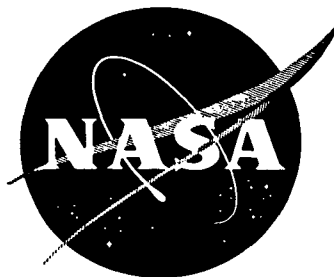


MSC-07626

NASA TECHNICAL MEMORANDUM

NASA TM X-58105
December 1972



A SOLID CERAMIC ELECTROLYTE SYSTEM FOR MEASURING REDOX
CONDITIONS IN HIGH-TEMPERATURE GAS MIXING STUDIES

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1. Report No. NASA TM X-58105		2. Government Accession No.		3. Recipient's Catalog No.	
4. Title and Subtitle A SOLID CERAMIC ELECTROLYTE SYSTEM FOR MEASURING REDOX CONDITIONS IN HIGH-TEMPERATURE GAS MIXING STUDIES				5. Report Date December 1972	
				6. Performing Organization Code	
7. Author(s) Richard J. Williams, MSC				8. Performing Organization Report No. MSC-07626	
9. Performing Organization Name and Address Manned Spacecraft Center Houston, Texas 77058				10. Work Unit No. 914-40-52-01-72	
				11. Contract or Grant No.	
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, D.C. 20546				13. Type of Report and Period Covered Technical Memorandum	
				14. Sponsoring Agency Code	
15. Supplementary Notes					
16. Abstract The details of the construction and operation of a gas mixing furnace are presented. A solid ceramic oxygen electrolyte cell is used to monitor the oxygen fugacity in the furnace. The system consists of a standard vertical-quench, gas mixing furnace with heads designed for mounting the electrolyte cell and with facilities for inserting and removing the samples. The system also contains the high-input impedance electronics necessary for measurements and a simplified version of standard gas mixing apparatus. The calibration and maintenance of the system are discussed.					
17. Key Words (Suggested by Author(s)) *Oxygen Fugacity *Gas Mixing *Electrochemical Cells *EMF Measurements *High-Temperature Systems			18. Distribution Statement		
19. Security Classif. (of this report) None		20. Security Classif. (of this page) None		21. No. of Pages 16	22. Price

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SUMMARY

A system that uses zirconia-calcia and thoria-yttria solid ceramic electrolyte cells to monitor the oxygen fugacity continuously in a standard vertical-quench furnace has been designed and built. The construction of furnace fittings using O-ring and Swagelock seals is illustrated. The use of such fittings produces a more durable and stable system. The design of the gas mixer used in this system is simpler than in other systems. Two 15-turn needle valves are used to proportion the gas, thus allowing more precise gas mixing to be done.

The operation of the system is discussed. The most common problems with the system and their resolutions are presented. Calibration procedures using solid metal/metal oxide buffers are given, and the maintenance of the system is discussed.

This system, in contrast to classical systems, is durable, simply operated, and highly accurate. Because the oxygen is measured directly, the system can be operated under conditions not possible in classical systems.

INTRODUCTION

In chemical, geological, and metallurgical investigations, it is often necessary to study the effects of high temperatures (873° to 1673° K (600° to 1400° C)) and changing redox state on chemical systems. Such studies provide information on the petrogenesis of natural and synthetic rock materials and thermochemical data. For pressures of 1 atmosphere, the most useful technique for controlling the redox state is that of gas mixing; that is, two gases that undergo reactions to produce oxygen (such as carbon monoxide (CO) and carbon dioxide (CO₂) or hydrogen (H₂) and carbon dioxide) are accurately mixed and flowed over a sample in a furnace. By using this technique, oxygen partial pressures between 10^{-24} and 10^{-3} , depending on the temperature, can be easily produced. The details of this technique are thoroughly covered in reference 1 and will not be discussed further here, except to note that expensive and delicate equipment must be used to meter the flows; that high-quality gases and special prepurification techniques must be used; and that graphite precipitation in the furnace (particularly under reducing conditions) can significantly alter the effective mixing ratio.

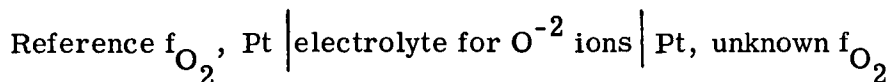
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A variety of ceramic materials are now available from which electrochemical cells can be constructed that directly sense oxygen fugacity in these high-temperature studies. The purpose of this report is to document one of these systems now in use at the NASA Manned Spacecraft Center (MSC). Hopefully, this report will answer some practical questions on how to set up such a system and aid others contemplating such studies.

