reaction mechanism), rather than the original molecules of the reactant.

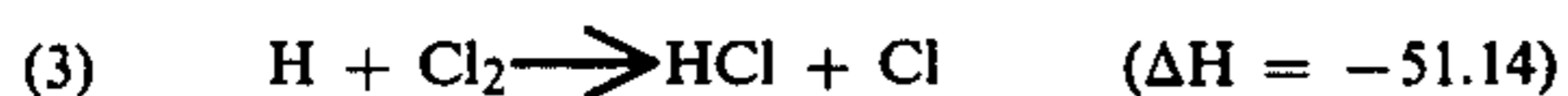
### CHAIN REACTION EXAMPLE NO. 1

The first example of chain reactions which we will consider involves the reaction of hydrogen gas  $H_2$  with Chlorine gas  $Cl_2$  to form HCL gas. When a  $Cl_2$  molecule absorbs radiated energy it passes to a higher energy or an excited state, and if the energy of this excited state is sufficiently high, the bond of the  $Cl_2$  molecule may be broken to form two Cl atoms. In this connection it may be noted that in order to dissociate a  $Cl_2$  molecule into its two atoms, a relatively large quantity of energy, in the order of 58.16 kilocalories per mole of  $Cl_2$  gas must be supplied. The decomposition of  $Cl_2$  molecules by absorption of radiated energy is illustrated by the following equations, which also involve the presence of hydrogen gas:





-continued



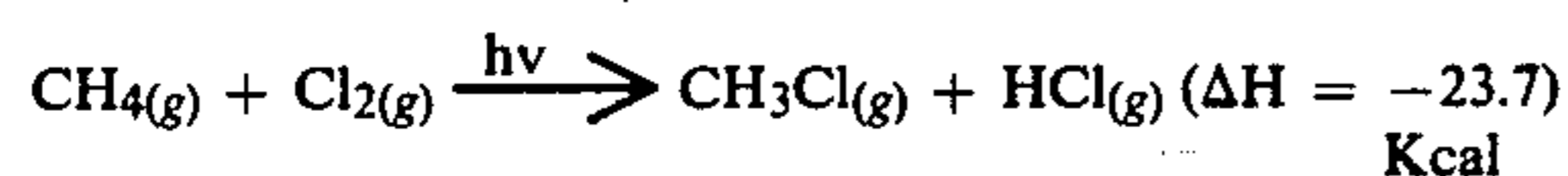
$$\Delta H + 7.02 + (-51.14) = -44.12 \text{ KCAL}$$

The chain reaction is eventually broken when a Cl atom collides with another Cl atom, perhaps absorbed on the wall of the reaction chamber, to reform a Cl<sub>2</sub> molecule. The chain reaction may also be interrupted when a Cl atom reacts with some impurity present in the system to form a product which no longer contributes to maintaining the chain reaction.

#### CHAIN REACTION EXAMPLE NO. 2

This second chain reaction example involves the reaction of methane CH<sub>4</sub> with Chlorine Cl<sub>2</sub> to form methyl chloride, CH<sub>3</sub>Cl, and hydrogen chloride HCl.

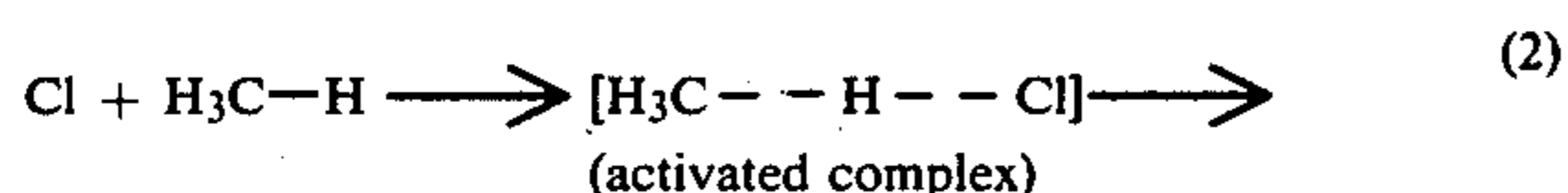
The primary reaction is as follows:



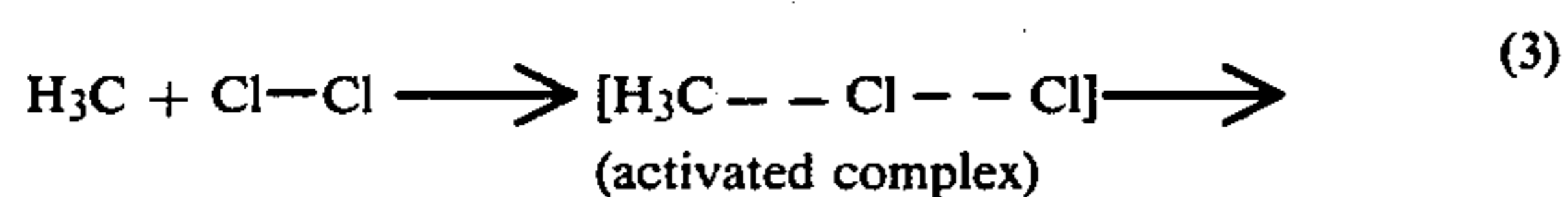
The chain initiation step involves the absorption of radiated energy by the Cl<sub>2</sub> molecule to break the bond as in the previous example:



Various chain propagation steps now follow. First, a Cl atom of high kinetic energy comes in contact with a CH<sub>4</sub> molecule, a carbon-hydrogen bond is broken, while a hydrogen-chlorine bond is formed. By losing an H atom, the CH<sub>4</sub> molecule becomes a CH<sub>3</sub> radical:



Now, a methyl radical CH<sub>3</sub> comes in contact with a Cl<sub>2</sub> molecule; a chlorine-chlorine bond is broken, while a carbon-chlorine bond is formed. The products are a methyl chloride molecule and a chlorine atom:



$$\Delta H = -183.0 + (+160.0) = -23.0 \text{ Kcal}$$

The two chain propagation steps 2 and 3 are repeated many times before the chain reaction is broken by adverse reactions or one of several chain terminating reactions of the type mentioned hereinabove.

The uniformity of radiation extending throughout the reaction chambers as disclosed in the present patent application is particularly advantageous in reactions such as the formation of methyl chloride CH<sub>3</sub>Cl. This advantage arises particularly from the fact that the substitution of chlorine atoms can proceed further, forming the di-, tri-, and finally the tetra-chloro compound, CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, and CCl<sub>4</sub>.

