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DETAILED CONCEPTUAL DESIGN OF A
HIGH-TEMPERATURE CO₂ SENSOR FOR GEOTHERMAL APPLICATIONS
FINAL REPORT - TASK I

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A Unit of General Signal Corporation

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March 1983

Prepared under Subcontract to
Pacific Northwest Laboratory for
The U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

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PREFACE

The investigation described in this report was authorized under prime contract DE-AC06-76RLO 1830 for the United States Department of Energy, Division of Geothermal Energy. It was performed by the Corporate Research Department of Leeds & Northrup Company, a unit of General Signal Corporation for the Pacific Northwest Laboratory, operated by Battelle Memorial Institute. This report covers work during the period June 1979 to October 1980. The constructive guidance provided by Dr. George A. Jensen, Project Officer for Pacific Northwest Laboratory, is gratefully acknowledged.

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I. INTRODUCTION & SUMMARY

In order to control scaling or corrosion in a geothermal power plant, one must monitor and verify the solution chemistry. At the present time, the fluid chemistry is determined by sampling and subsequent analysis. Sampling risks sample contamination or change due to cooling and only provides intermittent information. A much better method would be the insertion of chemical sensors down-hole or in-line. In particular, a means for measuring the partial pressure of carbon dioxide and other chemical constituents of geothermal brines must be developed to assure effective use of this valuable source of energy.

Leeds & Northrup Company was selected by the Pacific Northwest Laboratory (PNL) to develop a $p\text{CO}_2$ sensor in a probe configuration which will withstand the high temperature, corrosive environment of geothermal brines. This project is part of an extensive program undertaken by PNL for the U. S. Dept. of Energy to enable in situ measurements of critical geothermal fluid characteristics. Data from such measurements are required to prevent scaling, corrosion and other detrimental effects in the conversion of this resource to useful forms of energy. The PNL program is responsive to the recommendations of the National Materials Advisory Board (NMAB) of the National Academy of Science² and has prompted several investigations on adapting electrochemical devices to geothermal applications. The overall objective is to develop sensors for measurement of chemical properties such as redox potential, conductivity, pH, corrosivity, sulfide content and $p\text{CO}_2$.

This report documents the work performed by Leeds & Northrup Company, as a subcontractor to PNL, on the development of a $p\text{CO}_2$ probe. The recommended probe includes a solid state device which senses the pH of the internal electrolyte, a gas-permeable membrane that allows diffusion of CO_2 into the electrolyte, and a getter to inhibit incursion of H_2S . The results of the feasibility study indicate that such a probe holds promise of meeting all the operational and environmental requirements for in situ and down-hole measurement of carbon dioxide in geothermal fluids.

1. Background of Geothermal CO₂ Measurement

At present there is no way to obtain reliable in situ information concerning the three carbonate species (CO₂, CO₃⁼, HCO₃⁻) and hydrogen (H⁺) ion present in geothermal systems. An accurate analysis of at least two of the four of these species and the calcium ion activity is required to completely characterize the water chemistry relative to carbonate scaling by the brine in geothermal systems. The measurement of pH indicates the H⁺ concentration. Development of pH electrodes for this purpose is actively under way. The calcium ion concentration of the brine can be obtained analytically in the laboratory, the Ca⁺⁺ content of brine not being readily altered by the sampling process. Therefore, an in situ measurement of pCO₂ at various locations in the geothermal system would provide a means for deducing the scaling potential of the brine at these locations. Such information could be employed to prevent or alleviate corrosion, unwanted throttling or other unwanted problems associated with such information in geothermal systems.

In response to a Request for Proposal (RFP) from PNL, Leeds & Northrup proposed to develop an electrode system for in situ measurement of CO₂ in geothermal applications. The sensor must be operable to at least 250°C and up to 5000 psi. According to the NMAB report², geothermal brines contain CO₂ (up from 500 ppm), H₂S (up from 75 ppm), Na⁺ (up to 87,000 ppm), K⁺, Ca⁺⁺, Cl⁻, Mg⁺⁺, SO₄⁼, silica, and lesser constituents. The CO₂ sensor must operate for 24 hours in this environment and be free of any chemical interference. The development of this CO₂-sensing probe is divided into three stages in accordance with the tasks specified in the RFP; Task I - Detailed Conceptual Design, Task II - Fabrication and Test of Lead Units, and Task III - Fabrication of Additional Electrodes for Field Tests. This report covers the work undertaken to complete Task I - Detailed Conceptual Design.

2. Conclusions and Recommendations

The feasibility of developing a pCO₂ sensor for use in hot geothermal brine was demonstrated both theoretically and experimentally. A CO₂ sensing scheme was proposed and subjected to a critical evaluation,

with the development of a mathematical model predicting performance at elevated temperatures up to 300°C. The validity of the model predictions at room temperature were verified experimentally.

The essential components of the CO₂ sensing system include a pH sensor, a reference electrode, an internal electrolyte and a gas-permeable membrane. Those elements judged to be performance limiting at high temperatures were tested in the laboratory.

An electrode design using a proprietary ion selective field effect transistor (ISFET) is recommended. The possible use of the more conventional glass pH sensor was considered and rejected as reported in the Appendix (VI.2). The essential components of the ISFET pH sensitive device recommended for inclusion in the pCO₂ sensor were tested under simulated operating conditions in both sensor electrolytes and simulated brine. The best alternative maintained integrity and pH sensitivity after such exposure.

The recommended design also incorporates material selected from tests on polymers, glasses, thin film insulator, electrolytes and insoluble ion salts. Of paramount importance was the identification of a gas-permeable membrane which can withstand brine exposure and maintain CO₂ permeability. Mechanical and permeability testing were carried out on a variety of candidate polymer materials. EPDM membrane material is recommended that exhibited good survival in brine with a high CO₂ flux before and after 24 hours in simulated brine at 250°C.

The potential interference of acidic or basic gases (primarily H₂S) in the brine was assessed. Two systems were studied, one to avoid the influx of interfering gases and a second to compensate for their effects. A getter system using CuSO₄ was shown to be feasible and is recommended over the more complex interference compensation scheme, the latter reported in detail in the Appendix (VI.3).

The ISFET pH sensitive device recommended for inclusion in the pCO₂ sensor may also be applicable to in-situ brine pH determination. This possibility was explored by exposing the sensing surface to simulated geothermal brine and verifying room-temperature pH response before and after exposure.

Given the encouraging results of each component of the CO₂ sensor tested, a recommended design is presented with a project plan to fabricate and laboratory test complete units, with the anticipation of proceeding to field experimentation upon successful completion of the Task II effort.

II.

PROPOSED CO₂ SENSING SYSTEM

The recommended approach for a high temperature CO₂ sensor for use in geothermal applications is a "Stowe-Severinghaus" electrode system.^{3,4} In its simplest form, this pCO₂ sensor consists of a pH-reference electrode pair placed behind a gas permeable membrane in HCO₃⁻/CO₃⁼ solution. As CO₂ equilibrates with the internal solution, it determines the pH which in turn is measured by the electrode pair. Such a sensor is widely used to monitor blood pCO₂ in the clinical laboratory. Several challenges are evident when trying to apply this technique to the measurement of geothermal brines. High temperature pH and reference electrodes are required, as well as suitable membrane material and housing. Furthermore, acidic or basic gases may interfere (e.g. H₂S), and correction for this interference may have to be incorporated into the sensor. In order to evaluate the design requirements, a description of the reaction taking place in the sensor follows in Section II.1. The requirements of the various sensor components are discussed in Section II.2, while considerations of the potential interference problems and recommended corrective measures are described in Section III.

1.

Brine Carbonate Chemistry

As gaseous CO₂ diffuses through the sensor membrane from the sample it dissolves in the internal fill solution. Carbon dioxide dissolves in water to form solutions which obey Henry's Law quite satisfactorily.

$$K_{\text{Henry}} = \frac{\text{partial pressure of CO}_2(\text{in mm Hg})}{\text{mole fraction of CO}_2} \quad \text{II-1}$$

(The partial pressure of CO₂ in millimeters of mercury will hereafter be denoted "ppCO₂").

$$\text{Mole fraction of CO}_2 = \frac{\text{Number of moles CO}_2}{\text{Total moles of all species}} \quad \text{II-2}$$

As a rough approximation, the total number of moles in one liter of fill solution is taken to be 57. Therefore,

$$\text{Mole fraction of CO}_2 = \frac{\text{Number of moles CO}_2/\text{liter}}{57 \text{ moles/liter}} \quad \text{II-3}$$

$$\text{and, } \frac{\text{Number of moles CO}_2}{\text{liter}} = (\text{CO}_2) = \frac{(\text{ppCO}_2) (57 \text{ moles/liter})}{K_{\text{Henry}}} \quad \text{II-4}$$

(For simplicity, this discussion does not distinguish between activities of species and their concentrations. Activity coefficients are presumed to be constant and, as such, can be compensated by an offset voltage during calibration. Concentrations are expressed as moles/liter.)

The aqueous CO₂ is to some extent hydrolyzed,

$$K_{\text{Hydrolysis}} = \frac{(\text{H}_2\text{CO}_3)}{(\text{CO}_2)} \quad \text{II-6}$$

Rearranging II-6 and substituting for (CO₂) from II-4, one obtains

$$(\text{H}_2\text{CO}_3) = \frac{(\text{pp CO}_2) (57 \text{ moles/liter}) K_{\text{hydrolysis}}}{K_{\text{Henry}}} \quad \text{II-7}$$

Carbonic acid dissociates in two stages to yield H⁺, HCO₃⁻ and CO₃⁼.

$$K_1 = \frac{(\text{H}^+) (\text{HCO}_3^-)}{(\text{H}_2\text{CO}_3)} \quad \text{II-9}$$

$$K_2 = \frac{(H^+) (CO_3^{=})}{(HCO_3^-)} \quad \text{II-11}$$

In the internal fill solution, presumed for this discussion to be a $HCO_3^-/CO_3^{=}$ solution of the lithium salt, electroneutrality requires that the sum of all the positive charges equal the sum of all the negative charges. Therefore,

$$(H^+) + (Li^+) = (HCO_3^-) + 2(CO_3^{=}) + (OH^-) \quad \text{II-12}$$

Solving II-9 for (HCO_3^-) and II-11 for $(CO_3^{=})$, substituting into II-12 and solving for (H_2CO_3) , one obtains

$$(H_2CO_3) = \frac{(H^+)^2 + (H^+) (Li^+) - (H^+) (OH^-)}{K_1 (1 + \frac{2K_2}{(H^+)})} \quad \text{II-13}$$

But from II-5 and II-4,

$$(H_2CO_3) = \frac{K_{\text{hydrolysis}} (\text{pp } CO_2) (57 \text{ moles/l})}{K_{\text{Henry}}} \quad \text{II-14}$$

Equating II-13 and II-14 and noting that $(H^+) (OH^-)$ is equal to the dissociation constant of water K_w ,

$$\frac{K_{\text{hydrolysis}} (\text{pp } CO_2) (57 \text{ moles/l})}{K_{\text{Henry}}} = \frac{(H^+)^2 + (H^+) (Li^+) - K_w}{K_1 (1 + \frac{2K_2}{(H^+)})} \quad \text{II-15}$$

Assuming that an electrolyte near neutral pH is used as the internal fill and that (Li^+) is much greater than (H^+) , the first and third terms in the numerator on the right side of equation II-15 are negligible compared to the second term, and $2K_2/H^+$ is believed to be much smaller than one, so that equation II-15 may be approximated as

$$\frac{K_{\text{hydrolysis}} (\text{pp } CO_2) (57 \text{ moles/l})}{K_{\text{Henry}}} = \frac{(H^+) (Li^+)}{K_1} \quad \text{II-16}$$

Taking the logarithm of each side, letting $\text{pH} = -\log(\text{H}^+)$, and solving for pH, yields,

$$\begin{aligned} \text{pH} = & \log(\text{Li}^+) - \log K_1 - \log K_{\text{hydrolysis}} - \log (57 \text{ moles/l}) \\ & + \log K_{\text{Henry}} - \log (\text{pp CO}_2) \end{aligned} \quad \text{II-17}$$

For a given internal electrolyte and temperature, all the terms on the right side of equation II-17 are constant except the last, such that

$$\text{pH} = K - \log (\text{pp CO}_2) \quad \text{II-18}$$

or, since pCO_2 is defined as $-\log (\text{pp CO}_2)$

$$\text{pH} = K + \text{pCO}_2. \quad \text{II-19}$$

Therefore, if the internal solution is chosen to stay within the approximations used in the derivation, the measured pH will vary linearly with pCO_2 at any given temperature. At moderate temperatures it is easy to calculate the precise relationship since all the constants are known. However, at elevated temperatures not all the constants are known. For example, the hydrolysis reaction (II-5) has not been evaluated at elevated temperatures. It is possible to model the system by certain revisions in the comprehensive model described above to facilitate computations with the available high temperature data.

The dissolution of gaseous CO_2 is described by

where the subscript (app) indicates that the species referred to is the undifferentiated sum of $\text{H}_2\text{CO}_3(\text{aq})$ and $\text{CO}_2(\text{aq})$.^{5,p.777} The apparent Henry's Law constant is

$$K_{\text{Henry}}^{\text{app}} = \frac{(H_2CO_3(\text{app}))}{(CO_2(g))} \quad \text{II-21}$$

assuming (H_2O) is at unit activity. The fugacity of the gas, CO_2 , is the partial pressure corrected by an activity coefficient. At the gas pressures (up to a few bars) in most natural hydrothermal systems, it is sufficient to equate the partial pressure and fugacity of a gas.^{6,p.131} Therefore,

$$(CO_2) = pp \ CO_2 \ (\text{mm})/760 \quad \text{II-22}$$

The first and second ionizations of the carbonic acid are

$$K_1 = \frac{(H^+) (HCO_3^-)}{(H_2CO_3(\text{app}))} \quad \text{II-24}$$

and

$$K_2 = \frac{(H^+) (CO_3^{=})}{(HCO_3^-)} \quad \text{II-11}$$

The total of all carbonate species, ΣCO_2 , is defined as

$$\Sigma CO_2 = (H_2CO_3(\text{app})) + (HCO_3^-) + (CO_3^{=}) \quad \text{II-25}$$

The fraction of this total which is represented by each species is

$$\alpha_{H_2CO_3(\text{app})} = (H^+)^2/D \quad \text{II-26}$$

$$\alpha_{HCO_3^-} = (H^+) K_1/D \quad \text{II-27}$$

$$\alpha_{CO_3^{=}} = K_1 K_2/D \quad \text{II-28}$$

where

$$D = (H^+)^2 + (H^+) K_1 + K_1 K_2 \quad \text{II-29}$$

Recalling Equation II-12,

$$(Li^+) + (H^+) = (OH^-) + 2(CO_3^{2-}) + (HCO_3^-), \quad \text{II-12}$$

and substituting for (OH^-) , (CO_3^{2-}) and (HCO_3^-) from equation II-27, II-28, and K_w ,

$$(Li^+) + (H^+) = \frac{K_w}{(H^+)} + (2\alpha CO_3^{2-} + \alpha HCO_3^-) \Sigma CO_2 \quad \text{II-30}$$

But

$$\Sigma CO_2 = \frac{(H_2CO_3(app))}{\alpha H_2CO_3(app)} \quad \text{II-31}$$

$$= \frac{K_{Henry}^{app} (pp CO_2/760)}{\alpha H_2CO_3(app)} \quad \text{II-32}$$

Therefore,

$$(Li^+) + (H^+) = \frac{K_w}{(H^+)} + \frac{2\alpha CO_3^{2-} + \alpha HCO_3^-}{\alpha H_2CO_3(app)} \frac{K_{Henry}^{app} pp CO_2}{760} \quad \text{II-33}$$

and

$$(H^+)^2 + (H^+) \left[(Li^+) - \left(\frac{2\alpha CO_3^{2-} + \alpha HCO_3^-}{H_2CO_3(app)} \right) \frac{K_{Henry}^{app} pp CO_2}{760} - K_w \right] = 0 \quad \text{II-34}$$

For any temperature from 25 - 300°C, all of the parameters necessary to solve Equation II-34 are available⁵ so that for any specified initial concentration of Li_2CO_3 and $LiHCO_3$ in the internal electrolyte, the pH-pp CO_2 relationship can be rigorously evaluated (still ignoring the effects of activity coefficient variation). A computer program was developed, utilizing a previous effort of Dr. James G. Connery (L&N), to calculate the internal electrolyte pH as a function of pp CO_2 . A brief description of the program and its listing is included in the Appendix,

Section VI.1.1, followed by tabulations of the computed pH-pp CO₂ relationship at a variety of internal electrolyte bicarbonate and carbonate initial concentrations, at temperatures of 25, 100, 150, 200, 250 and 300°C. Discussion of these results is included in Sections II.1.1 and II.1.2 below.

1.1 Low Temperature Computation and Verification

The computer program based on the above derivation and listed in Section VI.1.1 calculates the pH of an electrolyte, the total carbonates and the carbonate in concentration given the initial carbonate and bicarbonate composition and appropriate values of K_w , K_{Henry} , K_1 and K_2 (the ionization constant of water, the Henry's law constant for CO₂, and the first and second ionization constants of carbonic acid, respectively) for the temperature selected.

There are many sources for these constants at 25°C. For example, one compilation includes 31 different references reporting K_w .⁷ It was decided to use values from a source⁵ which also had values up to 300°C, the consistency afforded by this being judged more important than the slightly improved accuracy possible if critical assesment of all the room temperature data were made. The values at 25°C selected were

$$K_w = 1.0 \times 10^{-14} \quad \text{II-35}$$

$$K_{\text{Henry}} = 3.47 \times 10^{-2} \quad \text{II-36}$$

$$K_1 = 4.47 \times 10^{-7} \quad \text{II-37}$$

$$\text{and } K_2 = 4.79 \times 10^{-11} \quad \text{II-38}$$

To verify experimentally the general approach and the mathematical model, a solution of 0.002 M Li₂CO₃ was adjusted with HCl to pH 7, and the response of a pH electrode immersed in this solution

was measured while exposed to varied partial pressures of CO_2 . The experimental set-up is shown schematically in Figure II-1.

From the computed values reported in Section VI.2, it can be seen that the pH varies with $\log(\text{pp } \text{CO}_2)$ at the expected Nerstian slope of 59.2 mv/decade at high CO_2 levels, with lessened response as a lower sensitivity limit is approached. The absolute pH and to a lesser extent the lower sensitivity limit are determined by the initial electrolyte composition selected.

Experimental results summarized in Figure II-2 confirm this behavior. The response was near-Nerstian, falling off as the concentration was decreased below about 300-400 ppm. This loss of sensitivity occurred at a slightly higher CO_2 partial pressure than the output in Section VI.2.2 predicts. There are several explanations for this behavior. There may be some error in the values of the constants used (Equations II-35 through II-38). The assumption made (i.e., ignoring activity coefficient considerations) may be significant, and the presumed system equilibration may not be reached. This latter case seems likely in that the kinetics of CO_2 hydrolysis is known to be somewhat slow at room temperature, as indicated by the use of carboxyanhydrase as a catalyst.

1.2 Computation of High Temperature Equilibria

Although the solubility and ionization of CO_2 in high temperature solutions has not been as extensively studied as it has at room temperatures, several reports⁷⁻¹¹ and summaries^{5,6} provide the constants required for use of the computer program listed in Section VI-1. For consistency, the data presented by Helgeson⁵ was chosen and is reported in Table II-1.

When the constants at a given temperature are substituted for the room temperature constants in statements 170, 180, 190, and 200 of the program, the pH- CO_2 relationship can be computed with the results tabulated in Sections VI.1.3 through VI.1.7. The most striking feature of

FIGURE II-1: SCHEMATIC OF pH VS. (CO_2) EXPERIMENTAL ASSEMBLY

ppm CO₂ VS. mv (pH) @ 25°C

○ WITHOUT LA₂(CO₃)₃

x WITH LA₂(CO₃)₃

--- IDEAL (NERNSTIAN) RESPONSE, 60 mv/DECADE

— BEST LINE (LEAST SQUARES FIT FOR LINEAR PORTION)

FIGURE II-2: ppmCO₂ VERSUS pH-REFERENCE VOLTAGE, No H₂S

TABLE II-1: DISSOCIATIONS AND SOLUBILITY CONSTANTS OF CO₂ AT ELEVATED TEMPERATURE

Temp., °C	K_w	K_1	K_2	K_{Henry}
100	5.49×10^{-13}	3.55×10^{-7}	6.92×10^{-11}	1.07×10^{-2}
150	2.29×10^{-12}	1.86×10^{-7}	5.13×10^{-11}	8.51×10^{-3}
200	5.37×10^{-12}	8.32×10^{-8}	2.09×10^{-11}	8.71×10^{-3}
250	7.41×10^{-12}	2.34×10^{-8}	3.72×10^{-12}	1.05×10^{-2}
300	4.07×10^{-12}	1.38×10^{-9}	4.17×10^{-14}	1.48×10^{-2}

the computed results is that the loss of Nernstian behavior runs at much higher CO₂ partial pressures as the temperature increases. Whereas near Nernstian behavior is observed at 7.6 mm CO₂ and 150°C, at 300°C and the same partial pressure there is virtually no response. Given the Henry's law constant of about 10⁻², this indicates that measurement of 10⁻⁴ M (≈5 ppm) H₂CO₃(app) would be feasible at 150°C but not at 300°C. There are many assumptions made in reaching this conclusion, and further work, both experimental and theoretical, is required before the sensitivity limit of the proposed system can be established.

2. Sensor Component Requirements

The CO₂ sensing system proposed in Section II.1 utilizes a pH sensing electrode, an internal electrolyte, a reference electrode, and a gas-permeable membrane. The fundamental requirements of each of these sensor components are discussed in Sections II.2.1 - II.2.4 below.

2.1 pH Sensing Electrode

Two types of pH sensing electrodes were selected for investigation. A recently developed type based on a solid state pH sensing field effect transistor is recommended for use. The background theory and the experimental results which dictated its selection are presented in Section II.2.1.1. A second alternative, based on the conventional glass membrane pH sensor, was investigated and rejected for use

in the geothermal CO₂ sensor as described in Section II.2.1.2, with the test results leading to this conclusion reported in Section VI.2.

2.1.1 Solid State pH Sensor

The pH sensing element recommended for use in the CO₂ probe is one of a class of recently developed ion-sensitive electrodes. These sensors combine the properties of ion selective electrodes with the field effect of semiconductor devices, for example the metal-oxide-semiconductor field effect transistor (MOSFET). Such ion sensitive field effect transistors (ISFET) offer several advantages compared to conventional types. They are inherently small, of some value for down-hole measurement. They have low impedance outputs, acting as intrinsic impedance converters, and as such, lessen the otherwise stringent electrical insulation and encapsulation requirements, a clear advantage. Furthermore, since the ISFET operates in a different manner than the conventional glass pH electrode, many of the limiting material requirements imposed upon good pH glasses are irrelevant, allowing the design and engineering process to include consideration of otherwise unuseable materials.

Recently, a pH sensitive ISFET has been developed with an extremely inert sensing "membrane," alumina.¹² Alumina is much less likely to dissolve in hot aqueous electrolytes than is conventional pH glass, a significant problem limiting the conventional approach in the CO₂ sensor (Section II.2.1.2). The brief presentation of ISFET theory is included in Section II.2.1.1.1 as background to the high temperature test results and capacitance-voltage testing presented in Sections II.2.1.1.2 and II.2.1.1.3. Tests of the sensor elements in simulated brine are described in Section II.2.1.1.4.

2.1.1.1 Background Theory

The underlying principles of ISFET design and operation are presented here in the expectation that a rationale of the experimental proof testing and design approach taken will result. Much of the discussion relates to an idealized model system and little detail is presented. The interested reader can refer to the extensive reference list

compiled during this work and categorized for convenience near the end of this Section.

The essential component of all ion-selective electrodes (ISE) is a membrane which responds selectively to chemical species in solution. The potential arising at the membrane-solution interface is indicative of the ion concentration of the measured species. In 1970, Bergveld described a novel ISE based on semiconductor technology.¹³ Essentially, it was a field effect transistor with output characteristics sensitive to ionic species in the solution in which it was placed.

Because the ISFET structure and operation is similar to MOS transistor technology, a brief description of the MOSFET device is presented below. More detailed reports are available elsewhere, for example reference 18.

A conventional MOS transistor consists of a semiconductive base covered with successive layers of insulation (1000-2000 Å) and metal (6000-7000 Å). The semiconductor is usually p- or n-type silicon, the difference due to the type of impurity giving rise to the conduction process. Most reported studies of ISFET devices employed p-type silicon, and this type was used almost exclusively in this study. For this reason, this discussion of MOS transistor operation will be limited to p-type devices.

When an atom of fewer valence electrons than silicon is substituted for silicon in the crystal lattice, an electron is accepted, giving rise to four covalent bonds to the impurity atom and creating a positively charged, mobile "hole." A fundamental requisite of semiconductor devices is the p-n junction, small regions of the p-type material adjacent to regions doped with an impurity which causes n-type conduction. In a field-effect transistor (FET) there are usually two p-n junctions, one at the "source" and one at the "drain," separated by a region of substrate called the "channel."

The channel area of a MOSFET is covered with a thin layer of insulation atop SiO_2 which is generally directly contacting the silicon. Other insulators which have been employed include SiO_2 , silicon nitride (Si_3N_4), alumina, and phosphosilicate, borosilicate and other silicate glasses. Techniques of insulation formation or deposition have included thermal oxidation, chemical vapor deposition (CVD), dc or rf reactive sputtering, electron beam evaporation and glass fusion from sedimented powders. The deposition method has a great effect on the properties of the dielectric films, and many studies have evaluated this important relationship in detail.¹⁴⁻¹⁷

The insulator film in an MOS device is covered with a metallic layer known as the gate, to which contact is made. Figure II-3 shows the complete MOS structure schematically.

When an ideal MOS (or more generally MIS for metal-insulator-semiconductor) structure is biased by application of a gate voltage, four basic situations may exist at the semiconductor-insulator interface. Consider the p-type semiconductor illustrated in Figure II-3. Application of a negative voltage to the gate causes the top of the valence band (E_v in Figure II-4) to bend upward toward the Fermi level, E_f . Since the hole density depends on the energy difference ($E_f - E_v$), the band bending causes an "accumulation" of the majority carriers (holes) near the semiconductor surface.

At zero applied bias, no band bending occurs. This is the so-called flatband condition. With a small positive bias, the bands bend downward and "depletion" of majority carriers occurs. At somewhat larger positive bias, the bands bend even further downward until the intrinsic level E_i at the surface crosses the Fermi level. When this occurs, the minority carrier (electron) concentration exceeds the hole concentration and the surface is said to be "inverted."

Another quantity of interest is the "turn-on" or threshold voltage, V_T , which is the voltage corresponding to the onset of strong inversion. V_T is a function of both the dielectric thickness and permittivity and the substrate doping level.

FIGURE II-3: STRUCTURE OF A METAL INSULATOR SEMICONDUCTOR FIELD EFFECT TRANSISTOR (MISFET)

FIGURE II-4: ENERGY BAND DIAGRAMS FOR IDEAL MIS TRANSISTORS WITH p-TYPE SILICON

In the idealized case being discussed, the flat band condition always corresponds to $V_g = 0$. However, in real cases there are often various sources of surface charges (fixed charges, mobile ions, ionized traps) located at or near the semiconductor interface which result in band bending even at zero applied bias. The value of the gate bias at which the true flat band condition occurs is known as the flat band voltage, V_{FB} . It is useful in characterizing "real" MIS structures and is a measure of how closely they approach ideal behavior. More will be said about V_{FB} in connection with the experimental results to be described later.

In applying these concepts to the MOSFET, it is seen how the gate voltage can be used to control the current flowing between the source and drain. Figure II-5 illustrates typical current-voltage characteristics for an n-channel (p-type substrate) depletion mode MOSFET. Note that for this device, a conducting channel (inversion layer) exists at zero gate bias. This device may be turned off by application of a suitable negative gate voltage, or made to conduct more strongly by application of a positive gate voltage.

When the gate voltage is greater than the threshold voltage, $(V_g - V_T)$, and the source to drain voltage is greater than the difference between the gate voltage and the threshold voltage $(V_{DS} > V_g - V_T)$, the device is said to be operating in the saturation region, with I_D relatively insensitive to variations in V_{DS} . Under these conditions

$$I_D = \beta (V_g - V_T)^2 \quad \text{II-39}$$

and

$$\beta = \mu C_0 W/L \quad \text{II-40}$$

where μ is the surface mobility of the electrons, C_0 is the capacitance per unit area, W is the channel width, and L is its length.¹⁸ When $V_g > V_T$ and $V_{DS} < V_g - V_T$, the device is operating in the linear region, with I_D varying with both V_g and V_D .

$$I_D = \beta \left(V_g - V_T - \frac{V_D}{2} \right) V_D \quad \text{II-41}$$

FIGURE II-5: OUTPUT CAPACITANCE-VOLTAGE CHARACTERISTICS OF AN N-CHANNEL MISFET

Note that in both equations II-39 and II-41, I_D is a function of the threshold voltage. Accordingly, the potential V_G applied to the gate in a circuit of high impedance modulates I_D in a low impedance circuit,¹⁹ giving rise to a major advantage of MOSFET and ISFET operation over conventional ion selective electrodes.

