# KINETIC STUDY OF ELECTRICALLY ACTIVATED REACTING SYSTEMS AT RELATIVELY LOW TEMPERATURE LEVELS

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Abstract

Further study on some basic theoretical aspects has been carried out. It was proposed that the local surface field resulted from the roughness of the surface of conductor be used in determining the density of field emission current by the Fowler-Nordheim equation, instead of the externally applied field. Accordingly, metal surfaces having definite roughness are being considered for the theoretical models as well as experimental electrodes. Once the surface field has been precisely defined the identification and characterization of the species under the influence of field emission may be properly analyzed and their interactions closely studied.

Due to the unexpected difficulty met in obtaining the high temperature reactor, a readily available Pyrex-glass reactor was used for the preliminary investigation of the reaction between $H_2$ and $I_2$ and that between $N_2$ and $H_2$ at temperatures below 200°C and 1 atm. (the conditions quite different from those originally planned). Many difficulties encountered were discussed with the experimental results obtained and recommendations for future work were made. These recommendations include the modification of reactor and electrodes, the better sampling technique and the quenching of the gas product.

I. Theoretical Work

Further theoretical analysis has been carried out, in particular, on the following aspects:

a) Field Emission from Surface of Definite Roughness - Metal surfaces having definite roughness are being used as theoretical model as well as experimental electrode for the exact determination of surface field strength needed in calculating the density of the field emission current $j$ by the Fowler-Nordheim equation:

$$j = 6 \times 10^{-6} \frac{\sqrt{E_F / e\varphi}}{E_F + e\varphi} X^2 \exp\left(\frac{-6.8 \times 10^7 \varphi^{\frac{3}{2}}}{X}\right)$$

where $X$ is surface field in v/cm

$E_F$ is the Fermi level in cv

$e\varphi$ is the work function in cv

$j$ is the current density in amp/cm$^2$

It is considered that the surface field resulted from the local roughness be used in the determination of the density of the field emission current instead of the external field applied. The local surface field strength may be indefinitely greater than the external field applied, depending on the dimension of the surface roughness of the conductor used. In this phase of the analysis the effects of adsorbed chemical species are not taken into consideration.

b) Identification and Possible Characterization of the Excited Species under Field Emission - Consideration is being given to the molecular orientation within the local surface field, the polarization of these species resulted from the changes in their electrostatic characteristics, and to the variation in bond lengths, angles and strength, etc.

c) Interaction between Excited Species in the Surface Field - Consideration in this respect is mainly on qualitative and semi-empirical bases. When sufficient data have been obtained some hypotheses developed would be tested using these data.

II. Experimental Work

1. Preliminary Investigation of Reaction, $H_2 + I_2 \rightleftharpoons 2HI$

As reported previously (1), aside from the Vycor-glass reactor all the components in the experimental devices to be used for the proposed study of this reaction were designed and constructed here at Villanova. These components were already described in the previous progress report (1). The Vycor-glass reactor as shown in Figure 1 was ordered to be made by the Corning Glass Company, Corning, New York in February, 1966 as reported previously; but after a long wait the order was cancelled by the Company in June, 1966 for reasons unknown. Therefore, it was immediately decided to use fused quartz as the material for the reactor; and two units of quartz reactors of the same dimensions were ordered to be made immediately by the Amersil Quartz Division, Engelheard Industries Corporation, Hillside, New Jersey. In spite of constant urging by Villanova University, the reactors were not received until the middle of December, 1966. Furthermore, the flanges needed for each reactor component were not made as specified, requiring some modification in the design before they can be used.

In June, 1966 when it was discovered that the Vycor-glass reactor would not be available and that there was no real guarantee that the quartz reactor would be available in four weeks as promised by the Amersil Quartz Division it was decided to change the original experimental plans and to try some gaseous reactions at much lower temperatures using Pyrex-glass reactor of the same design which was readily available.