Several people have been responsible for the ideas that have developed into the design of the system now in use. Most aspects are in one way or another an outgrowth of discussions with M. Sato of the United States Geological Survey. However, the greatest thanks must go to Oscar Mullins of Lockheed Electronics Corporation, who patiently helped with the building and designing of most parts of the system.

THEORY

There are various ceramics that may be used to construct electrochemical cells. Sato (ref. 2) lists these materials and extensively discusses their behavior, both in terms of the theoretical and practical details of their functioning. His article is the basic point for access to literature on electrochemical cells. For the present purposes, it is sufficient to point out that, schematically, the cell is arranged



where f_{O_2} is the fugacity of oxygen and Pt is platinum. The net reaction at the cell is $\text{O}_2 + 4e^- = 2 \text{O}^{-2}$ and thus the voltage across the cell is given by

$$E = \frac{RT}{4F} \ln \frac{f_{\text{O}_2} \text{ (unknown)}}{f_{\text{O}_2} \text{ (reference)}}$$

where E is the voltage, R is the universal gas constant, T is the temperature in °K, F is the Faraday constant, and ln is the exponential logarithm.

The two ceramic electrolytes commonly used at MSC are zirconia-calcia ((ZrO₂)_{0.85} (CaO)_{0.15}) and thoria-yttria ((ThO₂)_{0.92} (Y₂O₃)_{0.08}) ceramics. The main difference is the lower limit of the oxygen fugacity that the cells can measure; not the

voltage as a function of the oxygen fugacity. The lower response limit for the zirconia-calcia ceramic is given by

$$\log f_{\text{O}_2} = -\frac{60\,500}{T} + 23.5$$

The thoria-yttria ceramic functions to approximately 10 log units lower than the zirconia-calcia ceramic. The cells function perfectly above 873° K (600° C) and within their range of operation, and experience has shown that abnormal behavior is due to some other source of error than the cells.

SYSTEM DESCRIPTION

Furnace

The furnace used in these studies is a standard platinum resistance furnace operated in the vertical-quench mode. The heads have been modified to accommodate the electrode and quench systems. The modifications are detailed in figures 1 to 3. The most important modification is the use of a platinum-rhodium (Pt₉₀Rh₁₀) shield, composed of 0.0381-mm (0.0015-in.) thick foil, that is wrapped on the outer side of the inner muffle. Its purpose is to shield the electrode electrically from the alternating current interference from the heating coils. The shield must be continuous and must be firmly connected to the system ground. The electrode mounting must be firm to permit accurate positioning of the electrode in the furnace.

In practice, a 5.08-cm (2 in.) bore furnace is used and the heads are machined of aluminum; O-ring seals are used to position the heads and seal the gas system.

Electrode Mounting

The construction of the electrode and the fittings used to hold it in position are shown in figure 2. Several points must be made. The ceramic tubing that carries the electrode leads up the center must be continuous to ensure that the reference gas flow reaches the sensing head. It is convenient to mount the thermocouple as illustrated inside the electrode, but it must be totally insulated from the reference lead of the electrode. In this system, this is achieved by notching the four-hole thermocouple ceramic tubing and sealing the thermocouple with ceramic cement. The electrode contacts are of heavy gage 0.0762-mm (0.003 in.) platinum foil. The outer contact is perforated to permit maximum contact with the gas. The outer foil is cupped over the end of the ceramic and tied down with platinum wire. The inner contact is a crumpled piece of foil pressed against the ceramic by the four-hole ceramic tube. All lead wires are of 0.762-mm (0.03 in.) diameter platinum wire. The use of O-ring seals is most desirable because they easily take up the length changes caused by the differing thermal expansions of the ceramics. It is imperative that the metal contacts to the electrode be physically firm.

In practice, a 0.952-cm (0.375 in.) outside-diameter, 0.3985-cm (0.156 in.) inside-diameter electrolyte ceramic that is closed at one end is used. A 0.635-cm (0.25 in.) outside-diameter, four-hole, round alumina ceramic is used as the inner ceramic. The O-ring seal fittings are Cajon connectors modified to fit the ceramics used.