An ISFET structure is essentially that of a MOSFET without the metal gate. As shown in Figure II-6, the electrochemical potential developed at the solution-insulator interface effectively forms a "solution gate" to modulate channel conductance and thereby control the drain current. The response of the ISFET can best be described in terms of its effect on the threshold voltage, V_T . An expression relating V_T to various MOSFET characteristics²⁰ is

$$V_T = \phi_{MS} - Q_{SS}/C_0 + 2\phi_F - Q_B/\epsilon_0 \quad \text{II-42}$$

when ϕ_{MS} is the metal-semiconductor work function difference, Q_{SS} is the bulk Fermi level of the (p-type) substrate, Q_B is the depletion region charge per unit area, and C_0 is the insulation layer capacitance per unit area. A similar equation applies to an ISFET operating versus a reference electrode.²¹

$$V_T = \phi_I + V_R - \left[\frac{Q_{SS}}{C_0} + 2\phi_F + \frac{Q_B}{C_0} \right] \quad \text{II-43}$$

wherein ϕ_I denotes the potential formed at the solution-insulator interface and V_R is the liquid junction potential of the reference electrode. Note that all terms in equation II-43 are constant except ϕ_I , so that any change in V_T can be attributed to a change in the potential at the solution-insulator interface. Since ϕ_I is most likely governed by the electrochemical potential developed by ions in solution, a measure of V_T can be related to ionic activities or concentrations.

To date, most of the development of the ISFET has been empirical, focusing on various insulator materials to maximize sensitivity and selectivity of the device. Consequently, the nature of ϕ_I is

FIGURE II-6: SCHEMATIC OF ISFET OPERATION

not well understood. As opposed to the conventional type ISE, the change in ϕ_1 may or may not display the Nernstian relationship of $2.303(\frac{RT}{nF})$ mv change per decade change in concentration (i.e. 59 mv per decade at 25°C). In general, it has been found that if conventional ion-selective polymeric materials are used as the semiconductor insulator, a Nernstian response will be displayed.²¹ However, when the typical MOSFET insulator materials are used such as silicon dioxide (SiO_2), silicon nitride (Si_3N_4), alumina (Al_2O_3) etc., a non-Nernstian response may occur.

Two theories have been suggested to explain the potential generating mechanism of the electroactive species in solution. The first attributes ionic sensitivity of the ISFET to diffusion of the ion through the insulator to the insulator-semiconductor interface, causing changes in the interface charge.^{22,23} The second proposes that the mechanism of ionic response arises from surface reactions between the electrolyte and insulator.²⁴ The possible mechanism first presented seems to contradict certain observations. The mechanism apparently requires diffusion of a species through the insulating film, which is dependent on the diffusion constant and film thickness and potentially a very slow process. For example, the response of potassium ions (K^+) in a SiO_2 - Si system, has been reported by Siu et al²⁴ and found to be $>>10^4$ seconds for a 1000 Å thick oxide film at room temperature. This seems inconsistent with experimental observations.²¹ Secondly, there is evidence that films showing high sensitivity and selectivity to a particular ionic species can also be very effective diffusion barriers to that same ion. For example, the pH sensitivity of a SiN_4 film can be very good, yet as a hydrogen diffusion barrier it was shown to be better than SiO_2 .²¹ The diffusion mechanism would predict SiN_4 to be less responsive to pH than SiO_2 , contrary to observations. Finally, it would appear that the diffusion model predicts response time to vary with insulator film thickness, although measurements made of pH response at various film thicknesses showed no response time dependence on thickness.²⁴

The evidence presented seems to suggest that the primary mechanism of ISFET response is through electrolyte-insulator surface interactions, and that diffusion through the insulator, should it occur, contributes to slow drifts in the characteristics of the device.^{15,21,24}

Many of the interfacial parameters of ISFET systems may be experimentally investigated using the capacitance-voltage (C-V) characteristics of the system. C-V curves are frequently used in the study of MOS systems and can provide valuable information such as the work function difference between metal and semiconductor and surface state densities. The technique is widely used to determine the effects of temperature, moisture and bias on the electrical properties of the MOSFET. In ISFET studies, the C-V curves are especially useful in defining ionic selectivities and stabilities of alternative insulator films. To date, insulator materials with selectivity for K^+ , Ca^{++} , Na^+ , and H^+ have been identified using this technique. Because of its importance, the basis of C-V testing is reported below, expanding the dc considerations developed earlier in this section to include ac testing.

Earlier, the energy diagram for an ideal MIS structure was discussed for various conditions of applied dc gate bias. If a small ac signal is superimposed on this dc bias, the MIS capacitance may be readily measured. The resulting capacitance vs voltage curve has the form indicated by Figure II-7. Again, assuming a p-type semiconductor, application of a negative bias results in accumulation of majority carriers (holes) at the insulator-semiconductor interface so that the total capacitance is practically that corresponding to the insulator alone, i.e.,

$$C = C_i = \frac{\epsilon_i}{t_i} \quad \text{II-44}$$

when ϵ_i and t_i are respectively the dielectric constant and thickness of the insulator.

As the magnitude of the negative bias is reduced, a depletion region starts to form in the semiconductor, and the total capacitance is given by the semiconductor of the insulator capacitance and the voltage dependent depletion layer capacitance, i.e.,

$$C_{\text{tot}} = \frac{C_i C_D}{C_i + C_D} \quad \text{II-45}$$

Thus, as V_G becomes more positive, the depletion layer widens, and C_{tot} reflects the decrease in C_D . Finally, for some suitably large

FIGURE II-7: CAPACITANCE-VOLTAGE (C-V) CURVE FOR IDEAL MISFET

positive bias, inversion results, the depletion layer width remains essentially constant, C_D becomes fixed, and C_{tot} becomes relatively insensitive to further increases in applied bias. In this region, the total capacitance is at its minimum value given by

$$C_{min} = \frac{\epsilon_i}{t_i + \left(\frac{\epsilon_i}{\epsilon_s}\right) W_m} \quad \text{II-46}$$

where W_m is the maximum width of the depletion region and is a function of the semiconductor doping level N_A . (e.g. $W_m \approx \sqrt{4\epsilon_s kT \ln(N_A/n_i)/q^2 N_A}$).

At the flat band condition, which corresponds to $V_G = 0$ in the idealized model, the capacitance is called the flat band capacitance C_{FB} and is given by

$$C_{FB} = \frac{\epsilon_i}{t_i + \left(\frac{\epsilon_i}{\epsilon_s}\right) \sqrt{\frac{kt\epsilon_s}{p_0 q^2}}} \quad \text{II-47}$$

where p is the equilibrium hole density in the bulk of the semiconductor and is determined by the doping level.

Thus, from measurements in the accumulation region, where C depends on the insulator properties alone, and in the inversion region, where C depends on both the insulator properties and the semiconductor doping level, it is possible to predict the value of the flat band capacitance. The significance of this is better understood by considering the real (non-ideal) MIS behavior.

The most important distinguishing factor in real MIS devices is the presence of miscellaneous charges and surface states associated with the insulator itself and the insulator semiconductor interface. These take the form of fixed surface charges in the insulator but located near the insulator-semiconductor interface, ionized traps distributed throughout the insulator, mobile ions in the insulator which can migrate to and from the interface under different conditions of bias and temperature, and states (energy levels) associated with the interface itself. The effect of these various charges and states is

to shift the C-V curve along the voltage axis so that C_{FB} no longer occurs at $V = 0$, and to distort the shape of the curve in the region of transition from accumulation to inversion.

The amount of voltage shift is directly related to the incremental surface charge ΔV , and it is customary to describe such shifts in terms of the shift at the flat band condition, i.e.,

$$V_{FB} = \frac{Q_s}{C_i} \quad \text{II-48}$$

In a real MIS device, the metal semiconductor work function difference also affects V_{FB} so that

$$V_{FB} = \frac{Q_i}{C_i} - \psi_{ms} \quad \text{II-49}$$

In the ISFET, ψ_{ms} is replaced by ϕ_I which relates to the potential formed at the electrolyte-insulator interface. As the interfacial potential varies with changes of ionic species in the electrolyte concentration so does V_{FB} .

The overview presented above should facilitate the understanding of the experimental results reported in Section II.2.1.1.2.. Details on each subject described can be found in the literature. Selected references on MOSFET and ISFET technologies are categorized and presented in Table II-2 for the convenience of those desiring more information.

2.1.1.2 Experimental Results

The essential elements of an ISFET sensor were tested experimentally. Alternative insulator materials were fabricated on silicon substrates and exposed to various electrolytes and to simulated geothermal brines. The results of tests of film thermal and chemical stability, capacitance-voltage tests, and simulated brine exposure tests are reported in Sections II.2.1.1.2.1 - II.2.1.1.2.3, respectively.

2.1.1.2.1 Thermal and Chemical Stability

One of the most vital aspects of the high temperature CO_2 probe performance is the relationship of pH of the electrolyte to CO_2 content of the sample. As discussed in Section III, acidic gases in the sample (e.g., H_2S or NH_3) can interfere by altering internal electrolyte pH, but can be kept from contact with the electrolyte by

TABLE II-2: CATEGORIZED LITERATURE REFERENCES

<u>ISFET Technology</u>	<u>Reference Number</u>
General Review	— 19, 30-32
Theoretical Aspects	— 12, 13, 15, 22-24, 26, 33-44
C-V Characteristics	— 23, 26, 28, 30, 40, 45
Deposition Methods, Physicochemical properties of insulation material and contamination problems.	— 14, 16, 25, 28, 40, 46-53
Ion Selectivity Studies	— 12, 25, 27, 30, 34, 35, 46, 54-61
Polymeric insulation materials	— 58-60, 62-64
Solid state reference electrode	— 17, 63, 65
Temperature and moisture effects on surface characteristics	— 20, 27, 37
Microelectrodes and micro-electronics	— 12, 28, 66-68
Encapsulation techniques	— 31, 57, 60
<u>MOSFET Technology Related to ISFETs</u>	
C-V characteristics	— 20, 49, 69-76
Interface states	— 77-82
Moisture, temperature and bias effects on electrical properties	— 14, 74, 76, 79-81, 83-86

a gettering system in the membrane layers. Conventionally, the electrolyte pH measurement in a room temperature CO₂ probe, is accomplished with a glass pH electrode. At high temperatures, however, the glass is attacked and dissolved in the electrolyte, (Section VI.2), causing a pH change independent of CO₂ content and adding significant error to the measurement. Proposed for measurement of electrolyte pH at elevated temperatures is the ISFET pH sensor. As is the case with the glass electrode most of the sensor elements can be isolated from the electrolyte film trapped between the sensor surface and the gas-permeable membrane. Therefore, their slight dissolution or corrosion will not effect the measured pH. The sensing membrane of the ISFET, the gate-insulating thin film, is in direct contact with the solution to be measured; its physical integrity and chemical stability are essential. Formation or deposition of the ion-sensitive layer is usually carried out on a thin layer of thermally grown SiO₂ since this tends to result in a stable silicon-oxide interface. This SiO₂ layer, properly grown in dry heat, can provide an interface with the silicon substrate free of contamination and various undesirable surface states.

The selection of candidate film materials was facilitated by the earlier work of several researchers reported in the literature. Film materials were chosen based on demonstrated pH sensitivity and anticipated moisture resistance and mechanical and chemical stability. Films exhibiting high pH sensitivity have included silicon dioxide (SiO₂), silicon nitride (Si₃N₄), silicon oxynitrides (SiO₂-Si₃N₄ mixtures), and alumina (Al₂O₃).^{21,25,26} Of these, Si₃N₄ and Al₂O₃ have shown the greatest selectivity in pH measurement, a desirable but secondary consideration. SiO₂ is faulted in that it tends to dissolve in hot aqueous solutions. Silicon oxynitride and silicon nitride have been shown to oxidize and dissolve. Alumina, however, is a chemically inert substance with excellent resistance in high temperature, high pressure water environments.²⁷ Alumina was the material most scrutinized in these tests.

Pyrex borosilicate glass films (Corning 7740) were also tested for two reasons. Already recognized as being quite stable glass in hot aqueous solutions, relatively thick films of borosilicate glass could prove useful as a passivating material. Secondly, a hybrid sensor which incorporates an FET transistor, the gate metallizing of which is in direct contact with a thick film of pH glass (Corning 0150) has been reported.²⁸ A more inert glass, while having less selectivity for pH, might prove to be a suitable gate insulator film.

For screening purposes, the Al_2O_3 and borosilicate candidate materials were sputter deposited on p-type Si/SiO₂ wafers. The sputter deposition was selected mainly because the required equipment was readily available. Studies comparing the properties of dielectric films deposited by various methods are reported in the literature. In one,¹⁶ the stability of borosilicate glass (BSG) deposited by chemical vapor deposition (CVD), fused from sedimented powders, or rf sputtered was examined after exposure to boiling water. The B₂O₃ content of the glass was found to influence etch rate in both boiling water and dilute and buffered HF. (Pyrex glass, with a B₂O₃ content of ≈13%, is one of the most resistant of this class of glasses). Varying the deposition method was shown to have little effect. CVD films had properties most like the bulk material; similar results in etch rate tests and infrared band intensities were obtained using well annealed sputter deposited and fused glass films. Pyrolytic and rf sputtered alumina were observed to be good moisture barriers.¹⁶ Films deposited at low temperature looked clean and were uniformly dissolved, whereas films deposited at an elevated temperature or annealed appeared opaque. Non-uniformity of the film was postulated, the cloudy surface perhaps resulting from preferential attack at microcrystal grain boundaries.²⁷ Annealing was especially important with rf sputtered films, apparently reducing internal stresses in the material originating from the deposition process.

Finally, some tests were carried out on films deposited directly on silicon without the thermal oxide layer. The benefits of a thermal oxide middle layer used in the ISFET at room temperature have been noted previously. At the temperature required by this application, the utility of the thermal oxide layer was questioned. Since it will be perfectly isolated from electrolyte exposure, water contamination is not probable. However, in at least one study, micro crack formation in SiO_2 during manufacture has been noted and attributed to local surface imperfections in the Si surface. This may subsequently affect breakdown voltage of the ion sensing film. CVD Si_3N_4 over SiO_2 provided a satisfactory insulator with high dielectric strength in solution such that breakdown occurred at $\approx +15\text{V}$ dc. The rf sputtered Si_3N_4 over SiO_2 had a breakdown voltage of about half this value.²⁹ Since sputter deposition was used in this work, some Al_2O_3 and all Pyrex samples were prepared without SiO_2 . The total film thickness on Si was always $\approx 1000 \text{ \AA}$; when SiO_2 was used, each film was $\approx 500 \text{ \AA}$ thick.

All samples prepared were annealed at 1000°C for about 15 minutes. Chemical stability tests were carried out by immersion in $2 \times 10^{-3} \text{ M Li}_2\text{CO}_3$. A small cation was used as it typifies the worst case of likely ionic contamination and attack of the film. The effect of cation size was studied and is reported in Section II.2.1.1.2.2. Tests were carried out at 100, 200, and 250°C for from 21 to 24 hours. Each sample was observed microscopically (optical or electron microscope) before and after exposure. Color changes, indicative of a change in film thickness, as well as film characteristics such as cloudiness, pinholes, cracks, or partial loss were all noted. The samples were isolated from each other and from the vessel itself in glass containers; direct contact of the silicon with the Inconel test chamber resulted in electrolytic corrosion.

At 100°C three types of samples were tested: Al_2O_3 on a SiO_2/Si substrate, Al_2O_3 on a Si substrate, and Pyrex on Si substrate. (hereafter, samples will be represented as insulator/substrate, e.g., $\text{Al}_2\text{O}_3/\text{SiO}_2/\text{Si}$ on $\text{Al}_2\text{O}_3/\text{Si}$, etc.). The $\text{Al}_2\text{O}_3/\text{SiO}_2/\text{Si}$

and Pyrex/Si samples appeared unchanged. The $\text{Al}_2\text{O}_3/\text{Si}$ sample, originally brown in color had become somewhat purple. This indicated a possible thickness increase. Three new samples of the same types were tested at 200°C . The $\text{Al}_2\text{O}_3/\text{SiO}_2/\text{Si}$ sample showed no apparent physical changes. (In subsequent C-V testings at 100°C , some changes were noted and will be discussed.)

The $\text{Al}_2\text{O}_3/\text{Si}$ sample again appeared to have changed to a purple color. (Though the cause of this cannot be conclusively explained, the apparent thickness increase was confirmed in C-V tests.) The Pyrex/Si sample had changed from light yellow-green to blue, indicating a decrease in thickness. At one end, the film was completely removed exposing the silicon substrate. Under microscopic examination, the film appeared to terminate abruptly at a well-defined edge, inferring a loss of adhesion and subsequent cracking of the film, perhaps initiated at the exposed interface at the edge of the sample. Since some slight "pitting" of the surface was apparent, the Pyrex film was likely both eroded and to a slight extent dissolved.

All three film types, although affected in some minor way by 200°C electrolyte exposure, survived well enough for the intended use. The $\text{Al}_2\text{O}_3/\text{SiO}_2/\text{Si}$ system fared best and was ultimately selected for use in the sensor. While the insulator film survived, the aluminum metallizing on the opposite side of the chip was oxidized severely, as was the underlying reverse side of the silicon itself. This will not be a problem in the proposed design since contact will be made from the rear of the chip in a region completely sealed from electrolyte exposure. While not a problem in the final design, the corrosion of the non-passivated surface made evaluation of any insulator surface imperfection more difficult.

At 250°C , the silicon chip was severely oxidized on all surfaces except the one protected by the $\text{Al}_2\text{O}_3/\text{SiO}_2$ insulating film. All of the aluminum film on the back of the chip was lost and the underlying silicon corroded. In order to lessen the attack on the silicon, all exposed surfaces (except the $\text{Al}_2\text{O}_3/\text{SiO}_2$ film) were

covered with CVD platinum. After heating this system to 250°C for 20 hours, the platinum-covered silicon (n-type in this test) was unattacked. However, the surface insulated with $\text{Al}_2\text{O}_3/\text{SiO}_2$, although unattacked, lacked the characteristic color of the oxide film. A qualitative test was performed to ascertain the surface composition. The surface was determined to be hydrophobic, indicating that it was silicon since both SiO_2 and Al_2O_3 surfaces are hydrophilic. But, the silicon surface was uncorroded, unlike other silicon surfaces tested. The experiment was repeated with the same results. It appears that the Al_2O_3 film protected the silicon throughout most of the experiment and then adhesion of the film failed. The film was not recovered from the test solution. Since this was observed repeatedly, it would seem that some event precipitated film adhesion failure, an event occurring near the end of the experiment (since the silicon was uncorroded) such as the dimensional change in the chip on cool-down.

It is anticipated that CVD alumina, as opposed to the sputtered alumina employed in these tests, would exhibit better adhesion since it reportedly performs better under stress conditions.²⁹ The nature of the CVD process does not generate the stresses inherent in rf sputtering. More intimate contact to the SiO_2 may result, and a material with properties more nearly approaching the bulk substance is obtained. Confirmation of this within the time constraints of this project was not possible. Such tests are planned for inclusion in the Task II effort.

The experimental results are summarized in Table II-3. All sample films were visually unaffected by exposure to Li_2CO_3 for 24 hours at 100° or 200°C. Repeated exposure accelerated minimal localized attack, resulting in film destruction after several days. At 250°C, properly protected substrates were not attacked, but film adhesion seemed poor. An alternate deposition method is proposed to increase film adhesion to the point where the upper temperature limit will be determined by other considerations, among them substrate doping level.

TABLE II-3: SUMMARY OF STABILITY
TEST RESULTS

Sample	Temperature (°C) for About 24 Hours		
	100	200	250
Al ₂ O ₃ /SiO ₂ /Si	No change	No change	Film lost but Si unattacked
Al ₂ O ₃ /Si	Slight color change	Color Change (film thicker?)	Film lost, some Si attack.
Pyrex/Si	No change	Film thinner with edge erosion and pits	Film lost, Si attack.

2.1.1.2.2 Capacitance-Voltage Testing

As explained in Section II.2.1.1.1, capacitance-voltage (C-V) measurement techniques can be used to characterize several different bulk and interfacial properties of an electrolyte-insulator-semiconductor system. Sensitivity to ionic concentration changes at the electrolyte-insulator interface can be measured by noting shifts in V_{FB} . These can also be related to the presence of fixed surface charges at near the insulator-semiconductor interface, ionized traps and mobile ions in the insulator which can migrate to and from the insulator-semiconductor interface. Total capacitance (C_{tot}) and subsequent changes therein can be related to the insulator thickness. C-V tests are relatively simple to conduct since a dc bias with superimposed fixed-amplitude ac modulation is applied between a conventional reference electrode and the base of the chip, there being no need to fabricate FET structures for the screening of alternative insulator systems. C-V tests were used to determine the effects of high temperature electrolyte exposures, deducing changes in insulator thickness, mobile ion content, and pH sensitivity.

The three types of films discussed previously (Al₂O₃/SiO₂/Si, Al₂O₃/Si, and Pyrex/Si) were tested before and, where possible, after high temperature exposure. The experimental test cell used is

shown in Figure II-8. This high source impedance measurement mandates extreme cleanliness in sample and test cell preparation and handling, as well as shielded and guarded electronic measurements. Before and after each use, samples were washed first in deionized water, then in isopropanol, and finally ultrasonically cleaned in a 50:50 acetone/trichloroethylene mixture and dried at 110°C for 30 minutes. The test cell was ultrasonically washed in detergent, then deionized water followed by an isopropanol rinse and a thorough drying at 60°C.

The back side of each chip was metallized to assure electrical contact between the silicon and the metal base of the test cell. After assembly of the test cell, buffer was introduced via the inlet port. The cell was evacuated briefly to assure removal of entrained air bubbles. Buffer solutions could be changed by repeated flushing with the next test solution. A metal housing surrounded the test cell, providing electrical shielding and blocking all light (important since some of the devices were light-sensitive).

C-V curves were obtained by using an ac polarograph, Model 170 of Princeton Applied Research, Princeton, NJ. A 10 mv, 1000 Hz ac modulation was used, with ac current plotted versus the dc bias voltage. A phase lock detector amplifier was used so that the measured current could be correlated to device capacitance. A theoretical C-V curve is shown in Figure II-7.

Buffer solutions used were either L&N standard buffers at pH 4.0, 6.8 and 9.2, or specially prepared solutions made by neutralizing tetrabutylammonium hydroxide with phosphoric acid to the desired pH. The latter solution did not contain any of the small monovalent cations typically found in standard buffer solutions which have exerted a confusing effect on the test results.

Devices were heated in Li_2CO_3 , the results examined for evidence of film thickness and pH response changes, and also especially looking for changes in V_{FB} attributable to the penetration of the highly mobile, small Li^+ ion into the insulating film.

FIGURE II-8: EXPERIMENTAL TEST CELL FOR CAPACITANCE-VOLTAGE CHARACTERIZATION OF INSULATOR FILMS

Typical C-V curves obtained from $\text{Al}_2\text{O}_3/\text{SiO}_2/\text{Si}$ and Pyrex/Si films are shown in Figure II-9 and II-10 respectively. The non-ideality of the Pyrex/Si curve is apparent. For consistency in evaluation, the inflection point in the C-V curve was used to indicate the position of V_{FB} , a necessary approximation in these non-ideal curves. A computer program determined the location of the inflection point, assuring consistency of evaluation of the data generated. Since each sample was tested in at least three different pH values before and after high temperature testing, a vast amount of data was generated. Some inflection points were determined visually to save time, a procedure verified by selected comparison with the computer-determined values.

The dc voltage at the inflection point as a function of buffer pH is plotted for $\text{Al}_2\text{O}_3/\text{SiO}_2/\text{Si}$ films after 100 and 200°C exposure to Li_2CO_3 in Figures II-11 and II-12 respectively. While the pH response was still good after exposure, the shift in V_{FB} is evident, especially after 200°C exposure. This is believed due to Li^+ ions irreversibly penetrating the insulating film. Some decrease in film thickness was evidenced by the greater currents measured after exposure.

Similar data are shown in Figure II-13 for an $\text{Al}_2\text{O}_3/\text{Si}$ chip. (The data at pH=6.8 were ignored in determining the apparent pH sensitivity.) The C-V curves obtained from the sample were not ideal, but reasons for this were not further investigated.

Figure II-14 shows the results of Pyrex/Si film testing. The C-V curves were most difficult to characterize, as indicated in Figure II-10. Due to the non-reproducibility of the C-V tests, further use of this film was abandoned.

The effect of various cations in the high temperature solution was studied. $\text{Al}_2\text{O}_3/\text{SiO}_2/\text{Si}$ films were exposed to Li^+ , Na^+ , and Cs^+ solutions. The change in V_{FB} was markedly less as the size of the alkali cation increased, going from +1.8 V for Li^+ to +0.7 V for Cs^+ . Results for Cs^+ solutions at 200°C are shown in Figures II-15.

FIGURE II-9: TYPICAL C-V CURVE FOR $\text{Al}_2\text{O}_3/\text{SiO}_2/\text{Si}$ SYSTEM

CURRENT (5 nA PER DIVISION)

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FIGURE II-10: TYPICAL C-V CURVE FOR PYREX/Si SYSTEM

FIGURE II-11: V_{FB} vs pH FOR $Al_2O_3/SiO_2/Si$ SYSTEM

EXPOSURE: Li_2CO_3 , 24 Hrs., $100^\circ C$

FIGURE II-12: V_{FB} vs pH FOR $\text{Al}_2\text{O}_3/\text{SiO}_2/\text{Si}$ SYSTEM
EXPOSURE: Li_2CO_3 , 21 HRS., 200°C

FIGURE II-13: V_{FB} vs pH FOR Al_2O_3/Si SYSTEM
EXPOSURE: Li_2CO_3 , 21 HRS., $200^\circ C$

FIGURE II-14: V_{FB} vs pH FOR PYREX/Si SYSTEM
EXPOSURE: Li_2CO_3 , 21 HRS., 200°C

FIGURE II-15: V_{FB} vs pH FOR $Al_2O_3/SiO_2/Si$ SYSTEM
EXPOSURE: $CsCO_3$, 23 HRS., 200°C

The chip was tested from pH 2 to 13 in tetrabutylammonium phosphate buffer as described earlier. Since variation of V_{FB} as a result of exposure to the electrolyte causes a CO_2 measurement error in the proposed system, it is recommended that a cesium ion containing electrolyte be used with pretreatment of the sensor to minimize subsequent drift.

2.1.1.2.3 Tests in Simulated Brine

Although not the prime objective of this work, the recommended ISFET sensor insulation was C-V tested before and after exposure to simulated brine (25,000 ppm NaCl) to assess its viability as a pH in brine sensor. Figure II-16 shows its pH response before and after exposure, indicating that with proper design in-situ pH measurement should be feasible. The likelihood of sensor surface abrasion in the proposed CO_2 sensor is small due to the protective action of the rubber membranes. It should be recognized that abrasion is a greater potential problem in brine pH measurement due to the high level of suspended solids in the sample to which the sensing film must be directly exposed.

2.2 Internal Electrolyte

The internal electrolyte performs several functions. It must act as a pH buffer which changes in a prescribed manner with CO_2 partial pressure. It should not react with electrode components. It should have, if possible, the same osmotic pressure as the brine sample. Finally, it should contain whatever soluble species are required to stabilize the reference electrode potential. Each of these requirements is considered in turn.

2.2.1. Buffer Capacity

As indicated in the carbonate equilibria considerations discussed in Section II.1, the internal electrolyte should contain a carbonate or bicarbonate. The concentration must be high enough to avoid having the dissociation of water have a significant influence on the pH. On the other hand, a high buffer capacity requires a greater flux of CO_2 through the membrane to adjust the pH and from this point

FIGURE II-16: V_{FB} vs pH FOR $Al_2O_3/SiO_2/Si$ SYSTEM

EXPOSURE: BRINE (NaCl), 23 HRS., 200°C

of view a low concentration is desirable. The recommended compromise is an electrolyte containing 10^{-3} M carbonate and bicarbonate.

2.2.2 Corrosivity

The essential materials of the recommended sensor which contact the internal electrolyte have been tested in it and have been found to be relatively unaffected by such exposure. These include the pH sensing element, the pyrex stem upon which it is attached, the EPDM membrane and the Inconel housing. No corrosion problems which would jeopardize the minimum target lifetime of 24 hours are anticipated.

