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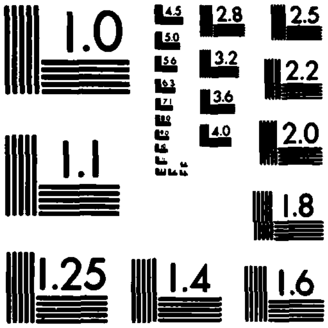

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Hydrogen and Oxygen from Water VI.
Quenching the Effluent from a Solar Furnace

by

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and Edward A. Fletcher

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HYDROGEN AND OXYGEN FROM WATER VI. QUENCHING THE EFFLUENT FROM A SOLAR FURNACE

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Abstract-- Numerical integration of a set of rate equations applicable to the hydrogen-oxygen system suggests that it should be possible to recover H_2 and O_2 by rapid cooling of low-pressure equilibrium mixtures from a solar furnace. Using the University of Minnesota 4.2 m solar furnace, we were able to recover explosive mixtures of H_2 and O_2 from water which had been heated to about 2100K. The numerical calculations and the experiment are described.

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INTRODUCTION

The use of sunlight for the production of H_2 and O_2 in a one-step thermochemical process is of current interest.[1-7] Bilgen[8] and his coworkers have conducted analytical and experimental studies and have concerned themselves with the possibility of quenching hot equilibrium products. A group at Los Alamos[9] considered quenching and concluded that it could not be done. Lede, Lapique, and Villermaux[10] concluded that equilibrium was quickly established when H_2O was heated. They also observed quenching in several types of zirconia nozzles and other devices when turbulent cold jets were injected into the streams which emerged from the focus of an arc image furnace. Our analytical studies[11-15] have emphasized our interest in high-temperature separation rather than quenching. We have presumed that quenched mixtures, even those in which a substantial measure of high-temperature separation has been achieved, should be avoided, at least until we are assured that they can be safely handled.

Quenched mixtures, from which most of the H_2O has been removed, would be brisantly explosive over a wide range of compositions.[16,17] Our concern with the possibility that our experimental work might produce hazardous mixtures prompted us, some time ago, to do numerical calculations of the rates of reactions which would be of interest to us.[18,19] Our analytical studies suggested that, under some conditions, dangerous mixtures might, indeed, be produced even in partially separated mixtures. But, in view of the fact that our kinetics program limited the number of concurrent reactions we could handle to thirty, we deferred publication of our results as a kinetic study. Inasmuch as we have now observed water quenching in a solar reactor, we believe they are of interest to the water-splitting community.

We recently built a solar furnace which can produce, in cavity receivers, temperatures at which the dissociation of H_2O becomes appreciable.[20] We are conducting developmental studies of a reactor-separator which will be used to study effusional separation in the Knudsen flow regime. It is too soon for us to have reached definite conclusions about the effusional technique. But, since quenching is of interest, we believe that some of our observations should be published now, especially inasmuch as some of the cooled products which emerge from our solar furnace are explosive.

THE KINETICS OF THE QUENCH REACTION

Oran, Young, and Boris[21] compiled an excellent set of rate constants for use with the H_2-O_2 system. It consists of 43 reactions involving the species H, H_2, O, OH, H_2O, O_2, HO_2, and H_2O_2. We used their rate constants in a computer program developed by Bittker and Scullin[22] to gain insights into the likelihood that our furnace might produce hazardous mixtures.

We found it necessary to eliminate some of the reactions of Ref. 21, since our computor program could handle only 30 simultaneous rate expressions. Even so, our results are adequate for the purpose for which they were intended, namely, to alert us to hazards.

We arbitratily chose to eliminate all reactions involving H_2O_2, leaving 34. We then did two sets of preliminary calculations, one in which HO_2 was not included and a second in which HO_2 was included, but in which the four slowest reactions in the set were excluded. There was a significant difference in the results, shown in Fig. 1. Thereafter, we included HO_2 and used the 30 fastest reactions in our reaction scheme.

Our primary interest is in whether the cooled effluent from a solar reactor-separator such as those we have described previously[11-14] would be explosive. We therefore concerned ourselves with the behavior of hydrogen-rich and oxygen-rich equilibrium mixtures such as those one might expect from an effusional separation process. Our examples thus yield mixtures that are probably safer than those which would be obtained in processes which quench without prior separation.

We did a series of calculations in which the equilibrium compositions at 2500K, shown in Table 1, were instantly cooled to lower temperatures. The hydrogen-rich mixtures have an H/O atom ratio of 2.2. Their pressure is a constant 0.01 atm. The oxygen-rich mixtures have an H/O atom ratio of 1.8. Their pressure is 0.04 atm. Starting with the compositions of Table 1, we integrated the rate expressions, using a very small time interval for one millisecond. After we had established the trends in the composition profiles, we continued the integration for one additional second, using a larger integration interval to save computor time. Details of the calculation can be found elsewhere.[19] We assumed that the compositions after 1.001 second would be indicative, of the amount of H_2O, H_2, and O_2 that would be found in the quenched product.