Quench System

In designing this system, an electrical quench system that allows rapid quenching of samples was incorporated. The components of this system are illustrated in figure 3. The bottom furnace head (fig. 1) incorporates a quench port that is sealed during furnace operation with a test tube and rubber hose that is slipped over the end of the quench port. This configuration allows easy and rapid opening and closing of the quench port without disturbing the electrode. With this type of system, it is important that the furnace be vertical and that the sample holder and quench port be carefully aligned.

Sample Holder

The sample holder is shown in figure 3. All connections are Swagelock and Cajon types to allow maximum adjustability. Because the top seal must be opened and closed often, a Teflon ferrule is used. The electrical leads are 0.762-mm (0.03 in.) Pt₉₀Rh₁₀ wire, and the actual holding wire is 0.1016-mm (0.004 in.) platinum. Gas sealing of the ceramic sheath is accomplished with RTV rubber sealant. When samples are not in the furnace, the port is sealed with a plug.

Electronics

A block diagram of the electronic components of the system is shown in figure 4(a). Because the ceramic electrolytes have an impedance of approximately 10^{14} ohms, precautions normal to high-impedance circuits must be taken. All leads must be shielded, and the metering system must be of the high-input impedance type. (In practice, electrometers or digital pH meters have been used.) All wiring must be stable and the contacts must be very firm. Finally, once a configuration of the wiring is obtained, it must not be disturbed. As a further precaution, it is wise to wipe all wires and insulation with alcohol to prevent losses because of grease or water films.

Gas Mixer

Because the electrolyte cells provide a direct indication of the conditions in the reaction zone of the furnace, gas mixer design can be much simpler than if redox conditions are adjusted by carefully controlling the ratio of gases mixed. The system used at MSC is illustrated schematically in figure 4(b). The central components of the system are two 15-turn needle valves that proportion the oxidizer and reducer. The flowmeters incorporated into the system need not be particularly accurate because

their main purpose is to monitor inflow and outflow. It is convenient to mount the whole system on a single panel and to use 0.635-cm (0.25 in.) soft copper tubing and Swagelock type connectors for the plumbing. This procedure minimizes leaks and facilitates safe operation.

In this system, gas flow in the furnace is directed from top to bottom — the reverse of classical systems. This configuration has proved to be the best for obtaining stable oxygen fugacities and for protecting the electrode.

Reference Gas

High-purity commercial oxygen is used as the reference gas. The flow is controlled with a needle valve and is monitored by a flowmeter. Small Teflon tubing (0.794-mm (0.031 in.) outside diameter), commercially available as electrical insulation, can be used to permit the introduction of the reference gas directly into the fourth hole of the inner ceramic insulator. The gas is exhausted directly into the laboratory. Small leaks in the electrode near the base will not affect the system because the gas flow pattern in the furnace will carry the reference gas out of the furnace before it reaches the hot zone. The reference gas must be flowed slowly (0.154 to 0.461 cm³/sec (0.02 to 0.06 standard ft³/hr)) to prevent cooling and thermal shocking of the electrode.

Simplification of the System

The system just described incorporates many features that would not be necessary if their convenience was not desirable. For example, the millivoltage source used to null the electromotive force (EMF) could be eliminated if the meters used can be read to the desired accuracy. The quenching system can be eliminated if the bore of the furnace is small. Quenching can then be performed by withdrawing the sample from the top. The gas distribution system can be simplified by eliminating the low-pressure regulators and using one flowmeter to monitor the flow into the furnace. Other simplifications are possible.

However, several things cannot be changed. The electronics must be of high quality. All grounds and shields in the system must be good. The electrode mounting must be as firm as possible. Gas flow should be from the top to the bottom of the furnace (that is, the gas stream should flow toward the electrode sensing head). All wiring must be physically stable.

CALIBRATION

Millivoltage Source Calibration

The millivoltage source must be calibrated against a good standard. At MSC, the calibration is against a potentiometer. If a battery-driven source is used, care must be taken to check the calibration of the source every few weeks.