2.2.3 Osmotic Pressure

It would be desirable to match the osmotic pressure of the internal electrolyte to the brine sample for two reasons. An osmotic pressure difference would cause a pressure differential across the polymer membrane, risking movement or rupture. Secondly, water will permeate through the polymer membrane if there is an osmotic pressure gradient as driving force. Unfortunately, it is impossible to match the osmotic pressure since the brine composition is uncertain. Moreover, the osmotic pressure varies with temperature. The variation of the osmotic coefficient with composition is estimated to be less than $\pm 3\%$ from over a concentration range from 1-4 M total ionic concentration.⁸⁷ However, the vapor pressure lowering can be severe, for example ≈ 550 mm Hg in simulated geothermal brine at 250°C . At lower temperatures the effect is less, e.g., ≈ 120 mm Hg at 175°C . It is recommended that the electrolyte used contain a high concentration of salt to minimize the vapor pressure gradient. The salt should have cesium as the cation to minimize ion penetration into the insulator film.

2.2.4 Stabilization of the Reference Electrode

A low level of chloride ion, 10^{-4} M is recommended to stabilize the Ag/AgCl reference electrode⁸⁸ (see Section II.2.3).

2.3 Reference Electrode

An Ag/AgCl reference electrode is recommended for use in this sensor. The fundamental electrochemistry of such an electrode has been studied and proved satisfactory in high temperature brine application. Since H_2S will not be present in the internal electrolyte because of the interference getter system recommended, no other

special precautions to avoid H_2S contamination are required as would be the case if the electrode were to be used unprotected in geothermal brine.

2.4 Gas-permeable Membrane

The proposed high temperature CO_2 measurement electrode requires a membrane which is gas permeable but ion impermeable. In the initial screening process, standards were set against which candidate materials were judged. The target specifications for the polymers were intermittent service temperature at least to $250^\circ C$, mechanical and chemical stability above $250^\circ C$, and reasonably high permeability to CO_2 in thicknesses greater than 0.020". Many polymer classes were scrutinized. Nine different polymers from three polymer classes were chosen. The fluorocarbons are noted for their excellent chemical resistance and thermal stability at elevated temperatures. In this class, Teflon FEP, Teflon PFA, Tefzel (all from Dupont Co., Wilmington, Delaware), Teflon TFE and Halar (both from Chemplast, Inc., Wayne, New Jersey) were tested. Elastomers have mechanical properties which facilitate installation and sealing in an assembly accommodating minor dimensional variances. Just recently, changes in the curing process for EPDM (ethylene-propylene-diene terpolymer) produced an improved elastomer, capable of continuous service in the thermal and chemical environment of geothermal brines.⁸⁹ Because of the great effect of compounding differences on polymer performance, three different EPDM compounds were obtained for testing: EPDM #692-75 (Parker Seal Co., Lexington, Kentucky), EPDM #79E60-24-1 and #79E32-25-2 (from Exxon Chemical Co., Linden, New Jersey). Also in this class Kalrez (Dupont Inc., Wilmington, DE), a fluoroelastomer typically used in well logging operations, was chosen. Finally, Parylene-C (Novatran Corp., Clear Lake, Wisconsin) was obtained. It has recently been found useful in space applications due to its ruggedness even as a thin film.

All samples, except for Parylene-C (0.0025") and Teflon TFE (0.010") were obtained in thicknesses of 0.020" to 0.060". It was felt that within this range would be the optimum thickness for a good combination of mechanical stability and acceptable permeability.

The literature permeability data on candidate membrane materials is summarized in Table II-4

TABLE II-4: LITERATURE PERMEABILITY VALUES FOR CANDIDATE POLYMERS

POLYMER	CO ₂ PERMEABILITY	(cm ³) (cm)			REF.
		(sec)	(cm ²)	(cmHg)	
Teflon FEP	1.7 x 10 ⁻¹⁰				90
Teflon TFE	1.7 x 10 ⁻⁹				91
Teflon PFA	Not Available				--
Halar	6.59 x 10 ⁻¹¹				92
Parylene C	4.6 x 10 ⁻¹²				93
Tefzel	1.5 x 10 ⁻¹⁰				94
EPDM	≈ 5.2 x 10 ⁻⁹				95
Kalrez	Not Available				--

2.4.1 Testing of Candidate Membrane Materials

All polymer samples were evaluated for their resistance to chemical attack when exposed to each of the following solutions:

- A. Synthetic brine (25000 ppm NaCl, 0.01M Na₂CO₃, 0.01M NaHCO₃ adjusted to pH 6.7)
- B. Synthetic brine (same composition as A) + H₂S (75 ppm)
- C. 0.002M LiCO₃, adjusted to pH 7 (possible pCO₂ internal fill solution)

Changes in the physical appearance and moisture absorption properties were noted. After these preliminary studies were completed and the results analyzed, three of the samples were chosen for further testing and evaluation, studying changes in the membrane's CO₂ permeability after brine exposure. Sections II.2.4.1.1 and II.2.4.1.2 contain descriptions of the procedures and apparatus used in the preliminary studies and in the permeability tests, respectively.

2.4.1.1 Thermal and Chemical Stability

All samples were labeled, weighed and placed in 100 mls of the test solution. The test apparatus was a 2" I.D. vessel (Fig. II-17)

FIGURE II-17: INCONEL TEST CHAMBER

machined from Inconel #625. The test solution was thoroughly deaerated with N_2 , or $N_2 + H_2S$, for 20 minutes. All solutions contained excess SiO_2 to better simulate the actual brine composition. The chamber was sealed, heated to $250^\circ C$ (in the first test, with brine but no H_2S , the temperature was limited to $220^\circ C$) for 22 hours, then cooled. Upon removal the samples were washed ultrasonically in deionized water, towel dried and reweighed. Changes in physical appearance were noted. After sitting in air for 24 to 48 hours, the samples were weighed a second time. The loss of moisture absorbed in polymers after exposure to a high heat and humidity environment is known to be a rapid, spontaneous process,⁹⁶ and this amount of time was allowed to assure that the material had reached equilibrium with the room humidity. Fluctuations in the room humidity can be ignored since only relative comparisons are being made between the different samples. The difference between the first and second post-exposure weights gives a minimum value for the moisture absorption that occurred in the sample.

2.4.1.2 Permeability Test

In order to measure the permeability of samples of the size and thickness required in this study, accurate detection of flux rate as low as 6×10^{-4} cc/min is necessary. Some of the detection methods considered, which basically met the above requirements, included measuring the rate of movement of a "liquid slug" along a capillary tube,⁹⁷ measuring conductivity changes in a solution of $Ba(OH)_2$, where $BaCO_3$ is precipitated by the influx of CO_2 , use of a thermal conductivity cell to detect the gas⁹¹, and detecting the rate of pressure increase as CO_2 permeates the sample with a thermocouple vacuum gauge. The first two methods are limited by the time requirements. Calculations from literature permeability values showed that two of the three samples to be measured would take at least 6.5 hours per experimental run. The third method required a thermal conductivity cell with a sensitivity greater than those which were available within the time limits of this contract. The final method necessitated only a vacuum system which was virtually leak-free, and this was successfully implemented.

The test assembly shown in Figure II-18 was used. All tubing and valves were #316 stainless steel. The oven is shown because measurements at 95°C were intended. This would then give two data points which could be extrapolated (using an Arrhenius Plot) to give an estimate of the permeability constant at 250°C. However, the difficulties encountered in setting up the vacuum system left no time for obtaining this data.

In the test procedure, a membrane was cut to size and fit in the sample holder as shown. A 0.210 standard size butyl rubber O-ring was placed on top of the membrane and the holder was sealed by tightening the outer ring.

The entire system was evacuated overnight to insure complete outgassing of the membrane. Next, valves #1 and #4 were closed, and valve #3 was opened to allow CO₂ up to the right side of the membrane. For complete diffusion through the membrane, to reach an equilibrium state, the fluoropolymer samples required about 8-10 hours. The elastomer sample required about 15-30 minutes. Therefore, for the first two samples, the "leak rate" was evaluated over a period of two to three hours, and it ranged from .167-.267 μ /min. For the final (elastomeric) sample the leak rate was determined within the first 15 minutes after the test was started, and it ranged from 1.2-4 μ /min. Sixteen more hours were allowed to insure CO₂ saturation. The permeation testing began with evacuation of the system to the same level it reached after the overnight evacuation, $\approx$ 25 μ . This took only 15 to 30 minutes because outgassing of the membrane was now not required. Next, valves #1 and #4 were closed off, valve #3 was opened, and the CO₂ "flux" rate was determined by taking readings every minute. The value, after subtracting out the leak rate, was the permeability (at 25°C) in units of μ /min. The permeability constant of each polymer was computed by including corrections for thickness, area, pressure differential across the membrane, and gas volume of the vacuum system. Sample calculations, using the data from the Teflon FEP membrane, are given below:

FIGURE II-18: PERMEABILITY EXPERIMENT ASSEMBLY

Gross flux rate: .86 μ /min

Leak rate: .15 μ /min

Net flux rate: .71 μ /min

Sample thickness = .060" = .152 cm

Sample area = 2.7 cm²

Pressure across membrane = 97 cm Hg

System volume = 29.2 cm³

$$\frac{.71 \mu}{\text{min}} \times 29.2 \text{ cm}^3 \times \frac{1}{760000 \mu} \times 0.152 \text{ cm} \times \frac{1}{2.7 \text{ cm}^2} \times$$

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$$\frac{1}{97 \text{ cm Hg}} \times \frac{\text{min}}{60 \text{ sec}} = 2.77 \times 10^{-10} \frac{(\text{cm}^3)}{(\text{sec})} \frac{(\text{cm})}{(\text{cm}^2)} \frac{(\text{cm})}{(\text{cm Hg})}$$

This compares favorably with the literature value of 1.7×10^{-10} .

Following initial permeation constant determinations, the samples were treated in brine + H₂S for 22 hours at 250°C, then re-evaluated for changes.

2.4.2 Test results and Discussion

For the preliminary screening of the samples, results are categorized with respect to each material in the polymer class.

2.4.2.1 Fluoropolymer Stability

2.4.2.1.1 Teflon FEP

This material was chosen for its chemical inertness and high temperature stability. It has a continuous use temperature to 260°C. In brine, at 220°C, it showed the greatest amount of moisture absorption, 0.17%. In the brine + H₂S and Li₂CO₃ solutions it darkened considerably, indicating some sort of thermal degradation. The weight gain found after

these tests was 0.05 and 0.12%, respectively. Since this was lower than that seen at the more moderate temperature in the first test, the measured gain was probably offset by the degradation loss. It was not tested for its high temperature mechanical properties, but is known to flow somewhat in dry heat.

2.4.2.1.2 Teflon TFE

Like Teflon FEP, this is a very chemically inert polymer. It has a continuous service temperature of $>250^{\circ}\text{C}$, and is noted for its zero moisture absorption properties. The sample was unaffected by brine exposure at 220°C , but in brine + H_2S at 250°C it lost 0.32% of its initial weight. This was as expected since the literature states that at 232°C , small amounts of decomposition products are given off. Moisture absorption (0.48%) was seen after testing in the Li_2CO_3 at 250°C . Teflon TFE was eliminated from further consideration as a candidate membrane because its decomposition products could interfere with the CO_2 measurement system if they change the electrolyte pH. Also, it has very little mechanical strength at elevated temperature, making maintenance of mechanical seals extremely difficult.

2.4.2.1.3 Teflon PFA

This polymer is based on the TFE backbone but has perfluoroalkoxy side chains. This modification greatly increases its high temperature mechanical stability. It reportedly maintains strength and stiffness up to 500°F , as well as being chemically inert and having zero moisture absorption, comparable to TFE.

This sample was the least affected of all polymers tested in any solution. The maximum amount of moisture absorption seen was 0.07%, in brine + H_2S at 250°C . There were no other physical signs of degradation, such as darkening or deformation, after any of the exposure tests.

2.4.2.1.4 Halar

Even though its maximum service temperature is given as 180°C, this fluoropolymer was tested to determine if it could withstand intermittent exposure to higher temperatures. However, it melted, and turned opaque and yellow after exposure to brine at 220°C and was not tested further.

2.4.2.1.5 Tefzel

Tefzel is a fluoropolymer with improved high temperature mechanical performance over TFE and FEP. It has a service temperature of 200°C, but when exposed to brine at 220°C it was not visibly attacked. Some weight loss (0.08%) did occur though, indicating degradation. When tested in brine and H₂S and a pCO₂ internal electrolyte (Li₂CO₃) at 250°C, the results were similar to that of Halar.

2.4.2.2 Elastomer Stability

2.4.2.2.1 Kalrez

This material is actually a fluoroelastomer, combining the chemical resistance and high temperature properties of Teflon with the mechanical properties of an elastomer. When the sheet material was tested in brine and brine + H₂S, it became slightly embrittled, and absorbed up to 2% moisture. In the Li₂CO₃ solution it blistered badly and weighed 36% more than initially. After 48 hours in air the net weight was only 2.52% lower than after the first post-exposure weighing. A microscopic examination of a cross-section of the sample showed the blistered sections filled with water. To remove this, it was heated to 65°C overnight. The net weight gain (due to moisture) was determined to have been 17%. It was concluded that this elastomer may have potential application as an O-ring, where exposure is limited. As a membrane material however, it would not be useful.

2.4.2.2.2 EPDM #E692-75

This EPDM compound is the same as that tested in O-ring form in an earlier study with good results⁹⁸. This particular compound recently gave encouraging results when tested as a packing material in geothermal well operations. It was recommended by Dr. A. R. Hirasuna, based on his work studying geothermal elastomeric materials⁹⁹. Brine exposure tests for this application were done on the sheet material, and the results were comparable to our previous testing. In the brine and Li_2CO_3 electrolytes at 250°C, about 1.45% moisture absorption occurred. In the brine + H_2S , a weight loss of around 5.8% occurred, probably due to degradation by H_2S attack. In all tests, there was no visual evidence of attack.

2.4.2.2.3 EPDM #79E32-25-2 and #79E60-24-1 (Exxon Corp.)

The compositions of each of the above elastomers are listed in Table II-5.

TABLE II-5: COMPOSITION OF EPDM ELASTOMERS

A) <u>79E60-24-1</u>	<u>Parts by Wt.</u>	B) <u>79E32-25-2</u>	<u>Parts by Wt.</u>
Vistalon 560V	100	MD-709A	100
N 650 Black	100	N 550	4
N 762 Black	100	Translink 37	120
Sunpar 2280 Oil	120	Zinc Oxide	5
Zinc Oxide	5	Stearic Acid	1
Stearic Acid	1	Agerite Resin MA	1
Sulfur	0.5	Sunpar 2280 Oil	53
TMTD	2.5	Silane A 172	1
ZDMDC	2.5	TE-80	4
DTDM	1.7	DiCup 40 KE	8
ZDBDC	2.5	Sulfur	.2

Both were cured for 20 minutes at 160°C. It has been shown that, in

general, the peroxide cured elastomer is superior to the sulfur cured in the geothermal environment⁸⁹. Compound A is sulfur cured and Compound B is peroxide cured. The intent was to compare these two in the exposure tests relative to this application, and the results were as expected. In the brine + H₂S, at 250°C, both samples showed a weight loss (1.1 to 2.3%) due to degradation from H₂S attack. However, in brine at 220°C, Compound A lost weight (0.14%) and Compound B gained .96%. The former was probably being thermally degraded, while the latter simply showed a typical moisture absorption characteristic. In the Li₂CO₃ electrolyte at 250°C, both compounds "blistered" slightly and gained weight, especially the sulfur cured Compound A, which had a net weight gain of 5.6%. Overall, these two formulations had less resistance to chemical attack than EPDM #E692-75, and this is probably a result of formulation and curing differences. Mr. Chris Otterstadt, Senior Engineer at Exxon who provided these samples, recommended a formulation which he felt would best meet the requirements of this application. Its composition is listed below. Although the material was not available for testing at the time, any EPDM formulation would have to be tested prior to use in the sensor.

TABLE II-6: COMPOSITION OF UNTESTED EPDM

Vistalon 707 (or 404)	100
N 650 Black	40
N 747 Black	30
Sunpar 2280 Oil	25
Zinc Oxide	5
Vulcup 40 KE	6.25
EDMA	2.0

2.4.2.3 Parylene-C Stability

Poly-para-xylene is a vapor deposited film, capable of withstanding temperatures as high as 250°C, and is extremely resistant to chemical attack. Currently, the technology allows production of films no thicker than 0.003", and even these are non-uniform and not guaranteed to be pinhole free. A 0.0025" sample was tested in brine at 220°C, and though its weight didn't change, it turned milky and slightly brittle. Mechanical problems of sealing such a thin film, and the necessity for an absolutely pinhole free membrane eliminated Parylene-C from further consideration.

2.4.2.4 Permeation Test Results

The three materials chosen for testing were those which survived the preliminary exposure tests with little or no signs of chemical attack, and had the high temperature mechanical properties such that they could maintain a leak-free seal in the geothermal environment. These were Teflon FEP, Teflon PFA, and EPDM #692-75. The first sample is the least desirable in terms of the requirements listed above, due to its tendency to "flow" at high temperatures. However, it is the only one for which literature permeability values were widely available, so it was most useful as a reference for verification of the accuracy of the detection system used. Approximate permeability values for the other two samples were obtained from persons with experience in characterizing the polymer in question. Dr. A. R. Hirasuna, whose work on geothermal elastomeric materials was previously cited, had done some qualitative permeability work with EPDM in which he had concluded that its permeability was about one order of magnitude greater than that of butyl rubber. He pointed out, though, that variations in compounding could have a large affect on this value. Dr. Larry Ferris, at DuPont's Plastic Product & Resins Department, reported that the crystalline structure of PFA, a major factor in gas permeability, was similar to that of TFE. Their respective permeabilities are thus likely similar, and greater than that of Teflon FEP. He also stated that FEP at 100°C becomes more permeable than TFE due to its activation energy. Unfortunately, this could not be confirmed. Therefore, from the sources available, the permeabilities of the samples should be ordered (at 25°C) as follows: EPDM > PFA > FEP. This was confirmed experimentally. Table II-7 gives the experimental data and the computed permeabilities. Though agreement with the literature values was not perfect, experimental values are within 40%. A prime factor contributing to this difference is variations in the sample processing. However, of greater significance in this study are the changes in permeability after exposure to brine + H₂S. In all cases the permeability dropped, with EPDM being the most affected and Teflon FEP the least. The loss seen in EPDM is attributed to the effect of crosslinking initiated by the H₂S present.

TABLE II-7: EXPERIMENTAL PERMEABILITY DATA AND COMPUTED VALUES

Brine Exposure	Membrane Sample	Sample Thickness (cm)	Area (cm ²)	Leak Rate (μ/min)	Net Flux (μ/min)	Experimental CO ₂ Permeability	Literature CO ₂ Permeability
						$\frac{(\text{cm}^3)(\text{cm})}{(\text{sec})(\text{cm}^2)(\text{cm Hg})}$	$\frac{(\text{cm}^3)(\text{cm})}{(\text{sec})(\text{cm}^2)(\text{cm Hg})}$
Before	Teflon FEP	.1524	4.41	0.213	1.21	2.77×10^{-10}	1.7×10^{-10}
After	Teflon FEP	.1524	2.70	0.15	0.71	2.66×10^{-10}	
Before	Teflon PFA	.1524	2.70	0.23	2.23	8.33×10^{-10}	≈FEP, Not Available
After	Teflon PFA	.1524	2.70	0.231	1.47	5.5×10^{-10}	
Before	EPDM	.0762	2.70	1.2	12.8	2.39×10^{-9}	$\approx 5.2 \times 10^{-9}$
After	EPDM	.0762	2.70	1.0	4.3	8.03×10^{-10}	

In conclusion, these test results show that EPDM #E692-75 remains the most permeable of the three candidates after exposure, even though it is the most affected by it. In the proposed design it is also the material most easily implemented, since it can easily be made to conform to the pH electrode surface, and easily sealed into the CO₂ electrode body. Though it is recognized that elevated temperature data would be necessary to finalize the conclusion, it is now the recommended material for use in the CO₂ electrode for measurement in geothermal brine. Alternate candidates, chosen mainly for the property of chemical inertness are PFA Teflon and FEP Teflon. Neither, however are superior to the EPDM in dimensional stability under pressure.

III. CHEMICAL INTERFERENCES

Chemical interferences originating in the brine are limited to those which can permeate through the polymeric membrane into the electrolyte and alter its pH. Only species soluble in the membrane, i.e. gases, can interfere, and only those in the brine at a significant vapor pressure. Various compilations of brine composition^{2,5,6} mention H₂S, N₂, NH₃, H₂, CH₄, Ar, O₂ and He, HCl, HF and SO₂ in addition to CO₂. Of these, NH₃, H₂S, HCl, HF and SO₂ can directly alter solution pH and are possible interferences. The latter three, however, are reportedly present in extremely low vapor pressures and should not interfere.

1. Estimate of the Magnitude of Interferences

In deep hot waters, the partial pressure of NH₃ has been reported to be from 0.0003 to 0.02 bars, of H₂S from 0.002 to 0.2 bars and of CO₂ from .06 to 11 bars.^{6,p73} To a first approximation, H₂S and CO₂ dissolve in aqueous solutions to a similar extent.^{5,p776} Over the temperature range 150-250°C, the Henry's law constant for CO₂ is 10⁻² while that of H₂S is 10^{-1.53}. The first ionization constant of H₂S is very nearly identical with that of H₂CO₃, so that it could appear that each gas would exert a comparable effect on the internal electrolyte pH. The corresponding effect of NH₃ is more difficult to assess because the necessary constants are not known, but it is likely that, except in the rare case where the ammonia partial pressure is unusually high, NH₃ will be a relatively slight concern.

2. Interference Avoidance versus Interference Compensation

Given the likely interference from H₂S and/or NH₃ in the brine, two alternative approaches to eliminate the problem were studied. In principle, one can take steps to exclude the interfering species from the immediate region of the sensor, thereby avoiding the deleterious effects of the interferences. Such an approach, recommended for inclusion in the CO₂ sensor, is described and tested in Section III 2.1.

Alternatively, the interfering species may be allowed to permeate the system, and a compensation scheme be included to lessen or eliminate measurement error. A compensation scheme was devised and tested and is reported (Section III 2.2) as an alternative should the interference avoidance approach fail.

2.1 Interference Avoidance

Interference from H_2S and/or NH_3 may be avoided by use of a getter or reactive material in the diffusion path between the geothermal brine and the sensor internal fill solution. This approach was used successfully for the amperometric measurement of dissolved oxygen in a high H_2S environment.¹⁰⁰ It employs a two-layer membrane with a sulfide reactive compound acting as a "getter" trapped between the layers. (The sulfide getter is not placed directly in the internal electrolyte since, as it converts H_2S to the insoluble sulfide, it would free H^+ and lower the internal pH, causing a measurement error. An increase in acidity between the layers of membrane is of no consequence). In the CO_2 sensor recommended, the getter system consists of CuSO_4 (sat'd) in a 1.0 M HCl solution. As will be shown, this system allows the passage of CO_2 , while reacting H_2S with the CuSO_4 to form the insoluble CuS . The other possible interferent, NH_3 , is neutralized to form soluble NH_4Cl before it reaches the internal electrolyte.

Unlike the interference compensation system studied (Section III.2.2 and VI.3), selective removal does not require an additional electrode. Furthermore, since H_2S does not enter the internal solution, the silver/silver chloride reference electrode need not be protected internally from sulfidation. The relative simplicity of the design and the favorable experimental results reported below require that interference avoidance be included in the brine CO_2 sensor system.

2.1.1 Experimental Proof Testing at Room Temperature

A test chamber, shown schematically in Figure III-1, was machined from TFE Teflon to accommodate the membrane-getter system. This

FIGURE III-1: EXPERIMENTAL CONFIGURATION FOR GETTER SYSTEM EVALUATION; WITH EXPLODED VIEW OF TEST CELL

system consists of a porous substrate, soaked in 1M HCl saturated with CuSO_4 , placed between two layers of the recommended membrane material (Section II.2.4), 0.030" thick EPDM. The substrate acts as a wick and provides a continuous film of solution between the membranes in the gas diffusion path. Since EPDM is an elastomer with excellent mechanical sealing capability, the membranes may be compressed between the cell halves as shown to form sealed chambers on either side.

The lower chamber contains inlet and outlet ports for flowing diluted H_2S gas past the membrane. A solution, used to measure any influx of H_2S through the membrane, is introduced into the top chamber via a thru-hole tapped to accommodate an O-ring screw. Thereby, a sealed system is maintained during all tests.

In the center of the solution chamber, extending slightly beyond the plane of the membranes, is a rounded post. Its purpose is to exert a slight force on the membranes to assure that no gap develops between them. The slightly concave membrane shape which results helps to accurately place and maintain a small volume of test solution directly atop the upper membrane surface.

Two areas were explored experimentally. First, it was shown that gases could permeate the system if the CuSO_4 getter were omitted, since diffusion of CO_2 through the membranes and aqueous film is required before it can be sensed by the internal electrodes. Secondly, the removal of H_2S by the CuSO_4 getter was demonstrated. Each is reported below.

2.1.1.1 Gas Permeation through the Membrane-Solution Layers

When CuSO_4 was omitted from the 1M HCl getter solution, H_2S could theoretically permeate the system and be collected in the solution chamber for subsequent analysis. Confirmation of H_2S permeation would infer unhindered CO_2 permeation as the two gases are comparable in molecular diameter, a major factor governing permeability.

It was necessary to determine the H₂S permeability constant to design the experimental test conditions and optimize parameters such as membrane area, H₂S partial pressure, temperature, and duration. Permeability values in EPDM are not available because the polymer has only recently been developed and has not been well characterized for use as a membrane material. In work reported in Section II.2.4, the permeability constant for CO₂ in EPDM was determined experimentally ($2.39 \times 10^{-9} \text{ cm}^3 \text{ cm sec}^{-1} \text{ cm}^{-2} (\text{cm. Hg})^{-1}$) and was found to be in reasonable agreement with the estimated value of another researcher. The CO₂ permeability can be used to estimate the H₂S permeability.

$$P_{ik} = F_i G_k H_{ik} \quad \text{III-1}$$

where P_{ik} is the permeability constant of gas k in membrane material i , F_i is a constant characteristic of the membrane material, G_k is a constant characteristic of the gas (24.2 for CO₂ and 21.9 for H₂S) and H_{ik} is a constant related to the interaction of the membrane and permeant. (H_{ik} is usually very close to unity for non-condensable gases and the values for CO₂ and H₂S in EPDM will be presumed to be one.)

Therefore:

$$F_{\text{EPDM}} = P_{\text{CO}_2, \text{EPDM}} / G_{\text{CO}_2} = 9.88 \times 10^{-11} \quad \text{III-2}$$

$$\text{and } P_{\text{H}_2\text{S}, \text{EPDM}} = F_{\text{EPDM}} \times G_{\text{H}_2\text{S}} = 2.16 \times 10^{-9} \quad \text{III-3}$$

This computation reportedly results in an estimate of $P_{\text{H}_2\text{S}, \text{EPDM}}$ accurate to within a factor of three.⁹⁰

Using this estimate of $P_{\text{H}_2\text{S}, \text{EPDM}}$, the test configuration selected included two EPDM membranes, each 0.030" thick, sandwiching a 0.005" thick micro-porous filter saturated with HCl. Nitrogen containing first 0.2% H₂S and later 2.0% H₂S was flowed through the gas chamber and 5 ml of deaerated 1M NaOH filled the liquid chamber and absorbed incoming H₂S. The gas was allowed to permeate the membrane layers for from 24 to 64 hours. The H₂S concentration in the solution computed using $P_{\text{H}_2\text{S}, \text{EPDM}}$ was from 3.3×10^{-5} to 8.8×10^{-4} moles/liter. This computation assumes that equilibrium conditions between membrane

and permeant are established immediately, i.e. that the amount of permeant entering the membrane is equal to the amount leaving it, and is governed solely by the rate of diffusion. Theoretically, permeation of small molecules through a polymer film occurs by the consecutive steps of solution of the permeant in the polymer and diffusion of the dissolved permeant. Thus, equilibration time is related to the solubility of the permeant in the barrier material as it diffuses in from the high concentration side. The experimentally determined value, therefore, may be somewhat less than that computed.

It proved difficult to analyze the H_2S concentration in the collection solution for a variety of reasons. Several analytical techniques possess the required sensitivity, and the first tried was direct potentiometric measurement with a sulfide selective electrode. It has been shown¹⁰¹ that when precautions are taken to avoid error due to sulfide oxidation, accurate measurements at $3.1 \times 10^{-6} \text{ M}$ have been achieved, and complexation of heavy metal impurities improved the sensitivity to approximately 10^{-7} M .

