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NASA TM-78,428

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SOME STUDIES ON A SOLID STATE SULFUR PROBE

FOR COAL GASIFICATION SYSTEMS

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August 1977

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ABSTRACT

Measurements on the solid electrolyte cell

$$(Ar + H_2 + H_2S/CaS + CaF_2 + (Pt) // CaF_2 // (Pt) + CaF_2 + CaS / H_2S + H_2 + Ar)$$

shows that the emf of the cell is directly related through the Nernst equation to the difference in sulfur potentials established at the two $Ar + H_2 + H_2S$/electrode interfaces. The electrodes are designed to convert the sulfur potential gradient across the calcium fluoride electrolyte into an equivalent fluorine potential gradient with the aid of the reaction, $CaF_2(s) + 1/2 \ S_2(g) \rightarrow CaS(s) + F_2(g)$. The response time of the probe varies from approximately 9 hr at 990 K to 2.5 hr at 1225 K. The conversion of calcium sulfide and/or calcium fluoride into calcium oxide should not be a problem in anticipated commercial coal gasification systems. Suggestions are presented for improving the cell for such commercial applications.

The ability to continuously monitor the sulfur potential in coal gasification reactors is of crucial importance for efficient gasifier operation and for accurate life prediction of corroding construction materials. From an engineering point of view, *in situ* solid state sensors that directly measure the sulfur potential are preferable to devices that employ liquid electrolytes or involve sampling of gases for low temperature analytical procedures. Despite the concerted efforts of many laboratories during the last decade to find suitable sulfide electrolytes, analogous to $CaO-ZrO_2$ or $Y_2O_3-ThO_2$ for oxygen potential measurements, no acceptable material has been identified in which the ionic transport number is higher than 0.99 over a large range of sulfur potentials and temperatures.

The prospect of designing a suitable sulfide electrolyte does not appear promising in the near future because the band gaps in the sulfides are generally narrower than in the corresponding oxides (1). An alternate approach may be to use calcium fluoride (CaF_2) as the electrolyte in a solid state cell, in which the electrodes are designed to convert the sulfur potential in the gas into an equivalent fluorine potential.

Calcium fluoride has been found to be a suitable electrolyte at high temperatures and over a large range of fluorine potentials (2-7). Colorless, pure CaF_2 contains virtually equal concentrations of interstitial anions and anion vacancies. The fluoride ions are the mobile species, and they migrate as interstitials and vacancies. At very low fluorine potentials or in the presence of calcium vapor, an excess of calcium dissolves in CaF_2 according to the reaction

$$Ca(g) \; + \; 2 \; F_F x \; \rightarrow \; CaF_2 \; + \; 2 \; e_F x \qquad\qquad [1]$$

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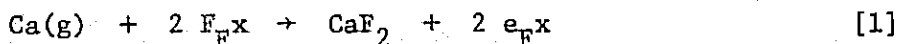
where F_Fx is a fluoride ion on a regular anion site, and e_Fx is an electron

substituted for an anion, producing a color (F) center. Wagner (8) has given

an analysis of the onset of electronic conduction in CaF_2 due to the dissolu-

tion of calcium metal. Patterson (9) has also discussed the electrolytic

conduction domain for CaF_2 at high temperatures. Because of the extreme

electronegativity difference between Ca^{2+} and F^- ions and the correspondingly

large forbidden bandgap for CaF_2, positive hole conduction will not be signif-

icant until the fluorine pressure is increased to several atmospheres. The

open-circuit emf (E) across the electrolyte is a direct measure of the chemical

potential difference, provided the fluorine pressures at the electrodes and

the temperatures of operation lie within the electrolytic conduction domain,

(that is the transport number of electrons or holes is less than 0.01).

An advantage of the solid electrolyte sensors is that the output is an

electric potential that can readily be used to actuate a control circuit. It

was, therefore, decided to study the efficiency of the solid electrolyte cell,

$$Ar + H_2 + H_2S/CaS + CaF_2 + (Pt) \; // \; CaF_2 \; // \; (Pt) + CaF_2 + CaS / H_2S + H_2 + Ar$$
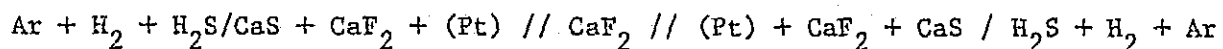
$$[2]$$

as a part of our program on the development of a sulfur probe. The experimental

results, the limitations of this technique to coal gasification systems, as

well as articipated improvements are presented in this paper.