Electrode Calibration

The electrode itself must be checked for correct EMF response. Most errors in calibration are due to incorrect electronic setup or incorrect placement of the sample relative to the electrode sensing area. The three most convenient calibrations are against air, the nickel-nickel oxide (Ni-NiO) buffer, and the iron-wüstite (Fe-''FeO'') buffer. The EMF of the cell in millivolts with pure oxygen as a reference is given in the following equations.

$$\text{Air:} \quad E = -0.0337T \text{ (}^\circ\text{K)}$$

$$\text{Ni-NiO:} \quad E = -1231 + 0.426T \text{ (}^\circ\text{K)}$$

$$\text{Fe-''FeO'':} \quad E = -1350 + 0.326T \text{ (}^\circ\text{K)}$$

Note that the electromotive forces are always negative; thus, the polarity of the electronic setup can be rapidly checked. The best procedure for calibrating is to check the metal/metal-oxide buffers by reversing the reactions using metal foils as starting material and duplicating as nearly as possible the physical conditions to be used in the experimentation. The use of foils is convenient because the calibration is a tarnish technique and the tarnish forms or dissipates in approximately 15 minutes.

Temperature Calibration

In this study, the thermocouple inside the electrode is used to monitor temperature. This couple is calibrated against the gold melting point again in the actual physical setup used for experimentation. Graphical temperature monitoring with automatic compensation for ambient temperature is used. Only occasional checks are made with a potentiometer.

RUN PROCEDURES

Assuming that one is starting from a completely down condition, the reference gas flow to the electrode is begun. Oxygen is used as a reference gas, and flows of 0.154 to 0.461 cm³/sec (0.02 to 0.06 standard ft³/hr) are sufficient. The temperature of the furnace is then increased generally to near 1473° K (1200° C). The EMF of the electrode is noted during heating; with the furnace open, the electromotive forces should be near those of the air/oxygen couple. In a dynamic system, these are rarely attained precisely but are used only as an indication of the status of the cell. At approximately 1473° K (1200° C), the furnace is sealed and carbon dioxide is flowed into the furnace for several hours to ensure that degassing is complete. (This degassing is particularly important with the thoria ceramics because they evolve large amounts of dissolved oxygen that must be purged from the system to ensure proper operation.)

After this "baking out," the gas flow is adjusted to an operating condition. The input and output valves to the furnace are opened full, and the mixing valves are both set half open. The gas pressure is set to approximately $2.069 \times 10^4 \text{ N/m}^2$ (3 psi) on the low-pressure regulators. The needle valve controlling the furnace outflow is slowly closed until a total flow of between 7.686 and 3.843 cm^3/sec (1.0 and 0.5 standard ft^3/hr) is attained. Then the needle valve on the input to the furnace is closed down until it just begins to affect the flow; it is then reopened slightly. From this position, the oxygen fugacity is controlled by adjusting the mixing valves. To effect a change in the fugacity of the oxygen, both valves must always be turned; one valve must be opened as the other is closed to prevent changing the total flow to the furnace.

The calibration procedure for the thermocouple and cell may now be done. Once this calibration is done, it is generally not repeated until the system is rebuilt, although the position of the buffer curves should be checked periodically. The procedure used pressurizes the furnace slightly to prevent leakage of air into the furnace. A sample is inserted into the furnace by removing the plug from the sample port and inserting the sample holder. Occasionally, a slight burnoff occurs at the top of the furnace. This is not serious if diluted gases are used; however, the sample should be inserted immediately to prevent the burnoff from entering the furnace. The temperature and the f_{O_2} may change slightly from readings made with all temperature and gas settings the same but without the sample. The orientation of the sample and the electrode can be examined with a mirror by opening the bottom quench port. Because of the gas flow pattern, the conditions in the furnace are not affected by opening this port. The quench is done by electrically burning the fine platinum wire and dropping the sample through the quench port.

After the initial run, further runs simply involve insertion and removal of samples and adjustments in gas mixing and temperature. Fluctuations of ± 2 to ± 5 millivolts are considered normal. The EMF is read by nulling the cell output with the millivoltage source and is monitored continuously by graphical output. The temperature is also continuously monitored.

Precautions

The ceramics used to make the electrodes are very sensitive to thermal shock at temperatures above approximately 773°K (500°C). Thus, once the electrode is emplaced and the heating process begun, it is best to restrict movement of the electrode to an absolute minimum. In this system, this is done by mounting the electrode so that the sensing head is in the center of the hot zone of the furnace. Any subsequent alignment is accomplished by adjusting the sample position only. To prevent thermal shocking, the reference gas flow rate is kept as low as possible.