Standard solutions were prepared by equilibrating a known volume of H_2S with deaerated 1 M NaOH . Low level standards (10^{-4} to 10^{-7} M) were prepared by dilution of the higher level standards with deaerated 1 M NaOH . The sulfide electrode was polished prior to use, and all analyses were carried out under a protective blanket of nitrogen.

Precise analysis of standard solutions with sulfide contents greater than 10^{-5} M was achieved. However, analysis of lower levels proved unreproducible due to drifting readings.

Rather than pursue the drift problem, the sulfide indicator electrode was used to detect the end-point of a sulfide titration with AgNO_3 . In this mode, neither the Nernstian performance of the electrode nor the absolute value of the output signal is critical to good analysis. The low level analyses were still imprecise, partly due to the difficulty of preparing the dilute AgNO_3 titrant and the very small volume additions required.

Coulometric generation of the silver ion titrant was employed, still using potentiometric end-point detection. Coulometric generation of titrant facilitates the addition of very small increments (10^{-8} gram equivalents or less) with no volume increase. The current used to generate the silver ion was controlled and was decreased to less than 10^{-6} ampere near the end point. The current integral was recorded automatically versus the potentiometric indicator signal using Princeton Applied Research Models 173 and 179.

Analysis of freshly prepared sulfide standards gave reasonable and precise results at all levels of interest, verifying the capability of the coulometric titration procedure in this application. However, repeated analysis of the NaOH collector solutions showed little or no sulfide present. Given the measurement sensitivity, either little or no H_2S was permeating the membrane system, or after entering the collection system it was being destroyed before analysis. The latter proved to be the case. It was demonstrated that as much as one-half of the sulfide in dilute samples was being lost in as little as 24 hours, presumably by oxidation even in "deaerated" solution.

Several steps could have been taken to eliminate the sulfide oxidation observed, including the use of soluble anti-oxidants such as ascorbic acid. The required experimental effort was circumvented by the indirect measurement of the sulfide permeant. The sulfide was reacted with Cu^{++} as soon as it reached the collection solution forming stable, insoluble CuS . The sulfide combined with Cu^{++} before oxidation could occur, and the consumption of Cu^{++} indicated by subsequent analysis was used to indicate the H_2S permeation.

A precisely known volume of dilute $CuSO_4$ solution was placed in the cell contacting the membrane surface. Only one milliliter of solution was required to cover the entire membrane surface on the concave side. The measurement of Cu^{++} was initially carried out using coulometric stripping analysis, a technique well-suited for the analysis of small samples of low concentration. This electrochemical technique includes two discrete steps. The copper in the analyte

is first reduced to metallic copper and deposited on the working electrode surface. Subsequently, it is oxidized to Cu^{++} and diffuses into the solution. During the deposition step, the electrode is held at a potential cathodic of the reduction potential of copper. The current is relatively low since the Cu^{++} arrives at the electrode surface from the sample at a low rate. The deposition results in a preconcentration of the copper into a small volume (on the electrode surface). To strip this material, the electrode potential is changed back in the direction required for oxidation (i.e. to the anodic potential). At the oxidation potential of the species, the faradaic current (or stripping current) produced by this oxidation is measured.

The stripping current of the analyte is proportional to the amount preconcentrated on the electrode and thus is proportional to the original unknown concentration.

In using stripping analysis, many variables must be optimized for the particular system being studied. Stirring or flow rate, working and counter electrode design (i.e. material, sizes, placement, etc.) and reference electrode type, fill solution, and isolation are all critical concerns for accurate results. A platinum foil working electrode was used, with a platinum wire counter electrode and a double junction Ag/AgCl (saturated with KCl) reference electrode with low leakage ceramic junctions. Initial results demonstrated the tremendous sensitivity of the technique, but the results were not of sufficient precision. The most likely improvement to be attempted was the use of a mercury film or hanging mercury drop working electrode, one of proven capability but greater experimental complexity.

Both the experimental results and theoretical considerations indicated that the Cu^{++} concentrations were high enough to use dc polarography at the dropping mercury electrode (DME). The DME is a reliable electroanalytical tool, largely because it provides a reproducible, continuously renewed working electrode surface. Polarography is a well-developed electroanalytical method, and for simpli-

city may be generalized for this study to be the control of the potential of the DME and the measurement of the resulting current. When a potential sufficiently electronegative to completely reduce all the available Cu^{++} is applied to the electrode, the concentration of Cu^{++} at the electrode surface is zero. A concentration gradient exists which causes Cu^{++} to diffuse to the electrode and give rise to a "diffusion-limited" current. This diffusion current, under properly controlled conditions, is directly proportional to the Cu^{++} concentration in the solution.

In this application, polarography has an advantage over stripping analysis since it measures copper concentration rather than quantity. Therefore, one need not measure precisely the small volumes of samples extracted from the test chamber and analyzed.

The DME was used in conjunction with a Ag/AgCl reference electrode and a platinum counter electrode. The supporting electrolyte to which the test sample was added was 1.0 M tetrabutylammonium hydroxide adjusted to a pH of 4 with H_3PO_4 . This electrolyte was concurrently being used for capacitance-voltage studies (Section II.2.1.1) and proved to suppress migration currents and polarographic maxima, and produce a stable, low residual current (i.e. blank). The standard deviation of measurements of known, low level (~ 0.0003 M) copper solutions was 4%.

This successful copper analysis system enabled study of the getter system with greater accuracy. The EPDM membranes were used with a 0.005" thick porous filter impregnated with 1M HCl and were placed in the test chamber and exposed on one side to 2% H_2S (balance N_2) for 96 hours. One milliliter of 7.2×10^{-3} M CuSO_4 solution was used as the collection solution. Subsequent analysis of the solution showed that 74% of the copper ion remained in solution, the apparent H_2S flux being 50% higher than computed based on the permeability constant estimate previously derived.

Given the poor thermal stability of the porous filter material (Section 2.1.2), the test was repeated twice with borosilicate glass paper (0.002" thick) replacing the filter material. The first test, lasting 70 hours, showed an H_2S flux 75% of that predicted, whereas the second, lasting 115 hours, resulted in a measured flux 25% of the anticipated value. This variation, while appearing significant, likely reflects the loss of H_2S by oxidation during the later stages of the long duration tests as the copper concentration in the collection solution decreases and fails to precipitate the sulfide before oxidation can occur. There are also many influences on membrane permeability which, acting in concert, could have affected the results. These include molecular morphology of the material, thickness variations, differences in molecular configuration of the elastomeric surface compared to the bulk, inhomogeneous filler content, and microcrystallinity and crosslinking in the polymer. All of these factors can vary in different areas of the same production sample; fresh sections of membrane were used for each experiment. The influx of H_2S at nearly the theoretical rate (in the absence of $CuSO_4$ in the membrane getter solution) indicates that a gas which is not absorbed in the getter solution does permeate both membranes and would reach the internal electrolyte and measuring electrode of the proposed CO_2 sensor. Therefore, carbon dioxide, which should not be impeded by the getter system, should be sensed at the electrode surface.

Data from these tests and that reported in Section 2.1.1.2 appear in Table III-1.

2.1.1.2 H_2S Removal by a $CuSO_4$ Getter

The efficacy of the proposed getter system was tested at room temperature. The two EPDM membranes and borosilicate glass paper structure described in Section III.2.1.1.1 was again used, but this time the getter solution was 1 M HCl plus $CuSO_4$ (sat'd at 25°C). The resultant solution was approximately 1.4 molar Cu^{++} .¹⁰² The collector solution placed in the test chamber with the membrane layers was one milliliter of 5×10^{-4} M $CuSO_4$, and 2% H_2S in N_2 was passed through

TABLE III-1 SUMMARY OF GETTER EXPERIMENTAL RESULTS

Getter Solution	Test Duration	Moles of Cu^{++} in Collection Solution	Moles Sulfide Permeant	Apparent EPDM Permeability Coefficient* $(\text{cm})^3(\text{cm})(\text{cm})^{-2}(\text{sec})(\text{cm Hg})$
1 M HCl in porous filter medium	96 hours	7.2×10^{-6}	1.9×10^{-6}	3.1×10^{-9}
1 M HCl in boro- silicate glass paper	70 hours	1.0×10^{-6}	6.7×10^{-7}	1.5×10^{-9}
1 M HCl in boro- silicate glass paper	115 hours	5.0×10^{-7}	4.2×10^{-7}	5.7×10^{-10}
1 M HCl + CuSO_4 (Sat'd) in borosili- cate glass paper	168 hours	5.0×10^{-7}	$<3 \times 10^{-8}$	Not applicable

* = the theoretical permeability coefficient computed for EPDM, $\text{P}_{\text{H}_2\text{S}}$, is 2.16×10^{-9} (see text).

the gas chamber of the cell for 168 hours. Within the detection limits of the analysis, no decrease of the copper content of the collection solution could be detected, but black CuS was observed to have precipitated in or on the glass paper between the membranes. The sensitivity was such that $\sim 3 \times 10^{-8}$ moles of H₂S flux could have been detected. This test result is also summarized in Table III-1.

The capacity of the H₂S getter system was estimated as follows. The glass paper, 0.005 cm thick and 2.54 cm diameter was presumed to have 50% void volume. The effective getter solution volume is therefore 1.3×10^{-5} ml, and given its 1.4 M copper content, there are 1.8×10^{-5} moles of available Cu⁺⁺ to precipitate an equal number of moles of H₂S as the sulfide. The range of permeabilities observed in earlier experiments (without the CuSO₄ in the getter solution) indicates an expected getter lifetime in the experiment of from 460 to 2400 hours.

2.1.2 High Temperature Use of the Getter System

The porous filter material, borosilicate glass alternative, and the EPDM membrane material were all subjected to 24 hour exposure to the proposed getter solution, 1 M HCl saturated with CuSO₄. The EPDM showed no visual sign of attack. The porous filter material was degraded beyond recovery. The borosilicate glass paper, only 0.002" thick, was not recovered intact, but the fibers which had separated were recovered. Given other experience with exposure of borosilicate glass to hot brine, and the fact that mechanical integrity of the glass paper is unimportant in this application, the chemical stability of the fibers suffices to justify their use in the CO₂ sensor.

While the integrity of the getter system materials was experimentally evaluated, no tests were conducted to determine the high temperature performance of the combined elements. Of special interest is the permeability of the EPDM membranes and the capacity (lifetime) of the getter system.

Factors which can effect permeation are determined by the type of diffusion process occurring in the polymer. As opposed to the "passive" process of flow through cracks and pores, transport through EPDM is governed by "activated" diffusion, wherein the permeant dissolves into the polymer. In an intact membrane, activated diffusion is little affected by hydrostatic pressure increases, is somewhat dependent (inversely) upon osmotic pressure and directly proportional to permeant vapor pressure. Since the ionic strength of the getter solution is comparable to that of the brine, effects of osmotic pressure differential are considered negligible. Thus, one can limit consideration of the vapor pressure of H_2S and the permeability constant of the membrane.

The room temperature permeability constant, P_{H_2S} , of EPDM was estimated in Section II.2.4. The permeability of H_2S is no-doubt highly temperature dependent, but no value at elevated temperature has been reported. It is possible to estimate the permeability constant at a second temperature if a value has been established at one temperature.⁹⁰

$$\log P_2 = \log P_1 + \frac{E_p}{.0046} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad \text{III-5}$$

Where P_1 and P_2 are the permeability constants at $T_1 < T_2$ ($^{\circ}K$) and E_p is the activation energy of the diffusion process in the material. The accuracy of this approximation is best if the temperature interval is small and if the polymer has no second order transition point in the temperature interval under consideration. Whether these conditions are met is suspect. Since P is only known at $25^{\circ}C$, it will be necessary to consider a $225^{\circ}C$ interval to estimate the permeability coefficient at $250^{\circ}C$. Secondly, no information regarding the occurrence of a second order transition, or lack thereof, was found in the literature. Finally, although the activation energies for most permeation processes lie between 5 and 16 kcal/mole, that of H_2S permeation through EPDM is not known. The system most closely resembling the one of interest for which data is known is thought to be CO_2 diffusion in

butyl rubber, wherein E_p is 8 kcal/mole. Using this value, the permeability coefficient of H_2S in EPDM is estimated to be about $7 \times 10^{-7} \text{ (cm}^3\text{)(cm)(cm}^2\text{)}^{-1}\text{(sec)}^{-1}\text{(cm Hg)}^{-1}$.

Ellis reports⁶ that the maximum level of H_2S ever measured in geothermal wells was 0.2 bars ($\approx 15 \text{ cm Hg}$). Another source² gives a maximum value of 75 ppm, which by using Henry's Law constant at 250°C can be expressed as an effective partial pressure of H_2S equal to 5.7 cm Hg. For the purpose of computing the maximum H_2S flux permeating the outer membrane layer, Ellis' value will be used, recognizing that it is a "worst case" value and typical H_2S levels to be encountered are much lower.

It is next necessary to estimate the amount of copper sulfate in the getter system recommended. The design includes a total getter solution volume estimated to be 10^{-2} cm^3 . For increasing capacity, a 1 M HCl solution saturated with CuSO_4 at 100°C ($\approx 4.2 \text{ M/L}^{102}$) is recommended. The number of moles of available Cu^{++} , and therefore the moles of H_2S which can be trapped, is approximately 4×10^{-5} . The volume of 4×10^{-5} moles of H_2S at standard temperature and pressure is 0.9 cm^3 .

The membrane thickness through which the H_2S must diffuse to reach the getter is 0.09 cm, and the effective membrane area, taken to be defined by the hole in the thin metal diaphragm separating the outer membrane from the getter solution, is 0.2 cm^2 .

Using the permeability coefficient estimate for 250°C and the other values derived above, one can compute the effective lifetime of the getter solution, t .

$$t \doteq \frac{(0.9)(0.09)}{(0.2)(15)(7 \times 10^{-7})} \doteq 40,000 \text{ sec} \doteq 10 \text{ hours} \quad \text{III-6}$$

This crude estimate, it must be recalled, presumes the highest H_2S level ever encountered at the relatively high temperature of 250°C . Furthermore, it was shown in Section II.2.4.2.4 that the permeability of EPDM decreased to about 1/3 of its original value

after exposure to simulated brine plus H_2S for 22 hours at $250^{\circ}C$. The level of H_2S in this test was ≈ 75 ppm, or about $1/3$ the "maximum" value used in the above computations. The decreased permeability, attributed to crosslinking of the elastomer initiated by the H_2S , would in use extend the getter lifetime beyond the estimated value. Within the limits of the approximations used to develop the lifetime estimate, it is believed that the getter system will effectively limit H_2S incursion for at least 24 hours, perhaps with the exception of the highest H_2S levels at the highest temperatures.

2.2 Interference Compensation

An alternative to the interference avoidance system described in Section III.2.1 was studied in detail. It involves allowing the acidic or basic gases (primarily H_2S) to permeate the system and, using an additional electrode (e.g. LaF_3), to develop a signal which effectively compensates for the erroneous component of the pH sensor signal. The interference compensation system was judged inferior to the interference avoidance approach because of its greater complexity and the possibility that it would fail due to unfavorable solubility and equilibrium relationships which might be encountered at elevated temperatures. A description of the theory behind the technique and experimental tests which resulted in the deferral of further effort along these lines are included in the Appendix, Section VII.3.

IV. PROPOSED PROBE DESIGN

1. Probe Components

The proposed probe design includes the essential components whose functions have been described in earlier sections. These are a pH sensing electrode, a reference electrode, an internal electrolyte, and a gas permeable membrane system incorporating an interference getter. In addition, it is necessary to include pressure relief to accommodate the net change in volume due to thermal expansion of the internal electrolyte and its compressibility under pressure. Each of these components are discussed in Section IV-1, with the probe assembly procedure, temperature compensation, calibration, unit cost, and potential sources of error discussed in subsequent sections.

1.1 pH Sensor

The ISFET pH sensor using an Al_2O_3 pH sensitive gate insulation is described in detail in Section II.2.1.1. Ohmic contact will be made through the back side of the chip, with the chip sealed to a glass tube which acts as a feed-through for the leads. The pH sensor is positioned behind the membrane-getter system as shown in Figure IV-1.

1.2 Reference Electrode

A simple chloridized Ag/AgCl reference element is placed in direct contact with the internal electrode as shown in Figure IV-1. Since the chloride content of the solution will be fixed, and the H_2S content negligible, no isolation of the reference electrode is required.

1.3 Internal Electrolyte

The internal electrolyte should have a reasonably low carbonate/bicarbonate content to minimize response time (i.e., a low buffer capacity) and a higher concentration of "inert" electrolyte to increase the ionic strength, more nearly matching that of the sample, to stabilize the internal activity, coefficients, osmotic pressure, and Henry's Law and dissociation constants. A solution 0.001 M in both cesium carbonate and cesium bicarbonate, plus 0.1 M cesium sulfate for increased ionic strength and 10^{-4} M CsCl for reference stabilization

FIGURE IV-1: PROPOSED pCO_2 PROBE ASSEMBLY

DET.	DESCRIPTION
1	Ag REFERENCE
2	INCONEL HOUSING
3	INTERNAL ELECTROLYTE RESERVOIR
4	DIAL MEMBRANE
5	COVER
6	GAS IMPERMEABLE METAL FOIL
7	H_2S GETTER
8	PH ISFET

is recommended. Cesium salts are recommended since they minimize the cationic penetration of the alumina surface of the ISFET pH sensor, and sulfate was selected because of its relative thermal stability, lack of ion association, and relative freedom from attack on other sensor materials.

1.4 Gas Permeable Membranes and Interference Getter System

Two EPDM membranes are used as shown in Figure IV-2.

Sandwiched between the two is a concentrated solution of CuSO_4 in 1M HCl. EPDM was selected because of a balance of desirable properties including mechanical survival in brine during our tests, maintenance of high permeability, and diffusion coefficient (at room temperature) after exposure to the brine, and favorable elastomeric qualities. Details of the test which mandated this choice are presented in Section II-2.4.

The interference gas getter system is described in Section III-2.1. It includes a thin layer of acidic solution containing concentrated CuSO_4 held in a porous glass paper matrix. A thin Inconel diaphragm prohibits gas permeation except through the central region behind which is located the ISFET pH sensor. This design permits the required influx of CO_2 to the pH sensor but minimizes the area through which H_2S (or NH_3) may diffuse and thereby extends getter lifetime.

1.5 Expansion System

Pressure gradients across the membrane system must be minimized to prevent damage to the membrane and to assure that the pH sensor is in intimate contact with the inner membrane. To accommodate differences in thermal expansion in the probe and the compressibility of the internal electrolyte, two alternatives were considered. The possibility of incorporating a metal bellows was rejected because of the significant engineering and testing required. Bellows dimensions (thickness and length) were not readily specified. Rather, it is recommended that the elastomeric properties of the membrane be utilized as indicated in Figure IV-1. By distending the membrane pair as shown,

FIGURE IV-2: EXPLODED VIEW OF pH SENSOR AND
MEMBRANE/GETTER SYSTEM

the pH sensor will remain in contact with the inner membrane even under a moderate pressure gradient, with higher external pressures assuring intimate contact so long as the membrane does not rupture. Given the cushion provided by the internal fill solution, the small movements anticipated due to electrolyte compression can be readily accommodated.

2. Probe Assembly Procedure

The recommended CO₂ sensing system is essentially modular in design, having four elements which may be replaced separately. The solid state pH sensing electrode, the reference electrode, and the getter membrane system are constructed separately and may be individually replaced. All fit into a housing which also contains the internal electrolyte. The electrolyte may also be replaced with fresh solution should that be deemed necessary.

The pH electrode and membranes are assembled into the housing first, with electrolyte then introduced via the reference electrode port. This subassembly is immersed in internal electrolyte solution and evacuated (under moderate vacuum) to remove all internal air. While the probe remains submerged in electrolyte, the reference electrode is inserted and seated against the metal housing. The assembly is stored, immersed in electrolyte, in an evacuated container.

3. Temperature Compensation

As is clear from the pH-CO₂ relationship presented in the Appendix (Section VII.1) and discussed in Section II.1.2, temperature compensation is required. No built-in compensation is included in the proposed design in the expectation that temperature will be determined by a separate temperature sensor and the required compensation can be computed after suitable calibration curves have been obtained over the temperature range of use.

4. Calibration

It will be necessary to develop a body of data over the temperature and CO₂ ranges of interest. Since this probe should be

able to operate over a very wide temperature range (from room temperature or lower to above 250°C), it will be possible to calibrate at moderately low temperatures, perhaps even 25°C. However, it is desirable to calibrate the sensor in a sample of brine content near that expected in use. By this technique, the deleterious effects of Henry's Law constant, osmotic pressure and activity coefficient uncertainties will be lessened.

5. Unit Cost

The manufacture cost for a preproduction lot of five prototype probes, as described for use in the laboratory test program, is estimated to be \$16,460. The per unit cost for five units is significantly higher than the per unit cost of units in larger quantities since it is anticipated that many solid state sensor chips can be produced from a single wafer, although the cost of manufacturing one wafer is high due to the many steps required.

6. Potential Sources of Error

The recognized potential sources of error in the measurement of CO₂ by the recommended approach are summarized in decreasing order of estimated severity in Sections IV.6.1 - IV.6.4 below.

6.1 Solid State pH Sensor Output Drift

Our experience, as reported in Section II.2.1.1.2, indicates that the solid state pH sensor will maintain a stable mv/pH response during and after brine exposure. However, if the cations from the electrolyte diffuse into (or out of) the insulator film, an offset in the flat-band voltage is expected. The internal electrolyte composition is selected to minimize this problem. In addition, an attempt will be made to pre-treat the ISFET sensor in hot electrolyte, anticipating that a near-steady ionic constant can be introduced into the film and thereby minimize sensor drift. In spite of these efforts, the possibility of sensor drift exists and will be quantitatively evaluated during Task II experimentation, if authorized.

6.2 Compositional Variations in Brine

The salt content of the brine should not infiltrate into the probe electrolyte. However, variations in salt content can cause osmotic pressure to vary significantly, eventually resulting in altered composition of the electrolyte behind the EPDM membranes as water passes through the polymer. This in turn can change the Henry's Law constant and vary activity coefficients, thereby changing the solution pH as described in Section II.1.2 and II.2.1.3.

6.3 Seal Failure

The seals must maintain their integrity in order to have sustained accuracy of the CO₂ measurement. O-rings must not allow leakage, membranes must seal and not leak, and glass-to-metal seals in the probes must not fracture. Infiltration of the brine into the probe will terminate its useful life, as will shunt paths in the potential measurement path caused by solution leakage to critical areas.

6.4 Pressure Compensation Failure

Rupture of the EPDM membranes, will terminate probe life. Movement of the membranes from close contact with the ISFET sensor will cause a significant response time increase and perhaps sustained measurement error.

7. Support Electronics

Support electronics to power the FET and to extract the signal will be required. The general configurations are outlined in reference 21. A constant current source and fixed source to drain voltage, each selected to operate the device in the saturation region, will allow a pH dependent gate voltage to be measured versus the silver reference electrode shown in Figure IV-1. The signal will have low source impedance, so that insulation requirements on the silver electrode will not be stringent. However, the constant current provided source to drain must not be shunted through insulation or through the internal electrolyte. One megohm or more isolation of the source and drain leads is likely to be necessary. It is recommended that the electronics be located atop the sensing element to minimize lead lengths and potential leakage paths.

V.

TEST PROCEDURES FOR LABORATORY PROOF TESTING

The recommended test procedure for proof testing the device is very similar to that used by PNL to test the geothermal brine reference electrode versus an in-situ hydrogen electrode¹ and that proposed for proof testing the geothermal pH sensor recently under development in this laboratory.⁹⁸ Solutions equilibrated with a known partial pressure of CO₂ and/or H₂S will be prepared, relying on literature values of solubility and dissociation constants to determine the CO₂ partial pressure at elevated temperatures. It is believed that uncertainties in these constants as a function of temperature will result in pCO₂ uncertainties of ± 0.4 . At a given temperature the dissociation constant errors still exist, although the absolute value of Henry's Law will not cause relative errors in comparing data taken at one temperature. Therefore, the estimated accuracy of pCO₂ solution preparation is ± 0.3 . It will be possible to relate probe output to brine composition at room temperature with greater accuracy and this will be of value since much of the reported brine analyses are actually results after cooling.

Tests will be conducted over a range of temperatures from 100°C to 250°C and beyond, varying the gas compositions, at total pressures ranging from atmospheric to 5000 psi. Ionic concentration of the brine will be varied to determine the indirect effects of this variable acting through activity, osmotic pressure, and gas solubility relationships. Time will not permit all combinations of variables, but the tests will be designed to determine the effect of each variable independently. Unexpected errors due to the effect of two or more variables acting in concert will not be thoroughly evaluated in this testing, but the likelihood of this type of error seems remote.

As performance limitations are encountered, corrective changes in probe design will be implemented.

If Task II is implemented as recommended, it would be possible to determine the CO₂ response of the probe from 100°C to 250°C and above, and to determine the extent of H₂S interference, if any, and the performance of the H₂S getter scheme in overcoming the potential interference. Performance limitations encountered would be investigated so that their source may be determined, corrective action recommended and attempted, and performance of the improved design characterized under the operating conditions anticipated.

An outline of the Task II program plan is shown in Figure V-1, indicating for each major task its starting time after project commencement and its approximate duration.

1. Design Pressure Vessel
2. Fabricate Pressure Vessel
3. Obtain Electrode Components
4. Assemble Recommended CO₂ Sensors
5. Test Recommended Sensors
 - T = 100, 150, 200, 250, 300°C
 - CO₂ = 0.5 - 500 ppm
 - H₂S = 0 - 75 ppm
6. Modify Design to Overcome any Observed Deficiencies
7. Repeat Tests with Modified Design(s)
8. Prepare, Submit, Review and Revise Final Report
 - (Δ = Submission of Report)

FIGURE V-1: PLAN FOR TASK II PROOFTESTING

VI.

APPENDIX

1. Computation of Carbonate Equilibria

Listed below is the program, written in Basic, which was used to compute pH, total CO_2 (all forms) and $\text{CO}_3^{=}$ concentration as a function of CO_2 partial pressure given initial carbonate and bicarbonate levels and $K_{\text{Henry}}^{\text{app}}$, $K_{\text{diss}}^{\text{H}_2\text{CO}_3(\text{app})}$, and $K_{\text{diss}}^{\text{HCO}_3^-}$ and K_w values appropriate for a specific temperature. Sample output is included for a selection of initial electrolyte compositions at six different temperatures.

1.1

Program Listing (Basic Language)

```

100 REM PROGRAM TO CALCULATE EQUILIBRIUM PH AND TOTAL CARBON
110 REM DIOXIDE STARTING WITH ANY CARBONATE SOLUTION IN EQUILIBRIUM
120 REM WITH ATMOSPHERIC CARBON DIOXIDE OF KNOWN PARTIAL PRESSURE
130 PRINT "SIMULATION OF EQUILIBRIUM PROPERTIES OF CARBONATE SOLUTIONS"
140 PRINT
150 PRINT "INPUT INITIAL BICARBONATE AND CARBONATE CONC'S";
160 INPUT N1,N2
170 K7 = 1.0E-14
180 K1 = 4.47E-7
190 K2 = 4.79E-11
200 K9 = 3.47E-2
210 PRINT
220 N=N1+2*N2
230 T=N1+N2
240 P=0
250 P2=10
260 P2=0.1*P2
270 IF P2<.0001 THEN 360
280 P = P+P2
290 H=10^(-P)
300 GO SUB 660
310 GO SUB 690
320 Z=H*H+H*N-1*H*(2*A3+A2)-K7
330 IF Z>0 THEN 280
340 P=P-P2
350 GO TO 260
360 GO SUB 630
370 PRINT "INITIAL SOLUTION PH ="; P
380 PRINT "CO SUB 2 PARTIAL PRESSURE =";(A1*T/K9)*760;"MM."
390 PRINT
400 PRINT "PARTIAL PRESSURE"," PH","TOTAL CO SUB 2","CARBONATE CONC."
410 PRINT
420 FOR I = 0 TO 30
430 C=760*10^(-0.2*I)
440 P=0
450 P2=10
460 P2=P2*0.1
470 IF P2<.0001 THEN 570
480 P = P+P2
490 H=10^(-P)
500 GO SUB 630
510 GO SUB 660
520 GO SUB 690
530 Z = H*H+H*(N-(2*A3+A2)*C/760*K9/A1)-K7
540 IF Z>0 THEN 480
550 P=P-P2
560 GO TO 460
570 PRINT C,P,C*K9/(A1*760),A3*C*K9/(A1*760)
580 NEXT I
590 STOP
630 REM SUBROUTINE TO CALCULATE ALPHA CARBONIC ACID
640 A1=H*H/(H*H+H*K1+K1*K2)
650 RETURN
660 REM SUBROUTINE TO CALCULATE ALPHA BICARBONATE ION
670 A2 = H*K1/(H*H+H*K1+K1*K2)
680 RETURN
690 REM SUBROUTINE TO CALCULATE ALPHA CARBONATE ION
700 A3 = K1*K2/(H*H+H*K1+K1*K2)
710 RETURN
720 END

```

1.2

Sample Output at 25°C

1.2.1

T = 25°C, $\text{HCO}_3^- = 0$, $\text{CO}_3^{2-} = 0$

SIMULATION OF EQUILIBRIUM PROPERTIES OF CARBONATE SOLUTIONS

INPUT INITIAL BICARBONATE AND CARBONATE CONC'S? 0.0

INITIAL SOLUTION PH = 6.99999

CO SUB 2 PARTIAL PRESSURE = 0 MM.