At first, the possibility of running the reaction, $H_2 + I_2 \rightleftharpoons 2HI$ at lower temperatures was carefully investigated, and some preliminary experiments were carried out on regulating the extremely small feed rates of $I_2$ vapor. As previously reported (1), this reaction was originally planned to be run at around 600°C in order to obtain the necessary conversion for chemical analysis of the product gases and at

the same time to avoid the significant reverse reaction usually accompanying the forward reaction at temperatures above 600°C (2). But, the reaction temperature highest permissible in Pyrex-glass reactor was about 200°C. Since the boiling point of $I_2$ is 185°C, the maximum temperature difference obtainable between the $I_2$ - sublimer and the reactor would be 15°C. This fact created considerable difficulties in maintaining the necessary temperatures between the two equipments. Furthermore, as shown in the table below the rate of the forward reaction decreases very rapidly as the temperature decreases.

| Temperature (°K) | Forward Rate Constants (g-mols/sec) |
|---|---|
| 556 | $4.44 \times 10^{-5}$ |
| 624 | $2.25 \times 10^{-3}$ |
| 666 | $1.415 \times 10^{-2}$ |
| 700 | $6.0 \times 10^{-2}$ |
| 781 | 1.336 |

The activation energy for the forward reaction was found to be 44.0 k. cal/g-mol and that of the reverse reaction was 39.0 k. cal/g-mol (3). This would give the rate constant value of about $10^{-7}$ g-mols/1/sec at around 200°C. Considering the minimum concentration of HI required for IR spectrometric analysis and the reaction rate obtainable at around 200°C the necessary feed rate of $I_2$ vapor that must be maintained in the reactor was determined to be:

0.0003245 moles/sec., or 0.0875 gms/sec.

After an extensive experimental study, it was concluded that it is just not practical to maintain this extremely small rate of sublimation since the sublimation process is controlled by the surface area of solid $I_2$ as well as by other factors including heat transfer rate etc. It was also found very difficult to prevent recondensation of this extremely small amount of $I_2$ vapor without overheating the reactor, which must be

maintained at a temperature below 200°C.

In addition to the operational difficulties encountered, the difficulties caused by the unfavorable kinetic behavior of the system at temperatures much lower than 600°C were also experienced. Consider the possibility of non-elastic, activated collision between $H_2$ molecules and $I_2$ molecules at temperatures between 200° and 600°C. Approximate calculation from the kinetic theory shows that the temperature co-efficient in terms of the activation energy included in the Boltzman Factor should be much greater than 44 k. cal for the forward reaction as experimentally determined (3). Considering also the facts that the heat of this reaction is only +3 k. cals and the bond dissociation energies of $I_2 \longrightarrow 2I$ is about 40 k. cals. It is very probable that the forward reaction may not proceed if $I_2$ molecules do not decompose into I atoms at low temperatures of around 200°C. Benson and Srinivasan have pointed out that at temperatures below 600°C $I_2$ molecules would not decompose into atoms to any appreciable extent (2). From the above reason it appears that some means such as photochemical technique would be necessary to decompose $I_2$ molecules into I atom in order to have the reaction between $H_2$ and $I_2$ at the lower temperatures employed. This had not been taken into account before this experiment was made since the reaction was originally planned to run at around 600°C, and had been considered to be a simple homogeneous bimolecular reaction. Furthermore, the role of the step of $I_2$ molecule decomposition and the interaction of this step with the probable next step, $H_2 + 2I \rightleftharpoons 2HI$ can only be studied after one has made the careful analysis of the theoretical aspects and the complete preparation of the necessary experiments. Effort is being made in this regard by the principal investigator. At the same time, some consideration on the possibility of decomposition of $I_2$ molecules by field emission is also being given. The progress made in this respect, would be reported in the future.