Finally, during the cooling of the furnace, the furnace must either be opened to the air or the gas flow continued during the cooling; otherwise, a substantial vacuum can be created. A vacuum is undesirable, particularly if liquid bubble columns are used at any point in the system, because it can draw the fluid back into the furnace, producing many problems.

Common Problems

Erratic EMF output. - All shielding, grounds, and electronic connections must be checked. Leads should be firmly connected to the electrode. It should be ensured that there is no short to the temperature measurement system. In dry weather, static charges that accumulate on personnel and on laboratory fixtures can affect the cell. This is generally seen as sudden fluctuations in EMF with movement in the general area. The only solution is to keep the relative humidity in the area relatively high.

Incorrect electromotive forces. - All ground loops must be eliminated. All metal surfaces must be grounded. If these sources of error have been eliminated, the only other sources of incorrect electromotive forces are miscalibration and misalignment of sample and electrode.

Drift. - At highly reducing conditions, graphite or water or both form in the system. These clog the output flowmeters and lines affecting the gas flow in the system. The lines should be checked for condensation and cleaned. The needle valves used for mixing can and do wear out and may slip. Drift caused by changes in gas composition will be noted when bottles begin to run out, particularly if gas mixes are used (hydrogen in nitrogen or carbon monoxide in nitrogen). Drift may also occur if the metallic contact to the electrolyte is not firm.

After a cell has been used for several months, the metallic contacts grow through the ceramic to produce partial electrical short circuits. Erratic EMF outputs, incorrect EMF response, and drift can result in an unpredictable manner. This problem results only in cells which have been in continuous use for several months, and the only correct procedure is to replace completely the used cell with a new one.

Overshoot. - In adjusting the mixing ratio, changes of the gas mixture take a finite time to be effective in the furnace. This time varies with the flow rates used and with the construction of the gas mixer. Thus, it is best to adjust the mixing slowly and in small steps to prevent overadjustments. The change in the f_{O_2} and that in the mixing ratio is not linear. Thus, depending upon the particular conditions of the experiments, varying amounts of adjustment are needed to effect the same change.

MAINTENANCE

Although the lifetime of the ceramic cells is theoretically very long, in practice they function only for 6 to 8 months before some component of the system breaks down. When this happens, it is wise to run through a complete maintenance of the system that includes the following items:

1. Replace all wiring and contacts in the cell.
2. Replace shielding.
3. Check all O-ring seals and replace if needed.

4. Check plumbing and clean flowmeters and valves.
5. Check water cooling system and clean.
6. Check furnace winding by noting if its cold resistance has increased significantly above the valve for new windings; replace if necessary.

By following this procedure, it is possible to reduce downtime significantly. All items used for maintenance are minor except the shielding and furnace winding, which are major expenses.

CONCLUDING REMARKS

In addition to the desirable qualities of providing rather precise in situ measurements of the redox conditions in high-temperature systems, use of the electrode system has several other advantages. Rather than using pure hydrogen with its manifold safety hazards, safe mixtures such as 10 percent hydrogen in nitrogen can be used to eliminate virtually all explosion hazards. It should be noted that neither high-precision mixtures, high-purity gas, nor prepurification techniques are necessary, and thus large savings are generated. Extreme mixing ratios (for example, 1:10 000) can be obtained by the use of judiciously chosen mixtures. Much lower flow rates also can be used, thus reducing gas usage rates to much lower values than those used classically. Gas mixer construction is much simpler and less costly than in conventional systems.

Manned Spacecraft Center
National Aeronautics and Space Administration
Houston, Texas, December 7, 1972
914-40-52-01-72

