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Technical Progress Report May 15, 1971 - May 14, 1972
and
Final Report

RESEARCH IN HIGH TEMPERATURE PHYSICAL CHEMISTRY

Principal Investigator: E. David Cater
Associate Professor
of Chemistry

Senior Investigator: H. Bruce Friedrich
Associate Professor
of Chemistry

Graduate Research Assistants: Terrance A. Rooney
Ronald G. Sommer

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Research in High Temperature Physical Chemistry

Final Report, Contract AT(11-1)-1182

May 15, 1962 - May 14, 1972

ABSTRACT

Investigations of transition metal, lanthanide, and actinide sulfides and oxides were carried out by five experimental approaches.

(1) X-ray diffraction studies at room temperature yielded lattice parameters and phase relationships for the solid phases ScS, YS, LaS, La_3S_4 , PrS, Pr_3S_4 , GdS, ZrS, US, UO_2 , UOS and their solid solutions. Equilibria between US, UO_2 , and UOS were studied at 1000-1500°C by a high temperature diffractometer.

(2) Vaporization studies by mass effusion and mass spectrometric techniques yielded enthalpies and entropies of formation of the above solid phases, heats of sublimation, and dissociation energies of the molecules ScS, YS, LaS, PrS, GdS, ZrS, US, UO, PrO, and UOS.

(3) Matrix isolation spectroscopy was used to determine vibrational frequencies and force constants for the molecules UO and UO_2 .

(4) High temperature solid state galvanic cells were used to measure the oxygen potentials of US-UOS- UO_2 mixtures and other metal-oxygen systems.

(5) The techniques of electron microscopy and electron diffraction were applied to mixed oxides of Ti, Ba, and Mg to investigate superlattice ordering in tunnel type structures.

Scientists trained as graduate assistants under the contract received seven Ph.D. and four MS degrees.

Final Technical Progress Report
Contract AT-(11-1)-1182
May 15, 1962 - May 14, 1972

The program under this contract had two purposes: (1) The study of chemical systems at high temperatures (roughly 500 to 2500°C) and (2) The training of scientists in the techniques of research at high temperatures. This report is in four parts: I. A summary of technical progress on high temperature systems; II. A listing of graduate students who have worked under this contract and their most recently available addresses and types of work; III. A list of publications and project reports; IV. A financial report for the final year May 15, 1970 to May 14, 1972.

I. Technical Summary, May 15, 1962 - May 14, 1972

A laboratory was organized and equipped during the decade of this contract, with the joint support of the University of Iowa and the AEC, in which several interrelated areas of high temperature chemistry were pursued. The largest effort was expended on the study of vaporization processes of transition metal and lanthanide monosulfides by Knudsen and mass spectrometric means, and spectroscopy of the high temperature molecules by matrix isolation techniques. However, reactions were studied in the $\text{US-UO}_2\text{-UOS}$ solid phase system by emf techniques and high temperature x-ray diffraction. Most recently interest has settled on the solid state emf technique and the use of the high resolution electron microscope for delectron diffraction and lattice imaging of refractory oxides.

A. Equipment purchased, constructed, and adapted specifically for these uses has included the following.

1. A Bendix model 12-101 time-of-flight mass spectrometer, equipped for interchangeable use with Bendix Knudsen cell assembly or the Knudsen cell assembly for the matrix isolation apparatus. This instrument is equipped to make effusion studies of the vaporization processes of refractory materials from room temperature to 2800°C.

2. A stable, well-regulated electron bombardment power supply capable of heating the Knudsen cell in the mass spectrometer or matrix isolation apparatus to approximately 2800°C.

3. A 25 KW Thermonic induction heating generator, equipped with continuously variable saturable reactor control, and capable of operating at either 250 kilocycles or 7 megacycles. This unit supplies power for heating our high temperature emf cell. Suitable vacuum apparatus is constructed adjacent to the generator for making effusion measurements or preparing and annealing samples.

4. An Ainsworth semi-micro vacuum balance equipped for continuous recording of weight, and adapted for use with the induction furnace in making effusion measurements on refractory materials or other thermogravimetric studies.

5. Two calibrated Leeds and Northrup optical pyrometers capable of precise temperature measurements in the range 800 to 3000°C.

6. A North American Philips X-ray diffraction unit equipped with Debye-Scherrer cameras, room temperature diffractometer, a high temperature diffractometer attachment capable of operating with samples in vacuum or inert atmosphere from room temperature to above 1500°C, and a Guinier-DeWolff Quadruple Focusing X-ray Camera.

7. A metal high vacuum furnace system built for high temperature ~~emf~~ studies. This is equipped with a Cary Model 31-CV vibrating reed electrometer, for measuring potentials of solid state galvanic cells and small currents in coulometric studies.