An example result is shown in Fig. 2. Table 2 summarizes the results of many such calculations. Section a of of Table 2 deals with oxygen-rich mixtures such as those one might expect from the uneffused fraction from a reactor-separator at 2500K; section b deals with the hydrogen-rich effusate. The first part of each section gives the mole fractions of the major products after 1.001 s at the quench temperature. The second part gives the mole fractions of the components that would be found in the cool product if the mass of H_2O did not change after 1.001 s and the remaining species recombined in such a way as to be completely converted into H_2 and O_2. The third part gives the mole fractions of hydrogen that would be found in the H_2-O_2 mixtures retrieved after liquid H_2O has been removed. The fourth part gives the components that would be retrieved if the fate of all oxygen bound to hydrogen either in H_2O or OH is to be found, ultimately, in water. The fifth part of each section gives the mole fraction of H_2 in the H_2-O_2 gaseous mixture that remains after the H_2O has been condensed from it. Mixtures having mole fractions of hydrogen between 0.15 and 0.90 are detonable;[16] they are explosive over an even broader composition range, 0.047-0.939.[17] Researchers working with them should be aware of the possible danger. Explosive compositions are printed in bold type in Table 2.

EXPERIMENTAL PART

Apparatus

Our solar furnace has been described elsewhere.[20] A schematic diagram of the apparatus is shown in Fig. 3. The reactor was a cavity receiver with a 4.45-cm aperture. It was equipped with an H_2O metering system which fed liquid H_2O to a bank of Lennox Model LSC18 flat-plate collectors to prevaporize it at low pressure, a water cooled heat-exchanger, pressure-regulator, and pump, at the exit of which the effluent gas was conducted through a Tygon hose to a large beaker, half-filled-with-water, through which the effluent was permitted to bubble to the atmosphere. From time to time, small samples were collected in beakers or graduated cylinders by downward displacement of water, to measure flow rates and to test them for explosiveness.

The actual concentration ratio, measured calorimetrically, was 4400. The average energy flux at the aperture, with a solar intensity of 700 W/m^2, was about 3080 kW/m^2. The power to the receiver was therefore about 4.9 kW.

Figure 4 shows a cross-section through the reactor. We made it by wrapping a 6.5 cm thick inner layer of yttria-stabilized zirconia, Zircar ZYF-100 felt, around a mandrel to shape the reactor cavity. We then wrapped the zirconia inner chamber in a 4 cm thick outer insulating layer of alumina-silica paper, Fiberfrax series 970 JH. The resulting refractory cavity receiver was encased in Inconel 600, which made the assembly vacuum tight and provided the means by which the chamber was connected with the 4.75 cm Inconel feed- and product-lines.

The window was a shallow quartz dome. It was made hemispheroidal for strength and to minimize refraction of the sunlight passing through it from the concentrator. It was held in place on the highly polished front plate of the reactor housing by the vacuum in the reactor. A thin strip of Teflon provided the seal.

To improve heat transfer to the H_2O, as well as to learn how a thin zirconia membrane might be expected to behave in such an environment, we supported a thin sheet of zirconia felt on a dense zirconia honeycomb, as shown in Fig. 4, and required the H_2O to flow through it. The membrane thus served as a significant absorber of sunlight as well as a heat exchanger to heat the H_2O.

Procedure and Results

With all the components in place, pump working, and the system evacuated, we gradually increased the furnace power by opening the two large doors which serve as the furnace's shutter. After about five minutes at full power, we permitted H_2O to flow into the system through the inlet valve, whose setting was not changed again during the course of an experiment.

We measured, at convenient intervals, incident flux, cavity temperature, pressure, and the gas delivery rate at the pump exit. After one hour, the feedwater supply was shut off. Measurements of the remaining experimental variables continued for an additional 25 minutes. Then the furnace doors were closed and the experiment terminated.

Figure 5 is a summary of our experimental observations. The solar intensity peaked near noon, near the start of our experiment, at about 700 W/m^2 and decreased, gradually, to about 650 W/m^2 by the end of it at about 13:40 local time. The temperature of our receiver rose rapidly after the doors were opened, to about 2100K. When the feedwater was turned on the temperature dropped slightly, and then continued its rise, reaching its highest value, about 2150K, at about 12:45. Thereafter the trend in temperature was generally downward, but, after the H_2O supply had been turned off near the end of the experiment, it started upward again. The pressure in the system rose continuously as H_2O was being fed to it, and started to decrease when the H_2O supply was turned off; the behavior of the system was what one would expect of a system with a large capacity and long characteristic fill and pump-down times. The gas production rate shown on the figure, actually the pumping rate, correlated well with the pressure. The gas is presumed to have been a stoichiometric H_2-O_2 mixture. The bubbles and samples we collected over water exploded noisily upon being ignited by small flames.