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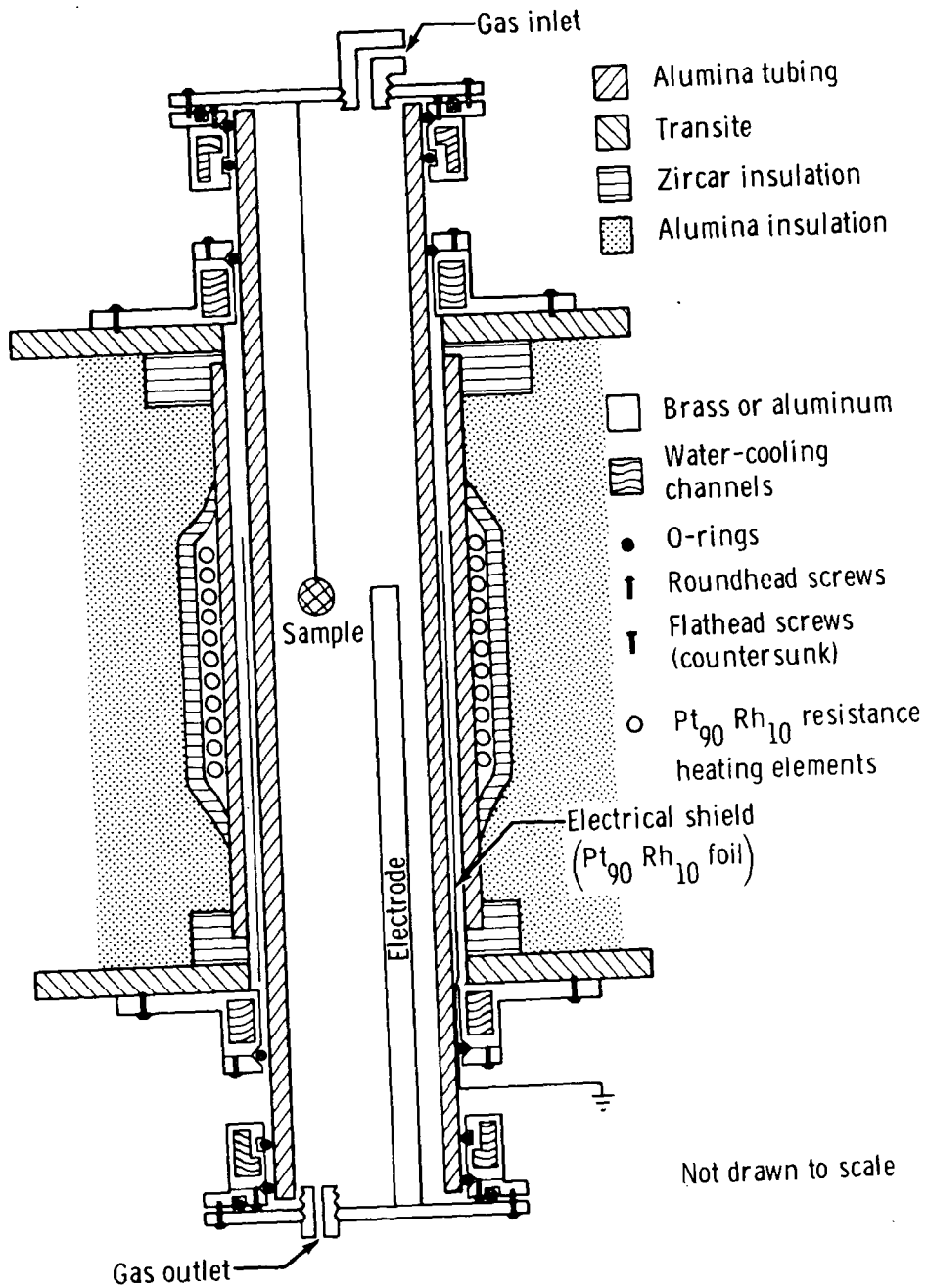


Figure 1. - Construction of furnace and water-cooling heads. The electrode and sample mountings are only schematic.