It is understood that an H atom of CH<sub>3</sub>Cl is more readily substituted, or replaced by a Cl atom than is an H atom of methane, CH<sub>4</sub>. Also, an H atom of CH<sub>2</sub>Cl<sub>2</sub> is more susceptible to further substitution by a Cl atom

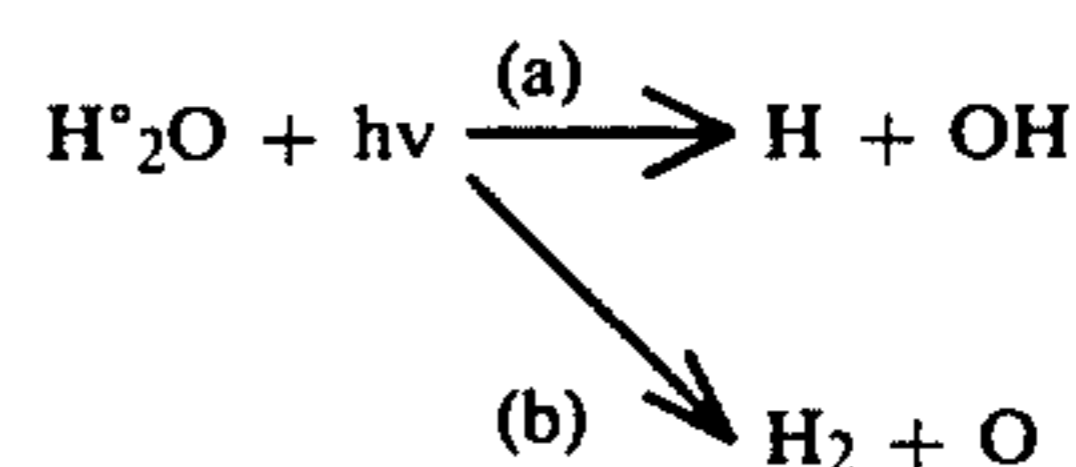
than an H atom of CH<sub>3</sub>Cl<sub>2</sub>, and similarly for CHCl<sub>3</sub>. In the present case, the C—H bond becomes more readily susceptible to substitution by a Cl—Cl bond as the number of Cl atoms already attached to the C atom increases. In terms of energetics, the compound CH<sub>3</sub>Cl is thermodynamically stable with respect to a mixture of CH<sub>4</sub> and Cl<sub>2</sub>, but the di-, tri-, and tetra-substituted compounds, CH<sub>2</sub> and Cl<sub>2</sub>, CHCl<sub>3</sub>, and CCl<sub>4</sub>, are even more stable, their stability increasing with the number of Cl atoms in the molecule.

If a reaction chamber were irradiated unevenly, with certain localized areas of very intense radiation, and others where there was little irradiation, then the reaction would proceed to the (undesired) final product CCl<sub>4</sub>. However, in the present case, by using reaction chambers which are very uniformly flooded with radiation, the bulk of the methane is only subject to a single substitution of the activated chlorine atom Cl, and it occurs very soon after these highly activated chlorine atoms are formed by the impact of radiation on the chlorine gas Cl<sub>2</sub>. In addition, a substantial excess of CH<sub>4</sub> is provided. Therefore, under these conditions, CH<sub>3</sub>Cl is the principal product of the chlorination of methane, although the more substituted products may also be formed in much smaller yields. In accordance with the teachings of the present invention, and the apparatus disclosed therein, precise amounts of energy of the proper energy level are delivered evenly throughout the reaction chamber, with the photons bombarding the target molecules, atoms or fragments of molecules from all directions simultaneously. In addition, as mentioned above, large amounts of intense energy of controlled wavelengths coupled to absorption bands of specific molecules or atoms is provided. This eliminates the steric factor, which is a normally expected problem.

#### PHOTOCHEMISTRY OF WATER VAPOR

The absorption spectrum of water vapor in the ultraviolet region is shown in FIG. 29. As compared with FIG. 10, it may be noted that FIG. 29 is directed to a band which starts just below 2,000 angstrom units. This would correspond to 0.2 microns. As mentioned hereinabove, the visible spectrum ranges from about 4,000 to about 7,000 angstroms, which is equal to 0.4 to 0.7 microns. Accordingly, the plot of FIG. 29 is in the ultraviolet, well below the visible spectrum, and the plot of FIG. 10 is in the infrared, above the visible spectrum. In comparing FIGS. 10 and 29 it may also be noted that in FIG. 29 peaks of absorption extend upwardly, whereas in FIG. 10 peaks of transmittance are plotted upwardly, and peaks for absorption extend down toward zero on the vertical scale.

There is considerable evidence that the photolysis of water at all wavelength regions leads to hydrogen and OH radicals. The following primary reactions are probably significant:



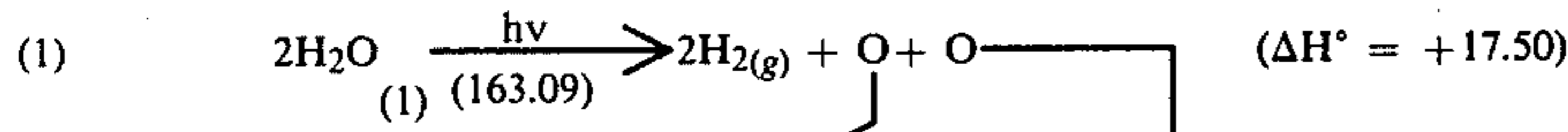
These reactions become possible energetically at wavelengths less than 2,420 angstrom and are probably the major reactions in the longer wavelength absorption



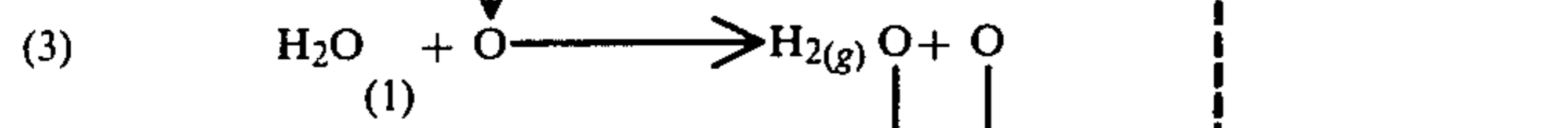
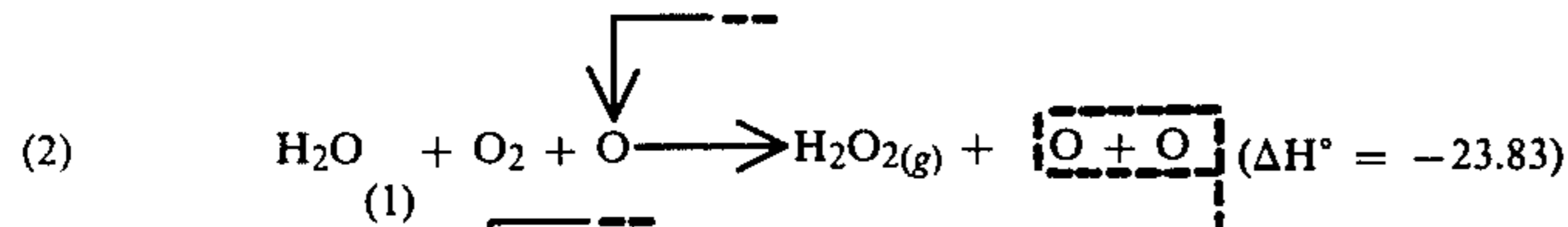
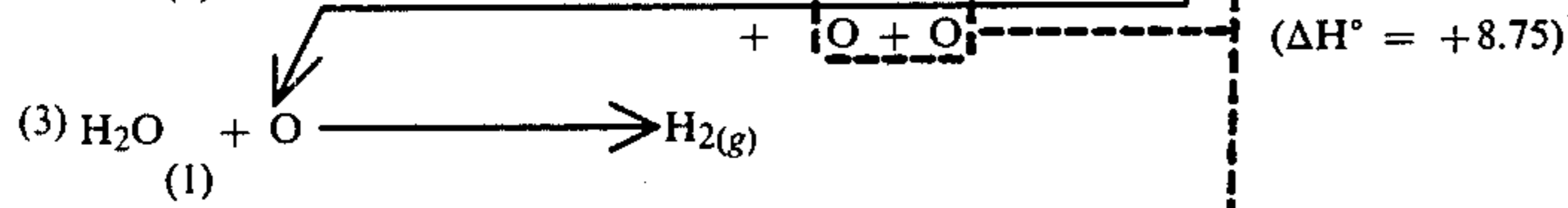
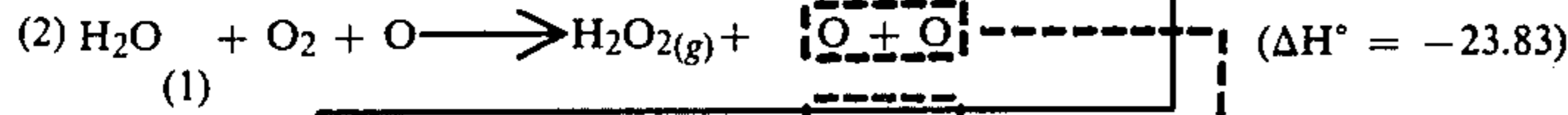