Experimental

Materials.—High purity $Ar+H_2+H_2S$ gas mixtures and their analysis were

obtained from Matheson. A slight decrease in the H_2S concentration of the

gases was observed over extended periods of storage, presumably due to the

reaction of H_2S with the storage tank. Correction factors for gas ratios

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were obtained by periodically observing the ion intensity ratios of H_2S to H_2 in a mass spectrometer. For the electrolyte, optical grade single crystals of CaF_2, in the form of discs of 1.5 cm in diameter and 0.2 cm thick, were obtained from Harshaw Chemical Company. High purity anhydrous CaF_2 and CaS powders were supplied by Apache Chemical Company and Ventron Corporation. Fine platinum powder and porous platinum sheet were obtained from Johnson and Mathey Company. The electrode pellets were made by double end compression of an intimate mixture of fine powders of CaF_2, CaS, and Pt in the molar ratio 1.5 : 1 : 0.2. The pellets were sintered in evacuated silica capsules at 1225 K for 12 hr.

Apparatus.—A schematic diagram of the apparatus is shown in Fig. 1. A disc of CaF_2 electrolyte was spring loaded against an alumina tube with a gold 'O' ring between them to obtain a gastight joint. The alumina tube was held firmly in a water cooled brass head, to which the springs were attached. Since gold softens at the high temperatures used in these experiments, low tension springs were sufficient to produce a gastight joint. Thus, the ceramic components of the assembly were not subjected to high applied stresses. Electrode pellets containing CaF_2+CaS+Pt were spring loaded on either side of the electrolyte, with a thin porous platinum sheet sandwiched between the pellet and the electrolyte. Platinum leads, flame sprayed with alumina, were spot welded to the porous platinum sheets. At the low sulfur potentials used in the experiments, no chemical attack on the platinum was observed in the hot zone of the furnace. At the cooler end, however, there was some evidence of reaction between platinum and H_2S gas. Therefore, in this region, the platinum leads were protected by an alumina sheath closed on both ends by alumina cement.

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The cell was designed to provide two separate gastight compartments around the two electrode pellets. Separate gas streams with differing sulfur potentials were passed through these compartments. The test gas was admitted to the system at the lower end of the reaction tube and flowed past the outer electrode pellet at a rate of 250 ml min^{-1}. The reference gas was passed around the inner electrode at a flow rate of 100 ml min^{-1}. The two gas streams were isolated in the reaction tube and escaped through different ports in the brass head. The escaping gases were bubbled through two 25 cm high columns of NaOH solution to remove H_2S and HF. The exit gases were further scrubbed before being pumped through the fume exhaust system.

The entire cell assembly, attached to the brass head, was lowered into a vertical alumina reaction tube. The cell was electrically shielded by connecting a platinum foil, wrapped around the reaction tube, to ground. The reaction tube was heated by a Kanthal resistance furnace. Temperatures of the furnace and of the cell were measured by two separate Pt–Pt (13% Rh) thermocouples. The furnace temperature was controlled to ±1 K by use of a stepless current-compensating controller.

Procedure.—The test cell was assembled as shown in Fig. 1, and the reaction tube was evacuated by a mechanical pump to a pressure of 0.5 Nm^{-2} and then backfilled with purified argon. The argon purification train con-sisted of magnesium perchlorate (to absorb the residual moisture), and copper turnings at 700 K and titanium turnings at 1100 K (to remove residual oxygen). The cell was heated to 500 K, evacuated, and refilled with argon. The tem-perature of the cell was then raised to 1225 K. The reference gas was introduced into the inner gas compartment of the cell, while argon flow was

maintained through the outer reaction tube. Gastightness of the 'O' ring seal

was checked by analyzing the argon stream exiting from the reaction tube

for traces of H_2S. After ensuring that the test cell was leaktight and the

two gas streams were isolated, the test gas was introduced into the reaction

tube. Cell voltage was monitored using a Kiethly digital voltmeter with an

internal impedance of 10^{12} Ohms. After the start of the experiment, approx-

imately 5 hr were required to obtain a steady emf.