DISCUSSION

During the course of the experiment, 106 moles of water was fed to the system. At the conclusion of the experiment, about half of it was recovered where it had condensed in the feed lines. The ambient temperature was about 270K. The total gas production, measured by integration of the gas flow rate shown in Fig. 5, was 0.35 moles, the product from 0.24 moles of H_2O. The fraction of the water which was recovered as H_2 and O_2 after having been passed through the reactor was 0.0045.

Table 3 gives the equilibrium composition of water at 2125K and 0.02 atm, a state which is representative of that of the reactor during the course of the experiment. The first column of the second section of Table 3 gives the mole fractions of the quenched products if the amount of water does not change at all during the quench process; the second gives the mole fractions of the quenched products if all the oxygen which is bonded to hydrogen is ultimately found in water. The third section of Table 3 gives the fraction of the water that would have been split in a perfect quench from 2125K according to the two schemes. The maximum yield, for a perfect quench, would thus correspond to a splitting of 0.038 to 0.047 of the feedwater. Our experiment thus yielded a split, achieved by quenching, of between 0.10 and 0.12 of the very best that might have been expected.

CONCLUDING REMARKS

Quenched mixtures of H_2 and O_2, especially those from which most of the H_2O has been condensed, could be brisantly explosive over an extremely wide range of compositions. We have observed that such mixtures can be produced by quenching the effluent from a solar furnace operating in the temperature range 2075-2150K at low pressures, of the order 0.01-0.02 atm. At higher pressures, the degree of quenching might be substantially less. Nevertheless, it would appear that quenching offers possibilities which deserve further exploration. However one conducting such studies should take appropriate precautions, especially when dealing with gaseous products from which H_2O has been removed.

Some time ago, Reppe[23] was able to develope techniques for handling acetylene at high pressures, although it is unstable and detonable, by making use of capillary tubes as reactors to quench incipient explosive reactions. Perhaps a similar approach might be used to safeguard H_2-O_2 mixtures as they are being separated by the appropriate low-temperature membranes.

Acknowledgement-- We would like to thank the Northern States Power Company for the gift of the flat solar collectors, and D. Bittker, V. Scullin, and K. Teichman for their help with the computor program. We were supported, in part, by grants from the Office of Naval Research, Contract N00014-82-k-0523, and by the Department of Energy, Contract DE-AC02-82ER12089.A000 during the period of this research. We are grateful for this support.

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Table 1. Mole Fractions of the Components of the Equilibrium Mixtures at 2500K. Although HO_2 is included in rate calculations, it is not included in the table because its mole fraction is $<10^{-7}$

Species	H/O = 1.8, P = 0.04 atm	H/O = 2.2, P = 0.01 atm
H	0.0360	0.1044
H_2	0.0820	0.1726
H_2O	0.7295	0.5840
OH	0.0590	0.0651
O	0.0210	0.0319
O_2	0.0725	0.0419

Table 2.a Mole Fractions of Components

Oxygen Rich Mixtures, H/O = 1.8, P = 0.04 atm.

T_{quench}	2400	2000	1600	1200	800
After 1.001 sec					
H	0.0205	0.0008	< 0.0001	< 0.0001	< 0.0001
H_2	0.0592	0.0070	0.0006	0.0007	0.0002
H_2O	0.7929	0.9293	0.9467	0.9460	0.9483
OH	0.0497	0.0101	0.0017	0.0007	< 0.0001
O	0.0115	0.0009	< 0.0001	< 0.0001	< 0.0001
O_2	0.0662	0.0518	0.0508	0.0524	0.0515
$HO_2 x 10^5$	0.301	0.0616	0.0068	0.0046	0.0083
With H_2O content frozen at 1.001 sec value and condensed to recombine remainder to H_2 and O_2					
H_2O (1)	0.8058	0.9301	0.9468	0.9461	0.9483
H_2 (g)	0.0958	0.0125	0.0015	0.0011	0.0002
O_2 (g)	0.0984	0.0574	0.0517	0.0528	0.0515
H_2 in gas mixt	0.4933	0.1789	0.0279	0.0203	0.0040
With H_2O content determined by OH and H_2O content after 1.001 sec.					
H_2O (1)	0.8784	0.9449	0.9490	0.9471	0.9484
H_2 (g)	0.0465	0.0024	---	0.0004	0.0002
O_2 (g)	0.0751	0.0526	0.0510	0.0525	0.0515
H_2 in gas mixt	0.383	0.044	---	0.007	0.003

Table 2.b Mole Fractions of Components

Hydrogen Rich Mixtures, H/O = 2.2, P = 0.01 atm.