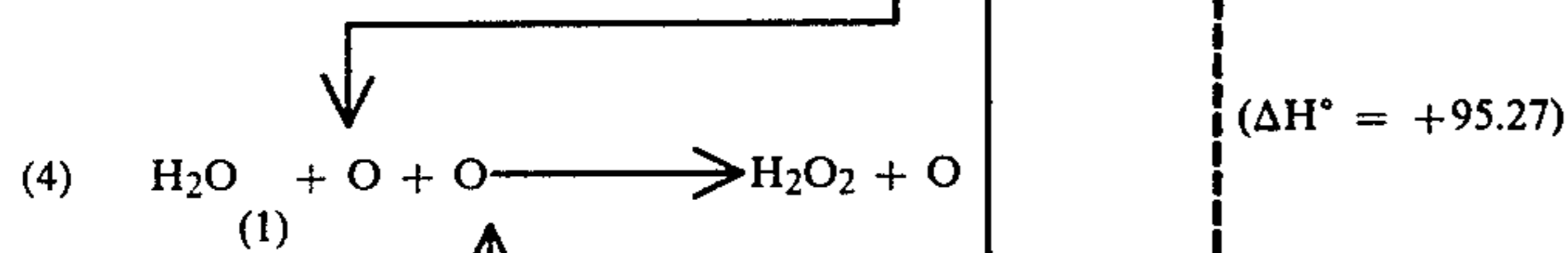
## PRIMARY REACTION



## CHAIN REACTIONS



## CHAIN TERMINATING REACTION



AVAILABLE FOR BRANCHING

$$+ \equiv 17.50 + (-23.83) + (+8.75) + (-23.83) + (+8.75) + (+95.27)$$

$$\Delta H^\circ = +82.61 \text{ Kcal}$$

NOTE:

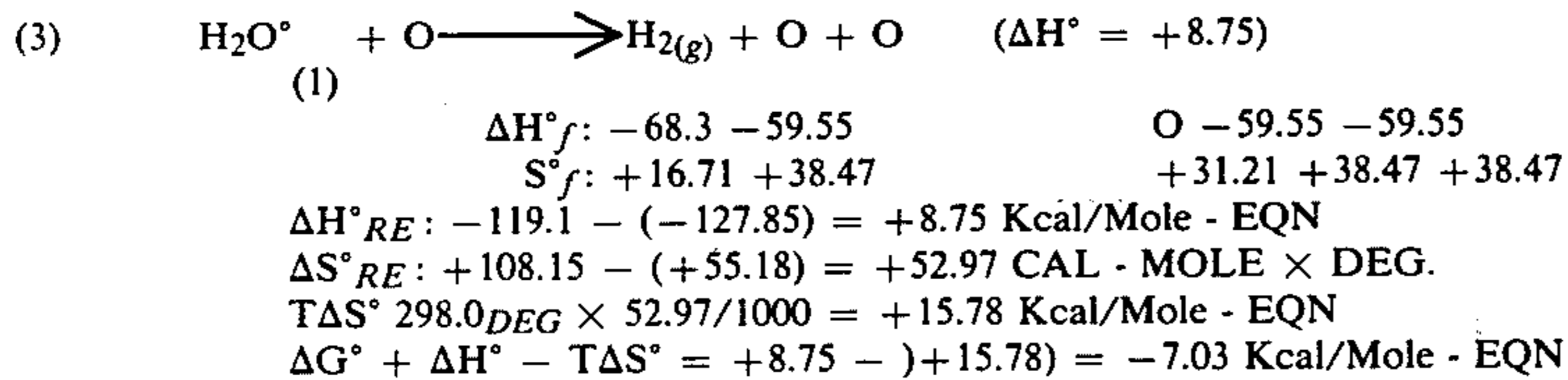
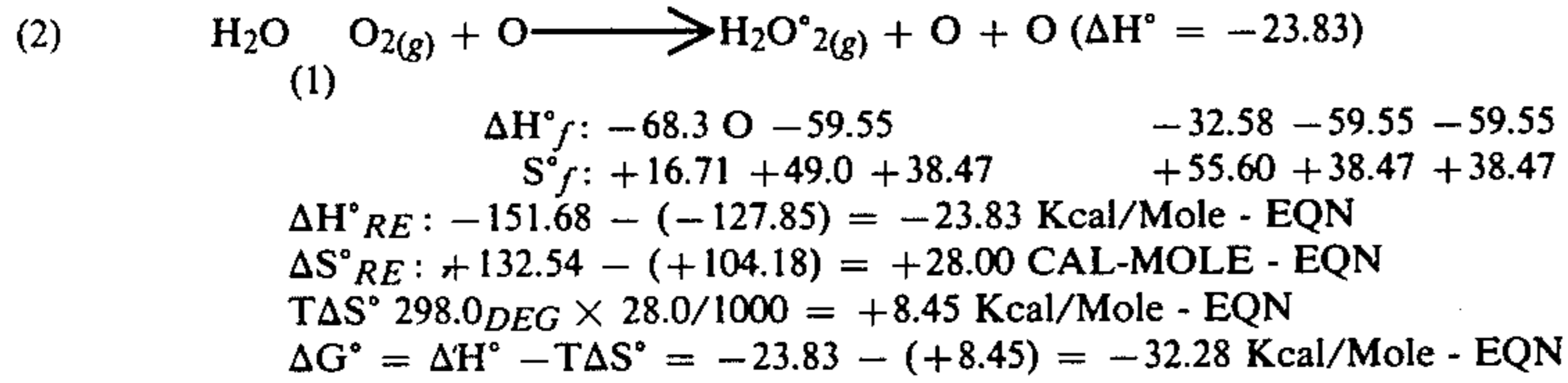
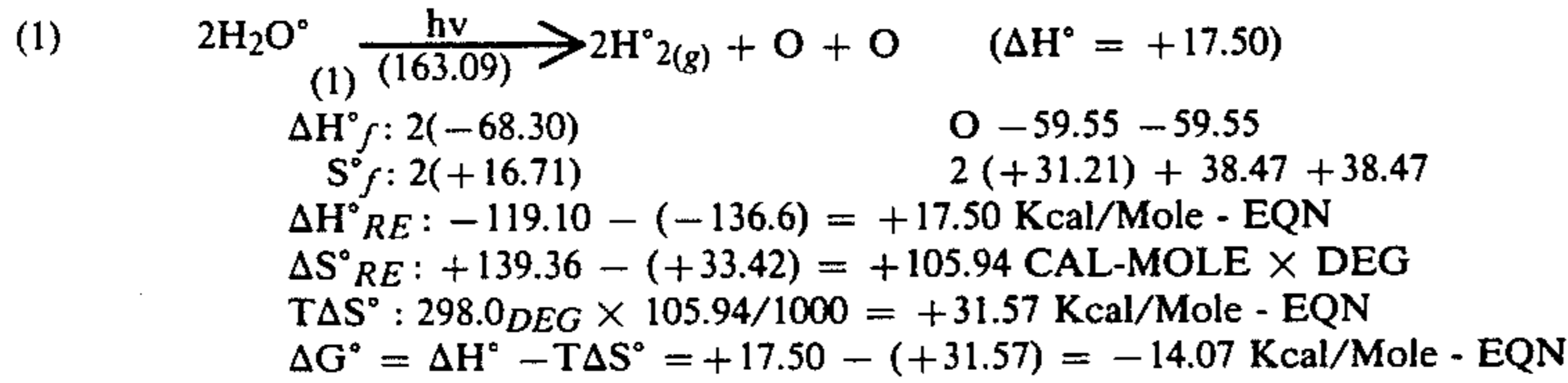
PRODUCT YIELD  $\bigcirc = (4) \text{ MOLES } \text{H}_2 + (3) \text{ MOLES } \text{H}_2\text{O}_2$