Two procedures were followed during the investigations: *(i)* During

isothermal runs, cell temperature was kept constant at 1073 K or 1173 K and

and the steady, reversible emf corresponding to different test gases was

measured, and *(ii)* For two selected test gases, the temperature dependence

of the steady, reversible emf was measured.

Results

Response time.—Composition of the test gases and the reference gas and

the emf obtained at 1073 K and 1173 K are shown in Table I. Generally, the

response time of the cell at 1225 K, after a small change in temperature or

gas composition, was 2.5 hr, while at a lower temperature of 990 K the

response time was approximately 9 hr. The cell emf was insensitive to

moderate increase in the flow rate of the test gas and/or the reference gas.

However, when the flow rate of one of the streams was increased by factors

greater than two, while keeping the flow rate of the other stream constant,

significant changes in the emf were noted — about 20 mV during the transient

period, and about 15 mV during the steady state period. The changes were,

however, not always reproducible. When the flow rates of both streams were

changed simultaneously by the same amount, the cell emf remained virtually

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constant. It is likely that a substantial increase in the flow of gas through one stream may have resulted in differential cooling, thus creating a thermal gradient across the electrolyte. Changes in emf resulting from the presence of a steady state thermal gradient are quantitatively related to the partial entropy of fluorine in the gas phase, as discussed by Fitzner, Jacob, and Alcock (10).
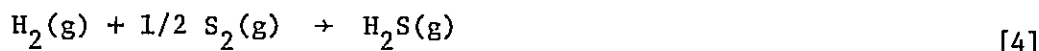
Reversibility of the emf was checked by passing small currents (5μA) through the cell in either direction for 2 min. It was found that the emf returned to the steady value before the titration in approximately 30 min. After several days of use, the electrode pellets became fragile and fractured easily.

Calculation of sulfur potentials.—Experimental emfs obtained at 1073 K and 1173 K for different test gases are compared in Fig. 2 with known values calculated from the difference in sulfur potential between the test gas and the reference gas. The emf developed across a CaF_2 electrolyte can be related through the Nernst equation to the partial pressure of fluorine (fluorine potential) across the electrolyte, provided the ionic transport number is close to unity:

$$E = \frac{\Delta\mu_{F_2}^R - \Delta\mu_{F_2}^T}{nF} = \frac{RT}{nF} \ln \frac{P_{F_2}^R}{P_{F_2}^T} \qquad [3]$$

where E is the emf, $\Delta\mu_{F_2}^R$ and $\Delta\mu_{F_2}^T$ are the fluorine potential at the reference and the test electrodes, F is the Faraday constant, n is the number of electrons (=2) involved in the transfer of one molecule of F_2 gas between the two electrodes, R is the gas constant, T is the absolute temperature, and P_{F_2} is the fluorine partial pressure. The gas phase containing $Ar+H_2+H_2S$

establishes a partial pressure of sulfur (sulfur potential) over the elec-
trode, depending on the ratio of H_2 to H_2S, by virtue of the reaction,

$$H_2(g) + 1/2 \ S_2(g) \rightarrow H_2S(g) \qquad [4]$$

$$1/2 \ \Delta\mu_{S_2} = RT \ \ln \ P_{S_2}^{1/2} = \Delta G_4^o + RT \ \ln \left(P_{H_2S} \Big/ P_{H_2} \right) \qquad [5]$$

where ΔG_4^o is the standard Gibbs' free energy change for reaction [4]. The
sulfur potential established by the gas phase, when in contact with the
electrode pellet consisting of CaS and CaF_2, fixes a fluorine potential
through the reaction

$$CaF_2(s) + 1/2 \ S_2(g) \rightarrow CaS(s) + F_2(g) \qquad [6]$$
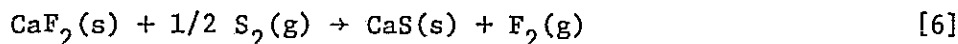
$$\Delta\mu_{F_2} = 1/2 \ \Delta\mu_{S_2} - \Delta G_6^o \qquad [7]$$

where ΔG_6^o is the standard Gibbs' free energy change for reaction [6]. The
platnium in the electrode pellet acts as a catalyst for the reaction. Since
there is no ternary compound or significant solid solubility in the
CaF_2-CaS system, the condensed phases in the electrode pellets are present
at unit activity. Combining equations [3] and [7], an expression is obtained
relating the emf to the difference in the sulfur potential between the
electrodes;

$$E = \frac{\Delta\mu_{S_2}^R - \Delta\mu_{S_2}^T}{2nF} = \frac{RT}{2nF} \ \ln \ \frac{P_{S_2}^R}{P_{S_a}^T} \qquad [8]$$