PARTIAL PRESSURE	PH	TOTAL CO SUB 2	CARBONATE CONC.
760	3.90458	3.48245E-02	4.79003E-11
479.528	4.00459	2.19931E-02	4.79014E-11
302.562	4.10459	1.38929E-02	4.79013E-11
190.904	4.20459	8.77867E-03	4.79013E-11
120.452	4.30459	5.54917E-03	4.79012E-11
76.0001	4.40459	3.50939E-03	4.79010E-11
47.9528	4.50459	2.22071E-03	4.79008E-11
30.2562	4.60459	1.40628E-03	4.79008E-11
19.0904	4.70459	8.91365E-04	4.79006E-11
12.0452	4.80458	5.65638E-04	4.79006E-11
7.60003	4.90458	3.59456E-04	4.79004E-11
4.79529	5.00459	2.28836E-04	4.79015E-11
3.02562	5.10459	1.46002E-04	4.79013E-11
1.90904	5.20459	9.34047E-05	4.79013E-11
1.20452	5.30459	5.99542E-05	4.79012E-11
.760003	5.40449	3.86377E-05	4.78792E-11
.479529	5.50439	2.50213E-05	4.78572E-11
.302562	5.60429	1.62977E-05	4.78352E-11
.190904	5.70409	1.06880E-05	4.77915E-11
.120452	5.80378	7.06467E-06	4.77241E-11
7.60003E-02	5.90319	4.71150E-06	4.75935E-11
4.79530E-02	6.00239	3.17378E-06	4.74194E-11
3.02562E-02	6.10109	2.16101E-06	4.71368E-11
1.90904E-02	6.19908	1.48802E-06	4.67023E-11
1.20452E-02	6.29598	1.03609E-06	4.60391E-11
7.60004E-03	6.39099	7.28750E-07	4.49932E-11
4.79530E-03	6.48348	5.16989E-07	4.34647E-11
3.02562E-03	6.57199	3.68713E-07	4.12236E-11
1.90904E-03	6.65499	2.63286E-07	3.81192E-11
1.20452E-03	6.73049	1.87227E-07	3.40521E-11
7.60004E-04	6.79648	1.31828E-07	2.91158E-11

1.2.2

T = 25°C, $\text{HCO}_3^- = 0.001$, $\text{CO}_3 = 0.001$

SIMULATION OF EQUILIBRIUM PROPERTIES OF CARBONATE SOLUTIONS

INPUT INITIAL BICARBONATE AND CARBONATE CONC'S? .001,.001

INITIAL SOLUTION PH = 10.1856

CO SUB 2 PARTIAL PRESSURE = 3.68394E-03 MM.

PARTIAL PRESSURE	PH	TOTAL CO SUB 2	CARBONATE CONC.
760	5.28718	3.77055E-02	2.78957E-02
479.528	5.48688	2.48977E-02	4.41494E-02
302.562	5.68668	1.68164E-02	6.99079E-02
190.904	5.88658	1.17177E-02	1.10745E-01
120.452	6.08648	8.50043E-03	1.75443E-01
76.0001	6.28638	6.47027E-03	2.77930E-01
47.9528	6.48638	5.18984E-03	4.40487E-01
30.2562	6.68628	4.38141E-03	6.97803E-01
19.0904	6.88608	3.87064E-03	1.10493E-01
12.0452	7.08588	3.54819E-03	1.74952E-01
7.60003	7.28558	3.34422E-03	2.76905E-01
4.79529	7.48508	3.21432E-03	4.37855E-01
3.02562	7.68438	3.13125E-03	6.91723E-01
1.90904	7.88318	3.07600E-03	1.09026E-01
1.20452	8.08129	3.03712E-03	1.71295E-01
.760003	8.27838	3.00672E-03	2.67876E-01
.479529	8.47378	2.97764E-03	4.15652E-01
.302562	8.66688	2.94582E-03	6.38137E-01
.190904	8.85648	2.90549E-03	9.64110E-01
.120452	9.04129	2.85208E-03	1.42477E-01
7.60003E-02	9.21999	2.78290E-03	2.04717E-01
4.79530E-02	9.39099	2.69443E-03	2.83881E-01
3.02562E-02	9.55329	2.56768E-03	3.78208E-01
1.90904E-02	9.70658	2.46726E-03	4.83423E-01
1.20452E-02	9.85088	2.33764E-03	5.92823E-01
7.60004E-03	9.98678	2.20464E-03	6.99386E-01
4.79530E-03	10.1152	2.07360E-03	7.97160E-01
3.02562E-03	10.2369	1.94671E-03	8.80915E-01
1.90904E-03	10.3529	1.82659E-03	9.48256E-01
1.20452E-03	10.4638	1.71247E-03	9.97069E-01
7.60004E-04	10.5701	1.60302E-03	1.02646E-01

1.2.3 $T = 25^{\circ}\text{C}$, $\text{HCO}_3^- = 0.005$, $\text{CO}_3^{2-} = 0.005$

SIMULATION OF EQUILIBRIUM PROPERTIES OF CARBONATE SOLUTIONS

INPUT INITIAL BICARBONATE AND CARBONATE CONC'S? .005,.005

INITIAL SOLUTION PH = 10.2862

CO SUB 2 PARTIAL PRESSURE = 1.31588E-02 MM.

PARTIAL PRESSURE	PH	TOTAL CO SUB 2	CARBONATE CONC.
760	5.98538	4.97015E-02	6.94910E-07
479.528	6.18538	3.68963E-02	1.10138E-06
302.562	6.38528	2.88136E-02	1.74476E-06
190.904	6.58528	2.37165E-02	2.76525E-06
120.452	6.78518	2.04980E-02	4.38060E-06
76.0001	6.98498	1.84640E-02	6.93638E-06
47.9528	7.18478	1.71805E-02	1.09832E-05
30.2562	7.38438	1.63651E-02	1.73751E-05
19.0904	7.58378	1.58448E-02	2.74618E-05
12.0452	7.78288	1.55079E-02	4.33432E-05
7.60003	7.98138	1.52786E-02	6.82234E-05
4.79529	8.17908	1.51107E-02	1.06986E-04
3.02562	8.37558	1.49711E-02	1.66849E-04
1.90904	8.57009	1.48268E-02	2.57837E-04
1.20452	8.76188	1.46590E-02	3.93475E-04
.760003	8.94958	1.44378E-02	5.89287E-04
.479529	9.13199	1.41487E-02	8.61282E-04
.302562	9.30759	1.37744E-02	1.21994E-03
.190904	9.47528	1.33167E-02	1.66623E-03
.120452	9.63419	1.27814E-02	2.18540E-03
7.60003E-02	9.78418	1.21935E-02	2.75123E-03
4.79530E-02	9.92588	1.15890E-02	3.33372E-03
3.02562E-02	10.0599	1.09897E-02	3.89879E-03
1.90904E-02	10.1874	1.04256E-02	4.42517E-03
1.20452E-02	10.3092	9.90420E-03	4.89265E-03
7.60004E-03	10.4265	9.44069E-03	5.29826E-03
4.79530E-03	10.5398	9.02537E-03	5.63272E-03
3.02562E-03	10.6498	8.65572E-03	5.89813E-03
1.90904E-03	10.7572	8.33090E-03	6.10280E-03
1.20452E-03	10.8621	8.03206E-03	6.24214E-03
7.60004E-04	10.965	7.75741E-03	6.32610E-03

1.2.4

T = 25°C, $\text{HCO}_3^- = .01$, $\text{CO}_3^{2-} = .01$

SIMULATION OF EQUILIBRIUM PROPERTIES OF CARBONATE SOLUTIONS

INPUT INITIAL BICARBONATE AND CARBONATE CONC'S? .01,.01

INITIAL SOLUTION PH = 10.3023

CO SUB 2 PARTIAL PRESSURE = 2.49068E-02 MM.

PARTIAL PRESSURE	PH	TOTAL CO SUB 2	CARBONATE CONC.
760	6.88638	6.47026E-02	2.77930E-06
479.528	6.48628	5.18915E-02	4.40286E-06
302.562	6.68628	4.38141E-02	6.97802E-06
190.904	6.88608	3.87063E-02	1.10493E-05
120.452	7.08598	3.54887E-02	1.75032E-05
76.0001	7.28568	3.34490E-02	2.77031E-05
47.9528	7.48518	3.21500E-02	4.38055E-05
30.2562	7.68438	3.13125E-02	6.91723E-05
19.0904	7.88328	3.07668E-02	1.09075E-04
12.0452	8.08139	3.03780E-02	1.71373E-04
7.60003	8.27856	3.00809E-02	2.68121E-04
4.79529	8.47418	2.98043E-02	4.16426E-04
3.02562	8.66748	2.94998E-02	6.39911E-04
1.90904	8.85738	2.91171E-02	9.68119E-04
1.20452	9.04269	2.86172E-02	1.43397E-03
.760003	9.22189	2.79591E-02	2.06505E-03
.479529	9.39368	2.71297E-02	2.87429E-03
.302562	9.55699	2.61310E-02	3.84716E-03
.190904	9.71159	2.50150E-02	4.94690E-03
.120452	9.85748	2.38265E-02	6.11118E-03
7.60003E-02	9.99538	2.26300E-02	7.27646E-03
4.79530E-02	10.1263	2.14844E-02	8.38967E-03
3.02562E-02	10.2512	2.04235E-02	9.40882E-03
1.90904E-02	10.371	1.94647E-02	1.03074E-02
1.20452E-02	10.4867	1.86206E-02	1.10794E-02
7.60004E-03	10.599	1.78876E-02	1.17853E-02
4.79530E-03	10.7084	1.72461E-02	1.22442E-02
3.02562E-03	10.8156	1.66966E-02	1.26571E-02
1.90904E-03	10.9208	1.62112E-02	1.29639E-02
1.20452E-03	11.0243	1.57751E-02	1.31747E-02
7.60004E-04	11.1263	1.53717E-02	1.32967E-02

1.2.5

T = 25°C, $\text{HCO}_3^- = 0$, $\text{CO}_3^{2-} = .002$

SIMULATION OF EQUILIBRIUM PROPERTIES OF CARBONATE SOLUTIONS

INPUT INITIAL BICARBONATE AND CARBONATE CONC'S? 0,.002

INITIAL SOLUTION PH = 10.7405

CO SUB 2 PARTIAL PRESSURE = 4.89804E-04 MM.

PARTIAL PRESSURE	PH	TOTAL CO SUB 2	CARBONATE CONC.
760	5.41179	3.87043E-02	4.95156E-08
479.528	5.61159	2.58967E-02	7.84048E-08
302.562	5.81149	1.78159E-02	1.24206E-07
190.904	6.01139	1.27171E-02	1.96768E-07
120.452	6.21139	9.50051E-03	3.11854E-07
76.0001	6.41129	7.47019E-03	4.94027E-07
47.9528	6.61119	6.18896E-03	7.82617E-07
30.2562	6.81109	5.38050E-03	1.23979E-06
19.0904	7.01099	4.87053E-03	1.96405E-06
12.0452	7.21069	4.54718E-03	3.10840E-06
7.60003	7.41029	4.34241E-03	4.91757E-06
4.79529	7.60968	4.21157E-03	7.77185E-06
3.02562	7.80868	4.12613E-03	1.22611E-05
1.90904	8.00709	4.06762E-03	1.92905E-05
1.20452	8.20459	4.02364E-03	3.02233E-05
.760003	8.40079	3.98589E-03	4.70697E-05
.479529	8.59488	3.94579E-03	7.25961E-05
.302562	8.78598	3.89753E-03	1.10442E-04
.190904	8.97288	3.83457E-03	1.64783E-04
.120452	9.15419	3.75204E-03	2.39632E-04
7.60003E-02	9.32839	3.64529E-03	3.37233E-04
4.79530E-02	9.49438	3.51496E-03	4.57018E-04
3.02562E-02	9.65139	3.36329E-03	5.94206E-04
1.90904E-02	9.79938	3.19737E-03	7.41169E-04
1.20452E-02	9.93888	3.02564E-03	8.89037E-04
7.60004E-03	10.0706	2.85440E-03	1.02881E-03
4.79530E-03	10.1956	2.69026E-03	1.15432E-03
3.02562E-03	10.3146	2.53446E-03	1.25989E-03
1.90904E-03	10.4286	2.38938E-03	1.34380E-03
1.20452E-03	10.538	2.25195E-03	1.40326E-03
7.60004E-04	10.6435	2.12198E-03	1.43925E-03

1.3

Sample Output at 100°C

1.3.1

T = 100°C, $\text{HCO}_3^- = 0$, $\text{CO}_3^{2-} = 0$

SIMULATION OF EQUILIBRIUM PROPERTIES OF CARBONATE SOLUTIONS

INPUT INITIAL BICARBONATE AND CARBONATE CONC'S? 0.0

INITIAL SOLUTION PH = 6.13019

CO SUB 2 PARTIAL PRESSURE = 0 MM.

PARTIAL PRESSURE	PH	TOTAL CO SUB 2	CARBONATE CONC.
760	4.21009	1.07616E-02	6.91995E-11
479.528	4.31009	6.80020E-03	6.91993E-11
302.562	4.41009	4.29863E-03	6.91992E-11
190.904	4.50999	2.71860E-03	6.91674E-11
120.452	4.60999	1.72037E-03	6.91672E-11
76.0001	4.70978	1.08948E-03	6.91000E-11
47.9528	4.80968	6.90591E-04	6.90683E-11
30.2562	4.90938	4.38252E-04	6.89735E-11
19.0904	5.00888	2.78513E-04	6.88154E-11
12.0452	5.10819	1.77309E-04	6.85956E-11
7.60003	5.20699	1.13120E-04	6.82182E-11
4.79529	5.30519	7.23532E-05	6.76546E-11
3.02562	5.40239	4.64179E-05	6.67877E-11
1.90904	5.49798	2.98813E-05	6.54460E-11
1.20452	5.59118	1.93075E-05	6.34288E-11
.760003	5.68078	1.25219E-05	6.04614E-11
.479529	5.76538	8.14798E-06	5.63223E-11
.302562	5.84288	5.31320E-06	5.07782E-11
.190904	5.91139	3.46598E-06	4.39229E-11
.120452	5.96938	2.25704E-06	3.61972E-11
7.60003E-02	6.01599	1.46422E-06	2.83075E-11
4.79530E-02	6.05149	9.45047E-07	2.10326E-11
3.02562E-02	6.07728	6.06706E-07	1.49447E-11
1.90904E-02	6.09538	3.87659E-07	1.02491E-11
1.20452E-02	6.10759	2.46735E-07	6.84055E-12
7.60004E-03	6.11559	1.56584E-07	4.47808E-12
4.79530E-03	6.12089	9.91821E-08	2.89528E-12
3.02562E-03	6.12429	6.27368E-08	1.85565E-12
1.90904E-03	6.12639	3.96458E-08	1.18220E-12
1.20452E-03	6.12778	2.50408E-08	7.50732E-13
7.60004E-04	6.12868	1.58103E-08	4.75649E-13

1.3.2

T = 100°C, $\text{HCO}_3^- = 0.001$, $\text{CO}_3^{2-} = 0.001$

SIMULATION OF EQUILIBRIUM PROPERTIES OF CARBONATE SOLUTIONS

INPUT INITIAL BICARBONATE AND CARBONATE CONC'S? .001,.001

INITIAL SOLUTION PH = 9.17258

CO SUB 2 PARTIAL PRESSURE = .243352 MM.

PARTIAL PRESSURE	PH	TOTAL CO SUB 2	CARBONATE CONC.
760	5.89758	1.37013E-02	1.64085E-07
479.528	6.09738	9.75130E-03	2.59825E-07
302.562	6.29728	7.25927E-03	4.11605E-07
190.904	6.49708	5.68611E-03	6.51750E-07
120.452	6.69678	4.69249E-03	1.03150E-06
76.0001	6.89638	4.06452E-03	1.63182E-06
47.9528	7.09578	3.66643E-03	2.57908E-06
30.2562	7.29468	3.41123E-03	4.06698E-06
19.0904	7.49308	3.24544E-03	6.39862E-06
12.0452	7.69058	3.13278E-03	1.00247E-05
7.60003	7.88668	3.04934E-03	1.56048E-05
4.79529	8.08059	2.97756E-03	2.40483E-05
3.02562	8.27129	2.90397E-03	3.65161E-05
1.90904	8.45718	2.81570E-03	5.42344E-05
1.20452	8.63638	2.70178E-03	7.81051E-05
.760003	8.80648	2.55184E-03	1.07863E-04
.479529	8.96498	2.35948E-03	1.41212E-04
.302562	9.10959	2.12435E-03	1.73413E-04
.190904	9.23858	1.85395E-03	1.98187E-04
.120452	9.35069	1.56142E-03	2.09543E-04
7.60003E-02	9.44548	1.26539E-03	2.04588E-04
4.79530E-02	9.52319	9.84952E-04	1.84626E-04
3.02562E-02	9.58458	7.36130E-04	1.54552E-04
1.90904E-02	9.63139	5.29650E-04	1.20972E-04
1.20452E-02	9.66568	3.68418E-04	8.93864E-05
7.60004E-03	9.68978	2.49112E-04	6.30176E-05
4.79530E-03	9.70639	1.64914E-04	4.29216E-05
3.02562E-03	9.71738	1.07434E-04	2.84889E-05
1.90904E-03	9.72458	6.92254E-05	1.85816E-05
1.20452E-03	9.72928	4.42821E-05	1.19806E-05
7.60004E-04	9.73229	2.81867E-05	7.66451E-06

1.3.3

T = 100°C, $\text{HCO}_3^- = 0.005$, $\text{CO}_3^{2-} = 0.005$

SIMULATION OF EQUILIBRIUM PROPERTIES OF CARBONATE SOLUTIONS

INPUT INITIAL BICARBONATE AND CARBONATE CONC'S? .005,.005

INITIAL SOLUTION PH = 9.66912

CO SUB 2 PARTIAL PRESSURE = .323687 MM.

PARTIAL PRESSURE	PH	TOTAL CO SUB 2	CARBONATE CONC.
760	6.59618	2.56972E-02	4.09524E-06
479.528	6.79598	2.17440E-02	6.48455E-06
302.562	6.99568	1.92455E-02	1.02626E-05
190.904	7.19528	1.76661E-02	1.62361E-05
120.452	7.39458	1.66593E-02	2.56490E-05
76.0001	7.59348	1.60107E-02	4.04462E-05
47.9528	7.79178	1.55805E-02	6.36013E-05
30.2562	7.98908	1.52753E-02	9.95556E-05
19.0904	8.18488	1.50315E-02	1.54764E-04
12.0452	8.37848	1.48021E-02	2.38164E-04
7.60003	8.56878	1.45442E-02	3.60966E-04
4.79529	8.75448	1.42235E-02	5.35639E-04
3.02562	8.93378	1.38008E-02	7.71747E-04
1.90904	9.10519	1.32582E-02	1.07224E-03
1.20452	9.26699	1.25773E-02	1.42521E-03
.760003	9.41829	1.17697E-02	1.80504E-03
.479529	9.55848	1.08521E-02	2.17204E-03
.302562	9.68748	9.85181E-03	2.48234E-03
.190904	9.80548	8.79781E-03	2.69701E-03
.120452	9.91288	7.71920E-03	2.79043E-03
7.60003E-02	10.0098	6.63791E-03	2.75093E-03
4.79530E-02	10.096	5.57240E-03	2.58156E-03
3.02562E-02	10.1714	4.54985E-03	2.30505E-03
1.90904E-02	10.2357	3.59795E-03	1.95560E-03
1.20452E-02	10.2889	2.74766E-03	1.57641E-03
7.60004E-03	10.3311	2.02251E-03	1.20807E-03
4.79530E-03	10.3634	1.43800E-03	8.84461E-04
3.02562E-03	10.3871	9.91247E-04	6.22405E-04
1.90904E-03	10.4037	6.65717E-04	4.23923E-04
1.20452E-03	10.4151	4.38511E-04	2.81892E-04
7.60004E-04	10.4227	2.84763E-04	1.84198E-04

1.3.4 T = 100°C, $\text{HCO}_3^- = 0.01$, $\text{CO}_3^{2-} = 0.01$

SIMULATION OF EQUILIBRIUM PROPERTIES OF CARBONATE SOLUTIONS

INPUT INITIAL BICARBONATE AND CARBONATE CONC'S? .01,.01

INITIAL SOLUTION PH = 9.82568

CO SUB 2 PARTIAL PRESSURE = .408314 MM.

PARTIAL PRESSURE	PH	TOTAL CO SUB 2	CARBONATE CONC.
760	6.89697	4.06862E-02	1.63630E-05
479.528	7.09658	3.67196E-02	2.58862E-05
302.562	7.29608	3.42091E-02	4.09338E-05
190.904	7.49538	3.26123E-02	6.46653E-05
120.452	7.69408	3.15687E-02	1.01878E-04
76.0001	7.89218	3.08708E-02	1.60056E-04
47.9528	8.08918	3.03621E-02	2.50193E-04
30.2562	8.28448	2.99339E-02	3.88036E-04
19.0904	8.47738	2.95117E-02	5.95212E-04
12.0452	8.66668	2.90177E-02	8.97969E-04
7.60003	8.85109	2.83963E-02	1.32460E-03
4.79529	9.02899	2.75908E-02	1.89623E-03
3.02562	9.19878	2.65622E-02	2.61493E-03
1.90904	9.35938	2.53156E-02	3.45681E-03
1.20452	9.51019	2.38789E-02	4.36806E-03
.760003	9.65088	2.22847E-02	5.26837E-03
.479529	9.78208	2.06035E-02	6.08252E-03
.302562	9.90419	1.88693E-02	6.73413E-03
.190904	10.0178	1.71144E-02	7.16928E-03
.120452	10.1234	1.53585E-02	7.35673E-03
7.60003E-02	10.221	1.35970E-02	7.27609E-03
4.79530E-02	10.3107	1.18418E-02	6.93882E-03
3.02562E-02	10.392	1.00965E-02	6.36620E-03
1.90904E-02	10.4646	8.39328E-03	5.61144E-03
1.20452E-02	10.5277	6.76420E-03	4.73451E-03
7.60004E-03	10.5809	5.26411E-03	3.81659E-03
4.79530E-03	10.6242	3.94868E-03	2.93960E-03
3.02562E-03	10.658	2.85532E-03	2.16711E-03
1.90904E-03	10.6832	1.99574E-03	1.53558E-03
1.20452E-03	10.7012	1.35532E-03	1.05268E-03
7.60004E-04	10.7137	9.00049E-04	7.03524E-04

1.3.5

 $T = 100^{\circ}\text{C}$, $\text{HCO}_3^- = 0$, $\text{CO}_3^{2-} = .002$

SIMULATION OF EQUILIBRIUM PROPERTIES OF CARBONATE SOLUTIONS

INPUT INITIAL BICARBONATE AND CARBONATE CONC'S? 0.002

INITIAL SOLUTION PH = 9.47958

CO SUB 2 PARTIAL PRESSURE = .109612 MM.

PARTIAL PRESSURE	PH	TOTAL CO SUB 2	CARBONATE CONC.
760	6.02239	1.47007E-02	2.91539E-07
479.528	6.22229	1.07512E-02	4.61844E-07
302.562	6.42209	8.25809E-03	7.31301E-07
190.904	6.62188	6.68459E-03	1.15793E-06
120.452	6.82158	5.69064E-03	1.83267E-06
76.0001	7.02119	5.06224E-03	2.89932E-06
47.9528	7.22039	4.66166E-03	4.57811E-06
30.2562	7.41929	4.40505E-03	7.21905E-06
19.0904	7.61748	4.23556E-03	1.13471E-05
12.0452	7.81458	4.11639E-03	1.77448E-05
7.60003	8.01019	4.02411E-03	2.75609E-05
4.79529	8.20329	3.93806E-03	4.23145E-05
3.02562	8.39278	3.84323E-03	6.38964E-05
1.90904	8.57718	3.72600E-03	9.42480E-05
1.20452	8.75428	3.57110E-03	1.34423E-04
.760003	8.92199	3.36895E-03	1.83605E-04
.479529	9.07788	3.11233E-03	2.37506E-04
.302562	9.22019	2.80418E-03	2.88600E-04
.190904	9.34748	2.45410E-03	3.27244E-04
.120452	9.45878	2.07817E-03	3.44720E-04
7.60003E-02	9.55388	1.69826E-03	3.37031E-04
4.79530E-02	9.63299	1.33647E-03	3.06120E-04
3.02562E-02	9.69658	1.01140E-03	2.58856E-04
1.90904E-02	9.74588	7.36831E-04	2.04959E-04
1.20452E-02	9.78268	5.18450E-04	1.53202E-04
7.60004E-03	9.80899	3.53955E-04	1.09114E-04
4.79530E-03	9.82728	2.36028E-04	7.48987E-05
3.02562E-03	9.83968	1.54643E-04	5.00347E-05
1.90904E-03	9.84778	1.00015E-04	3.27693E-05
1.20452E-03	9.85309	6.41381E-05	2.11877E-05
7.60004E-04	9.85648	4.08915E-05	1.35791E-05

1.4

Sample Output at 150°C

1.4.1

T = 150°C, $\text{HCO}_3^- = 0$, $\text{CO}_3^{2-} = 0$

SIMULATION OF EQUILIBRIUM PROPERTIES OF CARBONATE SOLUTIONS

INPUT INITIAL BICARBONATE AND CARBONATE CONC'S? 0.0

INITIAL SOLUTION PH = 5.76209

CO SUB 2 PARTIAL PRESSURE = 0 MM.

PARTIAL PRESSURE	PH	TOTAL CO SUB 2	CARBONATE CONC.
760	4.39978	8.54975E-03	5.12049E-11
479.523	4.49958	5.40100E-03	5.11580E-11
302.562	4.59918	3.41294E-03	5.10645E-11
190.904	4.69858	2.15748E-03	5.09229E-11
120.452	4.79768	1.36449E-03	5.07119E-11
76.0001	4.89618	8.63467E-04	5.03638E-11
47.9523	4.99378	5.46793E-04	4.98094E-11
30.2562	5.09019	3.46547E-04	4.89930E-11
19.0904	5.18448	2.19844E-04	4.77228E-11
12.0452	5.27578	1.39610E-04	4.58480E-11
7.60003	5.36268	8.87497E-05	4.31645E-11
4.79523	5.44339	5.64675E-05	3.94939E-11
3.02562	5.51588	3.59464E-05	3.47955E-11
1.90904	5.57848	2.28829E-05	2.92899E-11
1.20452	5.62978	1.45574E-05	2.34055E-11
.760003	5.66988	9.25037E-06	1.77628E-11
.479523	5.69958	5.86964E-06	1.28502E-11
.302562	5.72059	3.71914E-06	8.93162E-12
.190904	5.73499	2.35367E-06	6.02189E-12
.120452	5.74458	1.48811E-06	3.97122E-12
7.60003E-02	5.75088	9.40219E-07	2.57942E-12
4.79530E-02	5.75499	5.93772E-07	1.65856E-12
3.02562E-02	5.75758	3.74859E-07	1.05905E-12
1.90904E-02	5.75928	2.36610E-07	6.73475E-13
1.20452E-02	5.76029	1.49324E-07	4.26904E-13
7.60004E-03	5.76099	9.42320E-08	2.70231E-13
4.79530E-03	5.76138	5.94616E-08	1.70816E-13
3.02562E-03	5.76168	3.75202E-08	1.07925E-13
1.90904E-03	5.76178	2.36742E-08	6.81272E-14
1.20452E-03	5.76198	1.49381E-08	4.30246E-14
7.60004E-04	5.76199	9.42531E-09	2.71478E-14

1.4.2

T = 150°C, $\text{HCO}_3^- = 0.001$, $\text{CO}_3^{2-} = 0.001$

SIMULATION OF EQUILIBRIUM PROPERTIES OF CARBONATE SOLUTIONS

INPUT INITIAL BICARBONATE AND CARBONATE CONC'S? .001,.001

INITIAL SOLUTION PH = 8.52339

CO SUB 2 PARTIAL PRESSURE = 2.78435 MM.