2. Investigation of Homogeneous Reaction between $H_2$ and $N_2$

Because of the experimental difficulties encountered in carrying out the kinetic study of reaction $H_2 + I_2 \rightleftharpoons 2HI$ (or, $I_2 \rightarrow 2I$, $H_2 + 2I \rightarrow 2HI$) at lower temperatures as described above, it was considered desirable to experiment another gaseous reaction. The homogeneous reaction, $N_2 + 3H_2 \rightleftharpoons 2NH_3$ was chosen for the reasons:

(1) The reaction promoted by catalysts has been well investigated by a great many workers, and by the principal investigator. He has studied the effects of static charges and of field generated in the catalyst bed upon the rate and the conversion of this reaction at higher temperatures ($300^o$ - $400^oC$) and 1 atm (4). The possibility of carrying out this reaction with no catalyst has been studied by many workers, but no successful result has been reported in the literature. By the application of static electric field the principal investigator was able to initiate the homogeneous reaction at temperatures above $850^oC$ and 1 atm., and has confirmed that the homogeneous reaction in a static electric field is feasible at these temperatures without using high pressure (5). It was not known, however, if the same reaction is feasible at lower temperatures, viz. below $200^oC$.

(2) This reaction can be studied immediately using the available equipment without too much further preparation. (N. B. It should be recalled that all the original experimental plans were made for much higher temperatures; and as soon as quartz reactor has become available the experiments at higher temperatures would be started since they are much preferable for those reactions intended in this study).

2-a) Construction and Testing of Equipment:

The support equipment for the reactor such as the preheaters were to be designed so that they could be used at the low temperatures necessary in this preliminary investigation and also for higher temperatures when the quartz reactor arrived. Many unforseen difficulties were met in designing the preheaters and in preventing contamin-

ation. Heating and temperature controlling were problems because of the low gas flow rates necessary to give reasonable residence times within the reactor. These flow rates were in the laminar flow range where the heat transfer film coefficients are very small. Because of these low flow rates it was also difficult to maintain the temperature of the gas once it was reached. This was due to the low heat capacity of the small volume of gas relative to the great heat capacity of the system (reactor etc.)

The first preheater tried was made from a 2 in. diameter stainless steel (s. s.) pipe, 1 1/2 ft. long. The pipe was packed with s. s. wool (1/48 in width, 1/1000 in thickness) to increase the mixing and the linear flow rate of the gas and in turn the heat transfer coefficient. The packing also gives a much higher surface area for heat conduction. The pipe was heated on the outside wall by resistance wire and insulated with asbestos fiber. It was found that the s. s. wool could not be packed as tightly as presumed and therefore the porosity was not as small as expected when the preliminary calculations were made. Therefore, while the preheaters attained the temperatures necessary for the low temperature study they would not give the high temperatures required at the desired flow rates for later use.

Because of the above mentioned difficulties identical preheaters were constructed from 1 in diameter s. s. pipe. These preheaters gave the desired temperature range. However, after testing the preheaters it was found that there was a contamination problem. After experiencing much difficulty it was found the contamination was due to the three causes: (1) degeneration of teflon tape used in the fittings and threads, (2) evaporation of Zn from the silver solder used in constructing the preheaters, and (3) reaction of the fine s. s. wool with the $H_2$ gas. New preheaters of identical design were then welded and packed with almina pellets instead of s. s. wool but the almina pellets also reacted with the $H_2$ gas.

It was then decided to eliminate the packing completely. New preheaters were made by coiling 10 feet of 1/4 in diameter s. s. tube inside the 2 in diameter s. s. pipe,

filling the pipe with white sand and heating the entire apparatus, as shown in Figure 2. Reactant gases are supplied from standard gas cylinders equipped with pressure reducing valves. The two gas flow rates are regulated by two separate precision needle valves and measured by two separate rotometers. The gas streams passed through the two preheaters are introduced at either end of the T-shaped reactor (see Figure 3). The reactor and electrodes are the same as described in the previous report with the exception that the reactor is made of Pyrex glass.

For the first seventeen runs, each electrode used consists of 26.8550 gms. of s.s. wool (1/48 in width, 1/1000 in thickness), and the total surface area for each electrode is 1860 $cm^2$. The distance between the two electrodes was 2 ft. (If desirable, the size of electrodes and their total surface areas can be varied by varying the amount of s.s. wool used for each electrode. The electrodes can also be set at any desired distance from zero to a maximum of 2 feet).

