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GROUP VI ELEMENTS IN FUSED LiCl-KCl

by

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A THESIS

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FACULTY OF GRADUATE STUDIES

The undersigned hereby certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled

"GROUP VI ELEMENTS IN FUSED LiCl-KCl"

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This thesis is dedicated to my mother who contributed much which cannot be found on the following pages.

TABLE OF CONTENTS

Page

Approval Page ii

Acknowledgements iii

Table of Contents iv

List of Tables vi

List of Figures vii

PART I: Electrochemistry of S, Se, and Te in Fused LiCl-KCl

ABSTRACT 1

INTRODUCTION AND HISTORICAL 3

EXPERIMENTAL 10

Apparatus 10

Solvent 10

Chemicals 11

Electrodes 11

Cell Construction 13

Procedure 14

RESULTS 17

I. Sulfur 17

II. Selenium 30

III. Tellurium 39

DISCUSSION 41

BIBLIOGRAPHY 48

Page

PART II: Spectrophotometric Investigations of Sulfur-Sulfide Solutions in Fused LiCl-KCl

ABSTRACT 51

INTRODUCTION AND HISTORICAL 52

EXPERIMENTAL 54

Apparatus 54

Solvent 57

Chemicals 57

Electrodes 57

Procedure 57

RESULTS AND DISCUSSION 59

BIBLIOGRAPHY 64

APPENDIX I: Original data for $S/S^{=}$ and $Se/Se^{=}$ couples . . . 65

APPENDIX II: Computer programs for calculation of E°_{M} from Nernst equation and for least square analysis 72

LIST OF TABLES

Page

Table I Standard e.m.f. determinations for the $S/S^{=}$ couple 21

II Standard e.m.f. determinations for the $S/S^{=}$ couple, low concentrations 23

III Chronopotentiometric study of sulfide 28

IV Standard e.m.f. determinations for the $Se/Se^{=}$ couple 38

LIST OF FIGURES

Page

Figure 1 Temperature dependence of potential as a function of sulfide ion concentration 18

2 EMF of sulfide electrode as a function of sulfide concentration 20

3 Nernst plot for the $S/S^{=}$ couple (all data) 24

4 Voltammetric curve for sulfur 25

5 Current-potential curves for sulfide solutions . . . 27

6 Chronopotentiometric constant vs. sulfide concentration 29

7 Voltammetric curves for selenium and tellurium . . . 34

8 Current-potential curves for selenide solutions . . . 35

9 Temperature dependence of potential as a function of selenide concentration 36

10 EMF of selenide electrode as a function of selenide concentration 37

11 Furnace for Cary Model 14 Spectrophotometer 56

12 Spectra of fused LiCl-KCl without and with sulfide 60

13 Absorbance as a function of sulfide concentration . . 62

14 Absorbance as a function of sulfide concentration; low concentration detail from Fig. 13 63

It seemed quite natural to many scientists, not all of whom had a philosophical mind, to suppose that it was possible for the material world to have become known quite independently of the rules of the functioning of our mind, and especially of the processes necessarily associated with our faculties of sensation and perception through which we gain our knowledge of it. That our scientific theories should be connected with the rules of the functioning of our mind, to the structure of our reason, to the concepts of which we dispose, that is certainly a point concerning which no scientist endowed with a mind, let it be ever so feebly critical, has naturally ever been able entirely to rid himself; the science of man is human and can never cease to be so; on this point there is no possible doubt.

Louis de Broglie

PART I: ELECTROCHEMISTRY OF S, Se, AND Te IN FUSED LiCl-KCl

ABSTRACT

Liquid sulfur has been coulometrically reduced in fused LiCl-KCl eutectic at 420°C. Nernstian behavior is observed for the cell

$$C, S(l)/S^{=}, LiCl\text{-}KCl//Pt^{++}, LiCl\text{-}KCl/Pt.$$

The standard potentials of the sulfur/sulfide couple at 450°C with respect to the appropriate standard platinum reference electrode are -1.008, -1.039, and -1.219V on the molar, molal, and mole fraction scales, respectively. Voltammetric studies showed an anodic wave at +0.03 V ascribed to

$$2S + 2Cl^{-} \rightarrow S_2Cl_2(g) + 2e^{-}$$

and a cathodic wave at -0.92 V ascribed to

$$S + 2e^{-} \rightarrow S^{=}.$$

The diffusion coefficient of the (poly)sulfide ion was found to be 3.12×10^{-6} cm^2/sec at 420°C by chronopotentiometric measurements. The observed blue color of sulfur-sulfide solutions is ascribed to polysulfide ions.

Liquid selenium has been reduced coulometrically in fused LiCl-KCl eutectic at 400°C. Nernstian behavior is observed for the for the cell

$$C, Se(l)/Se^{=}, LiCl\text{-}KCl//Pt^{++}, LiCl\text{-}KCl/Pt.$$

The standard potentials of the selenium/selenide couple at 450°C with respect to the appropriate standard platinum reference electrode are -1.141, -1.172, and -1.252 V on the molar, molal, and mole fraction

scales, respectively. Voltammetric studies showed an anodic wave at +0.05 V ascribed to

$$2Se + 2Cl^- \rightarrow Se_2Cl_2(g) + 2e^-$$

and a cathodic wave at -1.07 V ascribed to

$$Se + 2e^- \rightarrow Se^=.$$

For tellurium an anodic wave at -0.15 V is ascribed to

$$Te \rightarrow Te(II) + 2e^-$$

and a cathodic one at -1.40 V to the plating of lithium into tellurium; the formation of free telluride does not appear to occur. The standard potential for the couple Te(II)/Te is estimated at -0.1 V.

INTRODUCTION

The electrochemical behavior of molten salts and of solutes dissolved therein has been studied intensively in recent years and much information of practical and theoretical interest has been gained from these studies. The majority of the work has concerned itself with metal-metal ion systems. Little has been done regarding non-metals and their anions, with the exception of cases where the anion is part of the melt itself, such as the halogen-halide couple in various halide melts. It therefore appeared desirable to extend the electrochemical studies to other anions. The LiCl-KCl eutectic was chosen as solvent since this electrolyte has probably attracted most attention so far and certainly the most extensive e.m.f. series has been compiled in it. The investigations were started with the sulfide ion and later extended to selenide and telluride.

An additional reason to undertake these studies was that fused salt cells with chalcogen cathodes have attracted considerable attention in recent years as a means of efficient energy storage. Little electrochemical research, however, has yet been done on these systems.

In the present study potentiometry, voltammetry, and chronopotentiometry were used to obtain insight into the electrochemical behavior of sulfur, selenium, and tellurium in fused LiCl-KCl eutectic.

HISTORICAL

Research in the field of molten salt chemistry has expanded rapidly during the last two decades and substantial efforts have been made to compile the extensive knowledge of this subject. Several monographs have been published dealing with fused salt chemistry in general (1,2,3,4). References to literature publications concerning physical properties of fused salt mixtures have been compiled by the Fused Salts Information Center of Sandia Laboratory (5). References to electrochemical studies in general have been compiled by Janz (4) and Delimarskii and Markov (6), while Plambeck (7) has compiled e.m.f. data in various molten salts. Electrochemical techniques used in molten salts have been reviewed (2,3).

The largest body of e.m.f. data exists in the LiCl-KCl eutectic which is a convenient solvent in view of its low melting point (352°C), large potential span (3.6 volts), and relative ease of purification and handling. Most common metals have now been investigated in this medium. Solutions of the metal ions are prepared by adding the appropriate metal chloride to the solvent or by anodization of a metal electrode. This last process produces the lowest oxidation state of the metal stable in the solvent; higher oxidation states are obtained by further oxidation of the metal ion with an inert electrode such as a graphite rod. In all cases the solutions of metal chlorides in LiCl-KCl are ionic and solubilities are fairly high so that few problems arise with electrochemical investigations on these systems.

Relatively little work has been done, however, with regard to non-metals. This may be due to the fact that many electrode reactions involving complex anions are difficult to interpret and construction of reversible electrodes presents formidable technical problems. Even in the case of simple anions the electrode reaction is often not reversible at convenient temperatures. It is then not possible to produce the anion by cathodization of the element, while addition of the anion to the solvent as its lithium or potassium salt presents the problems of obtaining and handling of small quantities of the pure salt. For instance, calcium and lithium carbide are known to dissolve ionically in fused chlorides (8) but it was not possible in the course of this study to produce carbide by cathodization of a graphite rod in LiCl-KCl at temperatures of up to 800°C.

Anions most commonly investigated are those that are constituents of the melt itself, e.g., sulfates (9), nitrates (10,11), and carbonates (12). Halides have been studied both as constituents of the melt (13,14,15,16) and as solutes in a variety of molten salts (13,17). In LiCl-KCl the hydrogen-lithium hydride electrode has been studied (18) in view of its possible use in thermally regenerative fuel cells and its standard potential has been estimated (7).

Reversible sulfur, selenium, and tellurium electrodes in solid electrolyte cells were used by Reinhold (19) in order to obtain thermodynamic data of the silver chalconides. He performed e.m.f. measurements on cells of the type

$$Ag/AgI(s)/Ag_2X(s)/X \text{ where } X = S, Se, Te$$

between 150° and 350°C. The solid silver iodide serves as electrolyte

involving migration of silver ions. Since the overall cell reaction taking place on passage of current is represented by

$$2Ag(s) + X \rightarrow Ag_2X(s)$$

the standard molar free energy of formation of solid silver chalconide is calculated from the reversible cell e.m.f. by means of the relationship $\Delta G = -nFE$. This work was repeated by Kiukkola and Wagner (20) in their studies of solid electrolyte cells.

Voltammetric studies of sulfide in fused potassium and sodium chloride mixtures have been conducted by Rempel and Malkova (21) in order to establish a sequence of discharge potentials of some industrially important anions. The order of discharge found was OH^-, NO_3^-, $S^=$, $SO_4^=$, Cl^-. This work and that of Delarue (22,23) clearly indicate that alkali sulfides form ionic solutions in alkali chloride melts. Delarue (22) studied sulfide solutions in fused LiCl-KCl eutectic by means of voltammetry with a platinum indicator electrode and obtained an anodic wave at $E_{\frac{1}{2}} = -0.45$ V with respect to the standard molar platinum electrode which he ascribed to the oxidation of sulfide to sulfur according to

$$S^= \rightarrow S + 2e^-.$$

Several redox reactions such as

$$S^= + I_2 \rightarrow 2I^- + S$$

were also carried out in this solvent. In all cases the sulfide was added as $Na_2S \cdot 9H_2O$. No attempts to obtain the cathodic wave for the reduction of sulfur to sulfide were reported. His quantitative results are subject to criticism (see Discussion section below).

Bell and Flengas (24) have investigated the concentration cell

$$Ag/AgCl,Ag_2S/AgCl/Ag$$

in the temperature range between 450° and 700°C. Their e.m.f. and conductivity measurements indicated that dilute solutions of silver sulfide in silver chloride are ideal and completely ionized.

While the investigations on the liquid sulfur electrode in LiCl-KCl for the present study were in progress Thompson and Flengas (25) reported on a reversible sulfur vapor electrode in fused silver chloride. This electrode, used in the formation cell

$$Ag/AgCl,Ag_2S/S_2(g),\ C,$$

followed the Nernst equation with respect to the partial pressure of sulfur in the range between 0.001 and 1.0 atm and to the silver sulfide concentration at a fixed sulfur vapor pressure in dilute silver sulfide solutions. The cell reaction on passage of current is

$$2Ag + \tfrac{1}{2}S_2(g) \rightarrow Ag_2S \text{ (solution)}$$

so that thermodynamic data of silver sulfide dissolved in silver chloride could be obtained from e.m.f. measurements.

The literature on selenium and tellurium in fused salt media is scanty. The deposition potential of tellurium from solutions of tellurium dioxide in fused $AlCl_3$-NaCl-KCl at 218°C has been determined by Verdieck and Yutema (26). Since this potential was obtained from current-voltage curves by means of a three electrode system it is comparable to an e.m.f. measurement. There is, however, uncertainty as to the oxidation state of the electroactive tellurium species in solution (7).

The free energy of formation of Li_2Te has been determined by Foster and Liu (27) using the cell

$Li_3Bi(s)$, Li in Bi(l)/LiCl-LiF/Li in Te(l), $Li_2Te(s)$

The potentials of the secondary reference electrode, Bi saturated with $Li_3Bi(s)$, had previously been measured against the Li reference electrode (28) so that the e.m.f. of the above cell could be converted to that for the cell

Li(l)/LiCl-LiF/Li in Te(l), $Li_2Te(s)$.

The free energy of formation of solid Li_2Te was calculated from the e.m.f. of this cell.

A similar cell has been used by Liu and Angus (29) to obtain thermodynamic properties of the bismuth-tellurium alloy Bi_2Te_3 and to investigate the bismuth-tellurium phase diagram by e.m.f. measurements. The cell employed was

Bi(l)/$BiCl_3$,LiCl-KCl/Bi-Te.

Advances in molten salt technology have resulted in efforts to develop energy conversion or storage cells employing fused electrolytes. Lithium has most frequently been used as anode material because of its low electronegativity and low equivalent weight. Many elements have been investigated as cathode material, such as chlorine (30) and bismuth (31). However, sulfur, selenium, and tellurium seem to combine many desirable characteristics such as relatively high electronegativity, low equivalent weight, ease in handling, and simple cell construction. At Argonne National Laboratory selenium (32), tellurium (33), and sulfur (34) cathodes have been used in conjunction with a lithium anode to construct cells with high power and energy densities. The electrolyte used was the ternary eutectic of LiF-LiCl-LiI (mp 341°C). On discharge the cell reaction is the

transfer of lithium from the anode to the cathode forming a lithium chalcogen compound at the cathode. A very interesting feature of these secondary cells is that recharge is possible within 15 minutes while on discharge current densities between 10 and 13 A/cm^2 can be obtained.

EXPERIMENTAL

Apparatus

Potentials were measured with a digital voltmeter (Model 3440A, Hewlett-Packard). Coulometric generations employed a Model IV Coulometric Current Source (E.H. Sargent and Co.). An Anotrol Model 4100 Potential Controller modified to operate with a Model 4510 linear scan unit (Magna Electronics) was used for voltammetric investigations. Chronopotentiometric investigations employed a Model 6824A power supply-amplifier (Hewlett-Packard) in a constant current configuration controlled by appropriate mercury-wetted relay switching circuitry; measurements were recorded on a Hewlett-Packard Model 175A oscilloscope equipped with 1750B and 1781B plug-in units and a Model 196B camera using ASA 3000 Polaroid film.

The temperature of the 3" diameter vertical tube furnace was controlled by a Model 3120-SCR-477 temperature controller (Marshall Products Co.). For the Lindberg Hevi-Duty Model 54381A furnace a Model 59344 temperature controller was employed. Temperatures were measured with a chromel-alumel thermocouple calibrated at the melting point of zinc.

Solvent

The LiCl-KCl eutectic solvent (59.5 mole% LiCl, mp 352°C) was prepared by the method of Maricle and Hume (35) modified as described below.

A total of 600 g of the component salts was mixed and melted without previous drying. Chlorine gas dried over magnesium perchlorate was bubbled through the melt for 2 hours. After purging the melt with nitrogen for 4 hours, magnesium ribbon was introduced to displace any heavy metal ions. Subsequently, chlorine was again introduced to oxidize any magnesium metal that may have dissolved in the melt, followed by nitrogen. The molten eutectic was transferred to large test tubes in charges of 120-140 g inside a drybox purged with nitrogen. The test tubes were sealed and stored for future use.

Chemicals

Reagent grade LiCl (Fisher Scientific Company) and KCl (Fisher Scientific Co. or Shawinigan Chemicals) were used. Selenium (99.99%) was obtained in 1/4" x 2" rods from A. D. Mackay, Inc. Tellurium (99.999%) was obtained from Atomergic Chemetals Co. The sulfur (sublimed; Fisher Scientific Co.) was dried at 100°C prior to use. Graphite electrodes were Special Spectroscopic Electrodes 1/8" in diameter (National Carbon Co.). Nitrogen was purified over hot copper turnings and dried by passage through a magnesium perchlorate column. Argon was dried by passage through a magnesium perchlorate column and two traps cooled by a dry ice-acetone bath.

Electrodes

A reference electrode based on the Pt(II)/Pt couple (0.03-0.04 M) was generated coulometrically for each experiment by anodization of a 3 cm^2 Pt foil sealed into Pyrex tubing; a current density of 7 mA/cm^2 was employed. All potentials were measured

against this reference electrode and are reported with reference to the Pt(II) (1.0 M)/Pt standard molar platinum electrode (S.M.P.E.) (36), conforming to the IUPAC "Stockholm" sign convention (37).

The boiling point of sulfur (444°C) being very close to the temperature of 450° at which the e.m.f. data were desired, it was necessary to work either with a vapor electrode or a liquid electrode and extrapolate from higher or lower temperatures to 450°. The liquid electrode appeared simpler [ref. (25) then not being available], and the sulfur electrode used consisted of an isolation compartment with a pool of liquid sulfur floating on the melt. Electrical contact with the pool was made by a graphite rod attached to Nichrome leads well above the sulfur pool. Sulfide was initially added to the compartment as Li_2S, but this proved unsatisfactory due to hydrolysis and difficulty in transferring known amounts to the compartment. The addition of sulfide by cathodic coulometric reduction of the sulfur pool proved more satisfactory and was used for all experiments reported here. Precautions were taken to ensure that an excess of liquid sulfur was always present, and more was added as necessary.

The selenium electrode consisted of a small Pyrex cup (7 mm diameter, 5 mm long) containing pieces of selenium. Contact with the selenium (liquid at operating temperature) was made with a graphite rod attached to Nichrome leads well above the melt level. The Pyrex cup rested on the bottom of the isolation compartment and was totally immersed in the melt.

The tellurium electrodes were made by melting lumps of tellurium in a 4 mm Pyrex tube under argon. A tungsten wire was

inserted into the liquid tellurium which was then allowed to solidify. The electrode was removed by carefully breaking the glass.

A graphite rod in an isolation compartment was used as the counter electrode.

The electrodes used in the chronopotentiometric investigations of the sulfide system were gold wires (0.05 cm in diameter) suspended in the melt or rhenium wires sealed in glass. Other metals such as tungsten or platinum were unsatisfactory because they became coated, presumably with insoluble sulfide. The geometric area of the gold electrode was calculated from its diameter and depth of immersion, that of the rhenium electrode from its diameter and the length of metal exposed.

Cell Construction

The electrolytic cell consisted of a Pyrex crucible inside a glass jacket that could be connected to a vacuum pump by means of a Pyrex cap. A 75 mm O-ring joint connected the jacket to the cap. The outer jacket could also be closed off with a machined Teflon stopper with holes for up to five isolation compartments, a thermocouple, and a nitrogen inlet tube. The isolation compartments were made of Pyrex sealing tubes with 10-20 micron frits (D porosity; Ace Glass Inc.) and protruded through the Teflon stopper. A hole below the Teflon stopper allowed entry of nitrogen into the otherwise closed compartments to equalize pressure.

The cell for the selenium and tellurium experiments was essentially the same, except that five 14/20 ground-glass joints were blown on the cap which were used to insert the thermocouple, the

electrodes, and an argon inlet tube.

The remainder of the electrolytic cell and glassware preparation have been described previously (38).

Procedure

The crucible containing the frozen eutectic, isolation compartments, and electrodes was placed inside the outer glass jacket of the electrolytic cell. Transfers of frozen eutectic to the crucible were made inside a dry box under nitrogen.

The 3" diameter tube furnace was used for the experiments with sulfur; the Lindberg furnace for those with selenium and tellurium.