PARTIAL PRESSURE	PH	TOTAL CO SUB 2	CARBONATE CONC.
760	6.27678	1.15048E-02	2.90615E-07
479.528	6.47628	8.36096E-03	4.59541E-07
302.562	6.67538	6.37347E-03	7.25304E-07
190.904	6.87408	5.11470E-03	1.14268E-06
120.452	7.07199	4.31214E-03	1.79360E-06
76.0001	7.26868	3.79292E-03	2.79967E-06
47.9528	7.46358	3.44613E-03	4.33433E-06
30.2562	7.65558	3.19723E-03	6.62093E-06
19.0904	7.84328	2.99585E-03	9.91552E-06
12.0452	8.02459	2.80465E-03	1.44185E-05
7.60003	8.19658	2.59475E-03	2.00872E-05
4.79529	8.35619	2.34854E-03	2.64313E-05
3.02562	8.49958	2.05735E-03	3.22775E-05
1.90904	8.62358	1.72898E-03	3.60508E-05
1.20452	8.72609	1.38539E-03	3.64689E-05
.760003	8.80709	1.05729E-03	3.34135E-05
.479529	8.86808	7.70553E-04	2.79204E-05
.302562	8.91209	5.39746E-04	2.15737E-05
.190904	8.94258	3.66238E-04	1.56646E-05
.120452	8.96328	2.42803E-04	1.08723E-05
7.60003E-02	8.97688	1.58267E-04	7.30308E-06
4.79530E-02	8.98578	1.02013E-04	4.80072E-06
3.02562E-02	8.99148	6.52532E-05	3.10969E-06
1.90904E-02	8.99508	4.15293E-05	1.99487E-06
1.20452E-02	8.99738	2.63483E-05	1.27208E-06
7.60004E-03	8.99887	1.66843E-05	8.38156E-07
4.79530E-03	8.99977	1.05499E-05	5.12033E-07
3.02562E-03	9.00039	6.66650E-06	3.23998E-07
1.90904E-03	9.00079	4.21023E-06	2.04798E-07
1.20452E-03	9.001	2.65784E-06	1.29345E-07
7.60004E-04	9.00119	1.67776E-06	8.16835E-08

1.4.3

T = 150°C, $\text{HCO}_3^- = 0.005$, $\text{CO}_3^{2-} = 0.005$

SIMULATION OF EQUILIBRIUM PROPERTIES OF CARBONATE SOLUTIONS

INPUT INITIAL BICARBONATE AND CARBONATE CONC'S? .005,.005

INITIAL SOLUTION PH = 9.16209

CO SUB 2 PARTIAL PRESSURE = 3.06532 MM.

PARTIAL PRESSURE	PH	TOTAL CO SUB 2	CARBONATE CONC.
760	6.97538	2.34769E-02	7.25295E-06
479.528	7.17468	2.03164E-02	1.14582E-05
302.562	7.37348	1.83002E-02	1.80598E-05
190.904	7.57168	1.69987E-02	2.83867E-05
120.452	7.76888	1.61303E-02	4.44123E-05
76.0001	7.96448	1.55087E-02	6.89780E-05
47.9528	8.15758	1.50018E-02	1.05906E-04
30.2562	8.34709	1.45147E-02	1.59927E-04
19.0904	8.53129	1.39648E-02	2.35685E-04
12.0452	8.70788	1.32764E-02	3.35363E-04
7.60003	8.87428	1.23932E-02	4.55317E-04
4.79529	9.02778	1.12856E-02	5.82532E-04
3.02562	9.16578	9.96030E-03	6.93925E-04
1.90904	9.28648	8.47638E-03	7.63333E-04
1.20452	9.38868	6.92531E-03	7.71102E-04
.760003	9.47238	5.42197E-03	7.15350E-04
.479529	9.53828	4.06682E-03	6.11400E-04
.302562	9.58828	2.93143E-03	4.85636E-04
.190904	9.62468	2.04027E-03	3.62338E-04
.120452	9.65019	1.37977E-03	2.57114E-04
7.60003E-02	9.66768	9.13256E-04	1.75834E-04
4.79530E-02	9.67928	5.94900E-04	1.17033E-04
3.02562E-02	9.68688	3.83297E-04	7.64712E-05
1.90904E-02	9.69178	2.45142E-04	4.93521E-05
1.20452E-02	9.69488	1.56007E-04	3.15870E-05
7.60004E-03	9.69688	9.89785E-05	2.01140E-05
4.79530E-03	9.69818	6.26774E-05	1.27676E-05
3.02562E-03	9.69898	3.96346E-05	8.08560E-06
1.90904E-03	9.69948	2.50422E-05	5.11336E-06
1.20452E-03	9.69977	1.58137E-05	3.23075E-06
7.60004E-04	9.69999	9.98381E-06	2.04052E-06

1.4.4

 $T = 150^{\circ}\text{C}$, $\text{HCO}_3^- = 0.01$, $\text{CO}_3^{2-} = 0.01$

SIMULATION OF EQUILIBRIUM PROPERTIES OF CARBONATE SOLUTIONS

INPUT INITIAL BICARBONATE AND CARBONATE CONC'S? .01,.01

INITIAL SOLUTION PH = 9.41109

CO SUB 2 PARTIAL PRESSURE = 3.2846 MM.

PARTIAL PRESSURE	PH	TOTAL CO SUB 2	CARBONATE CONC.
760	7.27599	3.84289E-02	2.89551E-05
479.528	7.47499	3.52361E-02	4.56792E-05
302.562	7.67348	3.31779E-02	7.18980E-05
190.904	7.87109	3.18050E-02	1.12701E-04
120.452	8.06738	3.08282E-02	1.75600E-04
76.0001	8.26159	3.00370E-02	2.70971E-04
47.9528	8.45268	2.92775E-02	4.12209E-04
30.2562	8.63938	2.84270E-02	6.14485E-04
19.0904	8.81958	2.73523E-02	8.89032E-04
12.0452	8.99138	2.59716E-02	1.23742E-03
7.60003	9.15229	2.42048E-02	1.63806E-03
4.79529	9.30029	2.20418E-02	2.04331E-03
3.02562	9.43378	1.95307E-02	2.38405E-03
1.90904	9.55178	1.67800E-02	2.59014E-03
1.20452	9.65368	1.39300E-02	2.61283E-03
.760003	9.73948	1.11460E-02	2.44748E-03
.479529	9.80968	8.58393E-03	2.13360E-03
.302562	9.86498	6.35863E-03	1.73661E-03
.190904	9.90688	4.54051E-03	1.32898E-03
.120452	9.93748	3.13955E-03	9.65406E-04
7.60003E-02	9.95908	2.11456E-03	6.72849E-04
4.79530E-02	9.97378	1.39520E-03	4.54256E-04
3.02562E-02	9.98358	9.07083E-04	2.99849E-04
1.90904E-02	9.98998	5.83690E-04	1.94858E-04
1.20452E-02	9.99418	3.73061E-04	1.25345E-04
7.60004E-03	9.99677	2.37275E-04	8.00395E-05
4.79530E-03	9.99848	1.50498E-04	5.08991E-05
3.02562E-03	9.99957	9.52779E-05	3.22773E-05
1.90904E-03	10.0002	6.02318E-05	2.04241E-05
1.20452E-03	10.0007	3.80620E-05	1.29163E-05
7.60004E-04	10.0009	2.40303E-05	8.15709E-06

1.4.5

T = 150°C, $\text{HCO}_3^- = 0$, $\text{CO}_3^{2-} = .002$

SIMULATION OF EQUILIBRIUM PROPERTIES OF CARBONATE SOLUTIONS

INPUT INITIAL BICARBONATE AND CARBONATE CONC'S? 0,.002

INITIAL SOLUTION PH = 8.81468

CO SUB 2 PARTIAL PRESSURE = 1.4121 MM.

PARTIAL PRESSURE	PH	TOTAL CO SUB 2	CARBONATE CONC.
760	6.40169	1.25029E-02	5.16574E-07
479.528	6.60109	9.35714E-03	8.16469E-07
302.562	6.80029	7.36870E-03	1.28924E-06
190.904	6.99887	6.10619E-03	2.03002E-06
120.452	7.19678	5.29937E-03	3.18644E-06
76.0001	7.39338	4.77266E-03	4.97180E-06
47.9528	7.58808	4.41384E-03	7.68985E-06
30.2562	7.77987	4.14730E-03	1.17356E-05
19.0904	7.96728	3.91957E-03	1.75516E-05
12.0452	8.14809	3.68914E-03	2.54641E-05
7.60003	8.31968	3.42590E-03	3.54093E-05
4.79529	8.47858	3.10704E-03	4.64422E-05
3.02562	8.62149	2.72696E-03	5.65883E-05
1.90904	8.74509	2.29564E-03	6.30842E-05
1.20452	8.84768	1.84426E-03	6.38430E-05
.760003	8.92888	1.41112E-03	5.85478E-05
.479529	8.99038	1.03147E-03	4.90362E-05
.302562	9.03499	7.24561E-04	3.79962E-05
.190904	9.06609	4.92851E-04	2.76647E-05
.120452	9.08718	3.27294E-04	1.92365E-05
7.60003E-02	9.10109	2.13610E-04	1.29403E-05
4.79530E-02	9.11019	1.37797E-04	8.51418E-06
3.02562E-02	9.11609	8.82027E-05	5.51998E-06
1.90904E-02	9.11988	5.61690E-05	3.54420E-06
1.20452E-02	9.12219	3.56402E-05	2.26012E-06
7.60004E-03	9.12379	2.25753E-05	1.43657E-06
4.79530E-03	9.12469	1.42754E-05	9.10181E-07
3.02562E-03	9.12529	9.02042E-06	5.75882E-07
1.90904E-03	9.12569	5.69703E-06	3.64023E-07
1.20452E-03	9.12588	3.59627E-06	2.29887E-07
7.60004E-04	9.12609	2.27027E-06	1.45191E-07

1.5

Sample Output at 200°C

1.5.1

 $T = 200^{\circ}\text{C}$, $\text{HCO}_3^- = 0$, $\text{CO}_3^{2-} = 0$

SIMULATION OF EQUILIBRIUM PROPERTIES OF CARBONATE SOLUTIONS

INPUT INITIAL BICARBONATE AND CARBONATE CONC'S? 0.0

INITIAL SOLUTION PH = 5.63499

CO SUB 2 PARTIAL PRESSURE = 0 MM.

PARTIAL PRESSURE	PH	TOTAL CO SUB 2	CARBONATE CONC.
760	4.56828	8.73682E-03	2.07515E-11
479.528	4.66738	5.51690E-03	2.06656E-11
302.562	4.76588	3.48434E-03	2.05230E-11
190.904	4.86358	2.20116E-03	2.03071E-11
120.452	4.95999	1.39092E-03	1.99738E-11
76.0001	5.05439	8.79217E-04	1.94652E-11
47.9528	5.14578	5.55962E-04	1.87091E-11
30.2562	5.23279	3.51684E-04	1.76220E-11
19.0904	5.31379	2.22536E-04	1.61457E-11
12.0452	5.38658	1.40842E-04	1.42445E-11
7.60003	5.44948	8.91407E-05	1.20074E-11
4.79529	5.50119	5.64067E-05	9.61322E-12
3.02562	5.54158	3.56794E-05	7.30561E-12
1.90904	5.57158	2.25575E-05	5.29240E-12
1.20452	5.59288	1.42544E-05	3.68335E-12
.760003	5.60748	9.00362E-06	2.48575E-12
.479529	5.61719	5.68507E-06	1.64006E-12
.302562	5.62358	3.58881E-06	1.06575E-12
.190904	5.62768	2.26511E-06	6.85252E-13
.120452	5.63039	1.42950E-06	4.37785E-13
7.60003E-02	5.63209	9.02073E-07	2.78397E-13
4.79530E-02	5.63309	5.69215E-07	1.76467E-13
3.02562E-02	5.63378	3.59170E-07	1.11700E-13
1.90904E-02	5.63419	2.26628E-07	7.06090E-14
1.20452E-02	5.63448	1.42996E-07	4.46124E-14
7.60004E-03	5.63468	9.02260E-08	2.81743E-14
4.79530E-03	5.63478	5.69292E-08	1.77849E-14
3.02562E-03	5.63488	3.59201E-08	1.12266E-14
1.90904E-03	5.63488	2.26641E-08	7.08352E-15
1.20452E-03	5.63488	1.43001E-08	4.46940E-15
7.60004E-04	5.63498	9.02282E-09	2.82129E-15

1.5.2

T = 200°C, $\text{HCO}_3^- = 0.001$, $\text{CO}_3^{2-} = 0.001$

SIMULATION OF EQUILIBRIUM PROPERTIES OF CARBONATE SOLUTIONS

INPUT INITIAL BICARBONATE AND CARBONATE CONC'S? .001,.001

INITIAL SOLUTION PH = 8.31219

CO SUB 2 PARTIAL PRESSURE = 9.61495 MM.

PARTIAL PRESSURE	PH	TOTAL CO SUB 2	CARBONATE CONC.
760	6.61368	1.16883E-02	2.55773E-07
479.528	6.81178	8.46103E-03	4.01839E-07
302.562	7.00879	6.41273E-03	6.28137E-07
190.904	7.20399	5.10110E-03	9.73793E-07
120.452	7.39668	4.24558E-03	1.49225E-06
76.0001	7.58528	3.66269E-03	2.24409E-06
47.9528	7.76778	3.23210E-03	3.28118E-06
30.2562	7.94148	2.87322E-03	4.60732E-06
19.0904	8.10289	2.53231E-03	6.11299E-06
12.0452	8.24819	2.17992E-03	7.53100E-06
7.60003	8.37368	1.80922E-03	8.46934E-06
4.79529	8.47708	1.43545E-03	8.60290E-06
3.02562	8.55808	1.08564E-03	7.88214E-06
1.90904	8.61838	7.84623E-04	6.56527E-06
1.20452	8.66148	5.45745E-04	5.05174E-06
.760003	8.69108	3.68257E-04	3.65296E-06
.479529	8.71088	2.43050E-04	2.52491E-06
.302562	8.72388	1.57957E-04	1.69136E-06
.190904	8.73229	1.01591E-04	1.10932E-06
.120452	8.73768	6.48924E-05	7.17538E-07
7.60003E-02	8.74119	4.12728E-05	4.60104E-07
4.79530E-02	8.74338	2.61719E-05	2.93253E-07
3.02562E-02	8.74468	1.65623E-05	1.86140E-07
1.90904E-02	8.74558	1.04716E-05	1.17935E-07
1.20452E-02	8.74618	6.61625E-06	7.46189E-08
7.60004E-03	8.74648	4.17741E-06	4.71461E-08
4.79530E-03	8.74668	2.63696E-06	2.97744E-08
3.02562E-03	8.74688	1.66456E-06	1.88036E-08
1.90904E-03	8.74699	1.05052E-06	1.18701E-08
1.20452E-03	8.74699	6.62836E-07	7.48950E-09
7.60004E-04	8.74708	4.18317E-07	4.72772E-09

1.5.3

T = 200°C, $\text{HCO}_3^- = 0.005$, $\text{CO}_3^{2-} = 0.005$

SIMULATION OF EQUILIBRIUM PROPERTIES OF CARBONATE SOLUTIONS

INPUT INITIAL BICARBONATE AND CARBONATE CONC'S? .005,.005

INITIAL SOLUTION PH = 8.96378

CO SUB 2 PARTIAL PRESSURE = 11.0407 MM.

PARTIAL PRESSURE	PH	TOTAL CO SUB 2	CARBONATE CONC.
760	7.31229	2.35937E-02	6.38347E-06
479.528	7.51029	2.03147E-02	1.00245E-05
302.562	7.70699	1.81800E-02	1.56479E-05
190.904	7.90188	1.67372E-02	2.42239E-05
120.452	8.09388	1.56774E-02	3.70034E-05
76.0001	8.28168	1.47915E-02	5.54433E-05
47.9528	8.46299	1.39110E-02	8.06221E-05
30.2562	8.63519	1.29164E-02	1.12422E-04
19.0904	8.79498	1.17228E-02	1.48063E-04
12.0452	8.93868	1.02942E-02	1.81067E-04
7.60003	9.06319	8.67338E-03	2.02704E-04
4.79529	9.16648	6.97073E-03	2.05800E-04
3.02562	9.24829	5.33512E-03	1.89255E-04
1.90904	9.30999	3.89787E-03	1.58660E-04
1.20452	9.35468	2.73649E-03	1.22984E-04
.760003	9.38588	1.86074E-03	8.95847E-05
.479529	9.40699	1.23521E-03	6.22958E-05
.302562	9.42089	8.05916E-04	4.19037E-05
.190904	9.42999	5.19797E-04	2.75717E-05
.120452	9.43588	3.32671E-04	1.78750E-05
7.60003E-02	9.43958	2.11786E-04	1.14721E-05
4.79530E-02	9.44199	1.34410E-04	7.31924E-06
3.02562E-02	9.44349	8.51132E-05	4.64994E-06
1.90904E-02	9.44439	5.38201E-05	2.94612E-06
1.20452E-02	9.44499	3.40077E-05	1.86404E-06
7.60004E-03	9.44538	2.14781E-05	1.17829E-06
4.79530E-03	9.44568	1.35615E-05	7.44471E-07
3.02562E-03	9.44578	8.55880E-06	4.69944E-07
1.90904E-03	9.44588	5.40154E-06	2.96651E-07
1.20452E-03	9.44599	3.40902E-06	1.87266E-07
7.60004E-04	9.44599	2.15095E-06	1.18157E-07

1.5.4

T = 200°C, $\text{HCO}_3^- = .01$, $\text{CO}_3^{2-} = .01$

SIMULATION OF EQUILIBRIUM PROPERTIES OF CARBONATE SOLUTIONS

INPUT INITIAL BICARBONATE AND CARBONATE CONC'S? .01,.01

INITIAL SOLUTION PH = 9.24439

CO SUB 2 PARTIAL PRESSURE = 11.4475 MM.

PARTIAL PRESSURE	PH	TOTAL CO SUB 2	CARBONATE CONC.
760	7.61299	3.84679E-02	2.54956E-05
479.528	7.81069	3.51104E-02	3.99804E-05
302.562	8.00709	3.28608E-02	6.23245E-05
190.904	8.20149	3.12392E-02	9.62617E-05
120.452	8.39278	2.99075E-02	1.46570E-04
76.0001	8.57948	2.86139E-02	2.18494E-04
47.9528	8.75948	2.71508E-02	3.15816E-04
30.2562	8.92999	2.53434E-02	4.36968E-04
19.0904	9.08788	2.30794E-02	5.70467E-04
12.0452	9.22978	2.03293E-02	6.91902E-04
7.60003	9.35319	1.72043E-02	7.70644E-04
4.79529	9.45638	1.39175E-02	7.82081E-04
3.02562	9.53899	1.07386E-02	7.21846E-04
1.90904	9.60229	7.91812E-03	6.09616E-04
1.20452	9.64888	5.60863E-03	4.76683E-04
.760003	9.68188	3.84314E-03	3.50133E-04
.479529	9.70449	2.56658E-03	2.45162E-04
.302562	9.71958	1.68223E-03	1.65823E-04
.190904	9.72948	1.08831E-03	1.09508E-04
.120452	9.73588	6.97881E-04	7.11601E-05
7.60003E-02	9.73999	4.44942E-04	4.57566E-05
4.79530E-02	9.74258	2.82594E-04	2.92179E-05
3.02562E-02	9.74419	1.79031E-04	1.85719E-05
1.90904E-02	9.74528	1.13275E-04	1.17772E-05
1.20452E-02	9.74599	7.15993E-05	7.45501E-06
7.60004E-03	9.74638	4.52218E-05	4.71242E-06
4.79530E-03	9.74668	2.85546E-05	2.97742E-06
3.02562E-03	9.74678	1.80212E-05	1.87948E-06
1.90904E-03	9.74688	1.13735E-05	1.18642E-06
1.20452E-03	9.74699	7.17814E-06	7.48945E-07
7.60004E-04	9.74699	4.52911E-06	4.72553E-07

1.5.5

 $T = 200^{\circ}\text{C}$, $\text{HCO}_3^- = 0$, $\text{CO}_3^{2-} = .002$

SIMULATION OF EQUILIBRIUM PROPERTIES OF CARBONATE SOLUTIONS

INPUT INITIAL BICARBONATE AND CARBONATE CONC'S? 0,.002

INITIAL SOLUTION PH = 8.58078

CO SUB 2 PARTIAL PRESSURE = 5.29661 MM.

PARTIAL PRESSURE	PH	TOTAL CO SUB 2	CARBONATE CONC.
760	6.73858	1.26807E-02	4.54618E-07
479.528	6.93668	9.44929E-03	7.14241E-07
302.562	7.13359	7.39346E-03	1.11595E-06
190.904	7.32888	6.07216E-03	1.73079E-06
120.452	7.52149	5.20009E-03	2.65123E-06
76.0001	7.70999	4.59229E-03	3.98529E-06
47.9528	7.89238	4.12497E-03	5.82422E-06
30.2562	8.06599	3.71405E-03	8.17441E-06
19.0904	8.22729	3.30234E-03	1.08405E-05
12.0452	8.37239	2.85923E-03	1.33429E-05
7.60003	8.49778	2.38253E-03	1.49981E-05
4.79529	8.60119	1.89589E-03	1.52356E-05
3.02562	8.68228	1.43706E-03	1.39651E-05
1.90904	8.74268	1.04027E-03	1.16373E-05
1.20452	8.78588	7.24407E-04	8.95855E-06
.760003	8.81568	4.89347E-04	6.48395E-06
.479529	8.83558	3.23177E-04	4.48373E-06
.302562	8.84868	2.10139E-04	3.00498E-06
.190904	8.85718	1.35205E-04	1.97173E-06
.120452	8.86258	8.63746E-05	1.27541E-06
7.60003E-02	8.86608	5.49391E-05	8.17800E-07
4.79530E-02	8.86828	3.48401E-05	5.21251E-07
3.02562E-02	8.86968	2.20531E-05	3.31001E-07
1.90904E-02	8.87048	1.39405E-05	2.09627E-07
1.20452E-02	8.87109	8.80807E-06	1.32633E-07
7.60004E-03	8.87148	5.56261E-06	8.38395E-08
4.79530E-03	8.87168	3.51137E-06	5.29476E-08
3.02562E-03	8.87178	2.21603E-06	3.34229E-08
1.90904E-03	8.87188	1.39854E-06	2.10981E-08
1.20452E-03	8.87199	8.82636E-07	1.33185E-08
7.60004E-04	8.87199	5.56907E-07	8.40343E-09

1.6

Sample Output at 250°C

1.6.1

T = 250°C, $\text{HCO}_3^- = 0$, $\text{CO}_3^{2-} = 0$

SIMULATION OF EQUILIBRIUM PROPERTIES OF CARBONATE SOLUTIONS

INPUT INITIAL BICARBONATE AND CARBONATE CONC'S? 0.0

INITIAL SOLUTION PH = 5.56509

CO SUB 2 PARTIAL PRESSURE = 0 MM.

PARTIAL PRESSURE	PH	TOTAL CO SUB 2	CARBONATE CONC.
760	4.79828	1.05154E-02	3.61163E-12
479.528	4.89458	6.63722E-03	3.55060E-12
302.562	4.98887	4.18966E-03	3.45854E-12
190.904	5.08009	2.64491E-03	3.32143E-12
120.452	5.16688	1.66986E-03	3.12542E-12
76.0001	5.24748	1.05435E-03	2.85835E-12
47.9528	5.31988	6.65744E-04	2.51715E-12
30.2562	5.38229	4.20372E-04	2.11698E-12
19.0904	5.43349	2.65423E-04	1.69090E-12
12.0452	5.47328	1.67572E-04	1.28149E-12
7.60003	5.50288	1.05783E-04	9.26652E-13
4.79529	5.52378	6.67686E-05	6.43745E-13
3.02562	5.53809	4.21391E-05	4.33829E-13
1.90904	5.54768	2.65928E-05	2.86094E-13
1.20452	5.55388	1.67808E-05	1.85741E-13
.760003	5.55799	1.05889E-05	1.19431E-13
.479529	5.56058	6.68144E-06	7.62631E-14
.302562	5.56219	4.21584E-06	4.84751E-14
.190904	5.56328	2.66007E-06	3.07409E-14
.120452	5.56388	1.67841E-06	1.94494E-14
7.60003E-02	5.56428	1.05902E-06	1.22946E-14
4.79530E-02	5.56458	6.68198E-07	7.76804E-15
3.02562E-02	5.56478	4.21605E-07	4.90576E-15
1.90904E-02	5.56488	2.66016E-07	3.09675E-15
1.20452E-02	5.56488	1.67845E-07	1.95392E-15
7.60004E-03	5.56499	1.05903E-07	1.23345E-15
4.79530E-03	5.56499	6.68203E-08	7.78257E-16
3.02562E-03	5.56499	4.21607E-08	4.91043E-16
1.90904E-03	5.56499	2.66016E-08	3.09827E-16
1.20452E-03	5.56499	1.67845E-08	1.95488E-16
7.60004E-04	5.56499	1.05903E-08	1.23345E-16

1.6.2

T = 250°C, $\text{HCO}_3^- = 0.001$, $\text{CO}_3^{2-} = 0.001$

SIMULATION OF EQUILIBRIUM PROPERTIES OF CARBONATE SOLUTIONS

INPUT INITIAL BICARBONATE AND CARBONATE CONC'S? .001,.001

INITIAL SOLUTION PH = 8.26798

CO SUB 2 PARTIAL PRESSURE = 27.1938 MM.

PARTIAL PRESSURE	PH	TOTAL CO SUB 2	CARBONATE CONC.
760	7.07378	1.34127E-02	1.28442E-07
479.528	7.26638	9.48866E-03	1.96747E-07
302.562	7.45488	6.96897E-03	2.95730E-07
190.904	7.63728	5.31578E-03	4.32230E-07
120.452	7.81088	4.18465E-03	6.06605E-07
76.0001	7.97198	3.35484E-03	8.03738E-07
47.9528	8.11669	2.69204E-03	9.87431E-07
30.2562	8.24149	2.12515E-03	1.10691E-06
19.0904	8.34378	1.62721E-03	1.11869E-06
12.0452	8.42359	1.20040E-03	1.01932E-06
7.60003	8.48378	8.58611E-04	8.44317E-07
4.79529	8.52458	5.85799E-04	6.46112E-07
3.02562	8.55329	3.92039E-04	4.65274E-07
1.90904	8.57238	2.57309E-04	3.20557E-07
1.20452	8.58498	1.66648E-04	2.14345E-07
.760003	8.59308	1.06932E-04	1.40382E-07
.479529	8.59828	6.82026E-05	9.07196E-08
.302562	8.60159	4.33304E-05	5.81185E-08
.190904	8.60369	2.74596E-05	3.70268E-08
.120452	8.60499	1.73728E-05	2.35025E-08
7.60003E-02	8.60578	1.09797E-05	1.48835E-08
4.79530E-02	8.60639	6.93644E-06	9.41697E-09
3.02562E-02	8.60668	4.37931E-06	5.94986E-09
1.90904E-02	8.60686	2.76431E-06	3.75755E-09
1.20452E-02	8.60699	1.74455E-06	2.37201E-09
7.60004E-03	8.60709	1.10096E-06	1.49733E-09
4.79530E-03	8.60719	6.94806E-07	9.45181E-10
3.02562E-03	8.60719	4.38392E-07	5.96368E-10
1.90904E-03	8.60719	2.76607E-07	3.76283E-10
1.20452E-03	8.60719	1.74527E-07	2.37419E-10
7.60004E-04	8.60729	1.10142E-07	1.49870E-10

1.6.3

T = 250°C, $\text{HCO}_3^- = 0.005$, $\text{CO}_3^{2-} = 0.005$

SIMULATION OF EQUILIBRIUM PROPERTIES OF CARBONATE SOLUTIONS

INPUT INITIAL BICARBONATE AND CARBONATE CONC'S? 0.002

INITIAL SOLUTION PH = 8.48138

CO SUB 2 PARTIAL PRESSURE = 17.8745 MM.