T_{quench}	2400	2000	1600	1200	800
After 1.001 sec					
H	0.0696	0.0286	0.0407	0.0536	0.0769
H_2	0.1519	0.1105	0.1049	0.0886	0.0644
H_2O	0.6762	0.8240	0.8249	0.8448	0.8517
OH	0.0549	0.0202	0.0118	0.0004	0.0003
O	0.0165	0.0041	0.0039	0.0003	0.0006
O_2	0.0309	0.0126	0.0138	0.0124	0.0060
$HO_2 x 10^5$	0.1058	0.0111	0.0022	0.0006	0.0002
With H_2O content frozen at 1.001 msec value and condensed to recombine remainder to H_2 and O_2					
H_2O (l)	0.7066	0.8377	0.8437	0.8682	0.8861
H_2 (g)	0.2238	0.1372	0.1342	0.1188	0.1072
O_2 (g)	0.0696	0.0251	0.0211	0.0131	0.0068
H_2 in gas mixt	**0.7628**	**0.8452**	**0.8585**	**0.9010**	**0.9405**
With H_2O content determined by OH and H_2O content after 1.001 sec.					
H_2O (l)	0.7865	0.8671	0.8607	0.8688	0.8866
H_2 (g)	0.1713	0.1179	0.1232	0.1184	0.1068
O_2 (g)	0.0421	0.0150	0.0162	0.0128	0.0066
H_2 in gas mixt	**0.8027**	**0.8870**	**0.8840**	**0.9021**	**0.9418**

Table 3. Mole Fractions of Components
H/O = 2, P = 0.02 ATM, T = 2125K

Equilibrium Composition	
H	0.00492
H_2	0.03700
H_2O	0.92766
OH	0.01319
O	0.00159
O_2	0.01564

	H_2O conserved	O-H conserved
H_2O (l)	0.93068	0.95020
H_2 (g)	0.04621	0.03320
O_2 (g)	0.02311	0.01660
Yield	0.047	0.038

FIGURE CAPTIONS

Fig. 1. Variation of the mole fractions of the components of stoichiometric (H/O = 2) mixtures. The initial composition is that of equilibrium H_2O at 3000K and 1 atm. The quench temperature is assumed to be constant and is 2000K; the pressure is 1 atm. The starred curves are the results of calculations which included HO_2 among the products. The unstarred curves are the results of the calculation which did not include HO_2 as a product. Although the presence of HO_2 is kinetically significant, it is present in very low concentrations. Its mole fraction has been multiplied by 1000 in this figure. The inclusion of HO_2 in the computation increases substantially the rate at which the fragments recombine to form H_2O during the first millisec., which is, incidentally, about the same period of time that would be required for passage of the gas through a de Laval nozzle, although in the nozzle, the temperature and pressure would be continuously decreasing. In our subsequent calculations, we conducted the integration in two steps. The first covered the first millisec.; the second covered the next second.