2-b) Procedure:

The procedure for each run was as follows: (refer to Fig. 3).

The preheaters (3) and the reactor (8) were allowed to heat up for several hours to attain the thermal equilibrium of the system. When the reactor reached the desired temperature, the controller (5) on the reactor heater (7) was adjusted to control at this temperature. The reactor was then purged with nitrogen and the desired nitrogen and hydrogen flow rates were set by setting the pressure reducer on the tanks to 10#/$in^2$ gage, and adjusting the needle valves (1) until the desired flow rates were obtained in the rotometers (2). The heat input to the two preheaters (3) was controlled by adjusting the Variacs until the two incoming gases reached equilibrium temperatures equal to the temperature of the reactor. The five thermocouples ($T_1$, $T_2$, $T_3$, $T_4$, $T_5$) whose location are shown in Figure 1 were checked with the potentiometer periodically to determine when thermal equilibrium was reached. It is normally reached about an hour after the flow rates are set.

Once thermal equilibrium was established within the reactor the thermocouples were disconnected from the potentiometer and the electrodes were set at the desired voltage and polarity by adjusting the two power supplies (4). About an hour was then allowed for the system to come to equilibrium under the influence of the field. At this point the exit stream from the reactor was diverted through the absorbing system, starting the actual run. The absorbing system was made up of two standard gas absorbing bottles (b) containing 100 ml. of a 4% by weight Boric Acid solution. The runs were continued anywhere from a half hour to two hours before the field was turned off and the final reading of the temperature was made. The duration of steady state run was then recorded. The absorbing fluid was then checked for any $NH_4$ + ions. These would have been formed by the reaction of any $NH_3$ in the exit stream with the Boric Acid. A qualitative test was first used to determine if any ammonia had been formed. A piece of filter paper was soaked with Nessler's reagent which was then dipped in a small sample of the absorbent. If there were even a small trace of $NH_4$ +ion the paper would turn yellow.

Table 1 is a summary of the first seventeen runs made. The average temperature in the reactor was determined from the temperature readings obtained from thermocouples, $T_2$ and $T_3$ shown in Figure 1. The two temperature readings in most of the runs carried out vary at most $1^o$ to $2^oC$. The volumetric gas rates were measured at the room temperature, but the values given were based on the average temperature in reactor. No trace of $NH_3$ was detected in the exit gases in all the runs. But in the separate runs identical to Runs 8, 9, 12, and 13, it has been found that detectable amounts of $NH_3$ were contained in $N_2$-electrode zone when the electrode was negatively charged.

Table 1. Experimental Results

NB - EX: sampled from the exit stream; $N_2$*, $H_2$*: sampled from $N_2$-side and $H_2$-side electrodes, respectively.

| Exp'l Run | Field Applied (volts) | | Average Temp. (°C) | | Feed Rates (cc/min) | | Partial Press. (atm) | | Reaction Duration (min) | $NH_3$ formed | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $N_2$ | $H_2$ | Low | High | $N_2$ | $H_2$ | $N_2$ | $H_2$ | | Ex. | $N_2$* | $H_2$* |
| 1 | 0 | 0 | 166.0 | 166.5 | 490 | 1475 | 0.25 | 0.75 | 30 | non | non | non |
| 2 | 0 | 0 | 157.5 | 159.0 | 477 | 1435 | 0.25 | 0.75 | 30 | non | non | non |
| 3 | 0 | -10,000 | 157.5 | 157.5 | 477 | 1435 | 0.25 | 0.75 | 30 | non | non | non |
| 4 | 0 | -10,000 | 157.3 | 157.5 | 477 | 1435 | 0.25 | 0.75 | 30 | non | non | non |
| 5 | 0 | -10,000 | 186.8 | 188.0 | 515 | 1545 | 0.25 | 0.75 | 120 | non | non | non |
| 6 | +10,000 | 0 | 186.8 | 186.8 | 515 | 1545 | 0.25 | 0.75 | 45 | non | non | non |
| 7 | +10,000 | 0 | 168.0 | 168.3 | 495 | 1480 | 0.25 | 0.75 | 240 | non | non | non |
| 8 | -10,000 | 0 | 189.0 | 189.0 | 295 | 2950 | 0.091 | 0.909 | 60 | non | trace | non |
| 9 | -10,000 | 0 | 189.0 | 189.0 | 295 | 2950 | 0.091 | 0.909 | 30 | non | trace | non |