Equation [8] may also be expressed in terms of the ratio of H_2S to H_2
in the gas phase over the two electrodes;

$$E = \frac{RT}{nF} \quad \ln \frac{\left(P_{H_2S}/P_{H_2}\right)^R}{\left(P_{H_2S}/P_{H_2}\right)^T} \qquad [9]$$

The measured emfs, as shown in Fig. 2, do not deviate by more than 2.5 mV from that calculated using equation [9]. Deviations from theoretical values have the same sign at different temperatures for each test gas. Thus, it is likely that these deviations arise from small errors in gas analysis.

The variation of the emf of the cell with temperature and with two test gases (3 and 4 in Table I) is shown in Fig. 3. Again, measured temperature dependence is in agreement with the theoretical value given by the derivative of equation [9] with respect to temperature.

$$\frac{dE}{dT} = \frac{R}{nF} \quad \ln \frac{\left(P_{H_2S}/P_{H_2}\right)^R}{\left(P_{H_2S}/P_{H_2}\right)^T} \qquad [10]$$

Discussion

The activity of calcium at the electrodes, during the present investigation, can be evaluated by considering the reaction,

$$CaS(s) + H_2(g) \rightarrow H_2S(g) + Ca(s) \qquad [11]$$
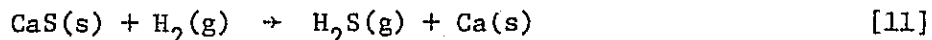
The activity of calcium, a_{Ca}, is given by

$$a_{Ca} = \left(P_{H_2}/P_{H_2S}\right) \exp\left(-\Delta G_{11}^O/RT\right) \qquad [12]$$

where G_{11}^O is the standard Gibbs' free energy change for reaction [11]. It can readily be shown from known thermodynamic data that the activity of calcium varies from 9.5×10^{-19} to 6.0×10^{-17} at 1113 K over the range of test gas composition (gases 1 and 4, respectively, Table I). Wagner (8) has suggested that

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the electronic transport number of CaF_2 is 10^{-2} when the activity of calcium is 6×10^{-6} at 1113 K. It is apparent, therefore, that the electronic transport number is much less than 10^{-2} and contributes very little to the results of the present study.

The exact factors affecting the slow response time of galvanic cells based on a CaF_2 electrolyte have not yet been determined. Clearly, the kinetics of the electrode reaction [6] may be rate controlling, or the transport of ions in CaF_2 may be slow, such that the composition gradient across the electrolyte cannot readjust rapidly after a perturbation in the chemical potential at the electrode. Additionally, since the fluorine potentials are low ($P_{F_2} \simeq 10^{-24}$ to 10^{-28} Nm^{-2}), gas phase polarization at the electrolyte-electrode interface may be the rate limiting step. This latter possibility seems rather improbable, however, because sufficient concentration of HF gas should be created by the reaction of H_2S with CaF_2 to transport the fluorine potential to the electrolyte surface.

Electrical current techniques, such as voltage recording after a galvanostatic pulse or impedance measurement at low frequencies, can be used to determine wherher the kinetics of the electrode reaction is responsible for the slow response of the cell (13). Heyne and Engelson (14) have recently suggested that for oxygen probes containing calcia-stabilized zirconia as the electrolyte, the uptake or release of oxygen by the electrolyte, when the partial pressure of oxygen in the ambient atmosphere is altered, is the main reason for the sluggishness in response and variation with time of the emf developed. If a similar mechanism is valid for CaF_2, a reduction in the thickness of the electrolyte or doping, to increase the effective diffusion coefficient, may accelerate the response of the probe to changes in sulfur potential. Another alternative is to use β-alumina as the electrolyte (15).

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β-alumina has much higher conductivity than CaF_2, especially at lower temperatures. Further, the electrodes would be redesigned to convert the sulfur potential gradient into an equivalent sodium potential gradient.

Although systematic studies on the catalytic behavior of platinum or other materials have not been undertaken, it was found in preliminary experiments that approximately 0.2 moles of platinum per mole of CaO is the optimum amount of catalyst in the electrode pellets. To use the cell for sulfur potentials higher than those studied in this investigation, a more suitable catalyst than platinum is needed. Platinum readily forms sulfides at higher sulfur potentials (12). Transition metal sulfides that do not react with CaS and in which cations exist in multivalent states may prove to be good catalysts.