$$4\text{H}_2 + 2\text{O}_2 = (4 \times 68.3 \text{ Kcal}) = 273.20 \text{ Kcal}$$

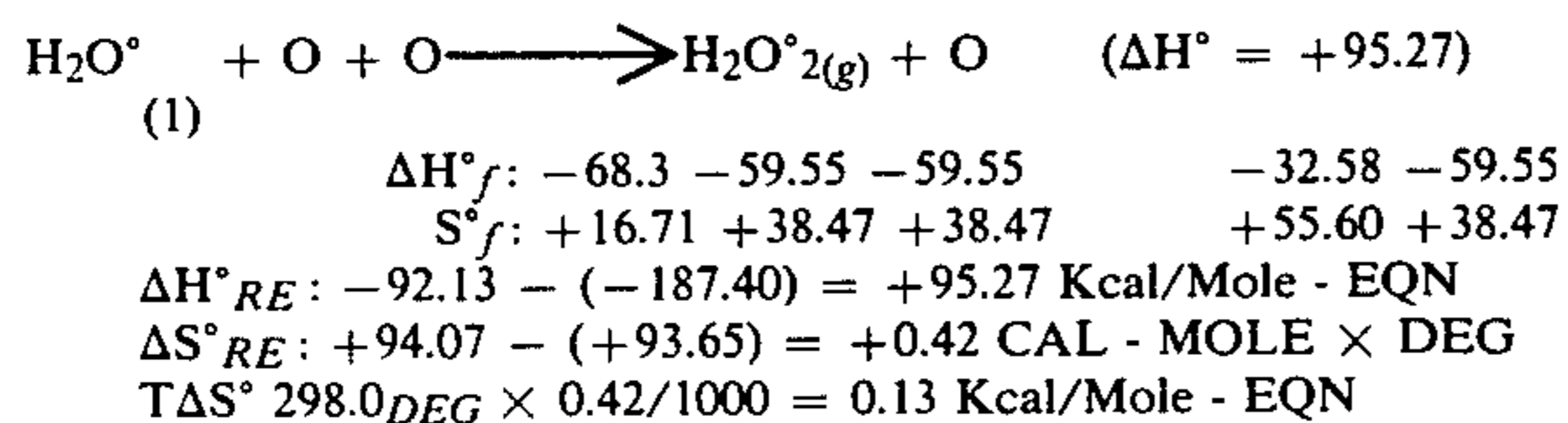
$$3\text{H}_2\text{O}_2 = (3 \times 32.58 \text{ Kcal}) = \underline{97.74 \text{ Kcal}}$$

$$370.94 \text{ Kcal}$$

## DETAIL ON REACTIONS



## (4) CHAIN BREAKING





-continued-

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = +95.27 - 0.13 = +95.14 \text{ Kcal/Mole EQN}$$

$$\Delta H^\circ$$

$$+17.50 + (-23.83) + (8.75) + (-23.83) + (+8.75) + (95.27)$$

$$\Delta H^\circ = +82.61 \text{ Kcal}$$

NOTE:

(A.) PRODUCT YIELD = (4) MOLES  $H_2$  + (3) MOLES  $H_2O_2$ 

$$4 H_2 + 2O_2 = (4 \times 68.3 \text{ Kcal}) = 273.20 \text{ Kcal}$$

$$3 H_2O_2 = (3 \times 32.58 \text{ Kcal}) = 97.74 \text{ Kcal}$$

$$\text{TOTAL} = 370.94 \text{ Kcal}$$

(B.) THEREFORE:  $370.94 - 82.61 - 136.60$ 

$$= 219.21 \text{ (Kcal - Net)}$$

(C.) PRODUCT QUANTUM YIELD,  $\Phi = \frac{370.94}{219.21} = 1.69$ 

## CHAIN REACTION EXAMPLE NO. 5

When water vapor alone, or when air including oxygen, and water vapor, are supplied to one of the reaction chambers, chain reactions occur which involve only the water vapor. The following example will consider such a chain reaction. In actual practice the reactions may follow a large number of branching patterns, but it has been determined that the example set forth below includes the principal reaction mechanisms which occur.