Table 1. Experimental Results (continued)

NB - EX: sampled from the exit stream; $N_2$*, $H_2$*: sampled from $N_2$-side and $H_2$-side electrodes, respectively.

| Exp'l Run | Field Applied (volts) | | Average Temp. (°C) | | Feed Rates (cc/min) | | Partial Press. (atm) | | Reaction Duration (min) | $NH_3$ formed | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $N_2$ | $H_2$ | Low | High | $N_2$ | $H_2$ | $N_2$ | $H_2$ | | Ex. | $N_2$* | $H_2$* |
| 10 | -10,000 | -10,000 | 183.3 | 183.3 | 290 | 2900 | 0.091 | 0.909 | 30 | non | non | non |
| 11 | -10,000 | -10,000 | 182.3 | 182.3 | 290 | 2900 | 0.091 | 0.909 | 60 | non | non | non |
| 12 | -10,000 | +10,000 | 188.8 | 188.8 | 295 | 2950 | 0.091 | 0.909 | 30 | non | trace | non |
| 13 | -10,000 | +10,000 | 188.8 | 188.8 | 295 | 2950 | 0.091 | 0.909 | 30 | non | trace | non |
| 14 | +10,000 | +10,000 | 179.8 | 180.0 | 288 | 2880 | 0.091 | 0.909 | 30 | non | non | non |
| 15 | +10,000 | +10,000 | 180.0 | 180.3 | 288 | 2880 | 0.091 | 0.909 | 30 | non | non | non |
| 16 | +10,000 | -10,000 | 178.5 | 179.0 | 287.8 | 2878 | 0.091 | 0.909 | 30 | non | non | non |
| 17 | +10,000 | -10,000 | 179.0 | 179.0 | 287.8 | 2878 | 0.091 | 0.909 | 30 | non | non | non |

III. Discussions and Recommendation

1. At about 200°C and 1 atm. the value of chemical equilibrium constant, K for reaction, $N_2 + 3H_2 \rightleftharpoons 2NH_3$ is predicted to be about 0.62, indicating that the reverse reaction of $NH_3$ decomposition under these conditions is proceeding in parallel with the forward reaction. The quenching of the gas products is definitely necessary for better results. Use of liquid air or dry ice for quenching is under consideration, and may be recommended for future work on this reaction.

2. Better technique is needed for sampling the gas product near each of the electrode zones. It is interesting to note that the trace of $NH_3$ was detected in the $N_2$ electrode zone charged negatively while no trace of $NH_3$ in the exit product gases was ever detected.

3. Sparking between the electrodes and the metal flanges of the Pyrex reactor used has been the most serious difficulty encountered in the experimental work carried out. Because of the design of the Pyrex reactor readily available it was impossible to apply a static field stronger than 10,000 volts per electrode. For this reason no experimental run was made using external field greater than 10,000 volts. The problem of sparking may become less significant in a quartz reactor. But, it seems necessary that the two electrodes be relocated to provide more distance between the electrodes and the metal flanges. This would result in shorter distances between the two electrodes.