PARTIAL PRESSURE	PH	TOTAL CO SUB 2	CARBONATE CONC.
760.	7.19868	1.43833E-02	2.28195E-07
479.528	7.39128	1.04430E-02	3.49714E-07
302.562	7.57978	7.89841E-03	5.25653E-07
190.904	7.76219	6.20838E-03	7.68254E-07
120.452	7.93568	5.02398E-03	1.07770E-06
76.0001	8.09678	4.12241E-03	1.42788E-06
47.9528	8.24159	3.36876E-03	1.75514E-06
30.2562	8.36628	2.69395E-03	1.96655E-06
19.0904	8.46858	2.08159E-03	1.98747E-06
12.0452	8.54838	1.54506E-03	1.81093E-06
7.60003	8.60748	1.10188E-03	1.50007E-06
4.79529	8.64948	7.59199E-04	1.14841E-06
3.02562	8.67818	5.08945E-04	8.26989E-07
1.90904	8.69728	3.34399E-04	5.69767E-07
1.20452	8.70988	2.16725E-04	3.80963E-07
.760003	8.71799	1.39127E-04	2.49526E-07
.479529	8.72319	8.87631E-05	1.61257E-07
.302562	8.72648	5.64011E-05	1.03301E-07
.190904	8.72858	3.57468E-05	6.58123E-08
.120452	8.72988	2.26170E-05	4.17726E-08
7.60003E-02	8.73078	1.42981E-05	2.64672E-08
4.79530E-02	8.73129	9.03124E-06	1.67385E-08
3.02562E-02	8.73158	5.70194E-06	1.05758E-08
1.90904E-02	8.73178	3.59922E-06	6.67896E-09
1.20452E-02	8.73199	2.27195E-06	4.21813E-09
7.60004E-03	8.73209	1.43381E-06	2.66268E-09
4.79530E-03	8.73209	9.04673E-07	1.68004E-09
3.02562E-03	8.73209	5.70809E-07	1.06003E-09
1.90904E-03	8.73219	3.60233E-07	6.69141E-10
1.20452E-03	8.73219	2.27292E-07	4.22200E-10
7.60004E-04	8.73219	1.43412E-07	2.66390E-10

1.6.4

T = 250°C, $\text{HCO}_3^- = .01$, $\text{CO}_3^{2-} = .01$

SIMULATION OF EQUILIBRIUM PROPERTIES OF CARBONATE SOLUTIONS

INPUT INITIAL DICARBONATE AND CARBONATE CONC'S? .01,.01

INITIAL SOLUTION PH = 9.15059

CO SUB 2 PARTIAL PRESSURE = 42.23 MM.

PARTIAL PRESSURE	PH	TOTAL CO SUB 2	CARBONATE CONC.
760	8.07339	3.96123E-02	1.28206E-05
479.528	8.26578	3.52391E-02	1.96200E-05
302.562	8.45409	3.20444E-02	2.94655E-05
190.904	8.63619	2.93913E-02	4.30042E-05
120.452	8.80928	2.68308E-02	6.02156E-05
76.0001	8.96987	2.40580E-02	7.95947E-05
47.9528	9.11419	2.09294E-02	9.76159E-05
30.2562	9.23858	1.74739E-02	1.09221E-04
19.0904	9.34088	1.39068E-02	1.10383E-04
12.0452	9.42089	1.05328E-02	1.00673E-04
7.60003	9.48048	7.61848E-03	8.35800E-05
4.79529	9.52288	5.29913E-03	6.41079E-05
3.02562	9.55209	3.57620E-03	4.62722E-05
1.90904	9.57158	2.36019E-03	3.19374E-05
1.20452	9.58438	1.53385E-03	2.13750E-05
.760003	9.59268	9.86528E-04	1.40120E-05
.479529	9.59798	6.30129E-04	9.05945E-06
.302562	9.60139	4.00727E-04	5.80650E-06
.190904	9.60359	2.54132E-04	3.70096E-06
.120452	9.60488	1.60826E-04	2.34909E-06
7.60003E-02	9.60578	1.01686E-04	1.48834E-06
4.79530E-02	9.60629	6.42343E-05	9.41259E-07
3.02562E-02	9.60668	4.05664E-05	5.94983E-07
1.90904E-02	9.60688	2.56074E-05	3.75752E-07
1.20452E-02	9.60699	1.61612E-05	2.37200E-07
7.60004E-03	9.60709	1.01994E-05	1.49732E-07
4.79530E-03	9.60719	6.43684E-06	9.45174E-08
3.02562E-03	9.60719	4.06137E-06	5.96364E-08
1.90904E-03	9.60719	2.56255E-06	3.76280E-08
1.20452E-03	9.60719	1.61686E-06	2.37417E-08
7.60004E-04	9.60729	1.02041E-06	1.49869E-08

1.6.5

T = 250°C, $\text{HCO}_3^- = 0$, $\text{CO}_3^{2-} = .002$

SIMULATION OF EQUILIBRIUM PROPERTIES OF CARBONATE SOLUTIONS

INPUT INITIAL BICARBONATE AND CARBONATE CONC'S? .005,.005

INITIAL SOLUTION PH = 8.87168

CU SUB 2 PARTIAL PRESSURE = 39.1967 MM.

PARTIAL PRESSURE	PH	TOTAL CU SUB 2	CARBONATE CONC.
760	7.77258	2.50605E-02	3.20849E-06
479.528	7.96508	2.09381E-02	4.91251E-06
302.562	8.15349	1.81188E-02	7.38104E-06
190.904	8.33578	1.60231E-02	1.07823E-05
120.452	8.50909	1.42567E-02	1.51119E-05
76.0001	8.66999	1.25645E-02	2.00040E-05
47.9528	8.81458	1.08049E-02	2.45647E-05
30.2562	8.93918	8.95072E-03	2.75110E-05
19.0904	9.04149	7.08342E-03	2.78045E-05
12.0452	9.12139	5.34273E-03	2.53463E-05
7.60003	9.18068	3.85152E-03	2.10140E-05
4.79529	9.22279	2.67226E-03	1.60956E-05
3.02562	9.25189	1.79997E-03	1.16013E-05
1.90904	9.27099	1.18647E-03	8.00047E-06
1.20452	9.28368	7.70484E-04	5.35191E-06
.760003	9.29188	4.95272E-04	3.50675E-06
.479529	9.29708	3.16208E-04	2.26625E-06
.302562	9.30049	2.01063E-04	1.45251E-06
.190904	9.30259	1.27469E-04	9.25384E-07
.120452	9.30389	8.06640E-05	5.87363E-07
7.60003E-02	9.30479	5.09999E-05	3.72143E-07
4.79530E-02	9.30529	3.22156E-05	2.35351E-07
3.02562E-02	9.30569	2.03450E-05	1.48769E-07
1.90904E-02	9.30588	1.28427E-05	9.39527E-08
1.20452E-02	9.30599	8.10512E-06	5.93091E-08
7.60004E-03	9.30609	5.11514E-06	3.74387E-08
4.79530E-03	9.30609	3.22744E-06	2.36222E-08
3.02562E-03	9.30619	2.03683E-06	1.49114E-08
1.90904E-03	9.30619	1.28515E-06	9.40847E-09
1.20452E-03	9.30619	8.10878E-07	5.93634E-09
7.60004E-04	9.30619	5.11630E-07	3.74559E-09

1.7

Sample Output at 300°C

1.7.1

 $T = 300^{\circ}\text{C}$, $\text{HCO}_3^- = 0$, $\text{CO}_3^{2-} = 0$

SIMULATION OF EQUILIBRIUM PROPERTIES OF CARBONATE SOLUTIONS

INPUT INITIAL BICARBONATE AND CARBONATE CONC'S? 0.0

INITIAL SOLUTION PH = 5.69518
CO SUB 2 PARTIAL PRESSURE = 0

MM.

PARTIAL PRESSURE	PH	TOTAL CO SUB 2	CARBONATE CONC.
760	5.30539	1.48041E-02	3.47738E-14
479.528	5.38528	9.34130E-03	3.16987E-14
302.562	5.45678	5.89431E-03	2.77994E-14
190.904	5.51809	3.71929E-03	2.32622E-14
120.452	5.56808	2.34684E-03	1.84775E-14
76.0001	5.60688	1.48083E-03	1.39392E-14
47.9528	5.63538	9.34375E-04	1.00287E-14
30.2562	5.65558	5.89567E-04	6.94445E-15
19.0904	5.66938	3.72000E-04	4.66912E-15
12.0452	5.67858	2.34719E-04	3.07350E-15
7.60003	5.68448	1.48099E-04	1.99268E-15
4.79529	5.68838	9.34448E-05	1.28007E-15
3.02562	5.69088	5.89599E-05	8.17020E-16
1.90904	5.69248	3.72013E-05	5.19324E-16
1.20452	5.69348	2.34725E-05	3.29182E-16
.760003	5.69408	1.48102E-05	2.08278E-16
.479529	5.69448	9.34457E-06	1.31654E-16
.302562	5.69468	5.89602E-06	8.31443E-17
.190904	5.69488	3.72015E-06	5.25085E-17
.120452	5.69498	2.34725E-06	3.31469E-17
7.60003E-02	5.69508	1.48102E-06	2.09239E-17
4.79530E-02	5.69508	9.34460E-07	1.32021E-17
3.02562E-02	5.69508	5.89603E-07	8.32992E-18
1.90904E-02	5.69508	3.72015E-07	5.25583E-18
1.20452E-02	5.69518	2.34726E-07	3.31772E-18
7.60004E-03	5.69518	1.48102E-07	2.09334E-18
4.79530E-03	5.69518	9.34460E-08	1.32081E-18
3.02562E-03	5.69518	5.89604E-08	8.33374E-19
1.90904E-03	5.69518	3.72015E-08	5.25824E-19
1.20452E-03	5.69518	2.34726E-08	3.31772E-19
7.60004E-04	5.69518	1.48102E-08	2.09335E-19

1.7.2

T = 300°C, $\text{HCO}_3^- = 0.001$, $\text{CO}_3^{2-} = 0.001$

SIMULATION OF EQUILIBRIUM PROPERTIES OF CARBONATE SOLUTIONS

INPUT INITIAL BICARBONATE AND CARBONATE CONC'S? .001,.001

INITIAL SOLUTION PH = 8.72388

CO SUB 2 PARTIAL PRESSURE = 59.3345 MM.

PARTIAL PRESSURE	PH	TOTAL CO SUB 2	CARBONATE CONC.
760	8.08799	1.73016E-02	1.27772E-08
479.528	8.24768	1.16181E-02	1.68203E-08
302.562	8.39068	7.89149E-03	2.05037E-08
190.904	8.51329	5.39072E-03	2.27530E-08
120.452	8.61329	3.67467E-03	2.27535E-08
76.0001	8.69088	2.48259E-03	2.05221E-08
47.9528	8.74798	1.65531E-03	1.68439E-08
30.2562	8.78838	1.08880E-03	1.28004E-08
19.0904	8.81588	7.07596E-04	9.16697E-09
12.0452	8.83428	4.55639E-04	6.29571E-09
7.60003	8.84618	2.91362E-04	4.19600E-09
4.79529	8.85399	1.85476E-04	2.74431E-09
3.02562	8.85888	1.17686E-04	1.77099E-09
1.90904	8.86209	7.45301E-05	1.13408E-09
1.20452	8.86408	4.71338E-05	7.22158E-10
.760003	8.86528	2.97808E-05	4.58176E-10
.479529	8.86608	1.88078E-05	2.90158E-10
.302562	8.86658	1.18738E-05	1.83497E-10
.190904	8.86698	7.49532E-06	1.15991E-10
.120452	8.86718	4.73035E-06	7.32547E-11
7.60003E-02	8.86728	2.98500E-06	4.62418E-11
4.79530E-02	8.86738	1.88362E-06	2.91899E-11
3.02562E-02	8.86738	1.18848E-06	1.84176E-11
1.90904E-02	8.86738	7.49883E-07	1.16207E-11
1.20452E-02	8.86748	4.73200E-07	7.33554E-12
7.60004E-03	8.86748	2.98569E-07	4.62842E-12
4.79530E-03	8.86748	1.88384E-07	2.92033E-12
3.02562E-03	8.86748	1.18862E-07	1.84260E-12
1.90904E-03	8.86748	7.49970E-08	1.16260E-12
1.20452E-03	8.86748	4.73200E-08	7.33555E-13
7.60004E-04	8.86748	2.98569E-08	4.62842E-13

1.7.3

 $T = 300^{\circ}\text{C}$, $\text{HCO}_3^- = 0.005$, $\text{CO}_3^{2-} = 0.005$

SIMULATION OF EQUILIBRIUM PROPERTIES OF CARBONATE SOLUTIONS

INPUT INITIAL BICARBONATE AND CARBONATE CONC'S? .005..005

INITIAL SOLUTION PH = 9.27988

CO SUB 2 PARTIAL PRESSURE = 141.481 MM.

PARTIAL PRESSURE	PH	TOTAL CO SUB 2	CARBONATE CONC.
760	8.78698	2.73091E-02	3.19467E-07
479.528	8.94668	2.07389E-02	4.20557E-07
302.562	9.08958	1.58882E-02	5.12419E-07
190.904	9.21219	1.20824E-02	5.68649E-07
120.452	9.31229	8.99174E-03	5.68923E-07
76.0001	9.38978	6.49258E-03	5.12895E-07
47.9528	9.44699	4.54190E-03	4.21159E-07
30.2562	9.48738	3.08766E-03	3.20057E-07
19.0904	9.51488	2.05125E-03	2.29208E-07
12.0452	9.53319	1.33989E-03	1.57344E-07
7.60003	9.54519	8.64947E-04	1.04916E-07
4.79529	9.55288	5.53830E-04	6.85845E-08
3.02562	9.55788	3.52805E-04	4.42812E-08
1.90904	9.56099	2.23940E-04	2.83432E-08
1.20452	9.56299	1.41839E-04	1.80484E-08
.760003	9.56428	8.97184E-05	1.14561E-08
.479529	9.56509	5.66958E-05	7.25504E-09
.302562	9.56558	3.58068E-05	4.58811E-09
.190904	9.56588	2.26056E-05	2.89888E-09
.120452	9.56608	1.42688E-05	1.83080E-09
7.60003E-02	9.56618	9.00473E-06	1.15569E-09
4.79530E-02	9.56628	5.68269E-06	7.29523E-10
3.02562E-02	9.56638	3.58621E-06	4.60509E-10
1.90904E-02	9.56638	2.26275E-06	2.90561E-10
1.20452E-02	9.56638	1.42770E-06	1.83332E-10
7.60004E-03	9.56638	9.00818E-07	1.15675E-10
4.79530E-03	9.56648	5.68486E-07	7.30192E-11
3.02562E-03	9.56648	3.58690E-07	4.60719E-11
1.90904E-03	9.56648	2.26318E-07	2.90695E-11
1.20452E-03	9.56648	1.42797E-07	1.83416E-11
7.60004E-04	9.56648	9.00991E-08	1.15728E-11

1.7.4

 $T = 300^{\circ}\text{C}$, $\text{HCO}_3^- = 0.01$, $\text{CO}_3^{2-} = 0.01$

SIMULATION OF EQUILIBRIUM PROPERTIES OF CARBONATE SOLUTIONS

INPUT INITIAL BICARBONATE AND CARBONATE CONC'S? .01,.01

INITIAL SOLUTION PH = 9.52288

CO SUB 2 PARTIAL PRESSURE = 183.341 MM.

PARTIAL PRESSURE	PH	TOTAL CO SUB 2	CARBONATE CONC.
760	9.08799	3.98176E-02	1.27775E-06
479.528	9.24768	3.21389E-02	1.68201E-06
302.562	9.39058	2.58843E-02	2.04942E-06
190.904	9.51319	2.04472E-02	2.27431E-06
120.452	9.61329	1.56380E-02	2.27534E-06
76.0001	9.69078	1.15054E-02	2.05126E-06
47.9528	9.74798	8.15026E-03	1.68438E-06
30.2562	9.78838	5.58636E-03	1.28003E-06
19.0904	9.81588	3.73094E-03	9.16689E-07
12.0452	9.83419	2.44536E-03	6.29278E-07
7.60003	9.84618	1.58199E-03	4.19597E-07
4.79529	9.85398	1.01455E-03	2.74421E-07
3.02562	9.85888	6.46743E-04	1.77103E-07
1.90904	9.86209	4.10818E-04	1.13407E-07
1.20452	9.86408	2.60297E-04	7.22175E-08
.760003	9.86528	1.64648E-04	4.58173E-08
.479529	9.86608	1.04060E-04	2.90156E-08
.302562	9.86658	6.57261E-05	1.83496E-08
.190904	9.86698	4.15056E-05	1.15994E-08
.120452	9.86718	2.61992E-05	7.32542E-09
7.60003E-02	9.86728	1.65340E-05	4.62415E-09
4.79530E-02	9.86738	1.04345E-05	2.91898E-09
3.02562E-02	9.86738	6.58368E-06	1.84175E-09
1.90904E-02	9.86738	4.15402E-06	1.16206E-09
1.20452E-02	9.86748	2.62156E-06	7.33549E-10
7.60004E-03	9.86748	1.65409E-06	4.62838E-10
4.79530E-03	9.86748	1.04366E-06	2.92031E-10
3.02562E-03	9.86748	6.58506E-07	1.84259E-10
1.90904E-03	9.86748	4.15489E-07	1.16260E-10
1.20452E-03	9.86748	2.62156E-07	7.33549E-11
7.60004E-04	9.86748	1.65410E-07	4.62839E-11

1.7.5

T = 300°C, $\text{HCO}_3^- = 0$, $\text{CO}_3^{2-} = 0.002$

SIMULATION OF EQUILIBRIUM PROPERTIES OF CARBONATE SOLUTIONS

INPUT INITIAL BICARBONATE AND CARBONATE CONC'S? 0.002

INITIAL SOLUTION PH = 8.86638

CO SUB 2 PARTIAL PRESSURE = 50.9748 MM.

PARTIAL PRESSURE	PH	TOTAL CO SUB 2	CARBONATE CONC.
760	8.21299	1.81360E-02	2.27222E-08
479.528	8.37268	1.23785E-02	2.99114E-08
302.562	8.51558	8.55778E-03	3.64449E-08
190.904	8.63818	5.94825E-03	4.04429E-08
120.452	8.73828	4.11792E-03	4.04612E-08
76.0001	8.81578	2.81668E-03	3.64776E-08
47.9528	8.87298	1.89594E-03	2.99524E-08
30.2562	8.91329	1.25530E-03	2.27531E-08
19.0904	8.94088	8.19610E-04	1.63015E-08
12.0452	8.95918	5.29303E-04	1.11901E-08
7.60003	8.97118	3.39179E-04	7.46170E-09
4.79529	8.97887	2.16161E-04	4.87766E-09
3.02562	8.98388	1.37286E-04	3.14933E-09
1.90904	8.98698	8.69770E-05	2.01574E-09
1.20452	8.98898	5.50234E-05	1.28358E-09
.760003	8.99028	3.47774E-05	8.14770E-10
.479529	8.99108	2.19663E-05	5.15986E-10
.302562	8.99158	1.38689E-05	3.26311E-10
.190904	8.99188	8.75410E-06	2.06165E-10
.120452	8.99208	5.52502E-06	1.30209E-10
7.60003E-02	8.99218	3.48652E-06	8.21938E-11
4.79530E-02	8.99228	2.20011E-06	5.18829E-11
3.02562E-02	8.99238	1.38836E-06	3.27509E-11
1.90904E-02	8.99238	8.75995E-07	2.06644E-11
1.20452E-02	8.99238	5.52716E-07	1.30384E-11
7.60004E-03	8.99238	3.48740E-07	8.22667E-12
4.79530E-03	8.99238	2.20040E-07	5.19067E-12
3.02562E-03	8.99238	1.38836E-07	3.27509E-12
1.90904E-03	8.99238	8.75995E-08	2.06644E-12
1.20452E-03	8.99238	5.52716E-08	1.30384E-12
7.60004E-04	8.99238	3.48741E-08	8.22667E-13

1.7.6

T = 300°C, $\text{HCO}_3^- = 0.02$, $\text{CO}_3^{2-} = 0$

SIMULATION OF EQUILIBRIUM PROPERTIES OF CARBONATE SOLUTIONS

INPUT INITIAL BICARBONATE AND CARBONATE CONC'S? .02,0

INITIAL SOLUTION PH = 9.19278

CO SUB 2 PARTIAL PRESSURE = .325.865 MM.

PARTIAL PRESSURE	PH	TOTAL CO SUB 2	CARBONATE CONC.
760	8.91188	3.14776E-02	5.67845E-07
479.528	9.07159	2.45382E-02	7.47553E-07
302.562	9.21459	1.92227E-02	9.11259E-07
190.904	9.33709	1.48699E-02	1.01076E-06
120.452	9.43719	1.12065E-02	1.01122E-06
76.0001	9.51478	8.16463E-03	9.12075E-07
47.9528	9.57188	5.74423E-03	7.48555E-07
30.2562	9.61229	3.92039E-03	5.68911E-07
19.0904	9.63978	2.61096E-03	4.07400E-07
12.0452	9.65818	1.70859E-03	2.79795E-07
7.60003	9.67009	1.10389E-03	1.86485E-07
4.79529	9.67788	7.07423E-04	1.21960E-07
3.02562	9.68278	4.50754E-04	7.87088E-08
1.90904	9.68598	2.86240E-04	5.04010E-08
1.20452	9.68798	1.81329E-04	3.20943E-08
.760003	9.68918	1.14686E-04	2.03623E-08
.479529	9.68999	7.24795E-05	1.28957E-08
.302562	9.69048	4.57771E-05	8.15526E-09
.190904	9.69088	2.89061E-05	5.15490E-09
.120452	9.69108	1.82463E-05	3.25570E-09
7.60003E-02	9.69118	1.15148E-05	2.05509E-09
4.79530E-02	9.69128	7.26679E-06	1.29727E-09
3.02562E-02	9.69128	4.58502E-06	8.18518E-10
1.90904E-02	9.69138	2.89353E-06	5.16687E-10
1.20452E-02	9.69138	1.82570E-06	3.26007E-10
7.60004E-03	9.69138	1.15194E-06	2.05697E-10
4.79530E-03	9.69138	7.26823E-07	1.29786E-10
3.02562E-03	9.69138	4.58594E-07	8.18893E-11
1.90904E-03	9.69138	2.89353E-07	5.16687E-11
1.20452E-03	9.69138	1.82570E-07	3.26008E-11
7.60004E-04	9.69138	1.15194E-07	2.05697E-11

2. Glass pH Electrode for CO₂ Measurement

A glass pH electrode was considered for inclusion in the geothermal CO₂ sensor.

This section describes these preliminary considerations for information only since the design described herein was rejected for use in geothermal CO₂ sensing.

A relatively flat glass membrane electrode, similar to that being developed for use in geothermal brine pH measurement under Subcontract No. B-57802-A-E, administered by PNL, is shown in Figure VI-1. It consists of a high temperature pH sensing glass sealed to stem glass and enclosed in a stainless steel jacket. The glass is sealed into the steel by four Bal-Seals (Bal-Seal Engineering Co.), and two potting compounds, CS-0954 (Castall, Inc.) and fluorosilicone, Dow-730 (Dow Chemical). Details of the design considerations are reported in reference 98.

Testing of pH glasses was carried out using the experimental configuration shown in Figure VI-2. The potential across the pH membrane can be measured at "zero" current. Alternatively, a current can be passed and, with appropriate voltage and current measurements made, the membrane impedance can be deduced.

In general, the results show 25°C membrane impedances of $\approx 10^{10} - 10^{11} \Omega$ which decreases to $\approx 10^9 \Omega$ after 24 hour exposure to simulated brine. The pH response at 25°C remained near the theoretical value predicted by the Nernst equation, even after 24-hour exposure to simulated brine at 200°C. Exposure to brine at 250°C for 24 hours reduced the probe sensitivity considerably, apparently limiting use to about 200°C.

Most of the materials which contact the internal electrolyte are relatively free from attack by the solution. There is one important exception to this; the pH sensing glass of the pH electrode is subject to attack. The corrosion of glass is a matter continually under investigation; a recent book on the subject¹⁰³ contains 148 references. However, very little is known of the high temperature effect of electrolyte solutions on glass. Very limited work has been done in high temperature pH measurement, and the concern is invariably the effect of

FIGURE VI-1: PROPOSED GEOTHERMAL pH SENSOR CONFIGURATION

FIGURE VI-2: EXPERIMENTAL CONFIGURATION FOR pH MEMBRANE TESTING

the solution on the glass and its pH response.^{98,104} In the case of the CO₂ sensor under consideration, of greater importance is the effect of the glass on the pH of the internal electrolyte contacting the glass surface. It is the pH of this thin film of solution which indicates CO₂ concentration. Nothing other than the varying CO₂ content of the sample should cause a pH change in the solution.

At low temperatures the mechanism of glass attack is primarily ion exchange. At elevated temperature, dissolution of the glass occurs. So long as the glass composition at the sensing surface remains unaltered, dissolution will not cause pH electrode failure. Tests of the glass electrode response after brine exposure are underway as part of other geothermal sensor development projects.

As the glass dissolves, the dissolution products are usually dispersed in the sample with little consequence. However, in the proposed design the dissolution products are trapped in the thin film of electrolyte between the glass and the polymer membrane. The dissolution product can be considered an alkali silicate since the glass is primarily Li₂O and SiO₂, and as such causes the electrolyte to become more basic. This serious potential problem is difficult to evaluate precisely without constructing the membrane-electrolyte-glass assembly, and this was not possible within the time constraint of the Task I effort. Instead, small quantities (1-2 ml) of various buffer solutions had been placed inside pH electrode assemblies to test their suitability as internal electrolytes for pH sensors, and these results are summarized in Table VI-1. The extreme pH change observed in these solutions, volumes large compared to the thin film confined against the electrode surface in the CO₂ sensor, indicates a severe problem may be encountered. Even a brief three-hour exposure at the relatively low temperature of 127°C resulted in a significant pH change in the buffers.

TABLE VI-1: ELECTROLYTE pH CHANGE IN CONTACT WITH GLASS
AT ELEVATED TEMPERATURE

	<u>Initial pH</u>	<u>Final pH</u>	<u>Time</u>	<u>Temp.</u>
Phosphate Buffer	6.4	10.0	7 days	105°C
Potassium Biphthalate Buffer	4.0	9.4	4 days	120°C
Acetate Buffer	5.0	5.6	3 hours	127°C

Only two factors make these results slightly inconclusive. First, the pH glass used was perhaps not quite as inert as the best high temperature pH glasses under development, although it was one of the better formulations studied.⁹⁸ Secondly, the experimental design permitted the electrolyte to come into contact with stem glass (Corning 010) known to be attacked in high temperature solutions. However, these reservations notwithstanding, it appears that glass dissolution into the electrolyte will be a factor limiting the probe performance. Unless a breakthrough is made in the attempt to find a more inert pH sensing glass, a ten-fold or more error in CO₂ analysis within the 24 hour target lifetime is likely.

At the present time, the best understood and most thoroughly tested pH sensing element is believed to be the glass pH electrode. However, the apparent likelihood of error caused by glass dissolution, a problem uniquely severe in the proposed CO₂ sensor, forces the choice of an alternative device for the application. The ISFET pH sensor, described in detail in Section II.2.1.1, was selected over several candidate approaches as the one most likely to fulfill the requirements of the geothermal CO₂ sensor. The results of tests described in Section II indicate the suitability of the ISFET sensor in the geothermal environment.

3. Interference Compensation Using a $\text{CO}_3^{=}\text{-F}^-$ System

Given the possible interference from acidic or basic gases in the brine, a compensation scheme was devised which might lessen or eliminate this problem. This compensation system allows the interfering species to permeate through the membrane (no getter system is required), and corrects the signal continuously so that no error results. The principle is described in Section VI.3.1 and solid electrolyte requirements and alternatives are presented in Section VII.3.2. A possible design is shown in Figure VI-3.

Although the system may have merit, it also has several drawbacks. The electrode complexity is high, equilibria of several chemical reactions is required, and the relative solubilities of certain salts (for which data is not available at elevated temperatures) must be correct. The getter system described in Section III.2.1 has none of these requirements and, given its high probability of satisfactorily avoiding any interference problem, it is recommended for inclusion in the proposed design without the $\text{CO}_3^{=}\text{-F}^-$ compensation systems.

The studies which evaluated the $\text{CO}_3^{=}\text{-F}^-$ system are reported in this section and will be of special use if this compensation scheme should be required. Secondly, the concept has secondary implications which may prove valuable. For example, the derivation of Section VI.3.1 indicate that CO_2 could be measured with the getter system (III.2.1) and a fluoride electrode without using a conventional pH sensor since the fluoride electrode potential varies with pH and possible interferences would be removed by the getter. At this time this approach is not recommended due to the limitations cited above.