Initially, the activation energies of the bonds of interest will be tabulated:

BONDS OF INTEREST	
	Activation Energies For Activated Complexes in Kcal
1. H—O <sub>2</sub> = 47.0	2.82
2. HO—O = 64.0	3.84

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-continued

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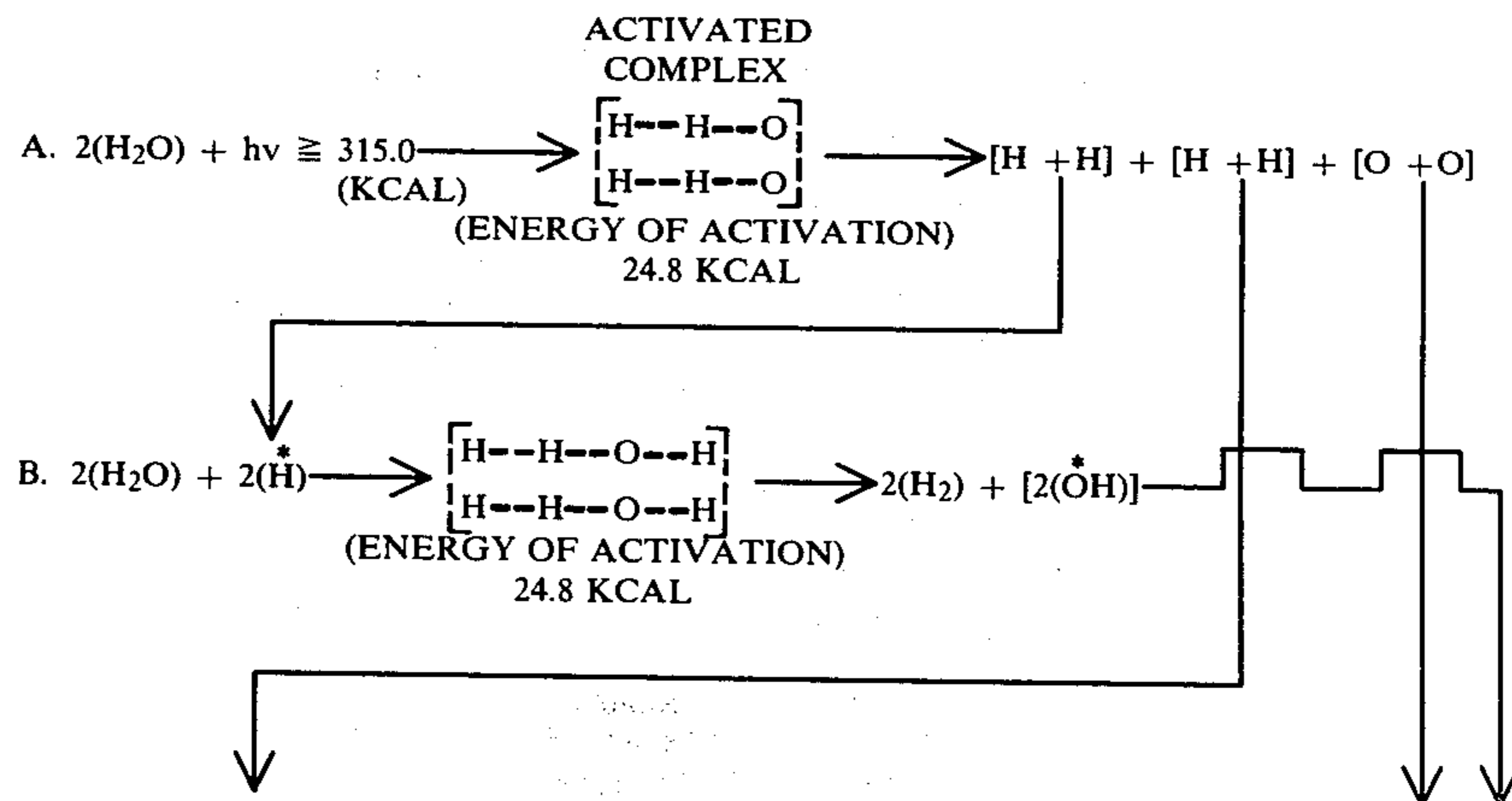
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## BONDS OF INTEREST

	Activation Energies For Activated Complexes in Kcal
3. HO—OH = 51.0	3.06
4. HO <sub>2</sub> —H = 90.0	5.40
5. H—H = 104.2	6.25
6. O—O = 119.1	7.15
7. H—OH = 119.0	7.14
8. H—O = 102.0	6.12

The activation energy will amount of ~5.5 percent minimum of the bond energy of the bond to be broken. Then, for the reaction  $A + BC \rightleftharpoons AB + C$ , if the reaction is exothermic from left to right, the activation energy estimated by the semiempirical method will be ~5.5 percent of the molecule BC. The activation energy of the reverse endothermic step will be this amount, plus the heat of the reaction. For our purposes, we used the figure of 0.06 (6.0) percent for our calculations.

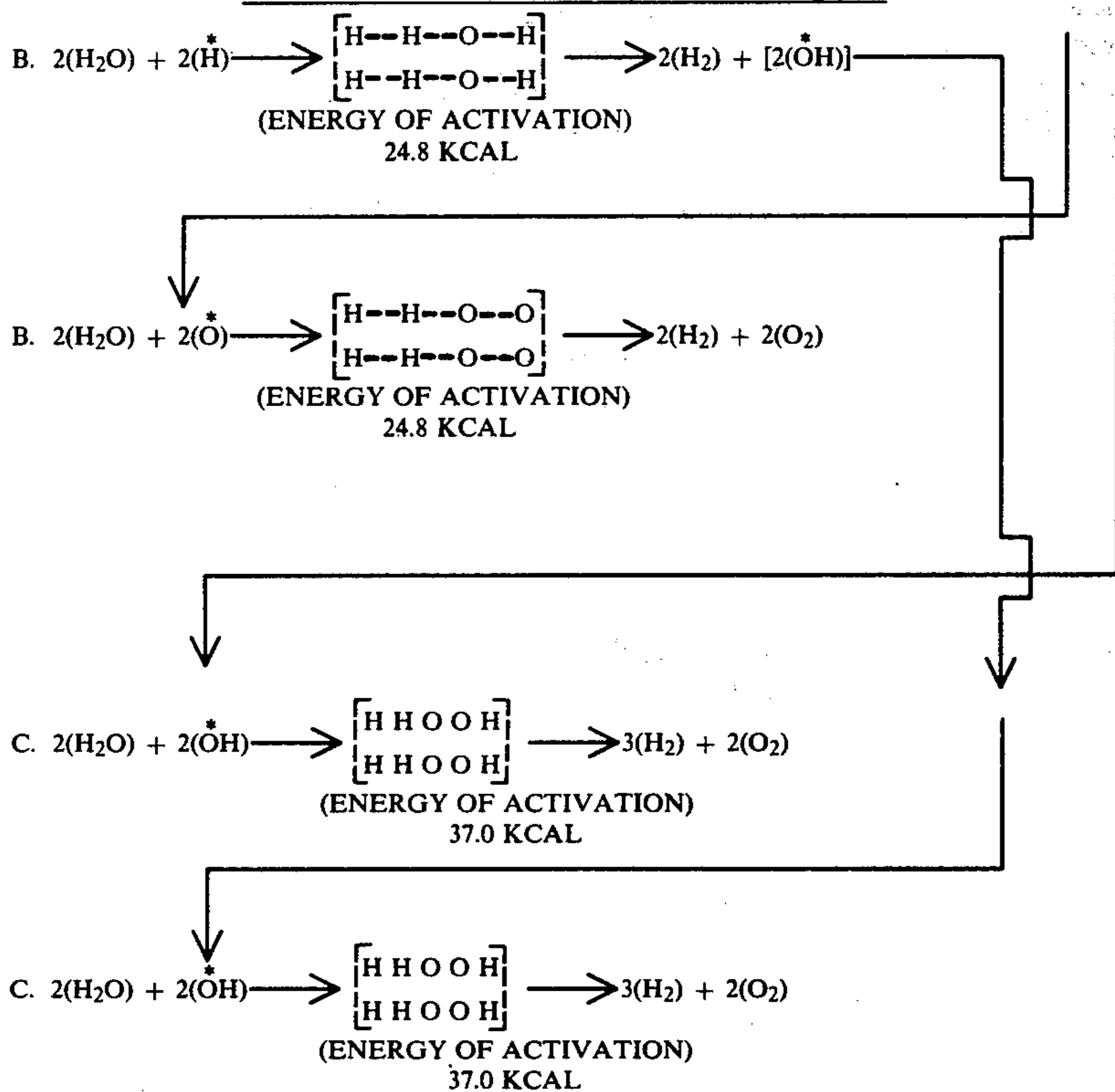
## REACTION MECHANISMS (Probable Average)