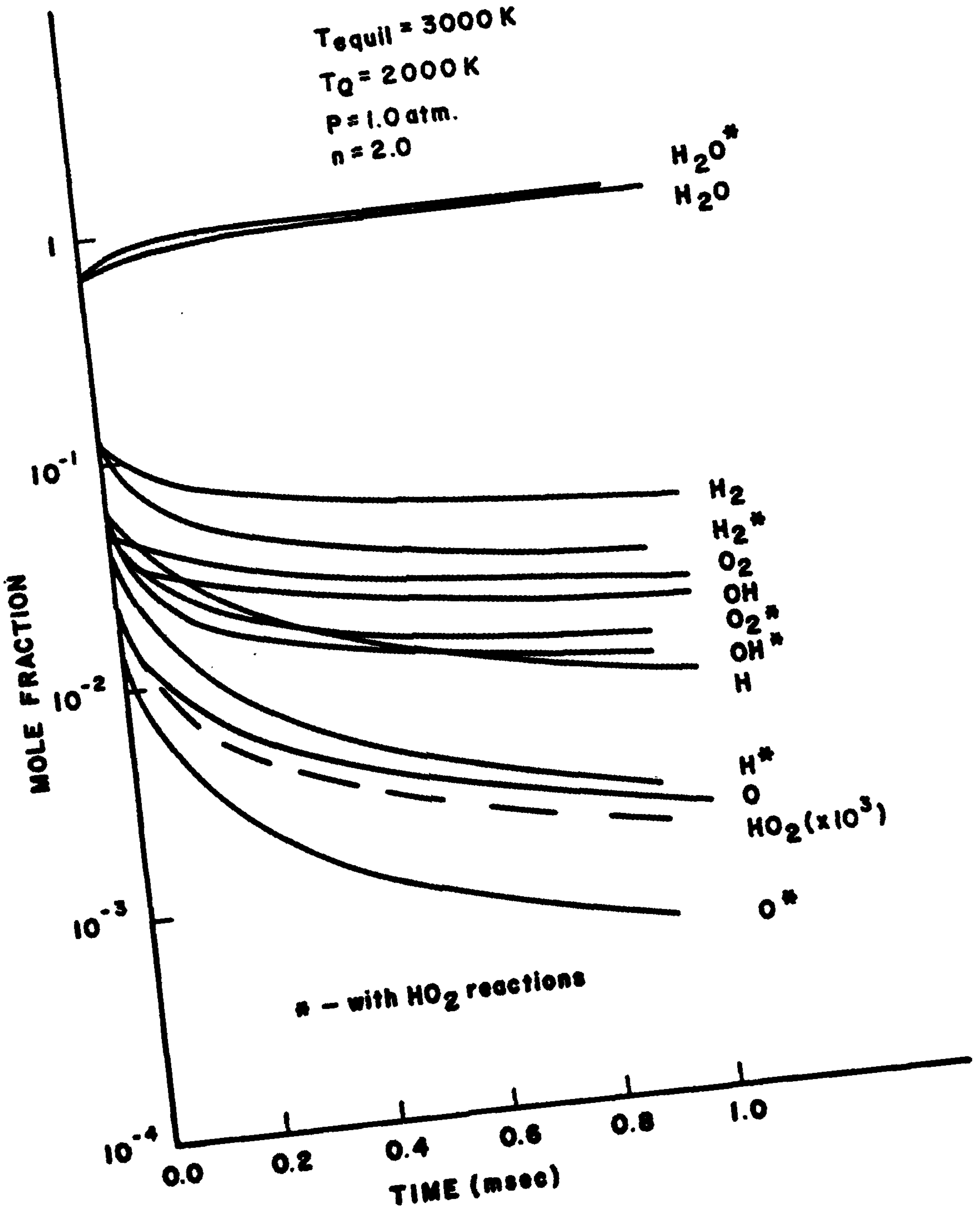
Fig. 2. Variation, with time, of the mole fractions of the components of a 2500K, 0.01 atm equilibrium mixture with H/O ratio equal to 2.2, when the temperature is instantly reduced to 800K; a, during the first millisecond; b, during the subsequent second. The equilibrium composition of such a mixture at 800K would consist only of H_2O (mole fraction 0.9091) and H_2 (mole fraction 0.0909). It is evident that there will be a substantial amount of unrecombined H_2 and O_2 in the mixture at 800K and, if the compo-

sition does not change much more as the mixture is also cooled and compressed to condense the H_2O, the remaining gas phase will be an explosive mixture of H_2 and O_2, with H_2 mole fraction of about 0.90.