4. As described above, each s.s. wool electrode used for the first seventeen runs had surface area of 1860 $cm^2$. Considering that the s.s. wool used has smooth surface the surface charge, S generated may be calculated by the following equation:

$$E = S/De$$

where:

E = 10,000 volts per 2 feet

$= 16,400$ volts/meter

$e = 8.85 \times 10^{-2}$ farad/meter

D = dielectric constant of 1 is assumed

S = density of surface current, farad./meter$^2$

$\therefore \quad S = DeE = 1.45/\times 10^{-7}$, coul./meter$^2$

$= 1.695 \times 10^{9}$ electrons per electrode used

For runs 8, 9, 12 and 13, the feed rate of $N_2$ used was 295 cc/min or $4.68 \times 10^{21}$ molecules/min. The mean residence time of the $N_2$ gas fed within $N_2$-electrode zone is calculated to be 0.34 min. Therefore at any given time there will be $1.58 \times 10^{21}$ molecules of $N_2$ in the $N_2$-electrode zone. This gives the number of electrons per molecule to be: $1.695 \times 10^{9}$ electrons/$1.58 \times 10^{21}$ molecules $\approx 1 \times 10^{-12}$ electrons/molecules.

If one may assume that the surface potential is the same as the external field applied in the s. s. wool electrodes used, then the value of $10^{-12}$ electrons/molecule is equivalent to $10^{-8}$ eV/molecule, which is negligible compared to the ionization potential of $N_2$ molecules (15.65 eV).

5. At present time, electrode consisted of a bed of pelletted $N_i$ metal power is being developed and tested. This electrode provides extremely large surface area per unit volume and would also generate extremely strong field across each thin layer of $N_i$ power within the pellet. The exact determination of the resultant surface field and then the density of field emission current is being studied. This information is essential for further analysis of the results obtained.

## References


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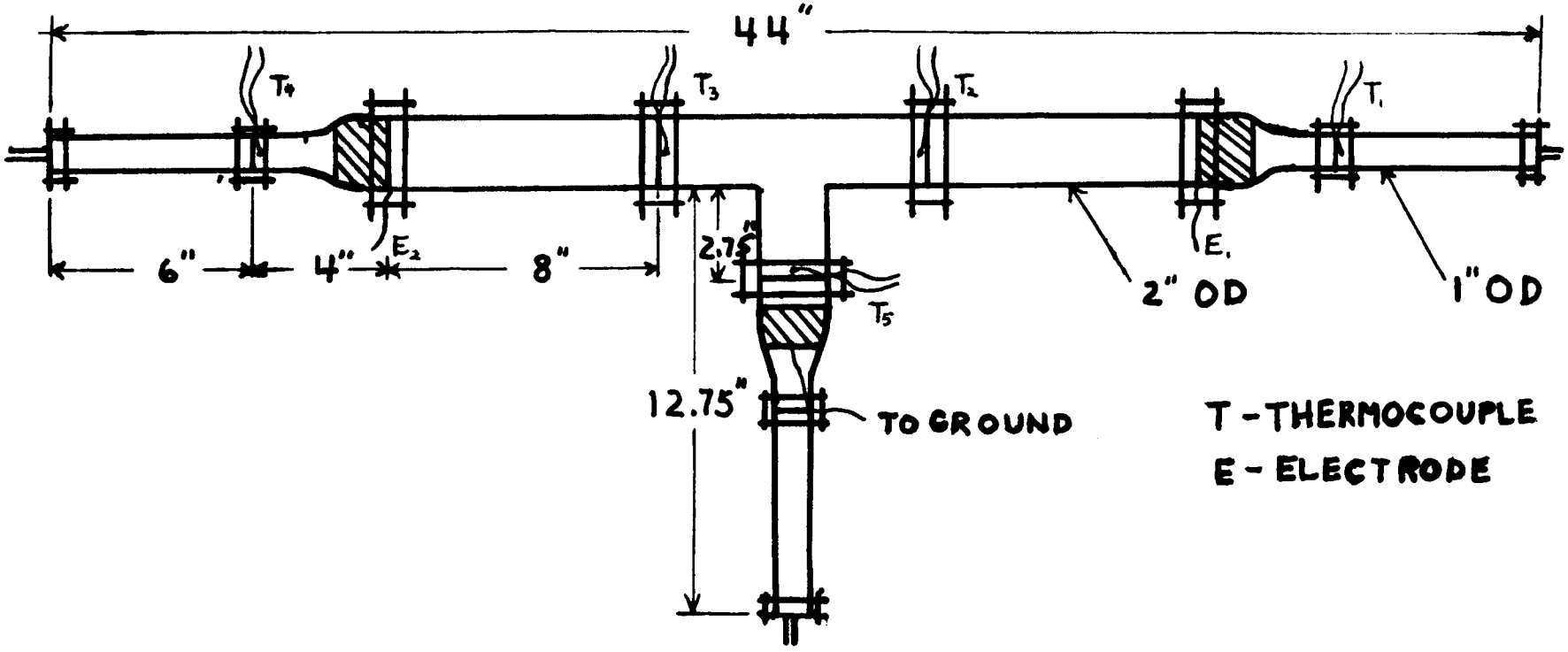