I. Sulfur - The temperature of the cell was raised slowly to 420-430°C under vacuum in order to thoroughly dry the glass equipment and electrode before fusion of the eutectic. The compartments were allowed to fill with eutectic during a further 8 hours at this temperature. Finally, purified nitrogen was introduced and allowed to pass over the melt during all experiments. After addition of sulfur to the compartments the sulfide concentration was successively increased by coulometric reduction of sulfur. The current density was 8 mA/cm^2. The reduction product was blue in color (see below). The sulfide electrode e.m.f. was measured against the same reference electrode for each run which normally included three different sulfide compartments.

The thermoelectric potential between the graphite and platinum electrodes was found to be +1.5 mV with respect to the platinum electrode in the temperature range of 400-450°C. All e.m.f. values were corrected accordingly.

II. Selenium and tellurium - The temperature of the cell was slowly raised to 370°C under vacuum in order to dry the glass equipment and electrodes before fusion of the eutectic. After fusion of the eutectic, argon was introduced and bubbled through the melt during all experiments. The compartments were allowed to fill with eutectic during a period of 8-10 hr. The selenium or tellurium was added as a final step. Ionic species were generated by anodization or cathodization of the selenium or tellurium. The cells were operated at 400 ± 2°C to minimize loss of volatile materials from the melt, which was still the most serious problem encountered in the investigation. The electrode potentials were measured against the platinum reference electrode. The thermoelectric potential of the graphite and leads was measured as +10 mV with respect to platinum. It was essentially invariant with temperature from 400° to 450°. The potentials were corrected for this effect.

In all cases the potentials were converted from the experimental temperature to 450°C using experimentally determined potential-temperature relationships (see below). This extrapolation to 450°C was done since all e.m.f. data in fused LiCl-KCl are reported at this temperature (7).

The voltammetric studies were done by the method of current-voltage curves in three electrode cells: a platinum reference, an indicator, and a graphite counter electrode, each in a separate isolation compartment. The amount of solvent in each isolation compartment was determined by a potentiometric chloride titration; when necessary, sulfide or selenide was removed from aqueous solution

by acidification with nitric acid. The concentrations of $S^{=}$, $Se^{=}$, and Pt^{++} ions were determined from the coulombs passed and the solvent volume as described previously (36).

Least square calculations were carried out on the University of Alberta IBM System/360 computer. The programs used are given in the Appendix.

RESULTS

I. SULFUR

Potentiometry

Five runs were carried out, with new compartments, electrodes, and eutectic charge used in each. A total of 89 concentration-potential data points were taken over the range 400-440°C, each point the mean of two potentials measured 15 minutes apart. In general the e.m.f. became constant, to within 0.5 mV, 15-30 minutes after coulometric reduction of sulfur had been terminated and did not change more than 1 mV over a period of several hours. The temperature of the melt was recorded at the time of each potential measurement. The effect of temperature on the e.m.f. was determined for various sulfide ion concentrations with both increasing and decreasing temperature. Plots of measured potential against temperature were linear over the range 400-440°C for a fixed sulfide ion concentration. Plots of $\Delta E/\Delta T$ against the logarithm of the molar concentration of sulfide (as moles $S^{=}$/liter of eutectic at 450°C) were linear over the concentration range 0.03-0.5 M as shown in Fig. 1. All data are given in the Appendix. Least square analysis gave, for the temperature dependence of the cell

$$(-)C,S(l)/S^{=},\ LiCl\text{-}KCl//Pt^{++},\ LiCl\text{-}KCl/Pt(+),$$

$$\Delta E/\Delta T = +0.124\ \mathrm{Log}[S^{=}] - 0.520\ mV/°C$$

with a relative standard error of 4.4% in the slope and of 1% in the intercept. This equation was used to extrapolate all measured potentials to 450°C. Linear Nernst plots were obtained for these

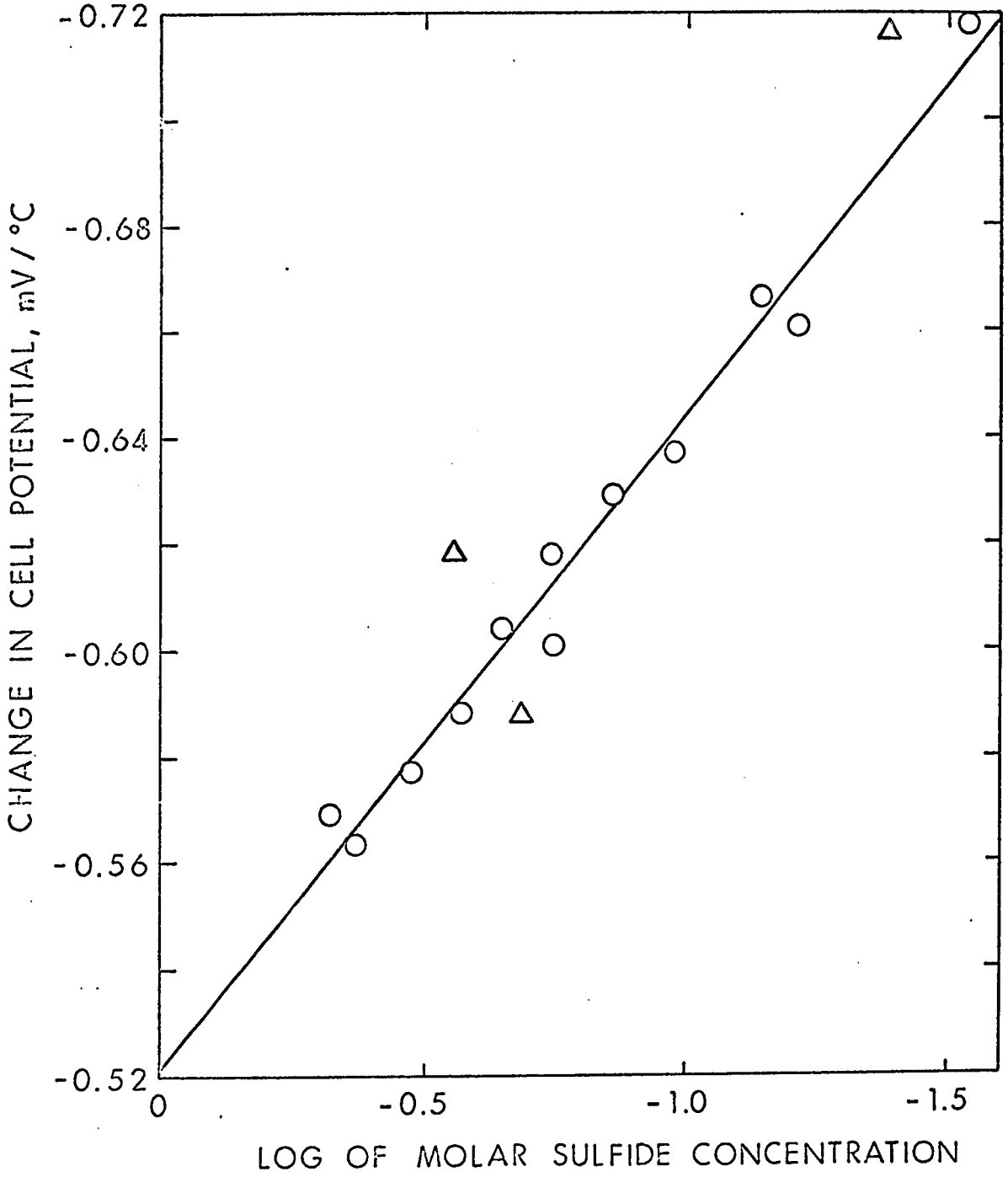

Fig. 1. Temperature dependence of potential as a function of sulfide ion concentration. Line is that given by least-squares analysis. Points indicated by triangles not included in least-squares analysis.

extrapolated potentials over the concentration range 0.03-0.5 M sulfide. Less stable potentials were obtained at lower sulfide concentrations. A typical plot of potentials against the logarithm of sulfide concentration (Fig. 2) shows that Henry's law is obeyed over the concentration range studied. A summary of all runs is given in Table I; the original data are given in the Appendix. Least square analysis of all points gave a standard potential (molarity scale) at 450°C of -1.008 V with a standard deviation of 0.002 V. This corresponds to values of -1.039 V and -1.219 V with the same standard deviation on the molality and mole fraction scales, respectively (36), all potentials being with respect to the appropriate standard platinum electrode. The slope of the Nernst plot was -0.0772 V/log unit with standard deviation of 0.0015, corresponding to a value of 1.86 ± 0.04 for the number of electrons taking part in the reaction. This is in good agreement with the theoretical value of 2 expected for

$$S + 2e^- \rightarrow S^=.$$

The above results were later checked on lower sulfide concentration (0.0017-0.032 M). A separate counter electrode was not used; the current from the coulometer was passed through the sulfur and platinum electrodes so that the concentrations of the platinum ion in the reference electrode compartment increased with each increase in sulfide concentration. The platinum ion concentration was therefore approximately equal to the sulfide concentration at a particular potential measurement and ranged from 0.0016 to 0.032 molar. The e.m.f. dependence on temperature was determined for each concentration and plots of measured potential against temperature were again linear.

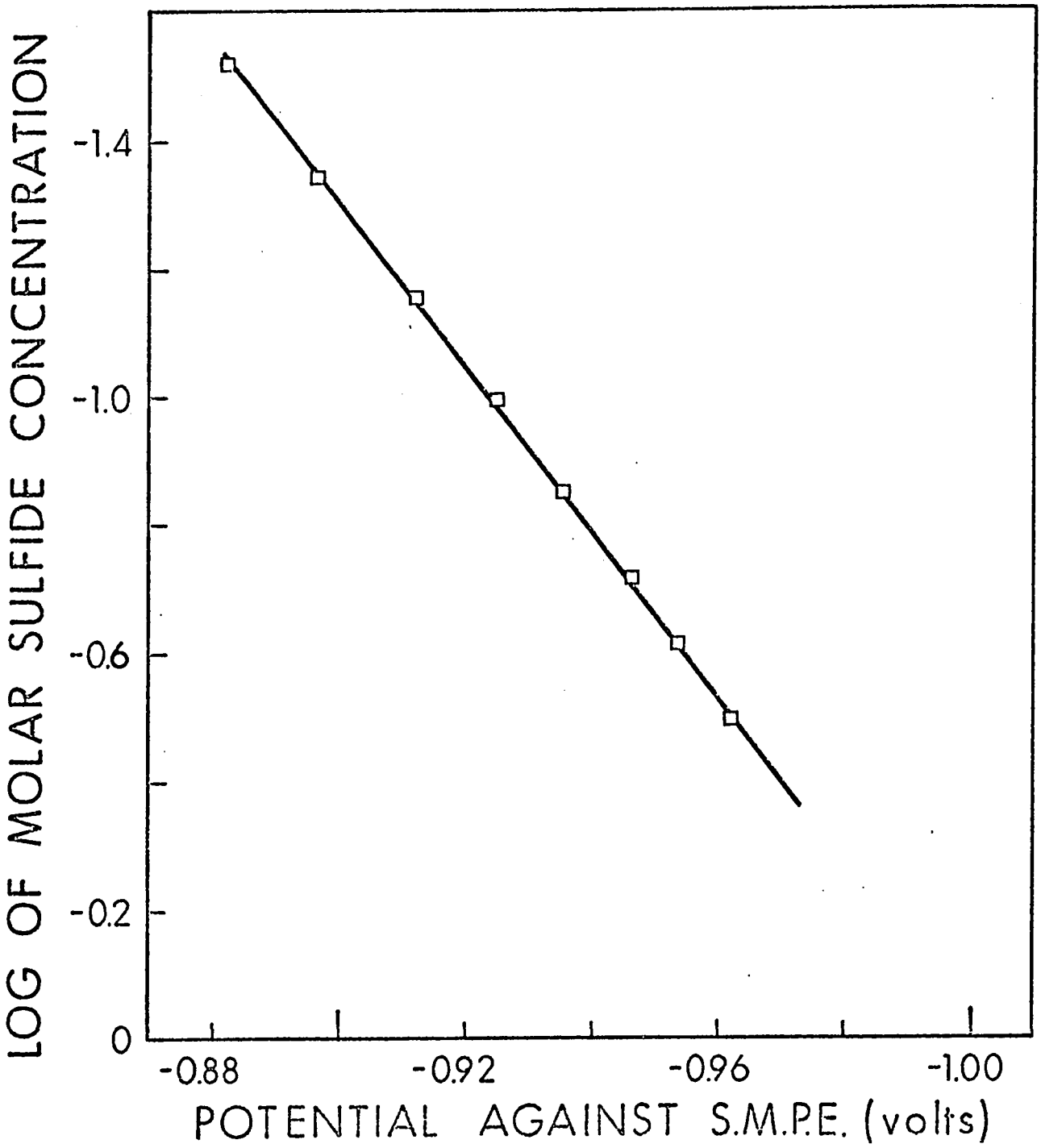

Fig. 2. Electromotive force of sulfide electrode (vs.S.M.P.E.) as a function of sulfide concentration in a typical run. Temperature (extrapolated) 450° C.

Table I*

Standard e.m.f. determinations for the $S/S^{=}$ couple

Sulfide Molarity	No. of points	E° (V) M	Standard deviation (mV)	Exper. n
0.093-0.15	6	-1.010	1.3	1.81
0.095-0.15	6	-1.008	6.7	1.80
0.054-0.25	7	-1.012	0.7	1.75
0.037-0.21	7	-1.012	0.8	1.80
0.045-0.20	7	-1.015	1.3	1.72
0.045-0.22	6	-1.007	0.4	1.98
0.036-0.18	6	-1.009	1.6	2.02
0.071-0.43	7	-1.004	0.2	2.09
0.055-0.20	5	-1.007	0.9	2.03
0.19-0.48	5	-1.006	0.3	2.19
0.092-0.28	5	-1.007	0.2	2.13
0.035-0.26	7	-1.004	0.9	1.79
0.030-0.32	8	-1.002	0.6	1.83
0.046-0.31	7	-1.004	1.3	1.72
Least square analysis of all points	89	-1.008	1.5	1.86

* two e.m.f. readings taken at each point 15 minutes apart, except for run 1; temperature converted to 450°C; all potentials given with respect to S.M.P.E.; each entry is a separate compartment, the first two being run 1 and the remainder. other runs with three compartments per run.

These plots were used to extrapolate all potentials to 450°C. Standard potentials calculated from these extrapolated values are given in Table II (for original data see Appendix).

A plot of all points is given in Fig. 3 where the line drawn is the one obtained from least square analysis of the points of Table I.

Voltammetry

Voltammetric scans of the pure eutectic melt with a graphite electrode gave the curve denoted by circles in Fig. 4. The potential was increased in the reduction direction and the current was measured after it had become constant (generally 5-10 sec.) After addition of sulfur to the compartment, the curve denoted by triangles in Fig. 4 was obtained. For the cathodic rise, which is ascribed to the reaction

$$S(l) + 2e^- \rightarrow S^=,$$

extrapolation of the lower part of the curve to zero current gave -0.92 ± 0.02 V for the "decomposition" potential (mean and std. dev. of 5 experiments), in agreement with the potentiometric measurements cited above. The anodic wave is ascribed to the reaction

$$2S(l) + 2Cl^- \rightarrow S_2Cl_2(g) + 2e^-$$

which Delarue (23) estimated to occur at about -0.05 V. The "decomposition" potential determined in this study is +0.03 ± 0.02 V (mean and std. dev. of 5 experiments). These measurements were carried out at 420 ± 2°C as were all other voltammetric and chronopotentiometric studies reported here.

Voltammetric curves were also obtained in compartments in which sulfur was present and sulfide had been generated coulometrically

Table II

Standard e.m.f. determinations for the $S/S^{=}$ Couple, low sulfide concentrations*

Sulfide Molarity	Potential Sulfide Electrode vs. S.M.P.E. (V)	E°_{M} (V)
0.00316	-0.8176	-0.9970
0.00789	-0.8521	-1.0030
0.0126	-0.8687	-1.0049
0.0221	-0.8905	-1.0093
0.0316	-0.9027	-1.0104
0.00171	-0.7772	-0.9757
0.00274	-0.8024	-0.9862
0.00428	-0.8236	-0.9935
0.00684	-0.8373	-0.9926
0.0106	-0.8540	-0.9966

*First five entries are run 1, remainder run 2.

Temperature converted to 450°C.

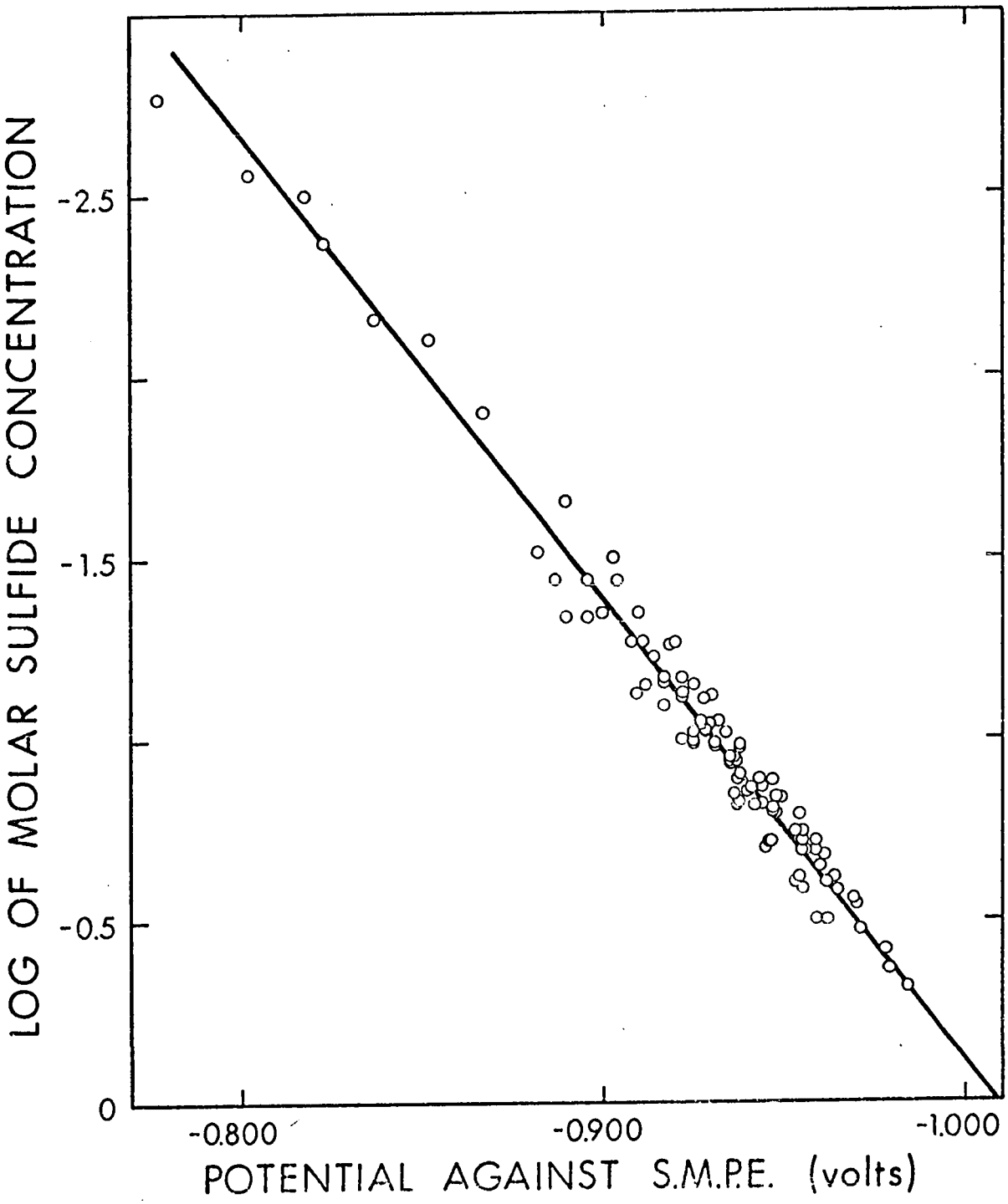

Fig. 3. Electromotive force of sulfide electrode (vs.S.M.P.E.) as a function of sulfide concentration. Temperature (extrapolated) 450°C.