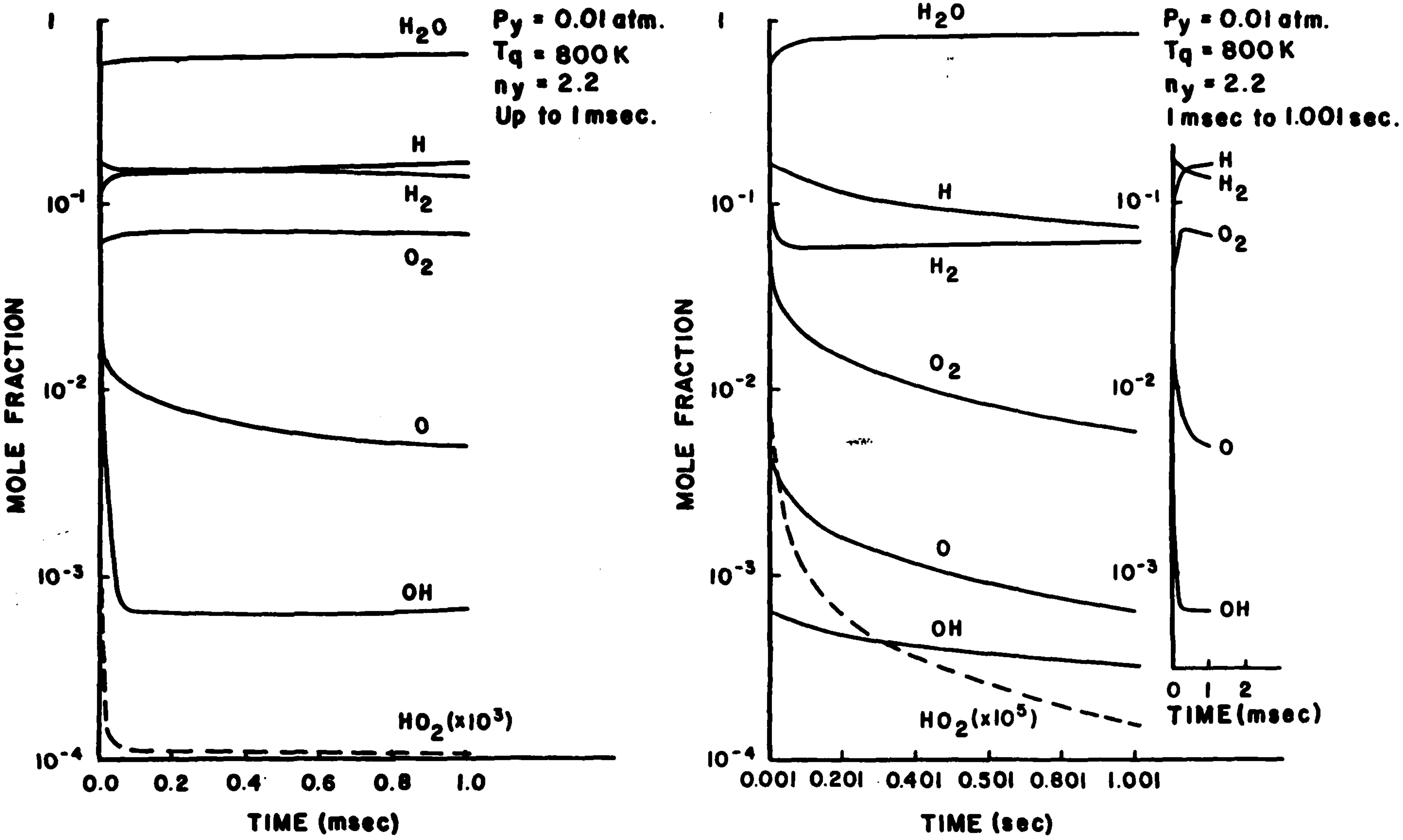
Fig. 3. Schematic diagram of the experimental apparatus.

Fig. 4. Schematic diagram of the reactor.

Fig. 5. Time history of the experimental variables and observations.