Fig. 1 REACTOR

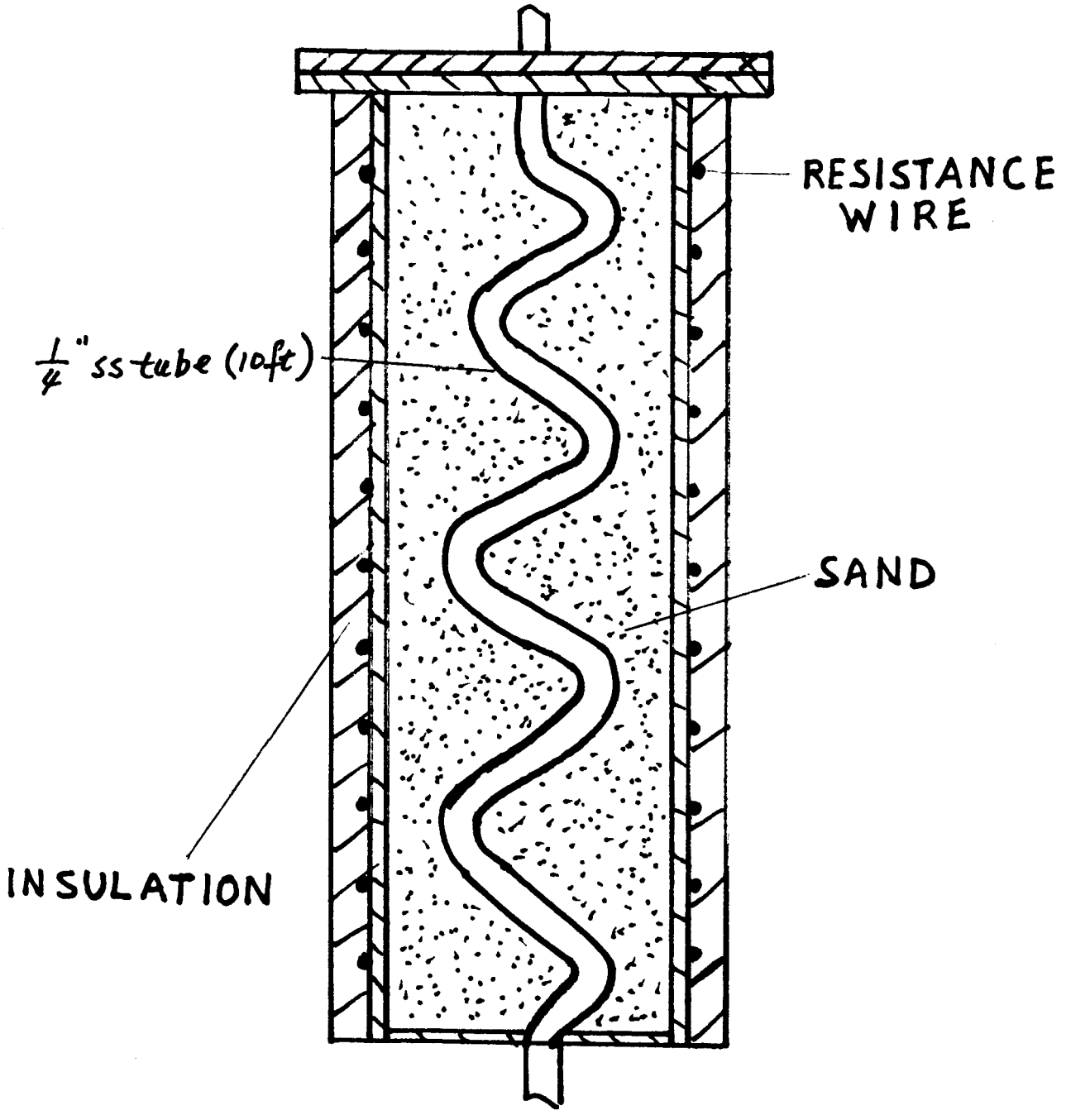


Fig. 2 Preheater