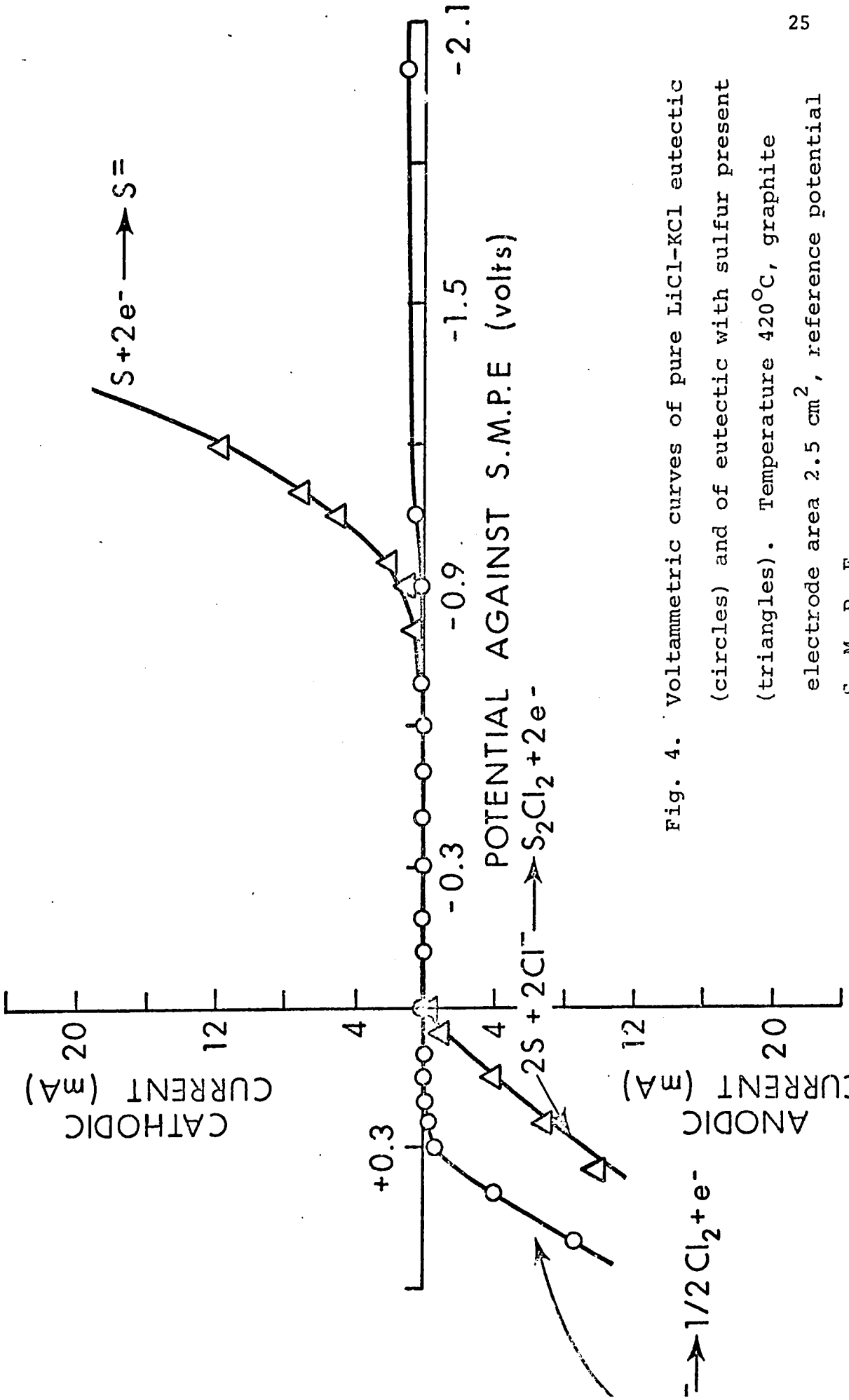

Fig. 4. Voltammetric curves of pure LiCl-KCl eutectic (circles) and of eutectic with sulfur present (triangles). Temperature 420°C, graphite electrode area 2.5 cm^2, reference potential S. M. P. E.

at concentrations ranging from 0.1 to 0.5 M. Two typical curves are shown in Fig. 5, obtained from two different sulfide concentrations in the same compartment. Identical straight lines were always obtained regardless of the direction of voltage change as long as precautions were taken to prevent significant change in the sulfide concentration between measurements. These precautions included stirring and, when necessary, oxidation or reduction such that the zero-current potential remained within 3 mV of its original value. The slopes of these lines ranged from 10-15 ohms and represent the cell resistance. These curves show the sulfur/sulfide couple to be reversible under these conditions.

Chronopotentiometry

One set of measurements was made with an uninsulated gold wire indicator electrode (diameter 0.055 cm, area 0.43 cm^2), others with rhenium wire (diameter 0.062 cm, area 0.34 cm^2) sealed in Pyrex so as to isolate it from the liquid sulfur pool. A total of 67 anodic chronopotentiograms were obtained. Each contained a single transition whose $E_{\tau/4}$ (corrected for IR drop) was within 30 mV of the equilibrium e.m.f. for that sulfide concentration. The times for this transition, which is ascribed to

$$S^{=} \rightarrow S + 2e^{-},$$

were measured and the results are summarized in Table III. All separate value of $i\tau^{\frac{1}{2}}/A$, except those obtained at 93.6 mmol/l sulfide, were subjected to least square analysis; this produced the linear plot of $i\tau^{\frac{1}{2}}/A$ against concentration shown in Fig. 6. This linearity indicates that the transition is diffusion-controlled and that the Sand equation

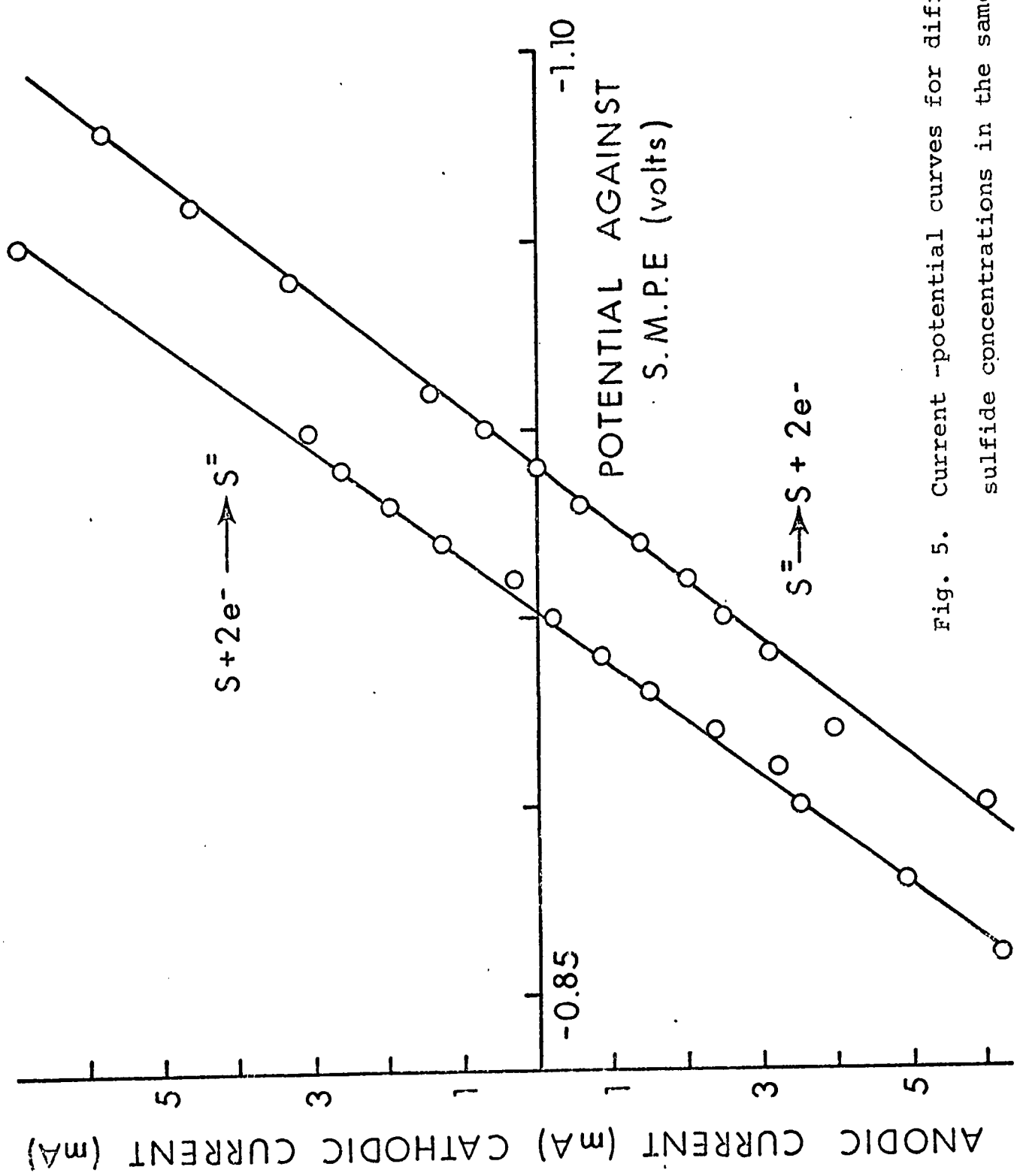

Fig. 5. Current -potential curves for different sulfide concentrations in the same compartment. Reference potential S.M.P.E., temperature 120°C

Table III*

Chronopotentiometric Study of Sulfide

Sulfide Concentration (mmol/l)	No. of Points	Mean $i_\tau^{1/2}/AC$ (amp cm $sec^{1/2}$ $mole^{-1}$)	Standard Deviation
23.2	7	349	20
27.9	6	335	12
37.2	8	331	6
51.1	9	321	20
65.1	8	299	10
37.4**	7	348	25
51.5**	7	352	13
74.8**	8	316	6
93.6**	7	281	9

* medium, fused LiCl-KCl eutectic at 420 ± 2°C; current density range, 26-101 mA/cm^2; each point taken at a different current density.

** rhenium electrode; otherwise, gold electrode.

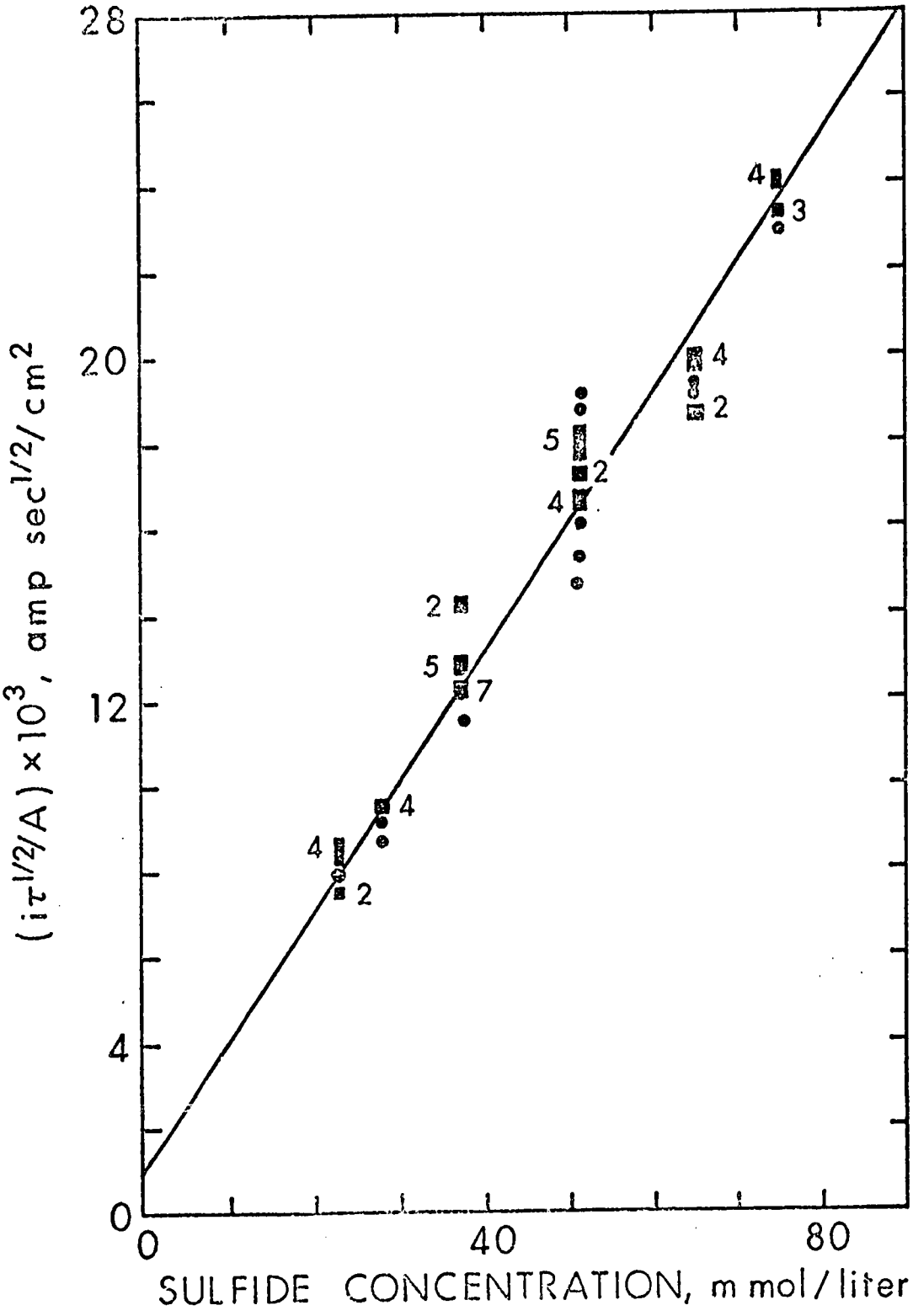

Fig. 6. Variation of chronopotentiometric constant $it^{1/2}/A$ with sulfide concentration, showing obedience to Sand equation. Solid circles, single points; solid rectangles, multiple points, with number given.

$$i\tau^{\frac{1}{2}} = \tfrac{1}{2}\pi^{\frac{1}{2}}nFACD^{\frac{1}{2}}$$

is obeyed by the sulfur/sulfide system with both rhenium and gold electrodes. From the slope of the line in Fig. 6 and the Sand equation, the diffusion coefficient of the diffusing sulfide species was calculated to be 3.12, std. dev. 0.11, x 10^{-6} cm^2/sec at 420 ± 2°C. This value is almost an order of magnitude smaller than the smallest value reported for a divalent metal ion, Pb^{++}, which is calculated as 1.3 ± 0.2 x 10^{-5} cm^2/sec at 420°C from literature data (39), indicating that the diffusing species is a somewhat larger entity, perhaps a polysulfide ion $S_x^=$. There appears to be a trend towards smaller $i\tau^{\frac{1}{2}}/AC$ values with increasing sulfide concentration (Table III), but it is doubtful whether any significance can be attached to this in view of the standard deviations of these values.

Some of the curves indicated a very ill-defined second transition whose $E_{\tau/4}$ was estimated as -0.08 ± 0.05 V and which we therefore ascribe to

$$2S + 2Cl^- \rightarrow S_2Cl_2 + 2e^-.$$

No measurements of the transition time were possible due to poor definition and the proximity of chlorine evolution.

Some difficulty was encountered with deposition of sulfur on the electrode. It was necessary to strip off the sulfur produced in each chronopotentiogram cathodically and wait 10 minutes between polarizations for the solution to become uniform. Erratic results (extremely short transition times, probably due to blocking of electroactive surface) were sometimes obtained, apparently due to attachment of sulfur from the pool to the electrode. A small residual

transition time was observed (intercept, Fig. 6), but it was much less than that reported by others (40) in fused salt media and can be ascribed to trace impurities and/or double-layer charging.

II. Selenium

Voltammetry

The voltammetric curve obtained for selenium is shown in Fig. 7, denoted by triangles. In the absence of selenium and tellurium, the only electrochemical phenomena observed are anodic chlorine evolution (+0.3 V) and cathodic lithium deposition (>-2.1 V) as in previous work (36).

The cathodic branch observed is ascribed to

$$Se(l) + 2e^- \rightarrow Se^=.$$

A red-brown color was observed leaving the electrode until the entire compartment contents were colored when cathodic current was passed. Extrapolation of the linear part of the curve to zero current gave -1.07 ± 0.02 V for the "decomposition" potential, in good agreement with the potentiometric results given below. The anodic wave is ascribed to

$$2Se(l) + 2Cl^- \rightarrow Se_2Cl_2(g) + 2e^-,$$

analogous to the reaction

$$2S(l) + 2Cl^- \rightarrow S_2Cl_2(g) + 2e^-$$

observed previously. The "decomposition" potential was +0.05 ± 0.02 V. Colorless gas bubbles were observed forming on the electrode at this potential and leaving the melt. No attempt was made to trap the gas since Se_2Cl_2 is reported as unstable at considerably lower temperatures

TABLE II.5

TIMES FOR THE DATA AT EDMONTON

(All times in GMT)

Record	Date	Digitized time (hrs)	Digitizing Interval	Length of the record	Record# on Too802	Record# on Tco472	Remarks
1	Jan. 1	1927-1932	0.25 seconds	5 minutes	1	25	
2		2156-2159			2	26	
3	Jan. 2	0001-0005			3	27	
4		0201-0206			4	28	
5		0551-0556			5	29	
6		0644-0649			6	30	
7		1038-1043			7	31	
8		1232-1237			8	32	
9		1454-1459			9	33	
10		1656-1659			10	34	
11		1754-1759			11	35	Total number of
12		1935-1940			13	37	digital points at
13		2217-2222			14	38	Edmonton
14		2332-2337			15	39	119,808
15	Jan. 3	0348-0353			16	40	
16		0434-0439			17	41	
17		0648-0653			18	42	
18		0832-0837			19	43	
19		1047-1052			20	44	
20		1312-1317			21	45	
21		1508-1513			22	46	
22		1643-1648			23	47	
23		1806-1811					Not on tape
24	Jan. 4	1239-1244			24	48	
25		1339-1344			12	36	
26		1439-1444			37	61	
27		1539-1544			38	62	

All data are given in the Appendix. A plot of $\Delta E/\Delta T$ against the logarithm of the molar concentration (as moles $Se^{=}$/liter of eutectic at 450°C) was linear (Fig. 9). Least square analysis of this plot gives

$$\Delta E/\Delta T = +0.123 \log [Se^{=}] - 0.510 \text{ mV/°C},$$

with a relative standard error of 6% in the slope and 1.5% in the intercept, for the temperature dependence of the cell

$$(-)C, Se(l)/Se^{=}, LiCl\text{-}KCl//Pt(II), LiCl\text{-}KCl/Pt (+).$$

This equation is identical to that obtained for the analogous sulfide cell within experimental error. It was used to extrapolate all measured potentials to 450°C.