Typical compositions of the raw gases in some coal gasification processes are shown in Table II. It can readily be shown that under the conditions of coal gasification, the conversion of CaS to CaO, according to the scheme,

$$CaS(s) + H_2O(g) \rightarrow CaO(s) + H_2S(g) \qquad [13]$$
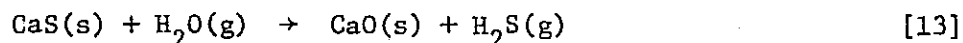
is not thermodynamically favorable. However, the reaction of $H_2S(g)$ with CaF_2,

$$CaF_2(s) + H_2S(g) \rightarrow CaS(s) + 2\ HF(g) \qquad [14]$$
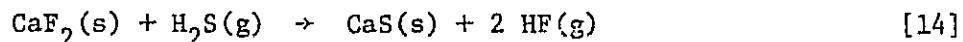
will result in a partial pressure of HF in the immediate neighborhood of the electrode that can vary from 2.8×10^2 Nm^{-2} to 80 Nm^{-2}. Since all the gas passing through the probe is not saturated in HF, the average HF concentration in the exit gas is estimated to be approximately 200 ppm, and therefore must be scrubbed for the removal of HF. Additionally, for commercial application, the probe must be designed in such a way as to prevent particulate material in the gas from depositing on the electrodes of the sensor.

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Conclusion

The theory, design and operation of a solid state sulfur probe based on CaF_2 electrolyte has been demonstrated. The cell responds to changes in sulfur potential in a manner predicted by the Nernst equation. Further research is needed to determine the main reason for the slow response of the cell. The rate limiting steps may be either the kinetics of electrode reactions or the rate of transport through the electrolyte. If the reaction kinetics is rate controlling, suitable catalysts may be developed to overcome the problem. If the slow transport of ions in the electrolyte is the reason for the sluggish response, a cell based on β-alumina electrolyte may be more suitable.

Acknowledgements

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Table I.   Composition of the test gas mixtures and the corresponding cell emfs

Test gas	Composition (vol. %)			emf (mV)	
Number	H_2	H_2S	Ar	1073 K	1173 K
1	40.6	8.3	51.1	−32	−34
2	50.4	2.05	47.55	43	47
3	54.0	0.79	45.21	87	96
4	55.1	0.18	44.72	160	174
5*	25.2	2.52	72.28	–	–

*Reference gas

Table II. Composition of raw gases in various coal gasification processes

	Battelle-Union Carbide Agglonerate Ash Process	BCR-Bi-Gas Process	Bureau of Mines Synthane Process	ICT Hygas Process
H_2	48.8	15	19	19
H_2O	14	52	36	20
CO	26	12	9	17
CO_2	5	13	21	16
H_2S	0.3	0.53	1.1	0.78
N_2	0.5	–	–	–
NH_3	0.002	0.25	0.6	0.4
CH_4	6	7	12	13

Compositions are given in vol. %

FIGURE CAPTIONS

Fig. 1.   Schematic diagram of the apparatus used for testing the CaF_2 electrolyte based sulfur probe.

Fig. 2.   Variations of the emf with H_2S/H_2 ratio of the test gas at 1073 K and 1173 K; — theoretical values [9].