DIVER - Figure 1



a

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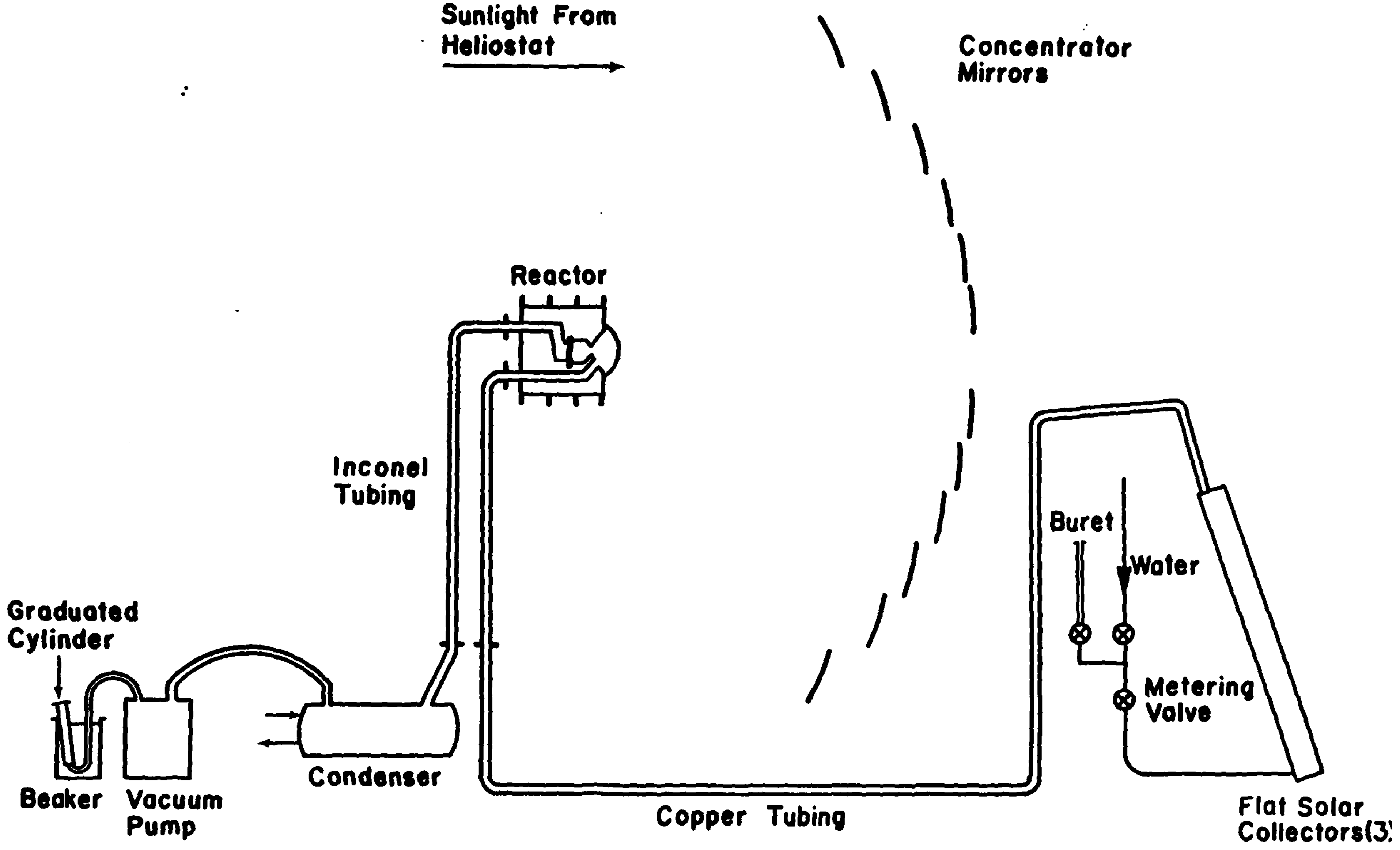
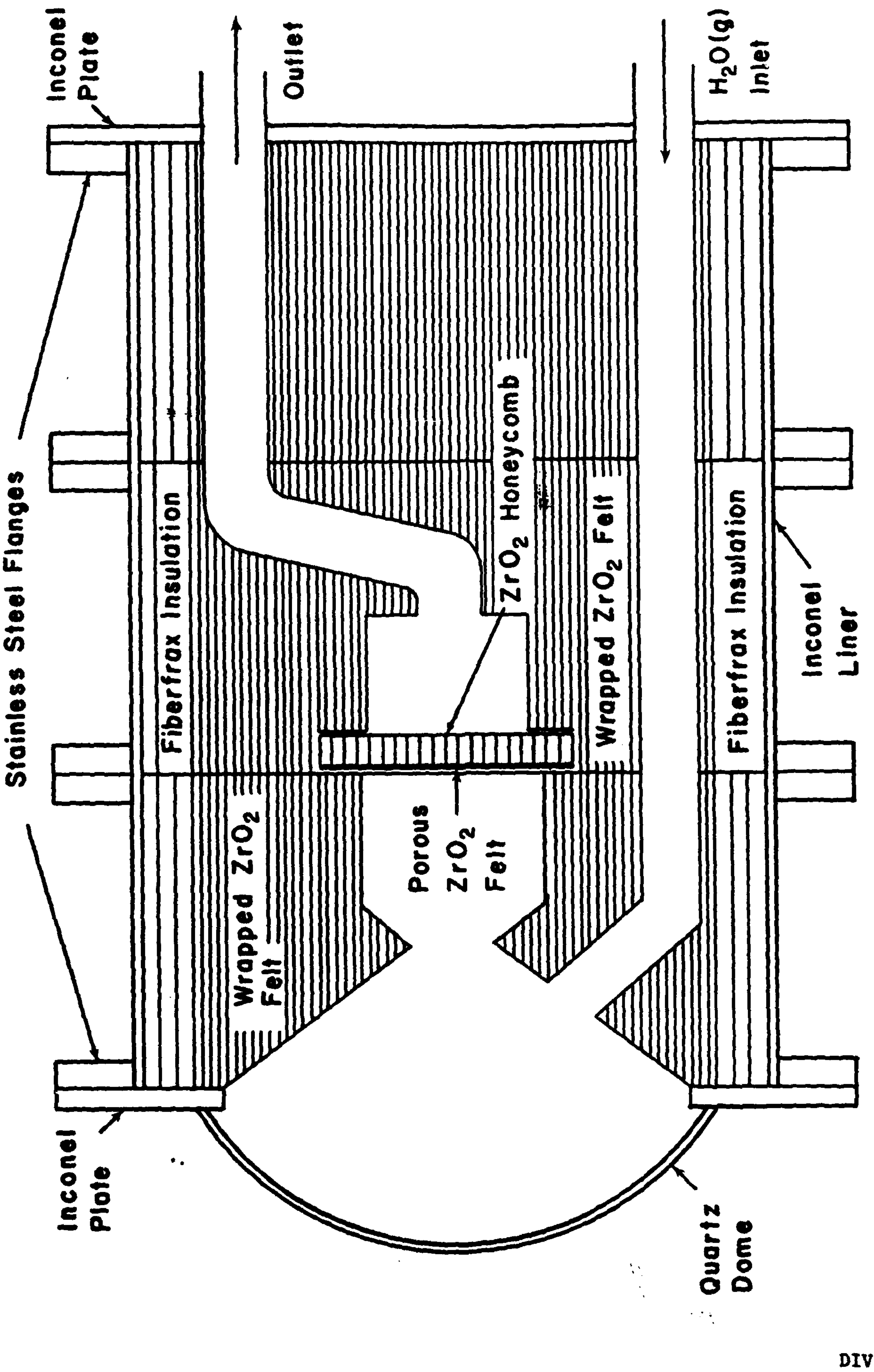
DIVER - Figure 2