These extrapolated potentials gave linear Nernst plots over the concentration range 0.015 - 0.35 molar selenide. A typical plot of potentials against the logarithm of selenide concentration (Fig. 10) shows that Henry's law is obeyed over the concentration range studied. A summary of all runs is given in Table IV; the original data are given in the Appendix. Least square analysis of all points gave a standard potential of -1.141 V for the $Se(l)/Se^{=}$ couple (molarity scale) at 450°C, with a standard error of 0.002 V. This corresponds to values of -1.172 V and -1.252 V, with the same standard error, on the molality and mole fraction scales, respectively (11), all potentials being with respect to the appropriate standard platinum electrode. The slope of the Nernst plot was -0.0660 V/log unit with a standard error of 0.0014, corresponding to 2.17 ± 0.05 electrons taking part in the reaction. This is in agreement with the theoretical value of 2 expected for $Se + 2e^{-} \rightarrow Se^{=}$.

Stable potentials could not be obtained on anodization of

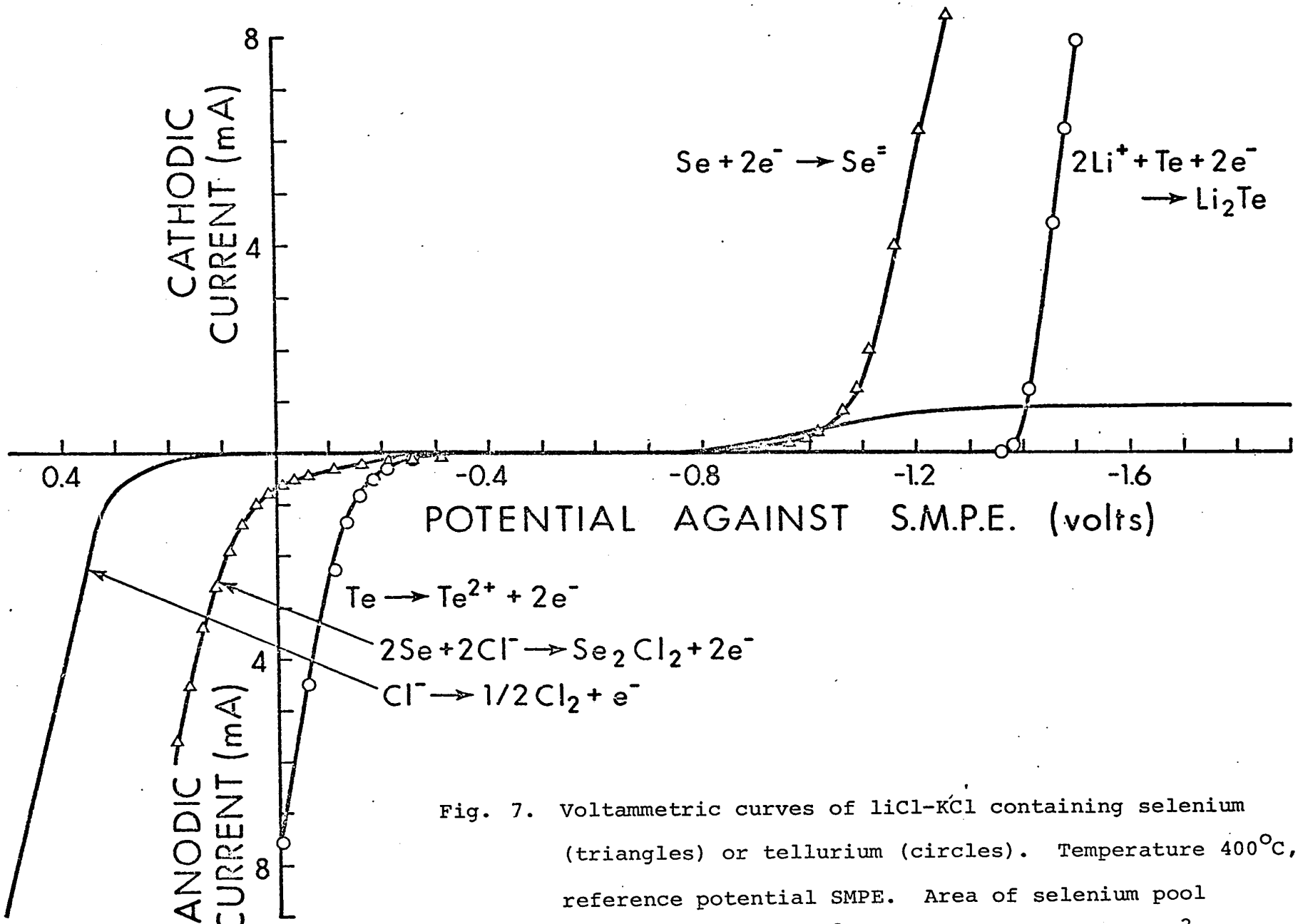

Fig. 7. Voltammetric curves of liCl-KCl containing selenium (triangles) or tellurium (circles). Temperature 400°C, reference potential SMPE. Area of selenium pool approximately 0.4 cm^2, of tellurium rod 1.1 cm^2.

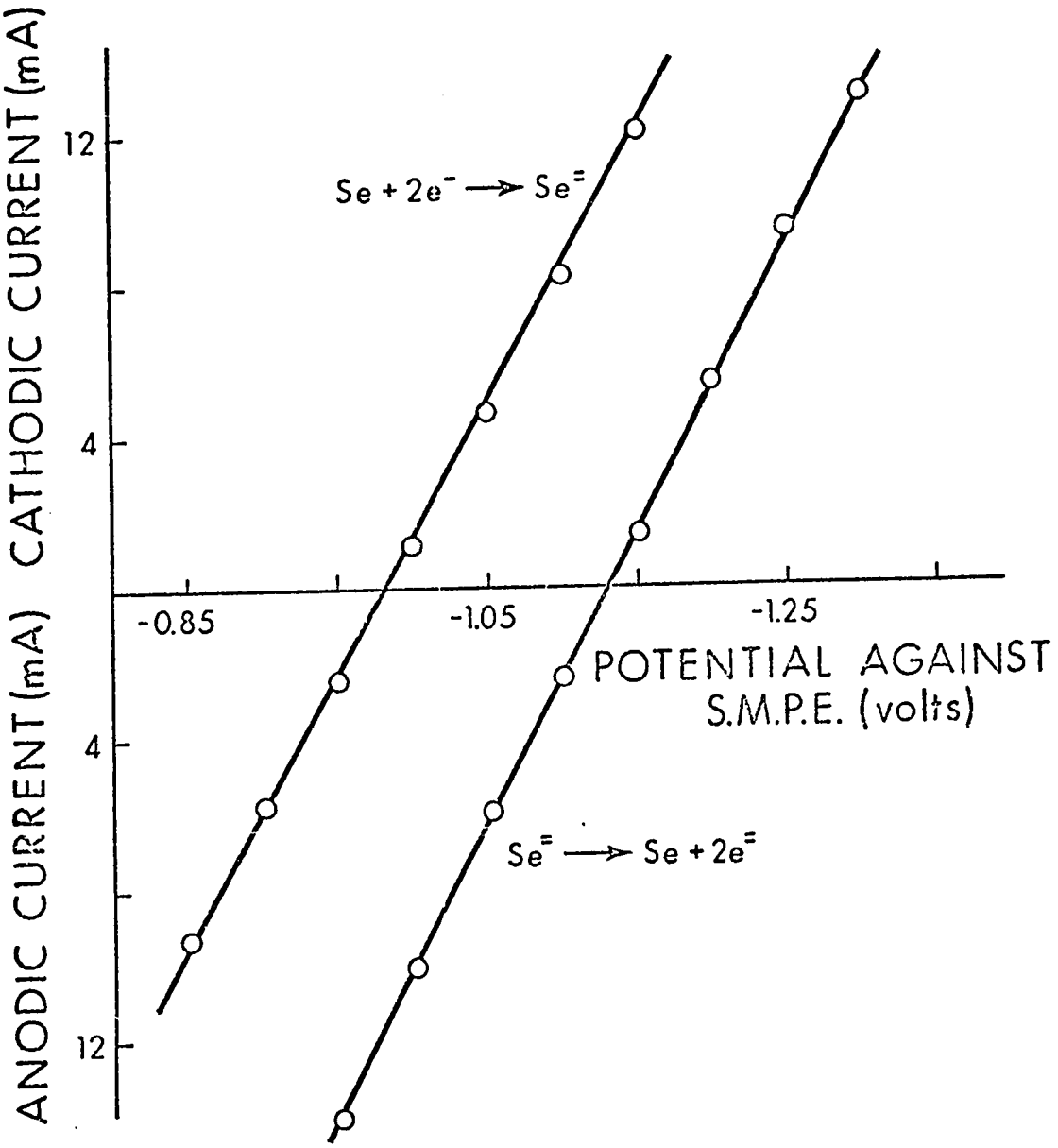

Fig. 8. Current-potential curves for different selenide concentrations in the same compartment. Reference potential SMPE, temperature 400°C.

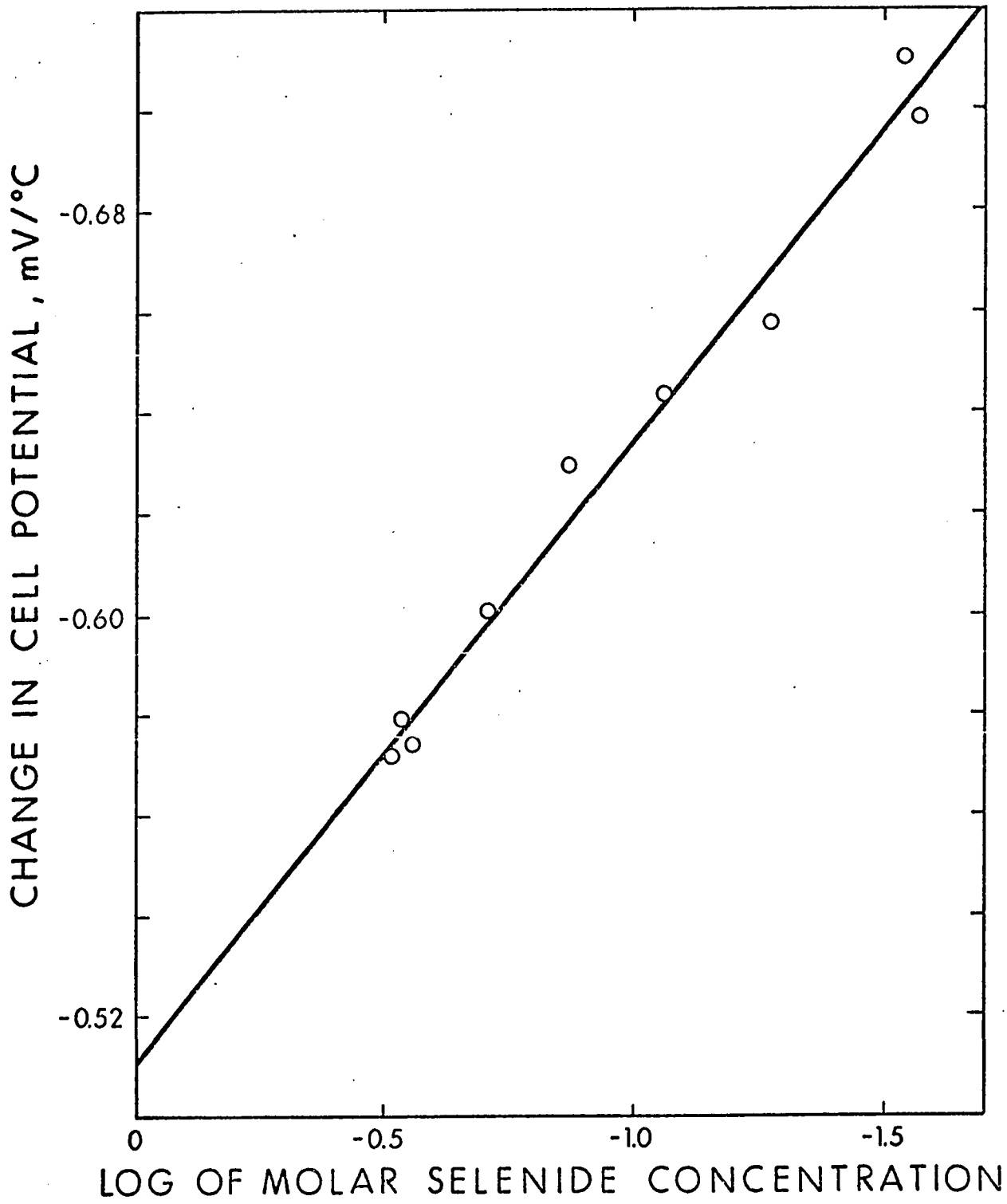

Fig. 9. Temperature dependence of potential as a function of selenide ion concentration. Line is that given by least-squares analysis. Temperature range 380-420°C.

Figure 1.13 HA activity of DGE Bands of Run 2 (gamma globulins).

Row No. 4 is a repeat test of Band 4, Run 1 (Band 4 in Fig. 1.14).

Row	Band	Titer ($-\log_2$) +	±
1	1 (Run 2)	-	-
2	2 (Run 2)	4	5, 6
3	3 (Run 2)	-	-
4	4 (Run 1)	6 - 8	4 - 5, 9 - 12

Figure 1.14 HA activity of DGE Bands of Run 1.

Note that most of the activity is found in Band 2. Note also the 'prozone' activity found in Band 4.

(Band 4 tested again in Fig. 1.13)

Row	Band	Titer ($-\log_2$) +	±
1	1 (Run 1)	-	1, 2
2	2 (Run 1)	7	8
3	3 (Run 1)	-	4
4	4 (Run 1)	7, 8	6

TABLE IV

Standard e.m.f. determinations for the $Se/Se^{=}$ couple*

Selenide Molarity	No. of Points	E°_{M} (volts)	Standard Deviation (mV)	Exper. n
0.015-0.10	7	-1.136	2.6	2.22
0.024-0.24	9	-1.141	1.1	2.27
0.018-0.16	9	-1.144	1.2	2.21
0.029-0.32	9	-1.143	2.4	2.08
0.029-0.33	9	-1.140	2.8	2.10
0.039-0.35	9	-1.143	2.3	2.10
Least square analysis of all points	52	-1.141	1.5	2.17

* values corrected to 450°C and SMPE; each entry is a separate compartment, the first being run 1, the next two being run 2, and the remainder being run 3.

selenium electrodes, for the reasons discussed above.

III. Tellurium

Voltammetry

The voltammetric curve obtained for tellurium is shown in Fig. 7, denoted by circles.

The cathodic branch observed is ascribed to the formation of stable lithium-tellurium intermetallic compounds whose limiting composition is Li_2Te (27); the reaction written as

$$Te(s) + 2Li^+ + 2e^- \rightarrow Li_2Te(s)$$

is probably an oversimplification. The potential characteristic of this reaction was -1.40 ± 0.02 V. Liquid alloys were observed to form on the tellurium rod on cathodization beyond this potential. Such alloy formation on cathodization has been observed in previous studies of the Li-Te system (27,41). The anodic wave is ascribed to

$$Te \rightarrow Te(l) + 2e^-.$$

An orange-brown color was observed leaving the electrode upon anodization. The "decomposition" potential for this reaction was -0.15 ± 0.03 V, in good agreement with the potentiometric measurements given below.

Potentiometry

Attempts were made to measure the standard potential of the $Te(s)/Te^=$ couple. These attempts were unsuccessful because the solubility of "Li_2Te" in the LiCl-KCl eutectic in the presence of excess tellurium is very low; even an attempt to produce 2×10^{-3} M $Te^=$ resulted in the formation of liquid on the surface of the tellurium

electrode. The potentials obtained in this manner were quite stable. They correspond, after correction for reference electrode, to those observed by Foster and Liu (27) for very tellurium-rich alloys of lithium and tellurium in a similar system, and therefore cannot be considered as true tellurium/telluride electrode potentials.

Anodization of tellurium produced an orange-brown solution. Long needles of tellurium were observed extending from the electrode. The potentials measured were unstable, however, and drifted in the negative direction continuously after anodization was completed. At the same time, the color of the solution slowly disappeared. A yellow powder sometimes condensed in the cooler top of the isolation compartment. This behavior would be expected if a volatile species such as $TeCl_2$ (b.p. 327°C) escaped from solution at 400°. The experiment was repeated at 375° but the species formed still volatilized from solution.

Attempts to produce meaningful Nernst plots from the potential data for this system were unsuccessful. The slope varied between 0.067 and 0.134 V/log unit. Since 0.033 V/log unit would be expected for a four-electron process, the ionic species produced should be Te(II) rather than Te(IV). From these plots and the voltammetric curves the standard potential (molarity scale) of the Te(II)/Te(s) couple is estimated as -0.10 ± 0.03 V, placing it between Rh(III)/Rh and Ir(III)/Ir couples in this medium (7). Attempts to further oxidize the Te(II) species at a graphite electrode were unsuccessful.

DISCUSSION

The standard molar potential difference between the sulfur and lithium electrodes, using data for lithium (7) and sulfur, is 2.232 V at 450°C. This is in good agreement with the open circuit potential of about 2.3 V obtained from the Li/S secondary cell at 385°C (31) for which the ternary eutectic of LiF-LiCl-LiI was used as electrolyte.

It is not possible to compare the potential data for the cell

$$Ag/AgCl,\ Ag_2S/C,\ S_2(g)$$

studied by Thompson and Flengas (25) with the results of this work since Ag_2S is completely miscible with AgCl but practically insoluble in the LiCl-KCl eutectic. Comparison would necessarily involve extrapolation of e.m.f. data and, more important, ignore a change in solvents. Potential data are experimentally accurate only within the concentration range where measurements were made and values extrapolated over several orders of magnitude on the concentration scale must be used with caution. Furthermore, the potential span between two couples may change from one solvent to another, especially if the electroactive ionic species are different in the two solvents.

Thermodynamic functions of metal sulfides in the LiCl-KCl solvent cannot be calculated from the potential data. For the cell

$$M/MCl_n,\ LiCl\text{-}KCl/LiCl\text{-}KCl,\ Li_2S/C,\ S(l)$$

(I) (II)

employed in this study, the overall cell reaction may be written as

$$2/n\ M + S(l) \rightarrow 2/n\ M^{n+} + S^{=}$$

(I) (II)

if it is assumed that the M^{n+} and $S^{=}$ ions do not take part in the transport of electricity and the activity of the Cl^{-} and (Li^{+}, K^{+}) ions are equal in solutions (I) and (II). The latter will hold in very dilute solutions. Any calculation, however, would refer to a hypothetical solution since most metal sulfides are quite insoluble in the melt and the metal and sulfide ions are here in two separate solutions. This difficulty could be overcome by constructing a cell of the type

M/MS, LiCl-KCl/LiCl-KCl, MS/S(l), C

(I) (II)

Now, however, another problem may arise, viz. that of different metal sulfide solubilities in solutions (I) and (II) due to the presence of liquid sulfur in solution (II). There is evidence (see below) of complex formation according to the equation

$$S^{=} + nS \rightarrow S^{=}_{n+1}$$

This would increase the sulfide solubility in solution (II) and render any cell potential measurement useless for a calculation of the free energy change of solid metal sulfide formation. Addition of sulfur to solution (I) is of course out of the question since it would quickly react with the metal electrode until no metal is left.