-continued

REACTION MECHANISMS (Probable Average)



INPUT ELECTRICAL ENERGY

(1) We have determined that we would like to supply the equivalent of 315.0 Kcal per second, so we convert this:

(a)  $1.0 \text{ Kcal} - \text{Sec} = 4.186 \text{ Kwatts} - \text{sec.}$

(b)  $315.0 (\text{Kcal/sec}) \times 4.186 = \boxed{1318.59 \text{ Kwatts} - \text{sec. (INPUT)}}$

- (2)  $1318.59 \text{ Kwatts-sec} \equiv 1,318,590 \text{ Joules per sec.}$
- (3)  $\text{Joule-sec.} = 1.5258 \times 10^{33} \text{ quanta.}$
- (4)

$\frac{1.5258 \times 10^{33} (\text{Joule-sec.})}{6.02 \times 10^{23} (\text{Avogadro's Number})} = 2.53455 \times 10^9 \text{ quanta (Per Joule)}$

(5)  $1,318,590 (\text{Joules-sec.}) \times 2.53455 \times 10^9 (\text{quanta})$

$\boxed{\text{Total Quanta-Sec.} = 3.342 \times 10^{15} (\text{INPUT})}$

(6) "Power" will be obtained in watts if W is expressed in joules ( $10^7$  ergs) and t in seconds.

$P = \frac{W}{t} = \frac{1,318,590}{1} = 1,318,590 \text{ Watt-Sec.}$   
 $= 1,318.59 (\text{Dwatt-Sec.})$   
 $= 315.0 (\text{Kcal-Sec.})$

(7) INFRARED = 2.5 (Peak) = ~24.0 Kcal/Mole/Photons

(8) U.V. =  $1847\text{\AA} = \sim 155.0 \text{ Kcal/Mole/Photons}$

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155.0	} 315.0 Kcal/sec (= DISTRIBUTION)
24.0	
24.0	
24.0	
24.0	
24.0	
24.0	
20.0	
20.0	
20.0	

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45 A. INPUT

315.0 (Kcal-Per-Unit-Time)

B. OUTPUT (Per-Same-Unit-Time) (Assuming 100% efficiency on reactions shown.)

50

- 1. 12 Moles  $\text{H}_2$  gas  
 $\therefore 12 \times 68.3 (\text{Kcal}) = 819.6 \text{ Kcal}$
- 2.  $\frac{819.6}{315.0} 2.60 = \Phi = \text{Product Quantum Yield.}$

55 C. OUTPUT (Per-Same-Unit-Time) (Assuming 50.0% efficiency on reactions shown.)

- 1. 6.0 Moles  $\text{H}_2$  gas  
 $\therefore 6 \times 68.3 (\text{Kcal}) = 409.8 \text{ Kcal}$
- 2.  $\frac{409.8}{315.0} 1.30 = \Phi = \text{Product Quantum Yield.}$

In summary, the apparatus described hereinabove may clearly be designed to provide the staged and compartmentalized irradiation of reactions to obtain conditions which are favorable to the reaction mechanisms of interest. Different radiation frequencies may be employed at the input feedstock area and at the output feedstock area to enhance the desired reaction. Certain

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selected reactions have been considered in some detail. Other reactions involving breaking molecular bonds and substituting new elements or radicals may be implemented by the same type of technique used in the apparatus as disclosed herein or similar apparatus. Typical products which may be input feedstocks include methane, ethane, propane, isobutane, N-pentane, isopentane, neopentane, and the alkyl amines. The apparatus as described in the present application are also particularly suited to hydrogenation and olefin formation, the dehydration of alcohols, addition reactions of olefins, and to reactions involving polysubstituted saturated hydrocarbons, benzene, unsaturated hydrocarbons including the alkyne series, alcohols, carboxylic acids, aldehydes, and ketones.

For completeness, certain matters relating to the gas discharge tubes and certain laser-type materials which may be used will now be reviewed. Initially, as mentioned above, the gas discharge tubes are preferably made of quartz and are mercury gas discharge lamps. One typical lamp available from Westinghouse is rated by the manufacturer at 39.0 watts, 0.420 amperes, for 115 volts A.C. operation. The emitted ultraviolet radiations are rated by the manufacturer at 38.5 percent of input power, or at about 15+ watts. Quartz, depending on its quality will transmit ultraviolet radiations with a cut-off of between 1000 Angstrom units and 2,000 Angstrom units.

The lines in the ultraviolet emission spectrum of mercury are set forth below, with particularly strong lines appearing at 2536 Å and at 1849 Å.

LINES IN THE ULTRAVIOLET  
EMISSION SPECTRUM OF MERCURY  
(Wavelength in Angstrom Units)

1269.7	2399.4	3125.6
1527.0	2482.7	3131.6
1592.0	2534.8	3131.8
1599.0	2536.0	3341.5
1650.0	2652.0	3650.2
1677.9	2698.9	3654.8
1783.3	2752.8	3662.8
1798.7	2803.5	3663.3
1849.0	2847.7	3906.4
1942.0	2893.6	3983.9
2224.7	2967.3	4046.6
2378.3	3021.5	

Four known laser type materials which may be used are as follows:

1. Aluminum Oxide ( $\text{Al}_2\text{O}_3$ ) doped with chromium ( $\text{Cr}^{3+}$ ), requiring input pumping radiation of from 0.32 to 0.42 microns, or from 3200 Å to 4200 Å, and having a fundamental output wavelength of 6934 Å.

2. Yttrium Oxide ( $\text{Y}_2\text{O}_3$ ) doped with europium ( $\text{Eu}^{3+}$ ), requiring input pumping radiation of from 2000 Å to 2800 Å, and having an output wavelength of 6113 Å.