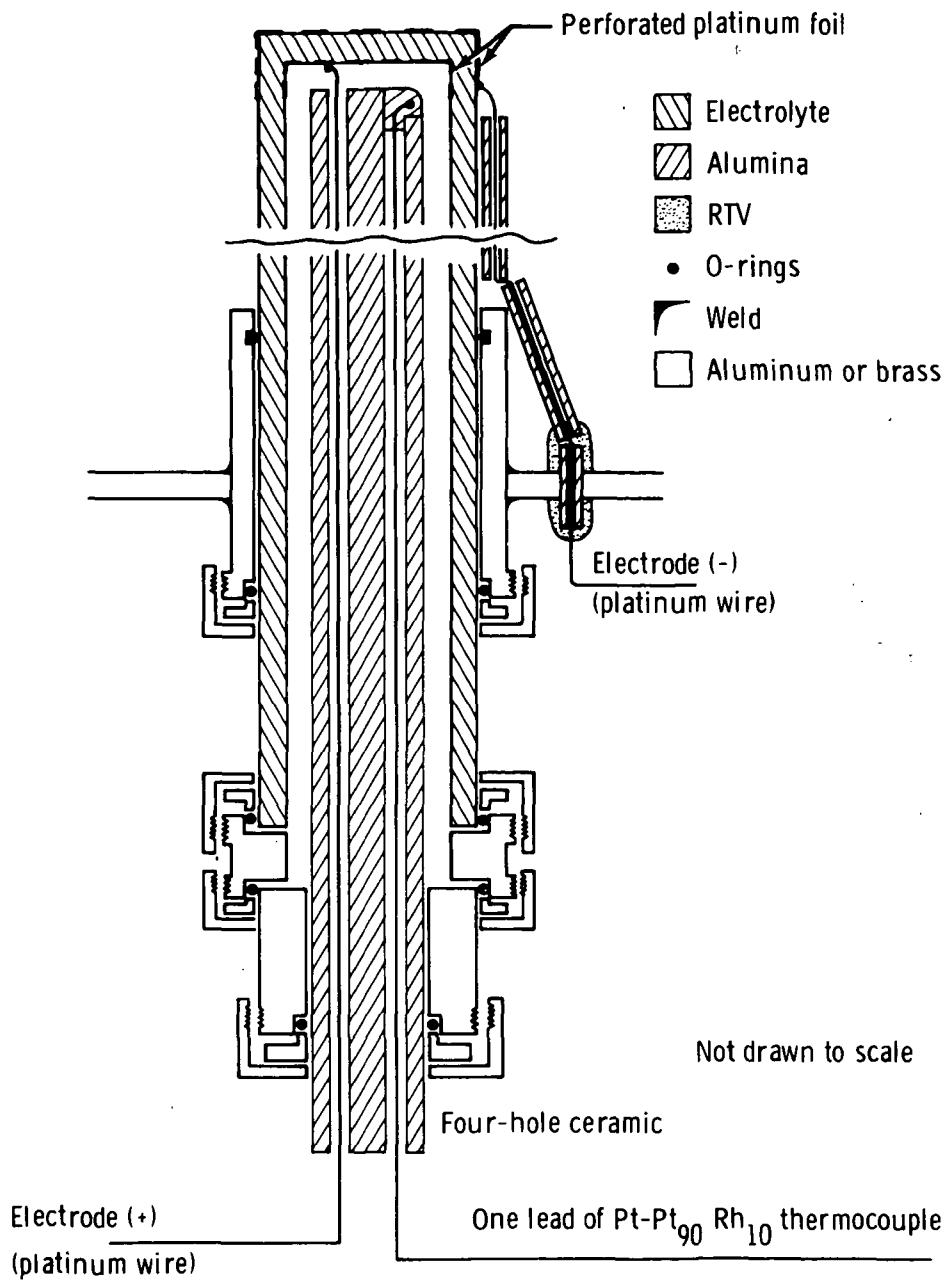
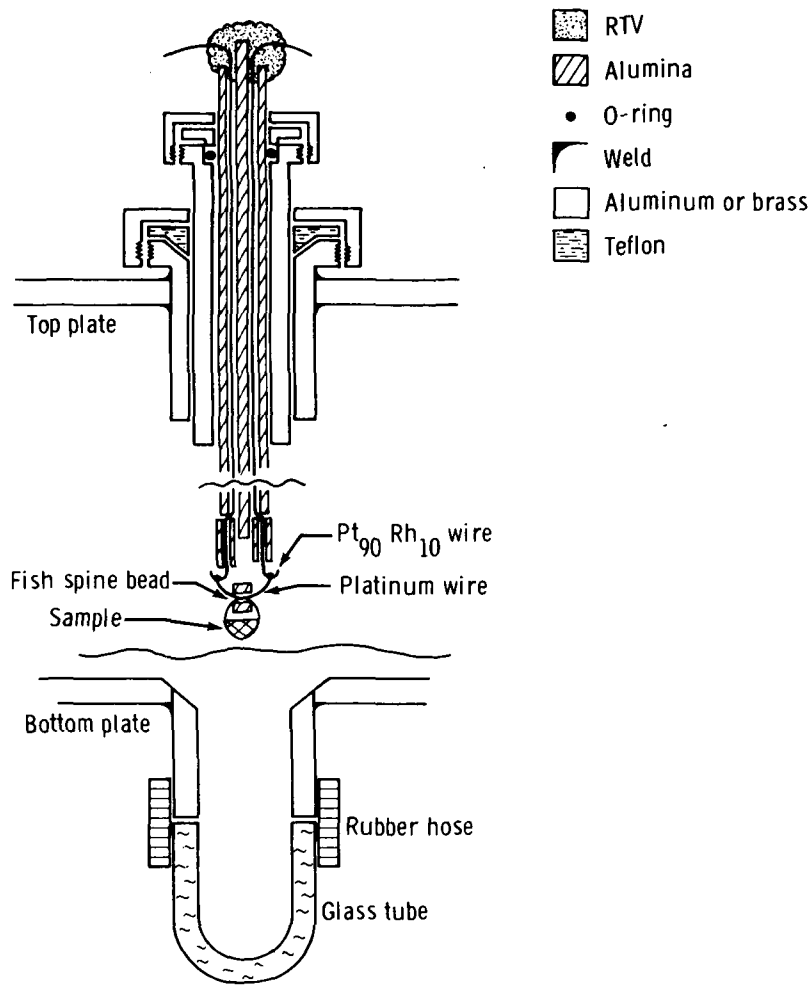
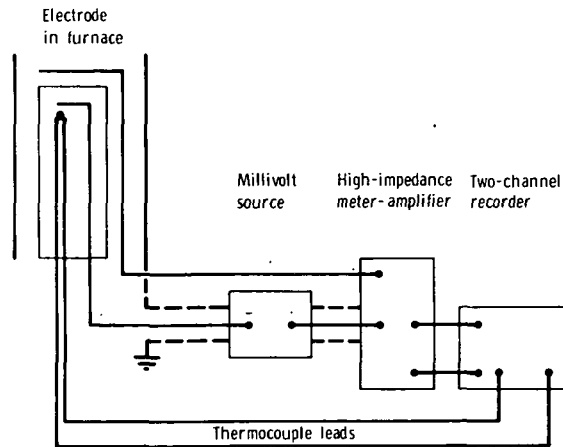