DIVER - Figure 3



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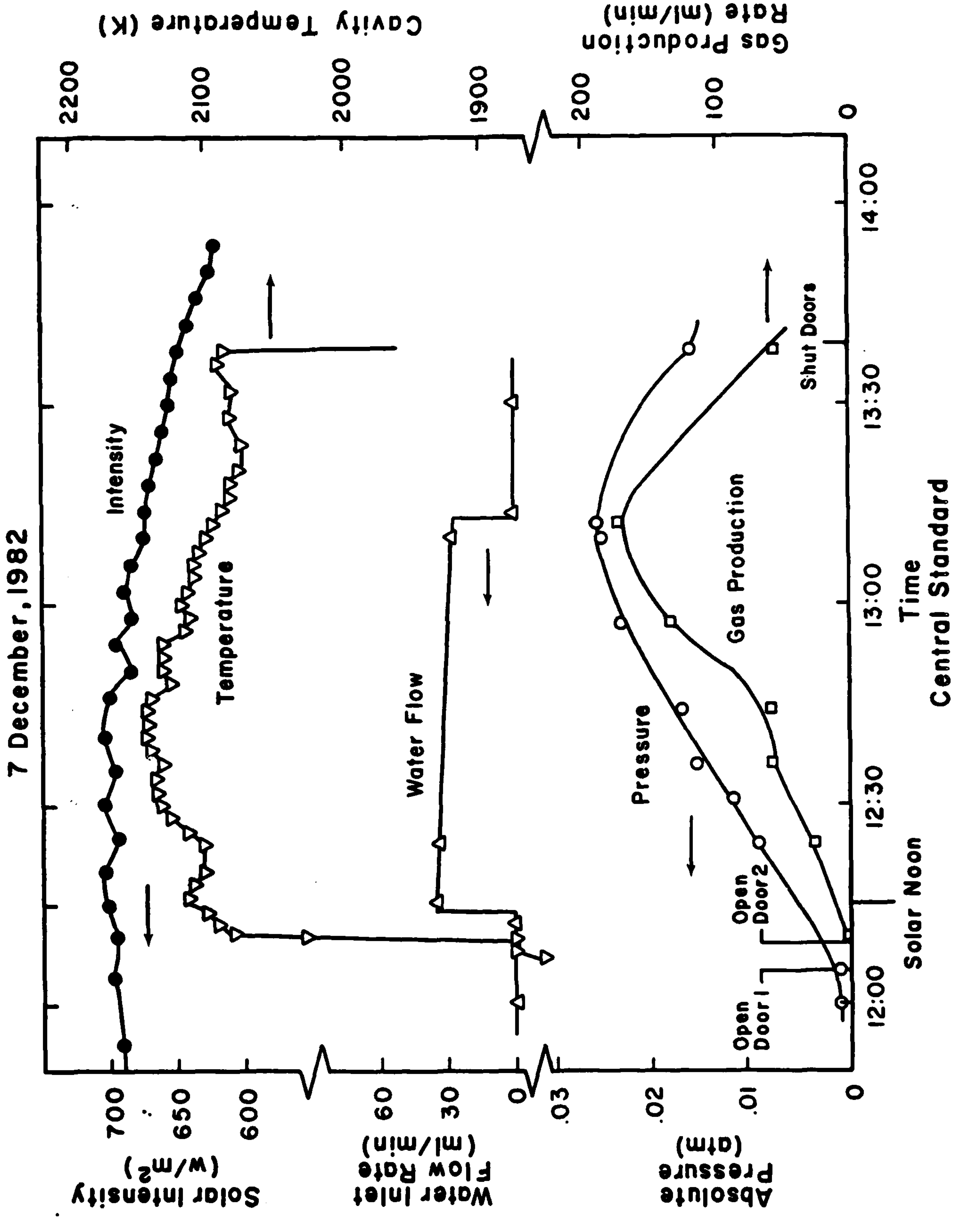

DIVER - Figure 5