3. Calcium Tungstate ( $\text{CaWO}_4$ ) doped with erbium ( $\text{Er}^{3+}$ ) requiring input pumping radiation between 2000 Å and 2800 Å and having a fundamental output wavelength of 16,120 Å.

4. Aluminum Oxide ( $\text{Al}_2\text{O}_3$ ) doped with erbium ( $\text{Er}^{3+}$ ) requiring input pumping radiation of between 3200 Å and 4200 Å, and having a fundamental output wavelength of 16,602 Å.

Considering Example No. 1 and Example No. 2, it is clear that mercury vapor spectral lines from 1942 Å through 2803.5 Å are available to supply pumping radiation for Example No. 2; and that mercury lines

3125.6 through 4046.6 are available for pumping Example No. 1.

Concerning another point, the use of the spheres of laser type material mounted on the quartz envelope of the mercury vapor tube has been noted. As discussed in detail, the mercury vapor discharge provides the radiant energy to pump the laser type material to the desired excited state to initiate coherent radiation. Instead of the mercury vapor discharge, the pumping energy for the laser-type material spheres may be provided from heated filaments coated with mullite suitably doped to provide the desired pumping frequency. The filaments could be of the configuration disclosed in FIG. 16, coated with an outer transparent sealing coating, to which the spheres could be secured as shown in FIG. 30, for example. Suitable variation in operating conditions could then be obtained by varying the power applied to the filaments, and their resultant temperature, and output radiation.

In closing, it is to be understood that the principles set forth in the foregoing description may be implemented by a number of different apparatus, with the constructions and materials specified herein only being exemplary of the types of apparatus and materials which may be employed. Reaction chambers of different configurations, and different laser type materials, as well as different feedstocks and products could be employed.

I claim:

1. A radiation apparatus comprising:
  - a filament composed at least in part of means including solid state material for producing substantially coherent output radiation at a predetermined frequency;
  - said filament including semi-reflective surface means extending generally concentric with the axis of said filament, said semi-reflective surface means including generally perpendicular surfaces spaced apart by a distance substantially equal to an integral number of half-wave lengths at said predetermined frequency.
  2. An apparatus as defined in claim 1 wherein two concentric semi-reflective surfaces are provided.
  3. An apparatus as defined in claim 1 wherein said filament is made up of a central resistive wire and an outer coating of said solid state material for producing substantially coherent radiation.
  4. An apparatus as defined in claim 1 further comprising:
    - means for applying pumping energy to said solid state material to raise said material to an excited state for producing coherent radiation.
    5. An apparatus as defined in claim 1 further comprising:
      - a reaction chamber,
      - means for mounting a plurality of said filaments in said reaction chamber; and
      - means for applying pumping energy to said solid state material to raise said material to an excited state, whereby said reaction chamber is flooded with output radiation from said solid state material.
      6. An apparatus as defined in claim 5 wherein said means for producing substantially coherent radiation includes solid state materials having different radiating frequencies in different ones of said filaments, whereby radiation of at least two different frequencies is applied to said reaction chamber.



7. An apparatus as defined in claim 6 further comprising means for supplying feedstock to said reaction chamber, thereby producing media discontinuities within said chamber, whereby sum and difference frequencies derived from different radiation frequencies present in said reaction chamber, are formed and are coupled to said feedstock.

8. An apparatus as defined in claim 7 further comprising means for supplying to said reaction chamber feedstock having an absorption band at the sum frequency of two or more radiations present in said reaction chamber, to cause dissociation of said feedstock.

9. An apparatus as defined in claim 5 further comprising means for supplying feedstock having an absorption band at said predetermined frequency of said radiation, to said reaction chamber, to cause dissociation of said feedstock.

10. An apparatus as defined in claim 9 further comprising means for supplying a second feedstock to said reaction chamber to react with one or more of the dissociation products of the first feedstock.

11. An apparatus as defined in claim 1 further comprising a plurality of gas discharge tubes, and wherein a plurality of said filaments are helically wrapped around said gas discharge tubes.

12. An apparatus as defined in claim 11 wherein said gas discharge tubes are mercury vapor gas discharge tubes.

13. An apparatus as defined in claim 1 wherein said solid state material includes host and sensitizer material for receiving incoherent radiant energy and for radiating substantially coherent monochromatic radiation at a different frequency than that of the input radiant energy.

14. An apparatus as defined in claim 1 wherein means are provided for directing radiation outward from said filament substantially transverse to the axis thereof.

15. An apparatus for controlled photochemical reactions comprising:

- a reaction chamber;
- means for supplying feedstock to said reaction chamber, said feedstock having a predetermined frequency absorption band or bands; and
- means for flooding said reaction chamber with radiation within at least one of the absorption bands of said feedstock;
- said means including at least one gas discharge tube having output radiation of a lower frequency than said predetermined band or bands and means in physical proximity to said gas discharge tube and also exposed to said reaction chamber for receiving said lower frequency radiation from said gas discharge tube and for supplying intense radiation to said reaction chamber within said predetermined band or bands.

16. An apparatus for controlled photochemical reactions comprising:

- a reaction chamber;
- means for supplying feedstock to said reaction chamber, said feedstock having predetermined absorption bands;
- means including a plurality of gas discharge tubes for flooding said reaction chamber with radiation within at least one of the absorption bands of said feedstock; and
- means including solid state material in close proximity to said gas discharge tubes for receiving pumping energy from said gas discharge tubes and for

radiating substantially coherent energy into said reaction chamber at a different frequency.

17. An apparatus as defined in claim 16 wherein said solid state material is in the form of filaments wound onto said gas discharge tubes.

18. An apparatus as defined in claim 16 wherein said solid state material is in the form of spheres mounted on said gas discharge tubes.

19. An apparatus as defined in claim 16 wherein said solid state material intercepts only a fraction of the radiation from said gas discharge tubes, whereby said reaction chamber is flooded with radiation of different frequencies forming sum and difference frequencies at the media discontinuities formed by the presence of the feedstock; and wherein said gas discharge tubes and said solid state material include means for producing at least one of the sum frequencies in an absorption band of said feedstock.

20. An apparatus as defined in claim 16 further comprising reflective coating means associated with said solid state material for increasing the coherency of said radiation.

21. An apparatus as defined in claim 20 wherein said reflective coating means reflects from 70% to 90% of incident visible radiation.

22. An apparatus as defined in claim 16 further comprising reflective coating means associated with said solid state material for reflecting infrared and visible frequencies and for transmitting shorter wavelength ultraviolet radiations to supply coherent harmonic radiations to said reaction chamber.

23. An apparatus for efficiently accomplishing photochemical reactions comprising:

- a reaction chamber;
- means for applying feedstock to said reaction chamber, said feedstock having predetermined frequency absorption band or bands;
- means located within said chamber for flooding said reaction chamber with substantially coherent energy within one of the absorption bands of said feedstock at energy levels sufficient to dissociate said feedstock, said radiation supplying means including solid state material; and
- low cost incoherent energy source means immediately adjacent said supplying means for pumping said solid state material to an excited state.