The present voltammetric studies appeared to be in disagreement with those of Delarue (22), who attributed an anodic wave in sulfide solutions at $E_{\frac{1}{2}} = -0.45$ V to the reaction $S^{=} \rightarrow S + 2e^{-}$. His melt was not purified nor was an inert atmosphere used, and the sulfide was added

as $Na_2S \cdot 9H_2O$ and an alkaline earth chloride. The necessity of scrupulously anhydrous and oxide-free melts has been discussed (35,42) and it originally appeared that impurities in his melt might account for the discrepancy. On duplicating his experiment with a purified melt and a platinum stationary microelectrode, it was found that the voltammetric curves were not reproducible but that waves of $E_{\frac{1}{2}}$ near -0.45 V were sometimes obtained. The poor reproducibility was unaffected by addition of sulfur, $CaCl_2$, and/or water. The equilibrium potential at the microelectrode was always near -0.9 V. The platinum surface immediately became dark on immersion in a melt containing sulfide. The discrepancy between this work and that of Delarue appears to be due to formation of a surface layer, probably PtS, on the platinum electrode in his work. It has not been possible to obtain reproducible voltammetric results with platinum electrodes in melts containing sulfide.

Delarue (22) has observed the formation of S_2Cl_2 in this solvent when a strong oxidizing agent was added to melts containing sulfur. The anodic wave, which is observed voltammetrically and, with less reproducibility, in the chronopotentiometric studies, is therefore ascribed to the reaction

$$2S(l) + 2Cl^- \rightarrow S_2Cl_2(g) + 2e^-.$$

From the data of Lewis and Randall (43) the free energy change for the reaction

$$2S(l) + Cl_2 \rightarrow S_2Cl_2(g)$$

is calculated to be -12.6 kcal/mole S_2Cl_2 at 420°C, while from the present voltammetric curves one calculates -12.4 ± 0.9 kcal/mole S_2Cl_2

at the same temperature, in excellent agreement. Attempts to trap and identify the gaseous product were, however, unsuccessful.

It has long been known that sulfur produces a blue color in certain solvents. This has been observed in fused KSCN (44,45) and fused LiCl-KCl (46). The nature of the colored sulfur species has not been established, and the following experiment was therefore performed.

Chlorine was generated in a compartment on a graphite electrode to remove any remaining traces of impurities which could reduce sulfur to sulfide ion. The chlorine was then removed by repeated alternation of vacuum and nitrogen purging. Sulfur pieces, obtained by heating sublimed sulfur to 200°C and cooling under vacuum, were added to the melt. No blue color developed even after 1 hour. When sulfide was then generated by cathodic coulometry the blue color developed close to the electrode surface. On stirring the color spread throughout the compartment and was clearly visible at a concentration of about 10^{-5}M calculated as sulfide ion. Further cathodic generation intensified the color. The color disappeared when chlorine was generated or when the potential of the graphite electrode was held at -0.3 V with respect to the S.M.P.E., both resulting in oxidation of sulfide to sulfur. The color also disappeared under vacuum after about 2 hours and reappeared on addition of sulfur to the melt. It appears impossible to explain these results, which indicate that both sulfide and sulfur are necessary to produce the blue color, other than by postulating that the color is due to a polysulfide ion formed by sulfur and sulfide, i.e., $S^{=} + xS \rightarrow S^{=}_{x+1}$ (blue). The molar absorptivity is so high, 16,600 (44), that a small amount of trace impurities present in

the fused LiCl-KCl (46) could reduce enough sulfur to sulfide to produce the color.

The situation in the fused KSCN system is more complex (44,45,47). The following reaction was proposed (44) at a temperature of about 400°C

$$xKSCN \rightarrow xKCN + S_x$$

and the conclusion drawn (44) was that sulfur itself produces the blue color. The reaction

$$S + 2CN^- \rightarrow S^= + (CN)_2$$

might also take place, however, even though it has been reported in the literature (see ref. 44) to occur only above 500°C. If this is the case then both sulfur and sulfide are present and can cause the blue color in agreement with the present experimental findings in the LiCl-KCl system.

The standard molar potential difference between selenium and lithium electrodes, using literature data for lithium (7) and the result of the present study for selenium, is 2.163 V at 450°C. This is in good agreement with the open-circuit potentials of 2.3-2.4 V obtained from the Li/Se secondary cell between 350° and 400°C (32), and implies that at nearly full charge the selenium electrode potential of that cell may well be determined by soluble $Se^=$ in the electrolyte rather than electrode composition. The free energy of the reaction $2Se(l) + Cl_2 \rightarrow Se_2Cl_2$ (g) can be estimated as -11 kcal/mole from the voltammetric curves. No literature data could be found with which to compare this value; it seems reasonable, however, as it is similar to that for the formation of gaseous S_2Cl_2 as determined above.

The Li/Te secondary cell is reported (27,33) to have an open-circuit voltage of 1.7-1.8 V which is in agreement with the value of 1.9 V obtained from the voltammetric curves of the present study.

As would be expected, the electrochemical behavior of sulfur is quite similar to that of selenium. Tellurium, on the other hand, exhibits some metallic character and does in first instance produce a soluble cationic species, presumably Te^{2+}, on anodization; the lithium-tellurium compound formed on cathodization is markedly less soluble in the LiCl-KCl solvent than the corresponding sulfur and selenium compounds.

It is a moot point whether sulfur and selenium react directly at the cathode according to

$$X + 2e^- \rightarrow X^=$$

or whether lithium is plated into the sulfur (selenium) pool forming the lithium compound which later dissolves and dissociates according to

$$2Li^+ + X + 2e^- \rightarrow Li_2X$$

and

$$Li_2X \rightarrow 2Li^+ + X^= .$$

The overall result is the same in both cases and no clear distinction between the different mechanisms is possible.

For tellurium the reaction taking place is apparently

$$2Li^+ + Te + 2e^- \rightarrow Li_2Te$$

as deduced from experimental observations. However, due to the low solubility of Li_2Te the reaction may still be in first instance

$$Te + 2e^- \rightarrow Te^=$$

and the liquid tellurium compound may only be formed after its solubility has been exceeded.

There is a significant point raised in the present work related to lithium-chalcogen cells. For both sulfur and selenium a soluble chalconide species determines the potential of the chalcogen electrode under the conditions of the present study. Such a species, whether $X^{=}$ or Li_2X, can be expected to be present in lithium-sulfur (34) and lithium-selenium (32) cells and to diffuse to the lithium electrode if cell construction so permits. This will lead to reduced cell efficiency and eventual cell failure. This problem appears to be less significant in the lithium-tellurium system due to lower solubility of the telluride species produced. For this reason the Li/Te secondary cell (33) seems more promising as a high power, high energy battery although it produces a lower terminal voltage than the analogous sulfur or selenium cell.

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PART II: SPECTROPHOTOMETRIC INVESTIGATIONS OF SULFUR-SULFIDE SOLUTIONS IN FUSED LiCl-KCl

ABSTRACT

The spectrum of a sulfide solution in fused LiCl-KCl eutectic with excess sulfur present has been determined at 400°C. One broad peak is observed with the maximum absorbance at 585 mμ. A plot of absorbance against sulfide concentration, where the sulfide was generated coulometrically in the spectrophotometric cell, showed that Beer's law is obeyed at sulfide concentrations less than about 2×10^{-5} molar. The molar absorptivity of the absorbing species was found to be 4,600 l $mole^{-1}$ cm^{-1}.

INTRODUCTION

As discussed above in Part I, the solution of sulfide ions in molten LiCl-KCl eutectic is blue in color if an excess of sulfur is present as a liquid pool floating on the melt. The blue color intensifies when more sulfide is added to the solution but disappears when the sulfur is pumped off, indicating that it is possibly due to a polysulfide species.

It appeared interesting to obtain the spectrum of this sulfide species and to investigate whether or not Beer's law is followed when the sulfide is generated coulometrically.

HISTORICAL

General aspects of molten salt spectrophotometry will not be discussed here since several reviews have been published on this subject (1,2).

The spectrum of molten KSCN has been published (3) and the blue color observed has been ascribed to sulfur (see Part I). An absorbance maximum was observed at 605 mμ between 250° and 450°C and below 250°C an additional one appeared at 415 mμ. The molar absorptivity for the 605 mμ maximum was estimated to be between 16,600 and 30,000.

A spectrum of molten LiCl-KCl eutectic saturated with sulfur has been published (4) and the blue color of the solution has been attributed to dissolved sulfur. The maximum absorbance was at about 600 mμ between 400° and 600°C. No value for the molar absorptivity was reported.

EXPERIMENTAL

Apparatus

Spectra were recorded on a Cary Model 14 spectrophotometer. Potentials and currents were measured with a digital voltmeter (Model 3440A, Hewlett-Packard). Two 45 V batteries in series were employed as current source from which currents between 50 and 500 μA were drawn through a resistor network.

The spectrophotometric cell consisted of square Pyrex tubing (Vitro Dynamics) of inside dimensions 22 x 10 mm with a top connected to it be means of a 34/45 ground-glass joint. Four 10/30 ground-glass joints were blown on this top which were used to insert a thermocouple, a gold foil electrode, an isolation compartment with a tungsten electrode, and an inert gas inlet tube. The isolation compartment for the anode was made of Pyrex sealing tubes (5D; Ace Glass Inc.). Part of this cell is shown in Fig. 11. The cell path length was 10 mm.

After several attempts a furnace was constructed that operated satisfactorily and fitted into the Cary sample compartment. It is shown in Fig. 11. Previously published oven designs did not allow insertion of the relatively large Pyrex cell used in the present study. Problems were also encountered in obtaining the uniform temperature necessary over a melt column of about 5 cm. The present design, which uses a large aluminum cylinder, accomplishes this; the temperature gradient in the unstirred melt was less than 2° over a

Fig. 11 Furnace for Cary Model 14 Spectrophotometer

1 Brass water jacket

2 Water inlet and outlet

3 Semicylindrical aluminum reflectors

4 Semicylindrical heating units, parallel, each 290 watts, length 4", i.d. 2 3/8" (Fisher Scientific Co.)

5 Stainless steel crucible, 59 mm dia.

6 Aluminum cylinder, 58 mm dia.

7 Square 22 x 10 mm (i.d.) Pyrex cell

8 Quartz window in water jacket, 20 mm dia.

9 Opening in aluminum cylinder, 7 x 17 mm

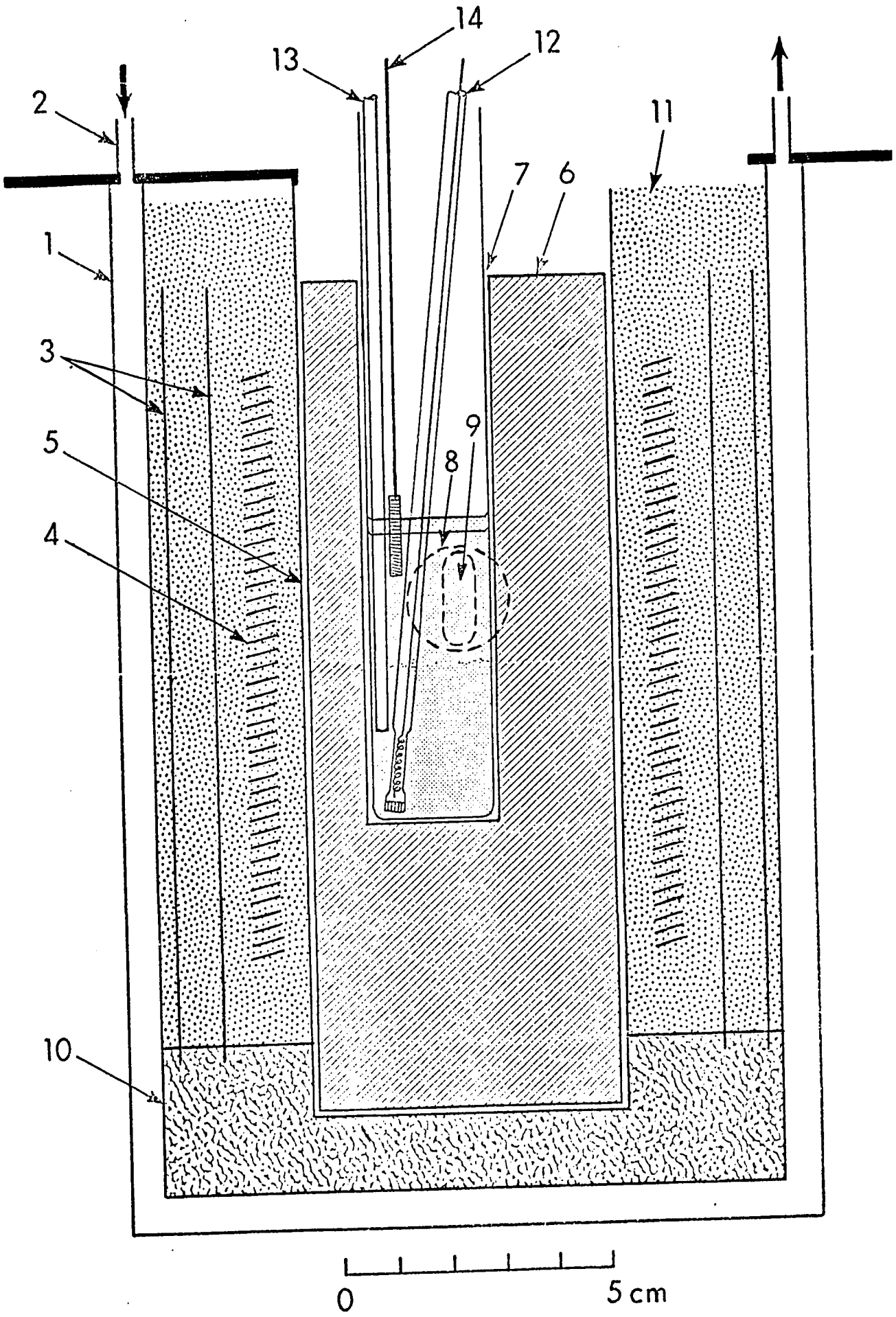
10 Insulation

11 Pyrex wool

12 Isolation compartment with tungsten electrode

13 Pyrex tube for thermocouple

14 Gold foil electrode making contact with sulfur pool


14
13
12
2
11
7
6
1
3
9
8
5
4
10
0
5 cm

vertical distance of 5 cm. The temperature of the oven was controlled by a Model 226 2-Mode solid state controller (API Instruments). The regulating thermocouple (not shown in Fig.11) was placed close to the heating elements.

Solvent

After preparation of the melt as described in Part I it was filtered through a Pyrex frit (B porosity; Ace Glass Inc.) before freezing and storage.

Chemicals

The chemicals used were described in Part I. Helium was used as inert gas. It was passed through three cold traps cooled with liquid nitrogen; the last cold trap contained activated carbon.

Electrodes

A gold foil electrode (Johnson, Matthey & Mallory Ltd.) was used to generate the sulfide from a sulfur pool. The anode consisted of a tungsten spiral in an isolation compartment which prevented mixing of anode and cathode products.

Procedure

The frozen eutectic was transferred to the cell and allowed to melt under a helium atmosphere. Once molten the eutectic was again treated with chlorine gas after insertion of the isolation compartment and the Pyrex tube for the thermocouple. After 10-15 minutes the chlorine was removed by purging with helium which was passed afterwards over the melt for the remainder of the experiment. The sulfide was

generated with a gold electrode in a sulfur pool floating on the melt. The current used was about 100 μA. After each coulometric generation the solution was made uniform by stirring it with the isolation compartment. The temperature of the melt was 400 ± 2°C. Spectra were recorded with a scanning speed of 25 A/sec. The concentration of the sulfide was calculated from the measured current, time of generation, and volume of melt obtained as before from a potentiometric chloride titration (5,6).

RESULTS AND DISCUSSION

The spectrum of the solvent with a sulfur pool floating on it is the lower curve in Fig. 12. The zero point on the absorbance scale is taken arbitrarily since the reference light beam passed through air. It shows no peaks between 400 and 800 mμ, contrary to an earlier report by Greenberg, Sundheim, and Gruen (4). In the present work no blue color develops when care is taken in the purification of both the melt and the inert gas. Impurities present in the melt might have reduced enough sulfur to sulfide to have produced the blue color observed in the earlier work (4). The spectrum after addition of sulfide to the melt is also given in Fig. 12. Only one maximum is observed at 585 mμ, not two as reported earlier (4).

Spectra of solutions with increasing sulfide concentrations were recorded at 400 ± 2°C. The absorbance at 585 mμ was measured as indicated in Fig. 12. For several experiments these absorbances were plotted as a function of the time of coulometric sulfide generation at constant current. In all cases the extrapolated lines passed through the origin. This indicates that the linear background line drawn under the upper curve in Fig. 12 is the zero absorbance line. It should be noted that the "zero absorbance" line shift from that of the solvent plus sulfur when sulfide was added to the solution. This was observed in all experiments.

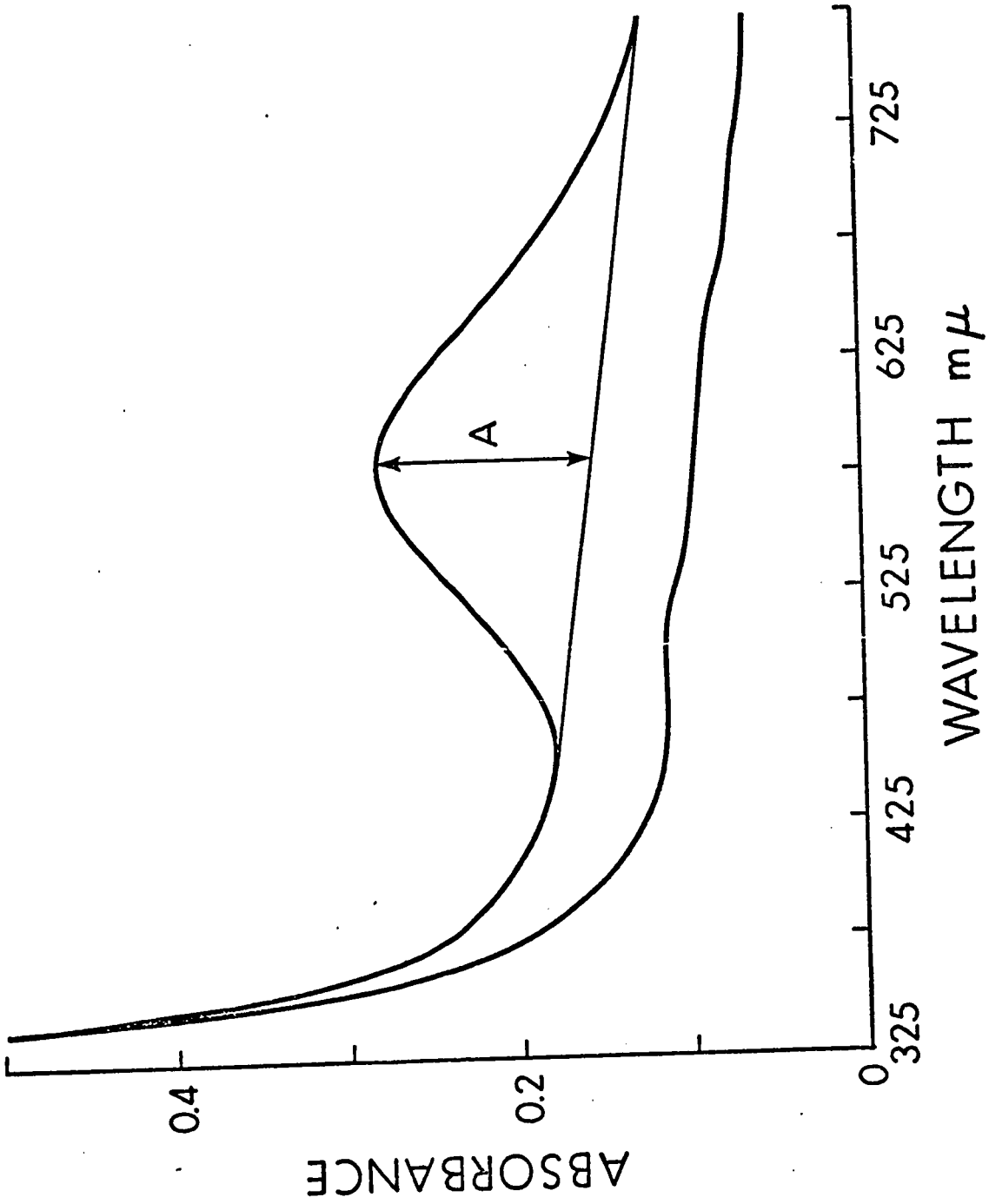


Fig. 12 Absorbance as a function of wavelength. Lower curve: fused LiCl-KCl with sulfur pool floating above it. Upper curve: same following coulometric generation of sulfide.