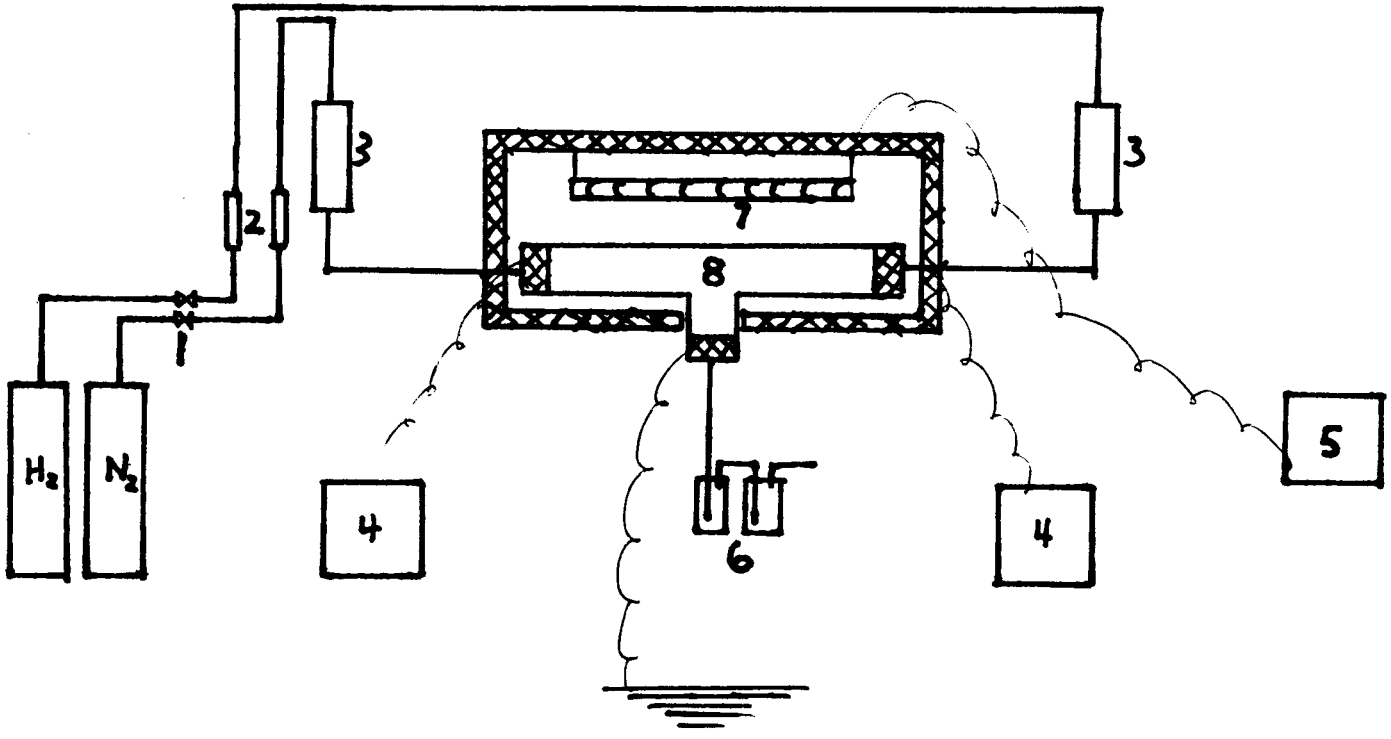


Fig. 3 Flow Sheet