Fig. 3.   The temperature dependence of the reversible emf with test gases 3 and 4 passing through the cell; — theoretical values [10].
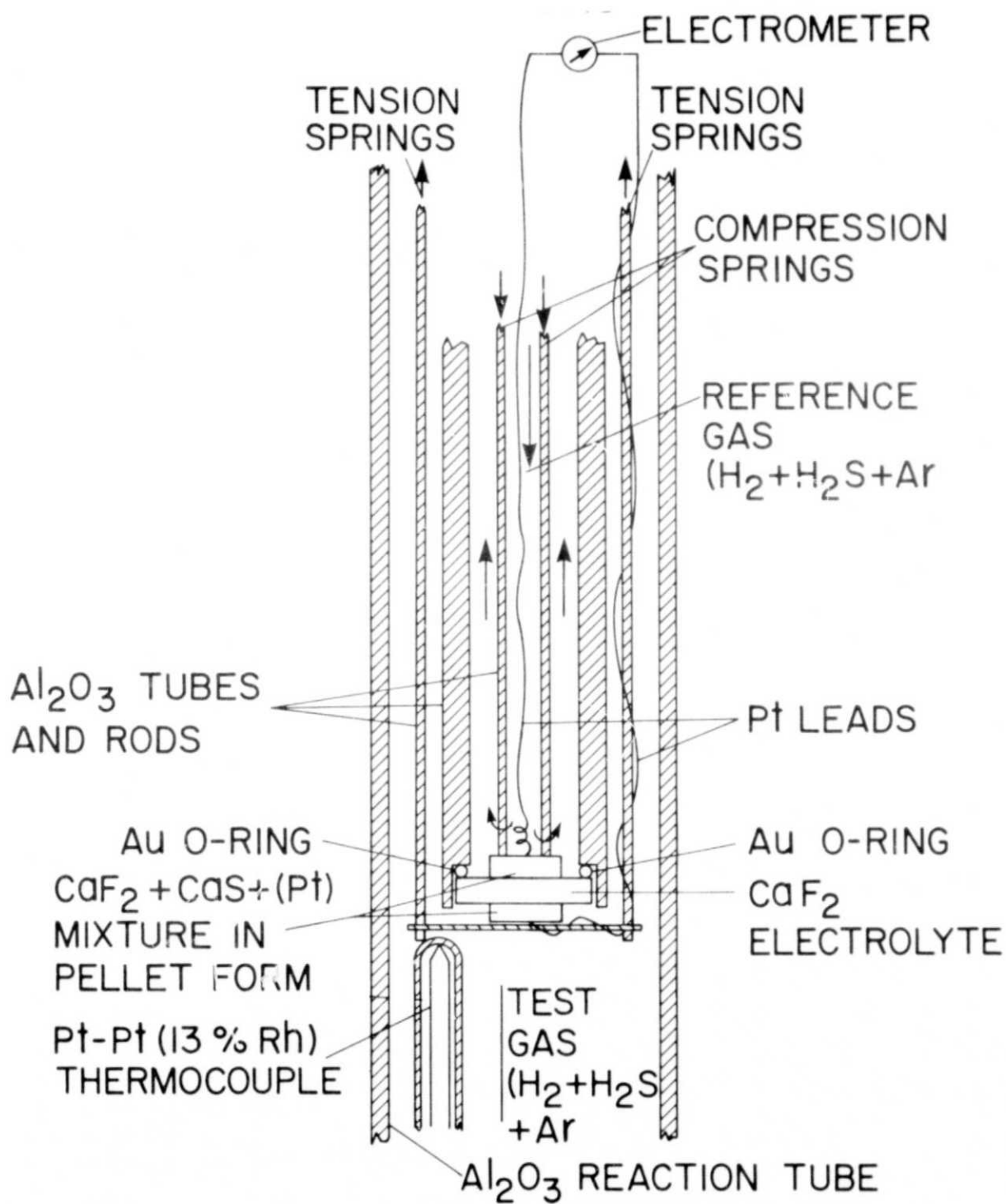
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