24. A source of radiant energy comprising:

- means including a sphere of solid state material for producing substantially coherent radiations;
- a semi-reflective coating on at least the major portion of the outer surface of said sphere; and
- means for pumping said solid state material to an excited state, whereby substantially coherent energy is radiated through said semi-reflective coating from said solid state material to an excited state, whereby substantially coherent energy is radiated through said semi-reflective coating from said material.

25. A source of radiant energy as defined in claim 24 wherein a plurality of said coated spheres are provided, and wherein said pumping means directs pumping radiation into said material through a portion of the surface of each of said spheres that is not coated with said semi-reflecting coating.

26. A source of radiant energy as defined in claim 25 wherein transparent envelope means are provided for supporting said spheres, and said pumping means



supplies radiant energy to said spheres through said transparent envelope.

27. A source of radiant energy as defined in claim 26 wherein said pumping means is a mercury vapor gas discharge tube.

28. A source of radiant energy as defined in claim 26 wherein said pumping means includes means for converting electrical power to radiant energy of the proper high frequency required to pump said laser material to the excited state.

29. A source of radiant energy as defined in claim 24 wherein said semi-reflective coating reflects from 70% to 90% of the incident visible radiation.

30. A source of radiant energy as defined in claim 24 wherein said semi-reflective coating comprises means for reflecting infrared and visible frequencies and for transmitting shorter wavelength ultra-violet radiations whereby coherent harmonic radiations emanate from said spheres.

31. An apparatus for controlled photochemical reactions including the radiant energy source as defined in claim 24 and further comprising:

means defining a reaction chamber for receiving the major portion of the radiation from said source;  
means for supplying a reactant to said chamber, said reactant having a frequency absorption band corresponding to the frequency of radiation from said source.

32. An apparatus for obtaining hydrogen or hydrogen peroxide from water vapor comprising:

means for directing water vapor through a predetermined reaction zone, said water vapor having predetermined absorption frequency bands;

means including at least one gas discharge tube within said reaction zone, for flooding said reaction zone with radiation within at least one of said absorption frequency bands, at sufficiently high intensities to produce combustible hydrogen or hydrogen peroxide from said water vapor, said means for flooding said reaction zone with radiation further including means in immediate proximity with said gas discharge tube for receiving radiation from said gas discharge tube having a predetermined frequency output, and for supplying higher frequency radiation to said reaction zone.

33. An apparatus as defined in claim 32 further comprising solid state means for producing substantially coherent output radiation within at least one of said absorption bands.

34. An apparatus as defined in claim 32 wherein said gas discharge means includes mercury vapor gas discharge means.

35. An apparatus as defined in claim 32 further comprising means for directing said water vapor into intimate reactive proximity to said means for supplying higher frequency radiation into said reaction zone.

36. An apparatus as defined in claim 32 further comprising means for continuously flowing water vapor through said reaction zone to continuously form combustible hydrogen or hydrogen peroxide.

37. An apparatus as defined in claim 32 wherein said gas discharge means is elongated; and wherein said means for receiving radiation from said gas discharge means is also elongated, and is spaced around said gas discharge means, and includes means for radiating said higher frequency radiation outward substantially transverse to the elongated gas discharge means.

38. An apparatus for controlled photochemical reactions comprising:

a reaction chamber;

means for supplying feedstock to said reaction chamber, said feedstock having a predetermined energy absorption vs. frequency characteristic, including at least one high energy absorption region;

means located within said radiation chamber for flooding said reaction chamber with high intensity radiation within said high energy absorption region of said feedstock;

said radiation flooding means including solid state means having outer surfaces of substantially circular cross-section for producing substantially coherent output radiation within or in immediate proximity to said reaction chamber; and

means for exciting said means for producing substantially coherent radiation to an excited state to radiate relatively coherent high frequency radiation through said outer surfaces at intensity levels sufficient to modify the form of a substantial proportion of said feedstock.

39. An apparatus as defined in claim 38 wherein said means for producing substantially coherent radiation is in the form of a plurality of elements of solid state material spaced apart within said reaction chamber.

40. An apparatus as defined in claim 38 wherein said solid state means are substantially spherical.

41. An apparatus as defined in claim 38 wherein said solid state means are elongated and are of substantially constant circular cross section.

42. An apparatus as defined in claim 41 wherein said solid state means include cylindrical rods.

43. An apparatus as defined in claim 41 wherein said solid state means include cylindrical filaments.

44. An apparatus as defined in claim 41 wherein said solid state means have a substantially cylindrical outer radiating surface.

45. An apparatus as defined in claim 38 wherein semireflective coating means are provided on the outside of said solid state means.

46. An apparatus as defined in claim 38 wherein semireflective coating means are provided on said solid state means to enhance the production of high frequency harmonic radiation and to supply it to said reaction chamber, said semi-reflecting coating being formed of material which is reflective to frequencies below ultraviolet radiation and which is relatively transparent to ultraviolet radiation.

47. An apparatus for controlled photochemical reactions comprising:

a reaction zone;

means for supplying feedstock to said reaction zone, said feedstock having a predetermined energy absorption vs. frequency characteristic, including at least one high energy absorption region;

means located inside said reaction zone for flooding said reaction zone with high intensity radiation within said high energy absorption region of said feedstock;

said means including at least one elongated gas discharge device within said reaction zone; and

means spaced around said gas discharge device for receiving radiation from said gas discharge device and for radiating high intensity radiation having a higher frequency content than the radiation from said gas discharge device, into said reaction zone.



48. An apparatus as defined in claim 47 including means for supplying water vapor to said reaction zone and means for drawing off hydrogen or hydrogen peroxide from said reaction zone.

49. In a system for subjecting material to high frequency radiation;

reaction chamber means for holding a reactant having a predetermined high frequency absorption band;

a high power source of lower frequency radiation;

interface means located between said source of lower

frequency radiation and said reaction chamber

means for receiving said lower frequency radiation

and for flooding said reaction chamber with high

intensity radiation in said predetermined absorp-

tion band, at an intensity level sufficient to dissoci-

ate said reactant, said interface means including

means mounted adjacent said reaction chamber for

reflecting the major portion of said lower fre-

quency radiation but transmitting the major por-

tion of radiation at said predetermined high fre-

quency.

50. A system as defined in claim 49 wherein said reflecting means is a thin metal layer.

51. A system as defined in claim 49 wherein said system includes means for supplying water vapor as said reactant to said reaction chamber, and means for drawing off hydrogen and/or hydrogen peroxide from said reaction chamber.

52. An apparatus for controlled photochemical reactions comprising:

a reaction zone;

means for supplying water vapor to said reaction zone, said water vapor having predetermined absorption band or bands in the ultra-violet frequency spectrum;

at least one elongated gas discharge tube mounted within said reaction zone and producing a predetermined lower frequency radiation output; and

means spaced around said gas discharge tube for receiving said lower frequency radiation output from said gas discharge tube, and for flooding said reaction zone with higher frequency output radiation within said predetermined absorption band or bands in the ultraviolet frequency spectrum, and at an intensity level sufficient to dissociate the greater portion of said water vapor and to form hydrogen and/or hydrogen peroxide.

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