A typical plot of absorbance as a function of sulfide concentration is shown in Fig. 13. Concentrations up to about 2×10^{-5} molar followed Beer's law accurately; the plot for these low concentrations is given in Fig. 14 on a larger scale. Negative deviations occurred at higher concentrations. The cell path was measured as 1.00 cm. From this and the slope of the line of Fig. 14 the molar absorptivity of the absorbing species was calculated to be 4,600 1 $mole^{-1}$ cm^{-1} for sulfide concentrations up to 2×10^{-5} molar. Lux and Anslinger (3) estimated this coefficient to be 16,600 or higher but this value was arrived at under the assumption that the absorbing species is S_2. Furthermore, it is not clear how these authors determined the zero absorbance line from which the absorbance was measured. The present value is therefore not strictly comparable with their value, especially in view of the fact that the fused salts used are significantly different.

It is not yet clear whether the negative deviations from Beer's law are due to chemical or physical interaction between the absorbing species or to other effects such as light scattering. Nevertheless, spectrophotometric measurements could be used to determine the solubility of metal sulfides in fused LiCl-KCl in the presence of excess sulfur. Suitable calibration curves would, however, be required.

It should be pointed out that it was quite difficult to prevent reduction of some sulfur to sulfide in every experiment. Further improvement in the purification methods for the melt and inert gas would help to ensure more easily reproducible results.

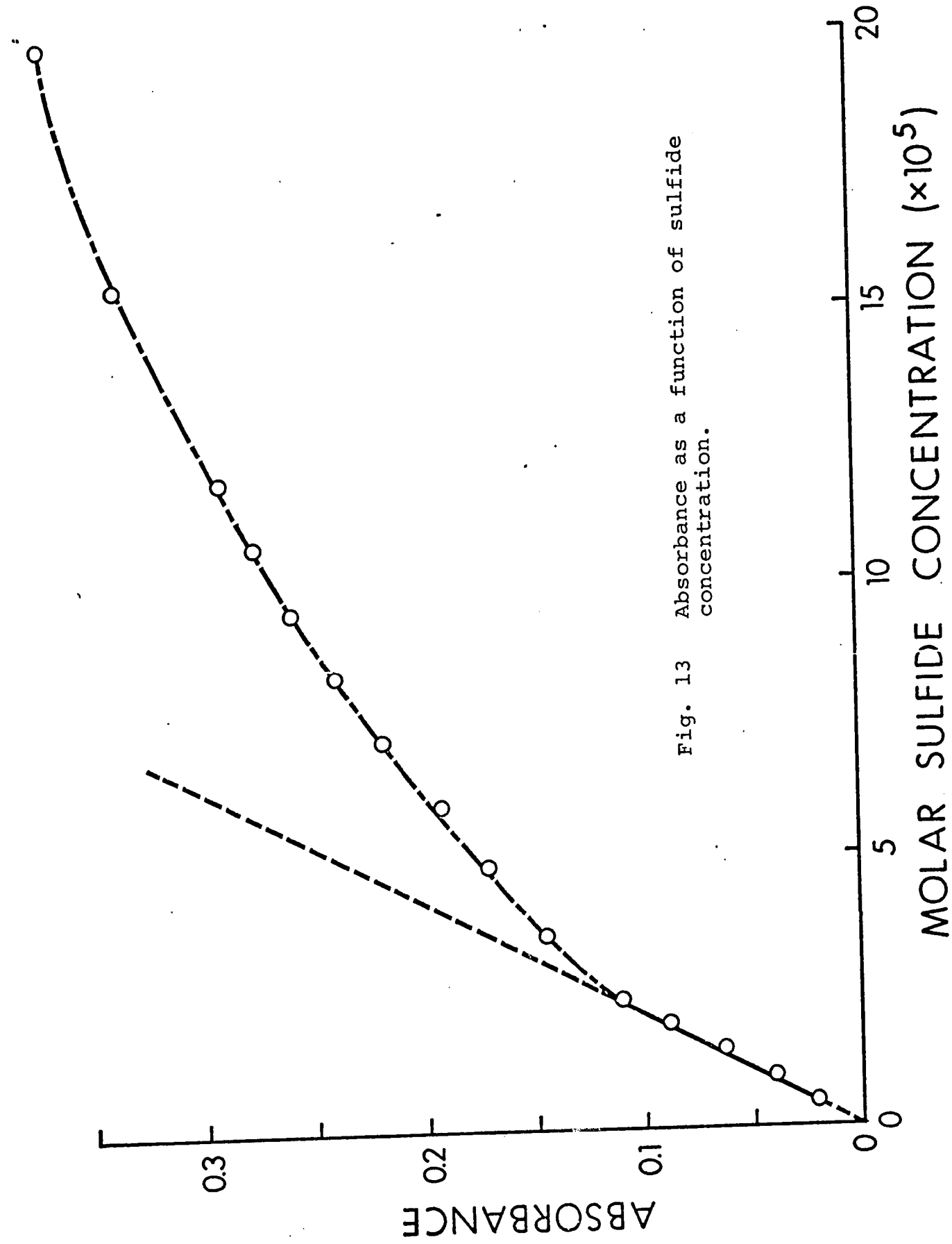


Fig. 13 Absorbance as a function of sulfide concentration.

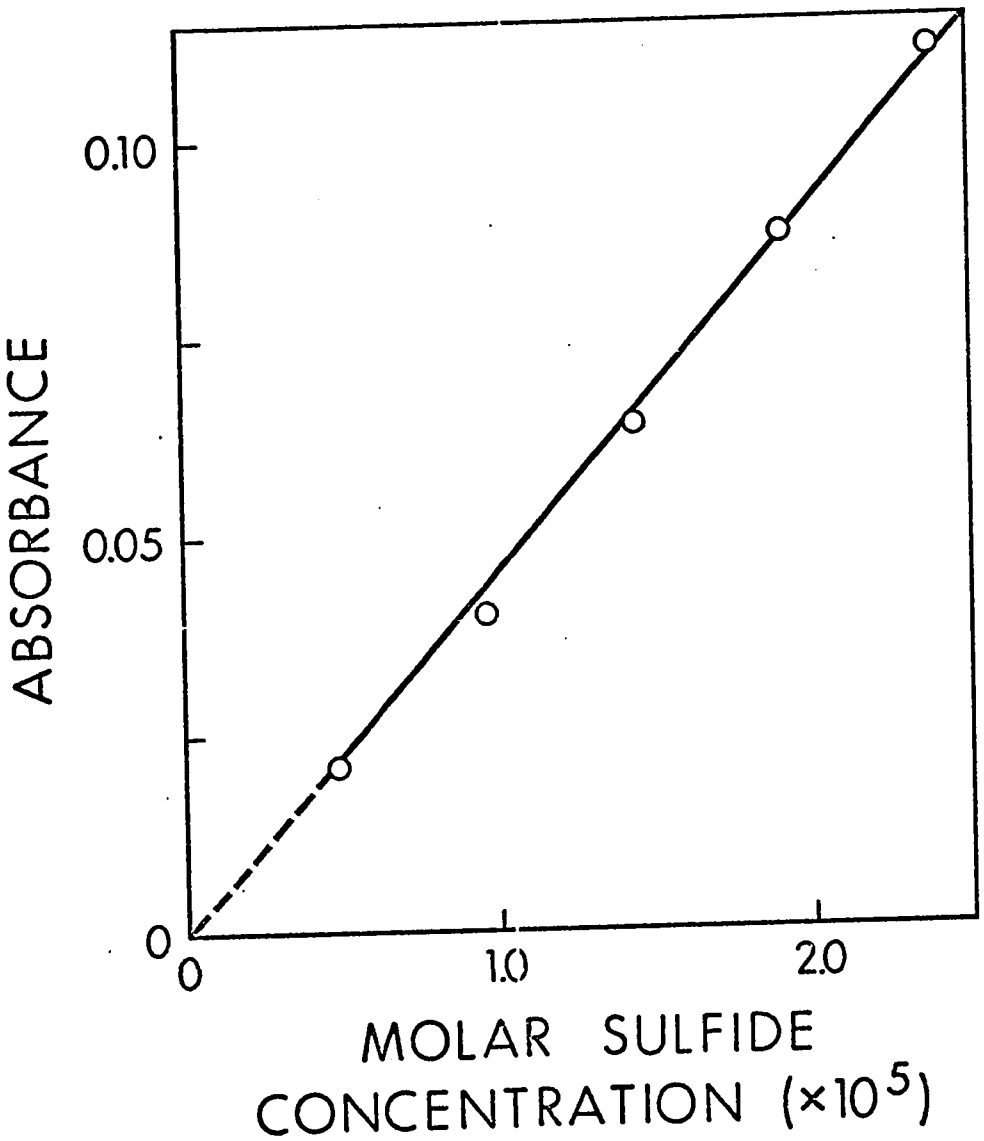


Fig. 14 Absorbance as a function of sulfide concentration; low concentration detail from Fig. 13.

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APPENDIX I

SULFIDE EMF DATA

COLUMN 1 SULFUR ELECTRODE EMF VS. REF. ELECTRODE (V)
COLUMN 2 TEMPERATURE CENTIGRADE
COLUMN 3 MICRO EQUIVALENTS OF SULFIDE GENERATED
COLUMN 4 MMOLE CHLORIDE IN SULFIDE COMPARTMENT
COLUMN 5 MICRO EQUIVALENTS OF PT ION IN REF. EL. COMPARTMENT
COLUMN 6 MMOLE CHLORIDE IN REF. EL. COMPARTMENT

BLANK ENTRY INDICATES SAME VALUE AS LAST PRINTED VALUE

-0.8477	421.0	400.00	64.055	200.00	70.769
-0.8510	420.8	440.00			
-0.8551	420.6	490.00			
-0.8575	421.3	540.00			
-0.8603	421.5	590.00			
-0.8633	421.5	650.00			
-0.8454	421.0	400.00	62.540		
-0.8507	420.8	440.00			
-0.8549	420.8	490.00			
-0.8567	421.3	540.00			
-0.8593	421.5	590.00			
-0.8611	421.5	640.00			
-0.8252	421.0	240.00	65.872	200.00	70.072
-0.8257	420.4	240.00			
-0.8336	421.0	300.00			
-0.8333	421.0	300.00			
-0.8440	420.6	400.00			
-0.8441	420.8	400.00			
-0.8515	420.6	500.00			
-0.8514	420.6	500.00			
-0.8627	420.4	700.00			
-0.8629	420.4	700.00			
-0.8720	420.2	900.00			
-0.8729	418.8	900.00			
-0.8783	418.5	1100.00			
-0.8785	417.8	1100.00			
-0.8143	421.0	160.00	64.712		
-0.8145	420.4	160.00			
-0.8317	421.0	260.00			
-0.8313	421.0	260.00			
-0.8389	420.6	320.00			
-0.8388	420.4	320.00			
-0.8461	420.6	400.00			
-0.8461	420.6	400.00			
-0.8535	420.4	500.00			
-0.8535	420.4	500.00			
-0.8645	420.2	700.00			
-0.8649	418.8	700.00			
-0.8733	418.5	900.00			
-0.8733	417.8	900.00			

-0.8184	421.0	200.00	66.378		
-0.8185	420.4	200.00			
-0.8340	421.3	300.00			
-0.8338	421.3	300.00			
-0.8386	420.6	340.00			
-0.8387	420.6	340.00			
-0.8444	420.8	400.00			
-0.8443	420.6	400.00			
-0.8527	420.4	500.00			
-0.8526	420.4	500.00			
-0.8639	420.4	702.40			
-0.8640	419.0	702.40			
-0.8723	418.5	900.00			
-0.8723	417.8	900.00			
-0.8307	419.3	200.00	65.972	204.00	75.185
-0.8308	419.5	200.00			
-0.8433	418.5	300.00			
-0.8431	418.8	300.00			
-0.8511	420.2	400.00			
-0.8511	420.0	400.00			
-0.8633	420.6	600.00			
-0.8634	418.5	600.00			
-0.8727	418.3	800.00			
-0.8726	418.5	800.00			
-0.8790	418.8	1000.00			
-0.8786	419.3	1000.00			
-0.8257	419.5	160.42	65.948		
-0.8257	419.3	160.42			
-0.8410	418.8	240.00			
-0.8412	418.8	240.00			
-0.8498	420.2	340.00			
-0.8501	420.0	340.00			
-0.8571	420.2	460.00			
-0.8582	418.8	460.00			
-0.8682	418.5	640.00			
-0.8682	418.8	640.00			
-0.8742	418.8	800.00			
-0.8737	419.3	800.00			
-0.8457	419.5	300.00	62.340		
-0.8457	419.5	300.00			
-0.8545	418.8	400.00			
-0.8543	418.8	400.00			
-0.8621	420.2	540.00			
-0.8623	420.0	540.00			
-0.8730	420.6	801.72			
-0.8742	418.8	801.72			
-0.8831	418.5	1100.00			
-0.8831	418.8	1100.00			
-0.8897	418.8	1400.00			
-0.8893	419.3	1400.00			
-0.8965	419.0	1800.00			
-0.8965	418.3	1800.00			
-0.8365	423.3	240.00	65.165	200.00	74.630
-0.8367	422.5	240.00			
-0.8464	421.5	340.00			

-0.8463	421.5	340.00			
-0.8554	422.0	460.00			
-0.8553	421.8	460.00			
-0.8656	421.5	640.00			
-0.8655	421.8	640.00			
-0.8756	421.5	900.00			
-0.8761	420.8	900.00			
-0.8747	422.5	800.00	62.365		
-0.8745	423.3	800.00			
-0.8810	421.5	1000.00			
-0.8810	421.5	1000.00			
-0.8859	422.0	1200.00			
-0.8858	421.8	1200.00			
-0.8940	421.5	1600.00			
-0.8939	421.8	1600.00			
-0.8999	421.5	2000.00			
-0.9004	420.8	2000.00			
-0.8545	422.8	400.00	64.155		
-0.8540	423.3	400.00			
-0.8644	421.8	560.00			
-0.8644	421.8	560.00			
-0.8706	422.3	700.00			
-0.8705	422.0	700.00			
-0.8777	421.8	900.00			
-0.8775	421.8	900.00			
-0.8857	421.5	1200.00			
-0.8861	420.8	1200.00			
-0.8117	419.0	160.00	66.450	200.00	67.000
-0.8117	418.5	160.00			
-0.8260	418.5	240.00			
-0.8255	417.8	240.00			
-0.8418	416.8	360.00			
-0.8411	417.3	360.00			
-0.8489	417.5	460.00			
-0.8487	417.5	460.00			
-0.8602	418.5	660.40			
-0.8601	418.5	660.40			
-0.8684	418.3	860.00			
-0.8683	418.3	860.00			
-0.8775	417.8	1160.00			
-0.8772	417.8	1160.00			
-0.8070	419.3	120.00	58.775		
-0.8211	418.5	180.00			
-0.8210	418.3	180.00			
-0.8362	417.8	280.00			
-0.8350	420.2	280.00			
-0.8491	417.3	400.00			
-0.8490	417.3	400.00			
-0.8595	417.5	560.00			
-0.8595	417.3	560.00			
-0.8685	418.5	760.00			
-0.8685	418.5	760.00			
-0.8755	418.0	960.00			
-0.8756	418.0	960.00			

-0.8835	417.8	1260.00	
-0.8835	417.8	1260.00	
-0.8149	418.3	200.00	64.775
-0.8145	418.0	200.00	
-0.8324	420.2	320.00	
-0.8322	420.2	320.00	
-0.8458	417.3	440.00	
-0.8455	417.5	440.00	
-0.8599	417.3	660.00	
-0.8599	417.0	660.00	
-0.8676	418.3	860.00	
-0.8675	418.3	860.00	
-0.8749	417.8	1080.00	
-0.8746	417.8	1080.00	
-0.8815	417.5	1360.00	
-0.8813	417.3	1360.00	

TEMPERATURE DEPENDENCE OF CELL POTENTIAL, SULFIDE

COLUMN 1 LOG OF MOLAR SULFIDE CONCENTRATION
COLUMN 2 CHANGE IN CELL POTENTIAL, MV/DEGREE

PT ION CONC. IN REF. EL. APPROX. 0.04M

-1.538	-0.718
-1.215	-0.661
-1.143	-0.667
-0.971	-0.637
-0.854	-0.629
-0.740	-0.618
-0.578	-0.588
-0.480	-0.577
-0.648	-0.604
-0.745	-0.605
-0.369	-0.564
-0.323	-0.569

SULFIDE EMF DATA, LOW CONCENTRATIONS

COLUMN 1 SULFUR ELECTRODE EMF VS. REF. ELECTRODE (V)
COLUMN 2 TEMPERATURE CENTIGRADE
COLUMN 3 MICRO EQUIVALENTS OF SULFIDE GENERATED
COLUMN 4 MMOLE CHLORIDE IN SULFIDE COMPARTMENT
COLUMN 5 MMOLE CHLORIDE IN REF. EL. COMPARTMENT

MICRO EQUIVALENTS PT ION IN REF. EL. COMPARTMENT EQUAL MICRO EQ. SULFIDE

BLANK ENTRY INDICATES SAME VALUE AS LAST PRINTED VALUE

-0.6856	398.3	20.00	93.92	97.42
-0.6695	414.5			
-0.6924	390.8			
-0.7084	373.3			
-0.6960	388.0			
-0.6885	397.0			
-0.7271	417.4	50.00		
-0.7422	400.5			
-0.7529	387.6			
-0.7628	375.0			
-0.7412	401.3			
-0.7518	424.5	80.00		
-0.7790	390.0			
-0.7908	376.8			
-0.7714	401.2			
-0.7955	415.0	140.00		
-0.8142	389.5			
-0.8288	369.0			
-0.8077	399.0			
-0.8150	419.0	200.00		
-0.8326	393.3			
-0.8446	376.0			
-0.8245	405.8			
-0.6183	411.3	10.00	86.67	91.80
-0.6098	419.8			
-0.6278	402.0			
-0.6419	390.0			
-0.6405	423.8	16.00		
-0.6765	385.3			
-0.6690	395.8			
-0.6554	410.0			
-0.7054	386.5	25.00		
-0.6933	400.5			
-0.6841	412.0			
-0.6734	424.3			
-0.7005	426.8	40.00		
-0.7133	411.8			
-0.7263	396.8			
-0.7366	385.3			
-0.7577	389.3	60.00		
-0.7480	401.6			
-0.7372	414.5			
-0.7306	423.8			

SELENIDE EMF DATA

COLUMN 1 SELENIUM ELECTRODE EMF VS. REF. ELECTRODE (V)
COLUMN 2 TEMPERATURE CENTIGRADE
COLUMN 3 MICRO EQUIVALENTS OF SELENIDE GENERATED
COLUMN 4 MMOLE CHLORIDE IN SELENIDE COMPARTMENT
COLUMN 5 MICRO EQUIVALENTS OF PT ION IN REF. EL. COMPARTMENT
COLUMN 6 MMOLE CHLORIDE IN REF. EL. COMPARTMENT