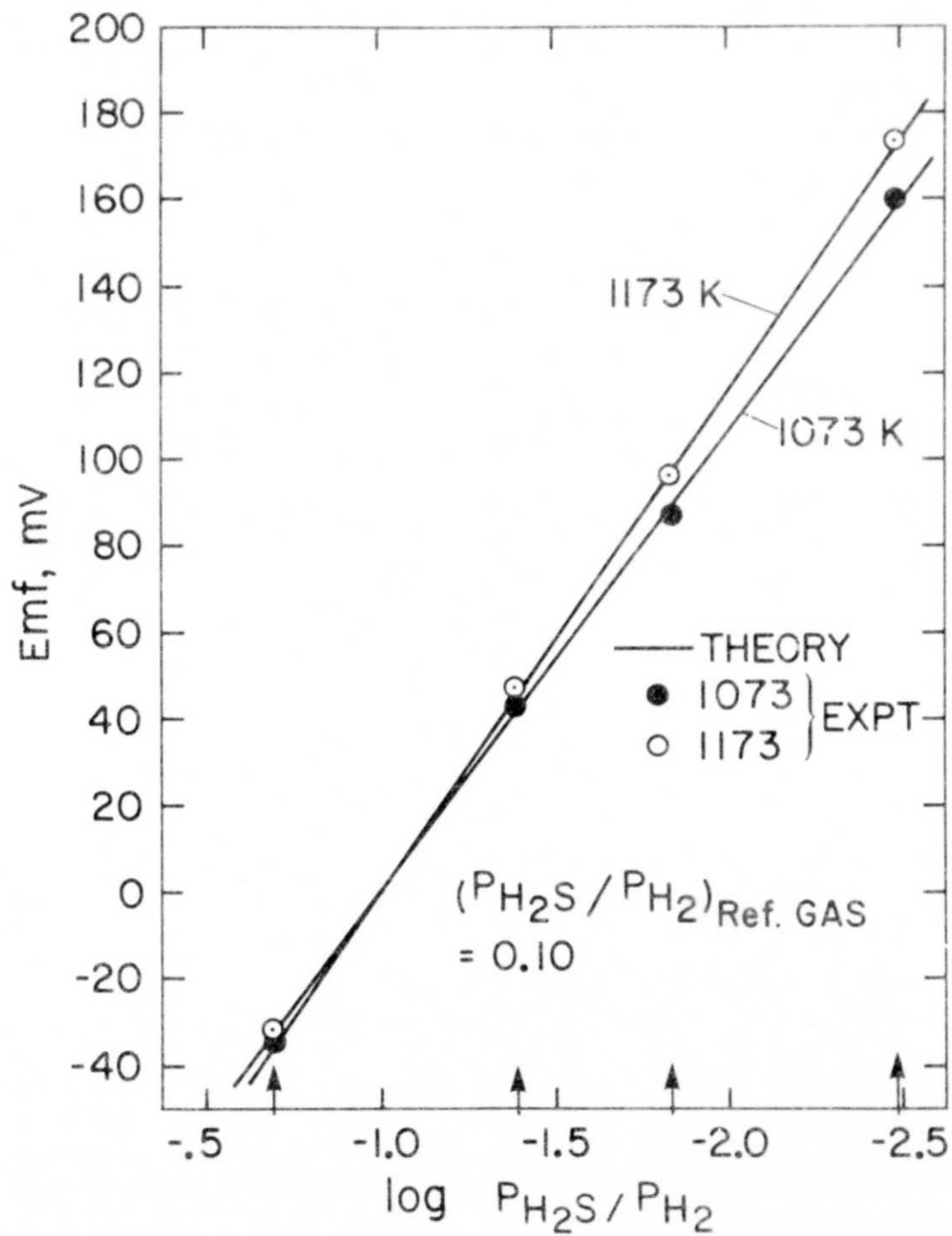
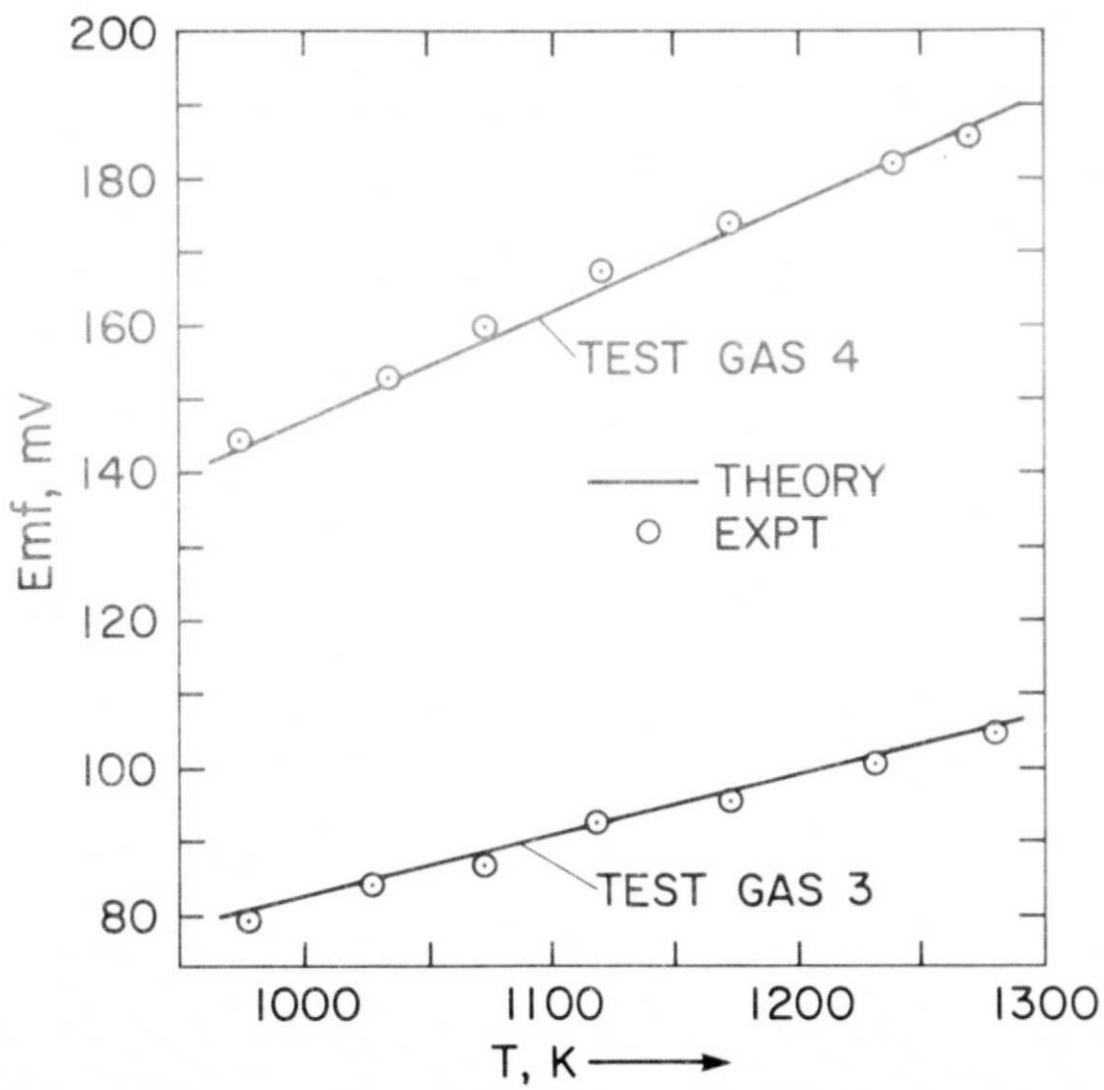Fig. 2. Variations of the emf with H_2S/H_2 ratio of the test gas at 1073 K and 1173 K; — theoretical values [9].