Figure 2. - Electrode construction and mounting.

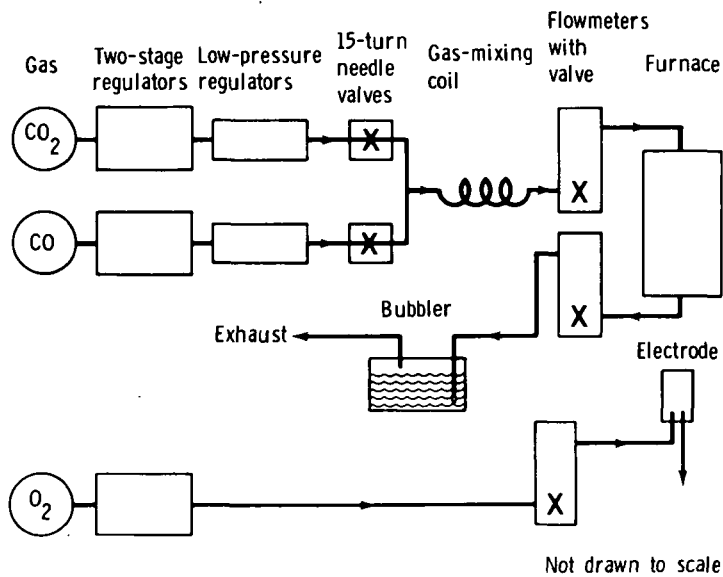


Not drawn to scale

Figure 3. - Quenching system and sample holder.



(a) Block diagram of electronic system.



(b) Block diagram of gas mixer and reference gas system. All tubing in the mixer is 0.635-cm (0.25 in.) copper; beyond the output flowmeter, the tubing expands to 1.27 cm (0.5 in.). The reference gas system is plumbed with 0.318-cm (0.125 in.) Teflon with a reduction to 0.794 mm (0.031 in.) at the electrode.

Figure 4. - Electrolyte system block diagrams.