BLANK ENTRY INDICATES SAME VALUE AS LAST PRINTED VALUE

-0.9876	398.4	200.00	76.213	200.00	94.047
-0.9900	398.2	250.00			
-0.9928	398.4	300.00			
-1.0000	398.7	400.00			
-1.0072	398.7	500.00			
-1.0198	397.6	750.00			
-1.0283	398.5	1000.00			
-1.0374	398.6	1400.00			
-1.0433	397.7	1800.00			
-0.9780	398.4	150.00	76.663		
-0.9823	398.2	200.00			
-0.9847	398.4	250.00			
-0.9934	398.7	350.00			
-1.0009	398.2	450.00			
-1.0143	397.6	700.00			
-1.0219	398.5	900.00			
-1.0327	398.6	1300.00			
-1.0410	397.7	1700.00			
-0.9786	398.4	150.00	77.789		
-0.9832	398.2	200.00			
-0.9865	398.4	250.00			
-0.9951	398.7	350.00			
-1.0032	398.2	450.00			
-1.0161	397.6	700.00			
-1.0237	398.5	900.00			
-1.0343	398.6	1300.00			
-1.0424	397.7	1700.00			
-0.9701	398.8	100.00	82.791	200.00	90.975
-0.9812	398.2	150.00			
-0.9890	398.2	200.00			
-0.9978	398.7	275.00			
-1.0032	399.0	350.00			
-1.0096	399.3	450.00			
-1.0168	398.7	600.00			
-1.0215	399.7	750.00			
-1.0252	399.2	900.00			
-0.9806	396.0	125.00	78.789		
-0.9855	398.2	175.00			
-0.9924	398.2	225.00			
-0.9983	398.7	275.00			

-1.0070	399.0	400.00			
-1.0124	399.3	500.00			
-1.0215	398.7	700.00			
-1.0279	399.7	950.00			
-1.0335	399.2	1250.00			
-0.9500	394.7	75.00	74.712	125.00	83.792
-0.9578	395.5	100.00			
-0.9668	393.5	135.00			
-0.9726	395.5	200.00			
-0.9815	395.0	275.00			
-0.9926	394.2	400.00			
-0.9996	394.2	505.00			

TEMPERATURE DEPENDENCE OF CELL POTENTIAL, SELENIDE

COLUMN 1 LOG OF MOLAR SELENIDE CONCENTRATION
COLUMN 2 CHANGE IN CELL POTENTIAL, MV/DEGREE

PT ION CONC. IN REF. EL. APPROX. 0.025M

-0.521	-0.572
-0.574	-0.579
-0.559	-0.574
-0.712	-0.600
-0.874	-0.629
-1.066	-0.643
-1.280	-0.657
-1.573	-0.697
-1.544	-0.709