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1. Report No. NASA TM-78,428	2. Government Accession No.	3. Recipient's Catalog No.

4. Title and Subtitle	5. Report Date
SOME STUDIES ON A SOLID STATE SULFUR PROBE FOR COAL GASIFICATION SYSTEMS	6. Performing Organization Code

7. Author(s)	8. Performing Organization Report No.
K. T. Jacob,* D. Bhogeswara Rao,** and Howard G. Nelson	A-7162

	10. Work Unit No.
9. Performing Organization Name and Address	778-11-02
University of California, Berkeley, CA 94720 and Ames Research Center, NASA, Moffett Field, CA 94035	11. Contract or Grant No.
	13. Type of Report and Period Covered
12. Sponsoring Agency Name and Address	Technical Memorandum
National Aeronautics and Space Administration Washington, D.C. 25046	14. Sponsoring Agency Code

16. Abstract

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shows that the emf of the cell is directly related through the Nernst equation to the difference in sulfur potentials established at the two $Ar + H_2 + H_2S$/electrode interfaces. The electrodes are designed to convert the sulfur potential gradient across the calcium fluoride electrolyte into an equivalent fluorine potential gradient with the aid of the reaction, $CaF_2(s) + 1/2\ S_2(g) \rightarrow CaS(s) + F_2(g)$. The response time of the probe varies from approximately 9 hr at 990 K to 2.5 hr at 1225 K. The conversion of calcium sulfide and/or calcium fluoride into calcium oxide should not be a problem in anticipated commercial coal gasification systems. Suggestions are presented for improving the cell for such commercial applications.

17. Key Words (Suggested by Author(s))	18. Distribution Statement
Sulfur Probe, Calcium Fluoride Sensor for Sulfur, Galvanic Cell, Solid Electrolyte Cell, Coal Gasification-Sulfur Control, High Temperature Sulfur Meter	Unlimited STAR Category - 23

19. Security Classif. (of this report)	20. Security Classif. (of this page)	21. No. of Pages	22. Price*
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