FIGURE VI-3: POSSIBLE pCO₂ PROBE DESIGN UTILIZING INTERFERENCE COMPENSATION SCHEME

3.1 Principle of Interference Compensation

For ease of understanding development of subsequent equations, equations II-7, II-9 and II-11, developed in Section II-1, are repeated below and renumbered VI-1, VI-2, and VI-3.

$$(H_2CO_3) = \frac{(pp\ CO_2) (57\ \text{moles/liter}) K_{\text{hydrolysis}}}{K_{\text{Henry}}} \quad \text{VI-1}$$

$$K_1 = \frac{(H^+) (HCO_3^-)}{(H_2CO_3)} \quad \text{VI-2}$$

$$K_2 = \frac{(H^+) (CO_3^{=})}{(HCO_3^-)} \quad \text{VI-3}$$

Combining equations VI-1, VI-2, and VI-3 and solving for $(CO_3^{=})$, one obtains

$$(CO_3^{=}) = \frac{(pp\ CO_2) (57) (K_{\text{hydrolysis}}) (K_1) (K_2) \text{ Moles}}{(K_{\text{Henry}}) (H^+)^2 \text{ Liter}} \quad \text{VI-4}$$

From equation VI-4 it is clear that if one could determine the (H^+) and $(CO_3^{=})$ concentration, the $ppCO_2$, could be computed.

It is proposed that a fluoride sensitive electrode be used in conjunction with a saturated solution of the carbonate salt of the fluoride electrode cation to measure the $CO_3^{=}$. Two alternative possible systems have been identified. One is the conventional LaF_3 -based fluoride electrode (an ambient temperature version of which is commercially available from Orion, Inc., Cambridge, Mass.) and $La_2(CO_3)_3$. A second, usable only at elevated temperatures, is a CaF_2 electrode in a saturated solution of $CaCO_3$.

The chemistry of the lanthanum fluoride-lanthanum carbonate system is described by way of example; an obvious parallel description could be written for the calcium based system.

It is assumed that no lanthanum species other than LaF_3 and $\text{La}_2(\text{CO}_3)_3$ are insoluble in this system, and that no stable lanthanum complex ions are present. If the solution at the surface of the electrode is saturated with lanthanum carbonate, the La^{+3} ion concentration is determined by the $\text{CO}_3^{=}$ concentration, the solubility product rule being applicable.

$$K_{\text{La}_2(\text{CO}_3)_3} = (\text{La}^{+3})^2 (\text{CO}_3^{=})^3 \quad \text{VI-6}$$

For brevity, the constants of equation VI-4 are combined to define the constant A, where

$$A = \frac{(57)(K_{\text{hydrolysis}})(K_1)(K_2)}{K_{\text{Henry}}} \left(\frac{\text{moles}}{\text{liter}} \right)^3 (\text{mm})^{-1} \quad \text{VI-7}$$

Substituting equations VI-4 and VI-7 into VI-6 and solving for (La^{+3}) , one obtains

$$(\text{La}^{+3}) = K_{\text{La}_2(\text{CO}_3)_3}^{1/2} (A)^{-3/2} (\text{H}^+)^3 (\text{pp CO}_2)^{-3/2} \quad \text{VI-8}$$

The (La^{+3}) concentration at the fluoride electrode surface determines (F^-) concentration, assuming that the solution at the surface is saturated with LaF_3 .

$$K_{\text{LaF}_3} = (\text{La}^{+3}) (\text{F}^-)^3 \quad \text{VI-10}$$

Assuming Nerstian behavior of the electrode,

$$E_{\text{F}^-} = E' + \frac{RT}{F} \ln(\text{F}^-) \quad \text{VI-11}$$

where R is the gas constant, F is Faraday's constant, and T is the absolute temperature. E_{F-} is the observed fluoride electrode potential, versus an arbitrary reference, and E' is a constant which includes the standard potential of the system (versus a specific reference) and correction for activities using the appropriate activity coefficients.

It can be seen that

$$E_{F-} = E' + \frac{RT}{F} \ln(K_{LaF_3})^{1/3} (A)^{1/2} - \frac{RT}{6F} \ln K_{La_2(CO_3)_3} + \frac{RT}{2F} \ln(ppCO_2) - \frac{RT}{F} \ln (H^+) \quad \text{VI-12}$$

which can be further reduced to

$$E_{F-} = E' - \frac{RT}{F} \ln(K_{LaF_3})^{1/3} (A)^{1/2} - \frac{RT}{6F} \ln K_{La_2(CO_3)_3} + \frac{RT}{2F} \ln(ppCO_2) + \frac{2.3 RT}{F} (pH) \quad \text{VI-13}$$

The potential of the pH sensitive glass electrode is defined as:

$$E_{H^+} = E'' - \frac{RT}{F} \ln H^+ \quad \text{VI-14}$$

$$= E'' + \frac{2.3 RT}{F} (pH) \quad \text{VI-15}$$

Substituting for $(2.3 RT/F)$ pH in equation II-13 and rearranging, one obtains

$$E_{F-} - E_{H^+} = E' - E'' - \frac{RT}{F} \ln (K_{LaF_3})^{1/3} (A)^{1/2} - \frac{RT}{6F} \ln K_{La_2(CO_3)_3} + \frac{RT}{2F} \ln (ppCO_2) \quad \text{VI-16}$$

Equation VI-16 shows that the difference in potential of the glass and fluoride electrodes varies linearly with CO_2 concentration.

3.2 Solid Electrolyte Requirements and Alternatives

Implied in the derivation in Section VI.3.1 are certain requirements of the ionic equilibrium. The solid electrolyte employed must have ionic conductivity, and LaF_3 , doped with europium, meets this requirement. CaF_2 also has ionic conductivity at elevated temperature resulting from fluoride ion mobility, although less than LaF_3 .

The carbonate salt of the cation must be more insoluble than most other corresponding complex ions. For example, the corresponding sulfide must not be more insoluble than carbonate under the H_2S and CO_2 levels encountered or else the carbonate would be converted to the sulfide. Both $\text{La}_2(\text{CO}_3)_3$ and CaCO_3 are stable and more insoluble than the corresponding sulfides. Finally, to function according to the model proposed in Section VII.3.1, the carbonate should be more soluble than the fluoride.

3.2.1 Literature Solubility Data

High temperature solubility data of lanthanum and calcium fluoride is summarized in Table VI-2. (Both La_2S_3 and CaS are either soluble or unstable in hot brine.) The data for the calcium salts indicates quite conclusively that both the carbonate and fluoride become less soluble as the temperature increases, with the carbonate remaining less soluble than the fluoride at all temperatures. This relative solubility relationship makes the calcium system unsuitable for interference compensation by the proposed scheme.

Two problems arose when trying to determine the feasibility of use of the lanthanum system for interference compensation. First, only data at 25°C could be found. Because the data did not show an extreme relationship, relative solubilities at high temperature could not be estimated. Furthermore, there was apparent scatter in the data reported for the solubility of $\text{La}_2(\text{CO}_3)_3$ at 25°C , whereas agreement on the solubility of LaF_3 was evident. Most of the apparent uncertainty in the solubility of $\text{La}_2(\text{CO}_3)_3$ is likely due to different conditions employed. Nonetheless, it makes evaluation of interference compensation using lanthanum salts impossible without more information.

TABLE VII-2: SOLUBILITY DATA OF LANTHANUM AND CALCIUM CARBONATES AND FLUORIDES

COMPOUND	TEMP. (°C)	CONDITIONS	K _{so}	SOLUBILITY (M/l)	REFERENCE
La ₂ (CO ₃) ₃	25	CO ₂ saturated H ₂ O γ = 0.21, Ionic Strength = 0.1	3.98 x 10 ⁻³⁴	1.46 x 10 ⁻⁷	105
"	25	CO ₂ saturated H ₂ O	1.5 x 10 ⁻²³	1.1 x 10 ⁻⁵	106
"	25	Aqueous acidified to pH 5.6 - 5.7	---	2.57 x 10 ⁻⁴	107
CaCO ₃	25	Aqueous, corr. to zero ionic strength	5.37 x 10 ⁻⁹	7.33 x 10 ⁻⁵	108
"	100	"	4.26 x 10 ⁻¹⁰	2.07 x 10 ⁻⁵	109
"	200	"	2.88 x 10 ⁻¹²	1.7 x 10 ⁻⁶	"
"	250	"	1.7 x 10 ⁻¹³	4.1 x 10 ⁻⁷	"
LaF ₃	25	Aqueous	1.4 x 10 ⁻¹⁸	2.6 x 10 ⁻⁵	110
	25	H ₂ O, Ionic Strength = 0.3M	1.2 x 10 ⁻¹⁸	2.5 x 10 ⁻⁵	111
CaF ₂	25	Aqueous	3.6 x 10 ⁻⁶	1.9 x 10 ⁻³	112
	199	"	5.2 x 10 ⁻⁸	2.3 x 10 ⁻⁴	"
	238	"	7.1 x 10 ⁻⁸	2.7 x 10 ⁻⁴	"
	250	"	6.5 x 10 ⁻⁸	2.5 x 10 ⁻⁴	"
	262	"	1.0 x 10 ⁻⁷	3.2 x 10 ⁻⁴	"
	367	"	9.2 x 10 ⁻⁸	3.0 x 10 ⁻⁴	"
	380	"	7.9 x 10 ⁻⁹	8.9 x 10 ⁻⁵	"
CaF ₂	250	H ₂ O, sat'd with amorphous silica	---	1.1 x 10 ⁻⁴	5, p. 142

Preliminary measurements have been completed to determine the lanthanum salt solubilities at both 25°C and elevated temperatures and are reported below.

3.2.2 Experimental Lanthanum Salt Solubility Results

Two experiments relate to the lanthanum salt solubilities. First, during tests of the proposed compensation system described in Section 2.3, a solution 10^{-3} molar in both $\text{CO}_3^{=}$ and $\text{HCO}_3^{=}$ was equilibrated with a known partial pressure of CO_2 which ranged from 56 to 791 ppm. The pH and the fluoride electrode potential were monitored, and with the CO_2 constant (stable readings achieved), $\text{La}_2(\text{CO}_3)_3$ was added to the solution. If $\text{La}_2(\text{CO}_3)_3$ were more soluble than LaF_3 , the lanthanum ion content of the solution, previously saturated with LaF_3 from the fluoride electrode, should have risen due to dissolution of the carbonate. The increased lanthanum concentration would have caused the dissolved fluoride level to decrease, and this would have been indicated by a change in the fluoride electrode potential. However, no such potential change was observed. This indicates that at 25°C the fluoride and lanthanum levels in the solution are determined by the LaF_3 solubility rather than the $\text{La}_2(\text{CO}_3)_3$, and indicates that the compensation system would not work as originally proposed. Nonetheless, the system was further tested with the results reported in Section VI.3.2.3.

In addition to the room temperature results described, several experiments were conducted to determine the solubility of LaF_3 at elevated temperatures. Initially, one LaF_3 crystal was placed in a sealed Pyrex ampule which was constricted in the center similar to an hour-glass. The ampule also contained 2.5 ml of 0.01 M of both $\text{HCO}_3^{=}$ and $\text{CO}_3^{=}$, saturated with $\text{La}_2(\text{CO}_3)_3$. The ampule was heated with the LaF_3 crystal immersed in solution for 22 hours, after which it was inverted. This caused the solution to flow to the other end of the ampule, and the ampule was cooled with the crystal held in the upper half of the container remote from the electrolyte. Recrystallization on the original crystal was thus prevented, and a small weight change could be attributed to

dissolution. Given the volume of the electrolyte and the weighing accuracy achieved (± 0.1 mg using a Torbal EA-1 balance), no weight change was detected and an upper solubility limit of 2×10^{-4} M/l at 250°C was established.

Due to the sensitivity limit encountered, a similar set of experiments was conducted in an Inconel test vessel containing 50 ml of electrolyte and using a Sierra Autobalance Model AM-1 with a repeatability of ± 0.02 mg. As a result, a solubility of approximately 2.0×10^{-6} M/l LaF_3 could be detected. The LaF_3 crystal was held in a wire screen so that it could be suspended above the solution during cooling in a manner similar to that described above for using the Pyrex ampule. Two separate tests were made at 240°C , with solubilities calculated from the measured weight loss of 1.08×10^{-5} and 1.04×10^{-5} M/l. Additional tests were run with mechanical stirring added rather than relying on thermal convection and diffusion. Similar results were obtained. It appears that the solubility of LaF_3 is only slightly different at 250°C than it is at 25°C .

3.2.3 Tests of the Interference Compensation System

The lanthanum fluoride electrode was tested at room temperature along with a pH sensor as shown in Figure VI-4. The partial pressures of CO_2 and H_2S could be independently varied with the balance of the gas being nitrogen. The response of a glass pH electrode (L&N #117169) measured versus a calomel reference electrode with ceramic junction (L&N #117203) is shown in Figure VI-5, plotted versus the ppm CO_2 . Note the two points diverging from the curve due to the presence of H_2S . H_2S at the test levels caused a lowering of the pH and an interference in this 25°C experiment.

During this experiment, the potential difference between a fluoride ion electrode (L&N #117405, or equivalent) and the same reference electrode was recorded. According to equation VI-16, the difference in the measured glass electrode and fluoride electrode potentials

FIGURE VI-4: SCHEMATIC OF INTERFERENCE COMPENSATION TEST ASSEMBLY

ppm CO₂ VS. mv (pH) @ 25°C

- WITHOUT LA₂(CO₃)₃
- x WITH LA₂(CO₃)₃
- Δ WITH H₂S
- IDEAL (NERNSTIAN) RESPONSE, 60 mv/DECADE
- BEST LINE (LEAST SQUARES FIT FOR LINEAR PORTION)

FIGURE VI-5: ppmCO₂ VERSUS pH-REFERENCE VOLTAGE, WITH H₂S

should indicate $p\text{CO}_2$ with a 30 mv/decade slope at 25°C. Figure VI-6 shows the pH-pF response of the system under varying $p\text{CO}_2$ and pH_2S levels, plotted versus the partial pressure of CO_2 . The slope of the curve is approximately 22 mv/decade CO_2 rather than 30 mv/decade, and curves where the pH electrode response is non-linear at low CO partial pressures as noted in Section II.1.1. The compensating effect is only partially successful, with both overcompensation and undercompensation occurring.

The limited data available make it difficult to assess the performance of the compensation system. Although the CO_2 measurement error is lessened, the system is not performing according to the theory presented, perhaps as a result of the relative insolubility of $\text{La}_2(\text{CO}_3)_3$. The results may involve the fluoride ion activity change due to protonation to form HF rather than fluoride ion activity being determined by the "soluble" $\text{La}_2(\text{CO}_3)_3$ and the more insoluble LaF_3 . The possibility that this mechanism is dominant hasn't been fully explored, but due to the unavailability of solubility and dissociation data at elevated temperatures, theoretical evaluation at this time is impossible. Given the favorable results obtained using the getter system described in Section III.2.1, further exploration of this compensation scheme was abandoned.

ppm CO₂ VS. pH-F (mv)

- WITHOUT LA₂(CO₃)₃
- x WITH LA₂(CO₃)₃
- Δ WITH LA₂(CO₃)₃ & H₂S
- IDEAL RESPONSE (30 mv/DECADE)
- BEST LINE (LEAST SQUARES FIT FOR LINEAR PORTION)

FIGURE VI-6: ppmCO₂ VERSUS pH-FLUORIDE VOLTAGE, WITH H₂S

VII.

REFERENCES

1. Danielson, M. J., Koski, O. H., and Shannon, D.W., "Development of Electrical and Electrochemical Probes for Down-Hole and In-Line Chemical Analysis of High Pressure, High Temperature Geothermal Fluids, Interim Report - Period Ending October 1977." U. S. Department of Energy Report under Contract EY-76-C-06-1830.
2. National Materials Advisory Board (NAS-NAE), "Assessment of the Characterization (In-Situ - Downhole) of Geothermal Brines," Publication NMAB-344, National Academy of Sciences, Washington, D.C., January 1978.
3. Stowe, R.W. et al., Arch. Phys. Med. and Rehab., 646, October 1957.
4. Severinghaus, J.W., and Bradley, A.F., J. Appl. Physiol., 13, 515 (1958).
5. Helgeson, Harold C., Am. J. Sci., 267, 729 (1969).
6. Ellis, A.J., and Mahon, W.A., Chemistry and Geothermal Systems, Academic Press, New York, NY, 1977.
7. Sillen, Lars Gunnar, and Martell, Arthur E., Stability Constants of Metal-Ion Complexes, The Chemical Society, London, 1964.
8. Malinin, S.D., Geochemistry, 3, 292-306 (1959).
9. Ellis, A.J., and Golding R.M., Am. J. of Sci., 261, 47 (1963).
10. Takenouchi, G., and Kennedy, G.C., Am. J. of Sci., 272, 1055 (1964).
11. Todheide, K., and Franck, E.U., Z. Physik. Chem., 37, 387 (1963).

12. Esashi, M., and Matsuo, T., IEEE Trans. BME-25 (2), 1978.
13. Bergveld, P., IEEE Trans., BME-17, 70, (1970).
14. Holmberg, G. L., Kuper, A. B., and Miraldi, F. D., J. Electrochem. Soc., 117 (5), 677 (1970).
15. Lauks, I. R., IEEE Trans. ED-26 (12), 1952 (1979).
16. Pliskin, W. A., J. Vac. Sci. Tech., 14 (5), 1064 (1977).
17. Comte, P. A. and Janata, J., 30th ACEMB, Los Angeles, Cal., 5-9 Nov., 1977.
18. Sze, S. M., Physics of Semiconductor Devices, Wiley - Interscience, New York, 1969.
19. Vlasov, Y. G., Zhurnal Prikladnoi Khimii, 52 (1), 3 (1979).
20. Grove, A. S., Deal, B. E., Snow, E. H., Sah, C. T., Sol. State Electron., 8, 145 (1965).
21. Cheung, P. W., Ko, W. H., Fung, D. J. and Wong, S. H. in Theory Design and Biomedical Applications of Solid State Chemical Sensors, edited by P. W. Cheung, D. G. Fleming, M. R. Newman and W. H. Ko (CRC Press, Inc., West Palm Beach, Fla., 1978) pp 91 to 115.
22. Bergveld, P., DeRoij, N. F., and Zemel, J. N., Nature, 273, June (1978).
23. Revez, A. G., Thin Solid Films, 41, L43 (1977).
24. Siu, W. M. and Cobbold, R.S.C., IEEE Trans., ED-26 (11), 1805 (1979).

25. Abe, H., Eshashi, M., and Matsuo, T., IEEE Trans., ED-26 (12), 1979.
26. Lauks, I. and Zemel, J. N., IEEE Trans. ED-26 (12), 1959 (1979).
27. Maeda, K., Sato, J. and Ban, Y., Jap. J. Appl. Phys., 16 (5), 729 (1977).
28. Afromowitz, M. A. and Yee, S. S., J. Bioeng., 1, 55 (1976).
29. Cohen, R. M., Huber, R. J., Janata, J., Ure, R., and Moss, S. D. Thin Solid Films, 53, 169 (1978).
30. Lundstrom, I., Physica Scripta, 18, 424 (1978).
31. Moss, S. D., Smith, J. B., Comte, P. A., Johnson, C. C. and Astle, L., J. Bioeng. 1, 11 (1976).
32. Zemel, J. N., Res. and Dev., 28 (4), 38 (1977).
33. Buck, R. P., Drug Res., 28 (I), Heft 4 (1978).
34. Buck, R. P., Anal. Chem., 45 (4), 654 (1973).
35. Esashi, M. and Matsuo, T., Proceedings of the 6th Conference on Solid State Devices, Tokyo, 1974, Supplement to J. Japan. Soc. Appl. Phys., 44, 1975.
36. Farrington, G. C. and Briant, J. L., Science, 204, 1371 (1979).
37. Janata, J. and Moss, S. D., Biomed. Eng., July 1976, p. 241.
38. Perram, J. W., Hunter, R. J. and Wright, H.J.L., Aust. J. Chem., 27, 461 (1974).
39. Schenck, J. F., J. Colloid and Interface Sci., 61 (3), 1 Oct. 1977.

40. Zemel, J. N., Anal. Chem., 47 (2), 255A (1975).
41. Zemel, J. N., U. S. Patent #4,103,227, 25 July 1978.
42. Zemel, J. N., Adv. in Auto. Anal., Technicon Int. Congr., Series 1, 68 (1977).
43. Zemel, J. N., Surface Science 86, 322 (1979).
44. Bergveld, P., Wiersma, J., and Meertens, A., IEEE Trans., BME-23 (2), 136 (1976).
45. Wen, C. C., Chen, T. C., Zemel, J. N., IEEE Trans., ED-26 (12), 1945 (1979).
46. Buck, R. P., and Hackleman, E. E., Anal. Chem., 49 (14), 2135 (1977).
47. Dell'Oca, C. J. and Barry, M. L., Solid State Electronics 15, 659 (1972).
48. Dunbar, P. M. and Hauser, J. R., J. Electrochem. Soc. 117 (5), 674 (1970).
49. Hu, S. M., J. Electrochem. Soc., 113 (7), 693 (1966).
50. Nannoni, R. and Musselin, M. J., Thin Solid Films 6, 397 (1970).
51. Pliskin, W. A. and Lehman, H. S., J. Electrochem. Soc., 110 (10), 1013 (1965).
52. Zemel, J. N., J. Franklin Inst., 296 (6), 475 (1973).
53. Franz, I. and Langheinrich, W., Solid State Electronics, 14, 499 (1970).

54. Bergveld, P., IEEE Trans., BME-19 (5), 1972.
55. Janata, J., U. S. Patent #4,198,851, 22 April 1980.
56. Leistiko, O., Physica Scripta, 18, 445 (1978).
57. Matsuo, T. and Wise, K., IEEE Trans., BME-21, 485 (1974).
58. Moss, S. D., Johnson, C. C. and Janata, J., IEEE Trans. BME-25 (1), 49 (1978).
59. Moss, S. D., Janata, J., and Johnson, C. C., Anal. Chem. 47 (13), 2238 (1975).
60. McBride, P., Janata, J., Comte, P., Moss, S., and Johnson, C. Anal. Chim. Acta., 101, 239 (1978).
61. Zemel, J. N., Surface Phys. Phosphors. Semicond. (Conf. Proc.), 523 (1975).
62. LeBlanc, O. H., Brown, J. F., Klebe, J. F., Niedrach, L. W., Slusarczuk, G.M.J. and Stoddard, W. H., J. Appl. Physiol. 40 (4), 644 (1976).
63. Matsuo, T. and Eashi, M., Extended Abstracts of the Electrochemical Society, Spring 1978, Abs #83,222 (1978).
64. Wen, C. C., Lauks, I, Zemel, J. N., to be published IEEE Trans.
65. Comte, P. A. and Janata, J., Anal. Chim. Acta, 101, 247 (1978).
66. Kelly, R. G., Owen, A. E. and Jordan, J. R., Proc. Anal. Div. Chem. Soc., Nov., 1977, p. 338.
67. Kelly, R. G., Electrochim. Acta., 22, 1977.

68. Wise, K. D., Angell, J. B. and Starr, A., IEEE Trans., BME-17 (3), 238 (1970).
69. Goetzberger, A., and Nicollian, E. H., The Bell Syst. Tech. J., 46 (3), 513 (1967).
70. Hofstein, S. R. and Warfield, G., Sol. State Electron., 8, 321 (1965).
71. Hofstein, S. R., Zaininger, K. H. and Warfield, G., Proc. IEEE, 52, 971 (1964).
72. Nicollian, E. H. and Goetzberger, A., The Bell Syst. Tech. J., 46 (6), 1055 (1967).
73. Nicollian, E. H. and Goetzberger, A., IEEE Trans., ED-12, 108 (1965).
74. White, M. H., Cricchi, J. R., Solid State Electronics, 9, 991 (1966).
75. Zemel, J. and Kaplit, M., Phys. Rev. Lett., 21 (4), 212 (1968).
76. Chen, M. C., J. Electrochem. Soc.: Solid State Science, 118 (4), 591 (1971).
77. Goetzberger, A., Klausmann, E. and Schulz, M., Report, European Research Office, U. S. Army Grant #DA-ERO-77-G-020, April, 1978.
78. Goetzberger, A., Klausmann, E., and Schulz, M. J., CRC Crit. Rev. in Sol. State Sci., 6 (1), 1 (1976).
79. Goetzberger, A., Lopez, A. D. and Strain, R. J., J. Electrochem. Soc. 120 (1), 1973.
80. Goetzberger, A., Deuling, H., and Klausmann, E., Solid. State Electron., 15, 559 (1972).

81. Ipri, A. C. and Zemel, J. N., J. Appl. Phys., 44 (2), 1973.
82. Nicollian, E. H., Annu. Proc. Reliab. Phys. (Symp) Series 12, 267 (1974).
83. Bergveld, P., Proc. IEEE, 57, 72 (1969).
84. Nicollian, E. H., Bergland, C. N., Schmidt, P. F. and Andrews, J. M., J. Appl. Phys. 42 (13), 5654 (1971).
85. Tarui, Y., Teshima, H. and Matsuoka, T., UDC 539,234: 621, 382-181.4 Japan.
86. Vadasz, L. and Grove, A. S., IEEE Trans., ED-13 (12), 863 (1966).
87. Liu, Chia-tsun, "Thermodynamics of Salt Solutions and Geothermal Brines at Elevated Temperature," Final Report, PB-250-733, OWRT/S-76/19, prepared for the U. S. Department of the Interior, Office of Water Research and Technology, Washington, D.C., 1975.
88. Seward, T. M., Geochimica et Cosmochimica Acta, 40, 1329 (1976).
89. Report of the Task Group on Geothermal Seals of ASTM Subcommittee D-11.36 on Seals, June 27, 1978.
90. Lebovits, Alexander, Modern Plastics, 139, March 1966.
91. Pasternak, R. A., Christensen, M. V. and Heller, J., Macromolecules, 3 (3), 366 (1970).
92. Halar Fluoropolymer Films, Allied Chemical Corp. data sheet, P. O. Box 1087R, Morristown, NJ, 07960.
93. Parylene Pellicles for Space Application, Novatran Corp. data sheet, 360 4th Street, Box 386, Clear Lake, Wisconsin 54005.

94. Properties of Tefzel Fluoropolymer Film, DuPont Inc. data sheet, Plastics Dept., Fluorocarbons Div., Wilmington, DE 19898.
95. Hirasuna, Dr. A. R., L'Garde, Inc., Newport Beach, CA, Personal communication, August 1979.
96. Browning, Charles E., "The Mechanism of Elevated Temperature Property Losses in High Performance Structural Epoxy Resin Matrix Materials After Exposure to High Humidity Environments", Air Force Materials Lab., Wright Patterson AFB, Ohio 45433, Report #AFML-TR-76-153.
97. Park, W.R.R., Anal. Chem., 29 (12), 1897 (1957).
98. Taylor, R. M., Phelan, D. M. and Rothstein, M. L., "Detailed Conceptual Design of a High Temperature Glass pH Electrode for Geothermal Applications", Final Report - Task I, PNL-3051, UC-66 prepared for the U. S. Department of Energy, Division of Geothermal Energy under prime contract EY-76-C-06-1830 with Battelle - Pacific Northwest Laboratories, Richland, Washington, May, 1979.
99. Hirasuna, A. R., Bilyeu, G. D., Davis, D. L., Stephens, C. G. and Veal, G. R., "Geothermal Elastomeric Materials", Twelve month progress report, October 1, 1976 - September 20, 1977. L'Garde, Inc., Newport Beach, CA, under contract EG-77-C-03-1308.
100. Schmid, M. and Mancy, K. H., Chimia, 23, 398 (1969).
101. Baumann, E. W., Anal. Chem., 46 (9), 1347 (1974).
102. Solubilities of Inorganic and Organic Compounds, edited by H. Stephen and T. Stephen (Pergaman Press, Long Island City, NY, (1963) pp378-379.
103. Clark, D. E., Pantano, C. G. Jr., Hench, L. L., Corrosion of Glass, Magazines for Industry, Inc., New York (1979).

104. Dolidze, V. A., "Electrodes for Potentiometric High Temperature Instrumentation of pH", pp 57-97 in Ion Selective Electrodes, Pungor, E., ed., Elsevier Scientific Publishing Co., New York, 1978.
105. Iordanov, N. and Khavezov, I., Z. Anorg. Allgem. Chem., 347 (1-2), 101 (1966).
106. Trombe, Felix, Glaise, Michele, and Caro, Paul, Comp. Rend. Ser. C, 263 (7), 521 (1966).
107. Vasil'ev, G. I., and Serebrennikov, V. V., Tr. Tomskogo Gos. Univ., Ser. Khim., 154, 103-4 (1962).
108. Troiluis, C., Tek Tid, 88, 211 (1958) as cited by Sillen, Lars Gunnar, and Martell, Arthur E., Stability Constants of Metal-Ion Complexes, The Chemical Society, London, 1964.
109. Ellis, A. J., J. Am. Sci., 257, 354 (1959).
110. Kury, John W., U. S. Atomic Energy Commission, Tech. Inform. Service UCRL-2271 (1953).
111. Lingane, James J., Anal. Chem., 40 (6), 1968.
112. Booth, H. S., and Bidwel, R. M., J. Am. Chem. Soc., 72, 2567 (1950).

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