APPENDIX II

```
C
C     NERNST EQUATION LEAST SQUARES PROGRAM USING LSQ1 (FORTRAN)
C
      IMPLICIT REAL*8 (A-H,O-Z)
      REAL*4 TITLE (20)
      DIMENSION A(20,15), B(20,1), X(500), Y(500,1), W(500), SUM(1),
     XPESID(500,1), EVAL(500), STD(15), XX1(50), X1(50), CTEMP(500), YTE
     XRM(500), RELDV(15), RELDEV(500), CONCTM(500), SPOT(500)
     X,STDPOT(500),YY(500)
      EQUIVALENCE (YTERM,STDPOT),(YY(1),Y(1,1))
C
      DATA R/8.3143/, F/96487.0/, T/273.16/, BASECH/0.43429448/
C
   10 CONTINUE
C
C     SET OF SUMMATIONS TO ZERO
C
      IREJ=0
      NREJ = 0
      MOREN = 0
      N1TOT = 0
      TOTAL1 = 0.
   11 READ (5,805) TITLE
      WRITE (6,1100) TITLE
C
C     PROGRAM CONTROL CARD
C     N=NO. OF POINTS IN EACH SET
C     IF IP.EQ.0 GRAPH SUBROUTINE IS NOT CALLED
C     IF IP.EQ.1 GRAPH SUBROUTINE IS CALLED
C     IF IP.EQ.2 GRAPH SUBROUTINE IS CALLED AND LEAST SQUARE LINE IS
C       ALSO PLOTTED
C     IF N1.NE.0 PROGRAM WILL CALCULATE POTENTIALS AT CONCENTRATIONS
C       SPECIFIED ON INPUT CARDS
C     IF IC.NE.0 ON ALL BUT LAST DATA SET, ALL DATA SETS ARE COMBINED
C       TO CALL GRAPH ONLY ON LAST DATA SET IP=1
C     IF IR.NE.0 ON LAST DATA SET (ALL OTHERS IR=0) REJECTION OF POINTS
C       WILL TAKE PLACE
C     IQ AND IT ARE DUMMIES
C
      READ (5,1000) N, IP, N1, IC, IR, IQ, IT
      IF (N.EQ.0) STOP
      TOTAL4 = 0.
      TOTAL5 = 0.
      TOTAL6 = 0.
      M = 2
C
C     DATA CARD FOR INDICATOR ELECTRODE COMPARTMENT
C     ZN    CHARGE OF ION INCL. SIGN
C     CONC    NUMBER OF MOLES OF CHLORIDE IN COMPARTMENT
C     DENS    DENSITY OF MELT IN G PER LITER
C     ZMMW    MEAN MOL. WEIGHT OF MELT
C     BASICT    TEMP. OF MELT IN CENTIGRADE
C
      READ(5,2000) ZN, DUMMY, CONC, DENS, ZMMW, BASICT
```

```
C
C     ASSUMPTIONS MADE BY PROGRAM FOR THE LICL-KCL EUTECTIC
C
      IF (BASICT.LE. 0.0) BASICT = 450.00
      IF (ZN.EQ.0.0) ZN = 1.0
      IF (CONC.LE.0.0) CONC = 0.1000
      IF (DENS.LE.0.0) DENS = 1648.00
      IF (ZMMW.LE.0.0) ZMMW = 55.5900
C
C     DATA CARD FOR REF. ELECTRODE COMPARTMENT
C     SEQIV   NUMBER OF EQUIVALENTS OF REF. ION GENERATED
C     SCONC   NUMBER OF MOLES OF CHLORIDE IN REF. COMPARTMENT
C     SN   CHARGE OF REF. ION INCL. SIGN
C     APOT   STD. POTENTIAL OF REF. ELECTRODE COUPLE
C     ORIGEQ   NUMBER OF EQUIVALENTS USED TO GENERATE ION OF LOWER
C       OXIDATION STATE WHEN PROGRAM IS USED FOR IONS OF TWO SOL.
C       OXIDATION STATES
C
      READ (5,2000) SEQIV, SCONC, SN, APOT, ORIGEQ
      WRITE (6,2100) SN, ORIGEQ, CONC, DENS, ZMMW, BASICT
      IF (SCONC.LE.0.0) SCONC = CONC
      IF (SN.LE.0.0) SN = 1.0
      NCHECK = MOREN + 1
      NSUM = N + MOREN
      WRITE (6,4100)
C
C     FIRST CALCULATION LOOP
C
      DO 33 I = NCHECK,NSUM
C
C     DATA CARD FOR INDICATOR ELECTRODE
C     EQIV   NUMBER OF EQUIVALENTS OF ION GENERATED
C     V   EMF VS REF. ELECTRODE IN VOLTS
C     CTEMP(I)   TEMP. IN CENTIGRADE
C     W(I)   WEIGHTING FACTOR OF POINT
C
      READ(5,2000) EQIV, V, CTEMP(I), DUMMY, DUMMY, W(I)
      IF (CTEMP(I).EQ.0.0) CTEMP(I)=BASICT
      IF (W(I).EQ.0.0) W(I) = 1.0
      WRITE (6,4000)  EQIV, V, W(I), CTEMP(I), DUMMY, DUMMY
      YTERM(I)=V
      TOTAL6=TOTAL6+(CTEMP(I)+T)
      CONCTM(I) = (EQIV*DENS) / (CABS(ZN)*CONC*ZMMW)
      IF (ORIGEQ.NE.0.0) CONCTM(I)=(EQIV/ZN)/(ORIGEQ-(EQIV/ZN))
   33 X(I) = DLOG10(CONCTM(I))
      AVTEMP = TOTAL6 / DFLOAT(N)
      TOTAL1 = TOTAL1 + TOTAL6
C
C     REFERENCE ELECTRODE CALCULATION LOOP
C
      DO 42 I = NCHECK, NSUM
      STEMP = CTEMP(I) + T
      SCNCTM = (SEQIV * DENS) / (SN * SCONC * ZMMW)
      SPOT(I) = APOT + ((R*STEMP) / (SN*F))*DLOG(SCNCTM)
      TOTAL4 = TOTAL4 + SPOT(I)
   42 Y(I,1) = SPOT(I) + YTERM(I)
```

```
      AVSPOT = TOTAL4 / DFLOAT(N)
C
C     ERROR AND DEVIATION CALCULATION LOOP
C
      SPTDEV=0.0
      IF(N.LE.1) GO TO 44
      DO 43 I = NCHECK, NSUM
   43 TOTAL5 = TOTAL5 + (((AVSPOT - SPOT(I))**2)/(DFLOAT(N)-1.0))
      SPTDEV = DSQRT(TOTAL5)
   44 WRITE (6,3100) APOT, SCONC, SEQIV, SCNCTM, AVSPOT, SPT
     XDEV, AVTEMP
      IF (N1.EQ.0) GO TO 46
      N1TOT = N1TOT + N1
      N1 = N1TOT - N1 + 1
C
C     DATA CARDS FOR CASE N1.NE.0
C
      READ (5,2000) (XX1(I), I = N1, N1TOT)
      DO 45 I = N1, N1TOT
   45 X1(I) = DLOG10(XX1(I))
C
   46 MOPEN = NSUM
      IF (IC.NE.0) GO TO 11
      AVGTMP = TOTAL1 / DFLOAT(NSUM)
   50 TOTAL2 = 0.0
      TOTAL3 = 0.
      DO 60 I = 1,NSUM
      STDPOT(I) = Y(I,1) - ((R*(CTEMP(I) + T))/(ZN*F))*(X(I)/BASECH)
      TOTAL3 = TOTAL3 + (STDPOT(I)*W(I))
   60 TOTAL2 = TOTAL2 + (((CTEMP(I) + T - AVGTMP)**2)/(DFLOAT(NSUM)-
     X1.0))
      TMPDEV = DSQRT(TOTAL2)
      AVGSPT = TOTAL3 / DFLOAT(NSUM - NREJ)
C
C     END OF CALCULATION LOOPS
C
      CALL LSQ1 (X,Y,W,RESID,NSUM,SUM,1,A,B,M)
C
      STDERR = DSQRT(SUM(1)/DFLOAT(NSUM - NREJ))
      EXPERN = (R * AVGTMP) / (B(2,1) * F * BASECH)
      DO 80 I = 1,M
      STD(I) = DSQRT(SUM(1)*A(I,1)/DFLOAT(NSUM - NREJ - M - 1))
   80 RELDV(I) = STD(I)/B(I,1)
      TOTAL1 = 0.
      DO 90 I = 1,NSUM
      TOTAL1 = TOTAL1 +(((AVGSPT-STDPOT(I))**2)*W(I))
      EVAL(I) = RESID(I,1) + Y(I,1)
   90 RELDEV(I) = RESID(I,1) / Y(I,1)
      SPOTDV = DSQRT(TOTAL1/DFLOAT(NSUM-NREJ-1))
      IF (IREJ.GT.0) GO TO 170
      IF (IREJ.GT.NSUM) GO TO 190
  100 WRITE (6,3000) NSUM, IP, N1TOT, IR, IQ, IC, NREJ, IT
      WRITE (6,5100) AVGTMP, TMPDEV, EXPERN, ZN, AVGSPT, SPOTDV
      WRITE (6,5000) (B(I,1), STD(I), RELDV(I), I = 1,M)
```

```
      WRITE (6,6000) SUM
      WRITE (6,6100) STDERR
      WRITE (6,6200)
      DO 160 I = 1,M
  160 WRITE (6,4000) (A(I,J), J = 1,M)
      WRITE (6,7000) (W(I), CONCTM(I), X(I), SPOT(I), Y(I,1),
     XEVAL(I), RESID(I,1), RELDEV(I), STDPOT(I), I=1,NSUM)

C
C     PLOTTING OPTION
C     HORIZONTAL AXIS IS POTENTIAL AGAINST STD.REF. IN VOLTS
C     VERTICAL AXIS IS LOG OF IONIC CONCENTRATION
C     X= EXPERIMENTAL POINT
C     *= LEAST SQUARES LINE
C     0 INDICATES OVERLAPPING POINTS
      IF(IP.NE.0) WRITE(6,1100) TITLE
      IF(IP.NE.0) CALL DGRAPH(NSUM,X,YY,EVAL,YY,IP,0.0,0.0,0.0,0.0,61)

C
      IF (IR.LE.0) GO TO 190
      IF (IREJ.GE.NSUM) GO TO 190
      IF (IREJ.GT.0) GO TO 180
      WSTORE=W(1)
      W(1) = 0.0
      IREJ = 1
      NREJ = 1
      GO TO 50
  170 NREJ = NREJ + 1
      IF (NREJ.GE.(NSUM-2)) GO TO 190
      IF (DABS(RESID(IREJ,1)).GE.2.576*STDERR) GO TO 100
      NREJ = NREJ - 1
      W(IREJ) = WSTORE
  180 IREJ = IREJ + 1
      WSTORE = W(IREJ)
      W(IREJ) = 0.0
      GO TO 50
  190 IF (N1TOT.LE.0) GO TO 10
      DO 194 I = 1,N1TOT
  194 EVAL(I) = POLY(X1(I), M, B, 1, 20, 1)
      WRITE (6,8000) (XX1(I), X1(I), EVAL(I), I = 1, N1TOT)
      GO TO 10
  805 FORMAT (20A4)
 1000 FORMAT (12I6)
 1100 FORMAT (1H1,20A4)
 2000 FORMAT (6D12.5)
 2100 FORMAT (84HJ   REF. CHARGE   ORIG.EQUIV.       CONC.       DENSITY
     X    MEAN MOL.WT.   BASE TEMP. /(1HJ1P6D14.5//))
 3000 FORMAT (48H1    LEAST SQUARE NERNST PLOT USING LSQ1          /
     X         3HJN=I3,5H  IP=I2,6H   N1=I2,6H   IR=I2,6H   IQ=I2,6H   IC
     X=I2,8H   NREJ=I2,6H   IT=I2)
 3100 FORMAT (80HJ                  INPUT DATA FOR AND CALCULATED VALUE OF
     XTHE STANDARD POTENTIAL       /105HJ   SCALE POT.      SOLV. CONC.
     XEQUIVALENTS   CONC. TERM     STD. POT.      STD. DEV.      AVG. TEMP.
     X          /(1HJ1P8D14.5//))
 4000 FORMAT (1HJ1P8D14.5)
 4100 FORMAT (86HJ   EQUIVALENTS    POTENTIAL       WEIGHT       TEMPERATU
                                    /)
     XRE
```

```
5000 FORMAT (62HJ          COEFFICIENT              ERROR              RELATIV
    XE ERROR/(1HJ3F20.8))
5100 FORMAT (82HJ AVERAGE TEMP.    DEVIATION     EXPER. N       THEOR. N
    X      MEAN          STD. DEV. /(1HJ1P8D14.5))
6000 FORMAT (36HJWEIGHTED SUM OF SQUARED DEVIATIONS=1PD13.5)
6100 FORMAT (29HJSTANDARD ERROR OF ESTIMATE =1PD13.5)
6200 FORMAT (13HJERROR MATRIX)
7000 FORMAT (124HJ      WEIGHT      MOLARITY          X      REFERENCE
    XPOT.   POTENTIAL    EVALUATION     RESIDUAL   RELATIVE DEV.   STD.
    XPOT./(1HJ1P9D14.5))
8000 FORMAT (43HJ      MOLARITY      EXTRA X      EVALUATION  /(1HJ1P3D1
    X4.5))
      END
```

```
C
      SUBROUTINE LSQ1(X,Y,W,RESID,N,SUM,L,A,B,M)
C
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION X(500),Y(500,1),RESID(500,1),A(20,15),B(20,1),C(500,15),
     XSUM(1),W(500)
C
      COMMON C
C
      DO 1 I = 1,N
    1 C(I,1) = 1.000000000
      DO 2 J = 2,M
      DO 2 I = 1,N
    2 C(I,J) = C(I,J - 1) * X(I)
      DO 3 I = 1,M
      DO 3 J = 1,M
      A(I,J) = 0.000000000
      DO 3 K = 1,N
    3 A(I,J) = A(I,J) + C(K,I) * C(K,J) * W(K)
      DO 4 J = 1,L
      DO 4 I = 1,M
      B(I,J) = 0.000000000
      DO 4 K = 1,N
    4 B(I,J) = B(I,J) + C(K,I) * Y(K,J) * W(K)
      CALL MATINV (A,M,B,L,DETERM)
      DO 6 J = 1,L
      SUM(J) = 0.000000000
      DO 6 I = 1,N
      RESID(I,J) = POLY(X(I),M,B,J,20,1) - Y(I,J)
    6 SUM(J) = SUM(J) + RESID(I,J)**2*W(I)
      RETURN
      END
```

```
C
C       MATRIX INVERSION WITH ACCOMPANYING SOLUTION OF LINEAR EQUATIONS
C
C
        SUBROUTINE MATINV(A,N,B,M,DETERM)
C
        IMPLICIT REAL*8(A-H,O-Z)
        DIMENSION IPIVOT(20), A(20,20), B(20,1), INDEX(20,2), PIVOT(20)
        COMMON PIVOT,INDEX, IPIVOT
        EQUIVALENCE (IROW,JROW), (ICOLUM,JCOLUM), (AMAX,T,SWAP)
C
C       INITIALIZATION
C
        DETERM = 1.000000000
        DO 20 J = 1,N
   20   IPIVOT(J) = 0
        DO 550 I = 1,N
C
C       SEARCH FOR PIVOT ELEMENT
C
        AMAX = 0.000000000
        DO 105 J = 1,N
        IF(IPIVOT(J) - 1) 60,105,60
   60   DO 100 K = 1,N
        IF (IPIVOT(K) - 1) 80,100,740
   80   IF(DABS(AMAX) -DABS(A(J,K))) 85,100,100
   85   IROW = J
        ICOLUM = K
        AMAX = A(J,K)
  100   CONTINUE
  105   CONTINUE
        IPIVOT(ICOLUM) = IPIVOT(ICOLUM) + 1
C
C       INTERCHANGE ROWS TO PUT PIVOT ELEMENT ON DIAGONAL
C
        IF (IROW - ICOLUM) 140,260,140
  140   DETERM = -DETERM
        DO 200 L = 1,N
        SWAP = A(IROW,L)
        A(IROW,L) = A(ICOLUM,L)
  200   A(ICOLUM,L) = SWAP
        IF (M) 260,260,210
  210   DO 250 L = 1,M
        SWAP = B(IROW,L)
        B(IROW,L) = B(ICOLUM,L)
  250   B(ICOLUM,L) = SWAP
  260   INDEX(I,1) = IROW
        INDEX(I,2) = ICOLUM
        PIVOT(I) = A(ICOLUM,ICOLUM)
        DETERM = DETERM * PIVOT(I)
C
C       DIVIDE PIVOT ROW BY PIVOT ELEMENT
C
        A(ICOLUM,ICOLUM) = 1.000000000
        DO 350 L = 1,N
  350   A(ICOLUM,L) = A(ICOLUM,L)/PIVOT(I)
```

```
      IF (M) 380,380,360
  360 DO 370 L = 1,M
  370 B(ICOLUM,L) = B(ICOLUM,L)/PIVOT(I)
C
C     REDUCE NONPIVOT ROWS
C
  380 DO 550 L1 = 1,N
      IF(L1 - ICOLUM) 400,550,400
  400 T = A(L1,ICOLUM)
      A(L1,ICOLUM) = 0.0
      DO 450 L = 1,N
  450 A(L1,L) = A(L1,L) - A(ICOLUM,L) * T
      IF (M) 550,550,460
  460 DO 500 L = 1,M
  500 B(L1,L) = B(L1,L) - B(ICOLUM,L) * T
  550 CONTINUE
C
C     INTERCHANGE COLUMNS
C
      DO 710 I = 1,N
      L = N + 1 - I
      IF (INDEX(L,1) - INDEX(L,2)) 630,710,630
  630 JROW = INDEX(L,1)
      JCOLUM = INDEX(L,2)
      DO 705 K = 1,N
      SWAP = A(K,JROW)
      A(K,JROW) = A(K,JCOLUM)
      A(K,JCOLUM) = SWAP
  705 CONTINUE
  710 CONTINUE
  740 RETURN
      END
```

```
      REAL FUNCTION POLY(X,M,COEFF,J,MR,MC)
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION COEFF(MR,MC)
      POLY = 0.0
      DO 1 N = 1,M
      MA = M - N + 1
    1 POLY = POLY * X + COEFF(MA,J)
      RETURN
      END
```

```
C
C
      SUBROUTINE DGRAPH(N,XI,YI,YPI,YQI,NYL,XLINC,XLOR,YLINC,YLOR,L)

C
C     N:  INTEGER GIVING THE NO. OF POINTS IN THE X-LIST (EQUALS THE NO.
C     OF POINTS IN EACH Y-LIST)
C
C     X:  REAL*4 X-VECTOR
C
C     Y,YP,YQ:  3 REAL*4 Y-VECTORS.  ALL Y(I),YP(I),YQ(I) SHARE THE SAME
C     X(I).
C
C     NY: INTEGER GIVING THE NUMBER OF Y-VECTORS TO BE ACTUALLY PLOTTED.
C     IF 1, Y IS PLOTTED; IF 2, Y AND YP ARE PLOTTED; IF 3, Y,YP,AND YQ
C     ARE PLOTTED.  IF NY<1 OR NY>3, PROGRAM ASSUMES 1.
C
C     XINC:  REAL*4 X-INCREMENT.  IF 0.0, SCALE IS CALLED, AND WILL GIVE
C     A FAIRLY REASONABLE SCALE.  IF NEGATIVE, THE ENTIRE AVAILABLE
C     SPACE (121 BY LINES)  WILL BE FILLED.
C
C     XOR:  REAL*4 X-ORIGIN.  IGNORED UNLESS XINC>0.0.
C
C     YINC:  REAL*4 Y-INCREMENT.  IF 0.0, SCALE IS CALLED.  IF NEGATIVE,
C     EACH Y-VECTOR IS SCALED SEPARATELY.
C
C     YOR:  REAL*4 Y-ORIGIN.  IGNORED UNLESS YINC>0.0.
C
C     LINES:  INTEGER GIVING THE MAXIMUM LENGTH OF THE GRAPH.  IF LINES
C     IS LESS THAN 10,  IT WILL BE ASSUMED TO BE 61 (ONE PAGE).  IF THE
C     PROGRAM DETERMINES ITS OWN SCALE(XINC=0.0), THE MAXIMUM LENGTH IS
C     500-1000 LINES, DEPENDING UPON THE RANGE.
C
C     ACCEPTABLE CALL STATEMENTS ARE:
C     CALL DGRAPH(N,X,Y,Y,Y,1,0.0,0.0,0.0,0.0,61)
C     CALL DGRAPH(N,X,Y,YP,YQ,3,0.0,0.0,-1.0,0.0,201)
C
C     THE PROGRAM PLOTS X IN THE VERTICAL DIRECTION AND Y IN THE HORI-
C     ZONTAL DIRECTION (ACROSS THE PAGE).  IF VALUES IN THE CALLING
C     SEQUENCE ARE RIDICULOUS, THE PROGRAM WILL EITHER RETURN OR MAKE
C     ASSUMPTIONS.  ALL MEMBERS OF THE CALLING SEQUENCE WILL ALWAYS BE
C     RETURNED UNCHANGED.
C          A POINT AT (X(I),Y(I)) WILL BE REPRESENTED BY AN X, ONE AT
C     (X(I),YP(I)) BY A *, AND ONE AT (X(I),YQ(I)) BY A +.  IF TWO OR
C     MORE POINTS FALL WITHIN THE SAME PRINTING BLOC, AN O WILL BE
C     PRINTED;  THERE WILL BE NO INFORMATION PROVIDED BY THE PROGRAM AS
C     TO WHICH POINTS ARE COINCIDENT.  ANY POINTS OFF SCALE ARE IGNORED
C          THE PROGRAM WILL NOT START A NEW PAGE OR PRINT A TITLE.
C          EXECUTION-TIME DIMENSIONING HAS BEEN USED AS MUCH AS POSSIBL
C     IN THE PROGRAM.  THE FOUR WORKING VECTORS, HOWEVER, HAVE BEEN
C     DIMENSIONED ARBITRARILY AT 200.  THIS CARD CAN READILY BE CHANGED
C     BY THE USER.
C
      IF (N.LE.1) RETURN
C
```

```
C       IF THERE ARE MORE THAN 200 POINTS, THE FOLLOWING CARD SHOULD BE
C       CHANGED.
C
        DIMENSION X(200),Y(200),YP(200),YQ(200)
        REAL*8    XI(N),YI(N),YPI(N),YQI(N)
        INTEGER*2 EX,BLANK,STAR,PLUS,DASH,VERT,ST,VEC(121)
        DATA EX/'X'/,BLANK/' '/,STAR/'*'/,PLUS/'+'/,DASH/'-'/,VERT/'|'/
        LOGICAL SWT
C
C       TRANSFER OF CALLING VALUES TO WORKING VALUES
C
        NY = NYL
        XINC = XLINC
        XOR = XLOR
        YINC = YLINC
        YOR = YLOR
        LINES = L
        DO 1  I = 1,N
        X(I) = XI(I)
        Y(I) = YI(I)
        YP(I) = YPI(I)
        YQ(I) = YQI(I)
      1 CONTINUE
C
C       SORTING OF WORKING VECTORS INTO ORDER OF INCREASING X.
C
        NT = N-1
        NL = NT
        DO 3  I = 1,NL
        SWT = .FALSE.
        DO 2  J = 1,NT
        IF (X(J).LE.X(J+1))  GO TO 2
        XTEMP = X(J)
        YTEMP = Y(J)
        YPTEMP = YP(J)
        YQTEMP = YQ(J)
        X(J) = X(J+1)
        Y(J) = Y(J+1)
        YP(J) = YP(J+1)
        YQ(J) = YQ(J+1)
        X(J+1) = XTEMP
        Y(J+1) = YTEMP
        YP(J+1) = YPTEMP
        YQ(J+1) = YQTEMP
        SWT = .TRUE.
      2 CONTINUE
        IF (.NOT.SWT) GO TO 4
      3 NT = NT - 1
      4 IF (LINES.LT.10)  LINES = 61
C
C       BRANCHING FOR SCALING OPTIONS.
C
        L = 0
        IF (XINC.LT.0.0)  L = 1
```

```
      IF (NY.GT.3.OR.NY.LT.1) NY=1
      IF (XINC.GT.0.0.AND.XOR.GT.X(1))  XOR = X(1)
      IF (XINC.LE.0.0)  CALL SCALE(X,X,X,0,XOR,XINC,LINES,N,L,BLANK)
      IF (YINC.LT.0.0)  GO TO 5
      IF (YINC.GT.0.0)  CALL AX(YINC,YOR,BLANK)
      IF (YINC.EQ.0.0)  CALL SCALE(Y,YP,YQ,NY,YOR,YINC,121,N,L,BLANK)
      IF (L.EQ.-1)  RETURN
      YPOR = YOR
      YQOR = YOR
      YPINC = YINC
      YQINC = YINC
      GO TO 104
    5 GO TO (101,102,103),NY
  103 CALL SCALE(YQ,YQ,YQ,1,YQOR,YQINC,121,N,L,PLUS)
  102 CALL SCALE(YP,YP,YP,1,YPOR,YPINC,121,N,L,STAR)
  101 CALL SCALE(Y,Y,Y,1,YOR,YINC,121,N,L,EX)
      IF (L.EQ.-1)  RETURN
  104 XVAL = XOR
C
C     GRAPH PLOTTING SEQUENCE BEGINS.
C
      NL = 1
      NP = 0
      DO 99  I = 1,LINES
C
C     INITIALIZATION OF PLOTTING VECTOR.
C
      ST = BLANK
      IF (I.EQ.1.OR.(NL.GT.N.AND.(I+4)/5*5.EQ.I+4).OR.I.EQ.LINES)ST=DASH
      DO 6  J = 2,120
      VEC(J) = ST
    6 CONTINUE
      VEC(1) = VERT
      IF ((I+4)/5*5.EQ.I+4)  VEC(1) = DASH
      VEC(121) = VEC(1)
      IF (ST.NE.DASH)  GO TO 8
      DO 7  J = 11,111,10
      VEC(J) = VERT
    7 CONTINUE
C
C     CHECKING IF NEXT UNPLOTTED X-VALUES ARE WITHIN CURRENT RANGE.
C
    8 IF (NL.GT.N)  GO TO 12
      DO 10  J = NL,N
      IF ((ABS(X(J) - XVAL)).LE.(XINC/2.0))  GO TO 9
      GO TO 11
    9 NP = J
   10 CONTINUE
   11 IF (NL.GT.NP)  GO TO 12
C
C     LOADING OF PLOTTING VECTOR
C
      GO TO (201,202,203),NY
  203 CALL POSY(YQ,NL,NP,YQOR,YQINC,VEC,PLUS,N)
```

```
  202 CALL POSY(YP,NL,NP,YPOR,YPINC,VEC,STAR,N)
  201 CALL POSY(Y,NL,NP,YOR,YINC,VEC,EX,N)
      NL = NP + 1
C
C     PRINTING OF PLOTTING VECTOR
C
   12 IF ((I+4)/5*5.EQ.I+4.OR.ST.EQ.DASH)  GO TO 13
      WRITE (6,100) VEC
      GO TO 14
   13 WRITE (6,200) XVAL,VEC
   14 IF (ST.EQ.DASH.AND.I.NE.1)  GO TO 15
   99 XVAL = XVAL + XINC
  100 FORMAT (' ',11X,121A1)
  200 FORMAT (' ',1PE11.4,121A1)
   15 RETURN
      END
C
C
      SUBROUTINE POSY(Y,NL,NP,YOR,YINC,VEC,SAVE,N)
C
C
C     LOADS PLOTTING VECTOR WITH APPROPRIATE CHARACTERS.
C
      DIMENSION Y(N)
      INTEGER*2 SAVE,VEC(121),STAR,PLUS,EX,O
      DATA O/'O'/,STAR/'*'/,PLUS/'+'/,EX/'X'/
      DO 2  J = NL,NP
      YPS = 1.0 + (Y(J)-YOR)/YINC
      JY = INT(YPS)
      IF ((YPS-AINT(YPS)-0.5).GT.0.0)  JY = JY +1
      IF (JY.LT.1.OR.JY.GT.121)  GO TO 2
      IF (VEC(JY).EQ.EX.OR.VEC(JY).EQ.STAR.OR.VEC(JY).EQ.PLUS.OR.VEC(JY)
     1.EQ.O)  GO TO 1
      VEC(JY) = SAVE
      GO TO 2
    1 VEC(JY) = O
    2 CONTINUE
      RETURN
      END
```

```
C
C
      SUBROUTINE SCALE(Y,YP,YQ,NY,YOR,YINC,LINES,N,L,ST)
C
C
      IF (L.EQ.-1)  RETURN
      DIMENSION Y(N),YP(N),YC(N),ASCALE(5),YA(6)
      INTEGER*2 ST
      DATA ASCALE/10.0,20.0,25.0,40.0,50.0/
      ALINE = FLOAT(LINES) - 1.0
      BSCALE = 0.0
      NY1 = NY + 1
C
C     BRANCHING TO DETERMINE RANGE.
C
      YMAX = Y(N)
      YMIN=Y(1)
      GO TO (104,101,102,103),NY1
  101 DO 1  I = 1,N
      YMAX = AMAX1(YMAX,Y(I))
      YMIN = AMIN1(YMIN,Y(I))
    1 CONTINUE
      GO TO 104
  102 DO 2  I = 1,N
      YMAX = AMAX1(YMAX,Y(I),YP(I))
      YMIN = AMIN1(YMIN,Y(I),YP(I))
    2 CONTINUE
      GO TO 104
  103 DO 3  I = 1,N
      YMAX = AMAX1(YMAX,Y(I),YP(I),YQ(I))
      YMIN = AMIN1(YMIN,Y(I),YP(I),YQ(I))
    3 CONTINUE
  104 YRANGE = YMAX - YMIN
      IF (YRANGE.EQ.0.0)  GO TO 10
      YOR = YMIN
      IF (L.EQ.1)  GO TO 7
C
C     DETERMINATION OF INCREMENT.
C
      YRLOG = ALOG10(YRANGE)
      JEXP = INT(YRLOG)
      IF (YRLOG.LT.0.0.AND.FLOAT(JEXP).NE.YRLOG)  JEXP = JEXP - 1
      DO 4  I = 1,5
      SINC = (ASCALE(I))*YRANGE/10.0**JEXP
      IF (SINC.GT.ALINE)  SINC = SINC/10.0
      IF (SINC*10.0.LE.ALINE) SINC = SINC*10.0
      IF (SINC.LE.ALINE) BSCALE = AMAX1(BSCALE,SINC)
    4 CONTINUE
      YINC = YRANGE/BSCALE
C
C     DETERMINATION OF ORIGIN.
C
      YL = ALOG10(YINC)
      IEXP = INT(YL) + 1
      IF (YL.LT.0.0.AND.FLOAT(IEXP).NE.YL)  IEXP = IEXP - 1
```

```
      DO 6  I = 1,2
      ORIG = 10.0**(I-1)*AINT(YMIN/10.0**(IEXP+I-1)*1.0001)
      IF (ORIG.EQ.0.0)  GO TO 5
      IF (YMIN.LT.0.0.OR.(YMIN/ORIG.LT.1.0001.AND.YMIN/ORIG.GT.0.99999))
     1ORIG = ORIG - 10.0**(I-1)
    5 AYOR = 10.0**IEXP*ORIG
      IF (((YMAX-AYOR)/YINC).LE.ALINE)  YOR = AMIN1(YOR,AYOR)
    6 CONTINUE
      IF (.NOT.(YMAX.GT.0.0.AND.YMIN.LT.0.0))  GO TO 8
      A = 10.0
      IF (NY.EQ.0)  A = 5.0
      ORIG = A*(AINT(-1.0001*YMIN/(YINC*A))+1.0)
      IF ((YMAX/YINC+ORIG+1.0).LE.ALINE)  YOR = -YINC*ORIG
      GO TO 8
    7 YINC = YRANGE/ALINE
    8 IF (NY.EQ.0)  GO TO 11
C
C     PRINTING OF Y-SCALE
C
      ENTRY  AX(YINC,YOR,ST)
      DO 9  I = 1,6
      YA(I) = YOR + YINC*(20.0*FLOAT(I) - 10.0)
    9 CONTINUE
      WRITE (6,500)  ST,YA
      GO TO 11
   10 L = -1
  500 FORMAT (' ',1X,A1,3X,'Y-AXIS IS',3X,1PE11.4,5(9X,1PE11.4))
   11 RETURN
      END
```

```
C
C     THIS IS A GENERAL PROGRAM FOR LEAST SQUARE POLYNOMIAL FIT
C     FORTRAN IV MODIFICATION OF UOI LSQI FOR 360 OPERATION,
C
C     DOUBLE PRECISION USED THROUGHOUT
C
C     LIST OF SYMBOLS USED FOR INPUT
C           N= NUMBER OF POINTS
C           M= NO. OF COEFFICIENTS OF POLY
C           N1= NO. OF ADDITIONAL POINTS AT WHICH EVALUATION OF FITTING
C               POLY. IS DESIRED.  MAX. N1=50
C           L= NO. OF DATA SETS TO BE FIT SIMULTANEOUSLY.  L=1-4
C           IEVAL= SIGNAL TO OUTPUT.  IF IEVAL>0, A TABLE OF THE INPUT
C                  DATA WITH POLY EVALUATIONS AND RESIDUALS IS PRINTED
C           X= INDEPENDENT VARIABLE
C           W= WEIGHTING FACTOR.  USE 1.0 FOR EQUAL WEIGHTING
C           Y= DEPENDENT VARIABLE
C           X1= EXTRA X AT WHICH POLY IS TO BE EVALUATED
C
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION A(20,15), B(20,4), X(500), Y(500,4), W(500), SUM(4),
     X          RESID(500,4), STD(15,4), EVAL(500), X1(50)
C
    1 READ (5,1000) N, M, N1, L, IEVAL
      IF (N) 1,1,2
    2 DO 3 I = 1,N
    3 READ (5,2000) X(I), W(I), Y(I,1),Y(I,2),Y(I,3),Y(I,4)
      IF (N1) 5,5,4
    4 READ (5,2000)(X1(I), I = 1,N1)
    5 CALL LSQ1(X,Y,W,RESID,N,SUM,L,A,B,M)
      DEG = N - M - 1
      DO 6 I = 1,M
      DO 6 J = 1,L
    6 STD(I,J) =DSQRT(SUM(J) * A(I,I)/DEG)
      WRITE (6,3000) N, M, N1, L
      DO 7 I = 1,M
    7 WRITE (6,4000) (A(I,J), J = 1,M)
      DO 8 J = 1,L
      WRITE (6,5000) (B(I,J), STD(I,J), I = 1,M)
      WRITE (6,6000) SUM(J)
      IF (IEVAL) 11,11,9
    9 DO 10 I = 1,N
   10 EVAL(I) = RESID(I,J) + Y(I,J)
      WRITE (6,7000) (X(I),W(I),Y(I,J),EVAL(I),RESID(I,J),I = 1,N)
   11 IF (N1) 8,8,12
   12 DO 13 I = 1,N1
   13 EVAL(I) = POLY(X1(I),M,B,J,20,4)
      WRITE (6,8000) (X1(I), EVAL(I), I = 1,N1)
    8 WRITE (6,9000)
      GO TO 1
 1000 FORMAT (12I6)
 2000 FORMAT (6D12.0)
 3000 FORMAT (48H1          LEAST SQUARE POLYNOMIAL FIT USING LSQ1  /
     X        3HON=I3,5H   M=I2,6H   N1=I2,5H   L=I2/13HOERROR MATRIX)
```

```
 4000 FORMAT (1H01P8D14.5)
 5000 FORMAT (37H0          COEFFICIENT              ERROR/(1H 1P2D20.7))
 6000 FORMAT (36HOWEIGHTED SUM OF SQUARED DEVIATIONS=1PD13.5)
 7000 FORMAT (70H0          X           WEIGHT           Y          EVALUATI
     XON      RESIDUAL/(1H 1P5D14.5))
 8000 FORMAT (29H0     EXTRA X      EVALUATION/(1H 1P2D14.5))
 9000 FORMAT (54H - - - - - - - - - - - - - - - - - - - - - - - - - - - - -)
      END
```

PROGRAM CONTINUES WITH
SUBROUTINE LSQ1
SUBROUTINE MATINV
REAL FUNCTION POLY
(SEE NERNST EQUATION LEAST
SQUARES PROGRAM)