8. An Andonian Associates modular liquid helium dewar with variable temperature tail with sample mounted on the cold finger outside of liquid helium, and with 360° rotary joint on outer tail and 1" height adjustment. This dewar has been fitted by us with a Knudsen cell assembly capable of attaining 2500°C in the cell for vaporizing refractory solids and depositing the vapors on the cold window in matrix isolation studies. The units are mounted on a manually operated hydraulic lift, fitted with wheels.

9. A Supairco storage and transfer dewar of 25 liter capacity for liquid helium, with transfer tube, also mounted on a manually operated hydraulic lift.

10. An Air Products and Chemicals, Inc. Model AC-3L Cryotip liquid hydrogen refrigerator which produces the liquid from compressed gas by Joule-Thompson expansion. The Knudsen cell assembly described above may be interchangeably attached to the helium dewar, the Cryotip, or the mass spectrometer. The Cryotip apparatus is light enough to be manually set in place in the spectrophotometers.

11. Departmental spectrophotometers used in the matrix isolation work included a Beckman IR-11 with capabilities for operating in the range 33 to 800 cm^{-1} and a Perkin Elmer Model 421 for use from 600 to 4000 cm^{-1} .

12. Available for use in this project in the Botany Department, which shares the same building with the Chemistry Department, is a Hitachi HU-12 electron microscope, installed in November, 1971. This instrument is capable

of $2\text{\AA}$ (lattice) or $3\text{\AA}$ (point to point) resolution, and is now (1973) in use with a tilting goniometer stage for electron diffraction and lattice imaging.

B. Mass spectrometric and vaporization studies.

High temperature mass spectrometric and Knudsen cell studies of the vaporization of refractory sulfides (1-7) were carried out for the determination of heats of formation and entropies of the solids and dissociation energies of transition metal and lanthanide monosulfides and monoxides, specifically SrS, US, LaS, YS, ZrS, ScS, GdS, PrS, PrO, and UO. The purpose was to demonstrate the existence and stability of such monosulfide molecules and to compare their properties with corresponding oxides. Prior to the principal investigator's own thesis research (8-9) on the sublimation of solid US, it had been predicted that such gaseous sulfide species would not be stable enough to exist in appreciable quantities in high temperature vapors. The studies showed that the monosulfides of transition, lanthanide, and actinide metals are quite stable, and have dissociation energies of approximately 65 to 75% those of the corresponding monoxides. The actual dissociation energies ranged from 114 to 137 kcal/mole or 4.8 to 5.8 electron volts. Other workers, particularly Drowart and his co-workers in Brussels (10-12) pursued dissociation measurements simultaneously with ours, using isomolecular equilibrium studies. However by also performing direct sublimation experiments we were able to determine heats of sublimation and heats of formation of the solid phases. More recently Gilles and his colleagues at Kansas University (13-15) have produced similar work. Table 1 Summarizes some of these data.

Table 1

Comparison of Dissociation Energies of Monosulfides and Other Thermochemical Data for Monosulfides

Dissociation energies of monosulfides are preferred values from work under this contract. In each case the uncertainty expressed is a limit of accuracy obtained by considering all experimental uncertainties in this work and values obtained from the literature. Dissociation energies of monoxides are taken from the reviews by L. Brewer and G. Rosenblatt, Advances in High Temperature Chemistry, L. Eyring, editor, Academic Press, Vol. 2, 1970, pp. 1ff. Reference numbers refer to the list at the end of this section of this report. Dissociation energies of monoxides determined in this project are also listed with the notation (this work). The enthalpies of formation $\Delta H_{f,298}^{\circ}$ are for the reaction $M(s) + S(rh) = MS(s)$ at 298.15 K. The enthalpies of sublimation $\Delta H_{sub,T}^{\circ}$ refer to the reaction $MS(s) = MS(g)$ at the mean temperature indicated.

Table 1

Compound and Ref. no.	D_o (MS) kCal/mole (This work)	D_o (MO) kCal/mole (Brewer & Rosenblatt)	D_o (MS)/ D_o (MO)	ΔH_f^{298} (MS) kcal/mole	ΔH_{sub} (MS) kcal/mole
SrS ⁴	80+ <u>4</u>	92+ <u>6</u>	0.87+ <u>.08</u>	-108+ <u>4</u>	124+ <u>4</u> , 2000K
ZrS ⁶	137.4+ <u>3.5</u>	180+ <u>10</u>	0.76+ <u>.06</u>		
ScS ⁶	113.5+ <u>3.0</u>	154+ <u>5</u>	0.74+ <u>.04</u>		
YS ⁵	125.4+ <u>2.5</u>	161+ <u>5</u>	0.78+ <u>.04</u>	-110+ <u>3</u>	142.9+ <u>2.5</u> , 2250K
LaS ^{2,3}	136.0+ <u>3.9</u>	187+ <u>5</u>	0.73+ <u>.03</u>	-108+ <u>4</u>	131.5+ <u>3.0</u> , 2240K
PrS ⁷	120.0+ <u>4.0</u>	179+ <u>8</u>	0.67+ <u>.06</u>		
		179.5+ <u>4.0</u> (this work)			
GdS ⁷	124.5+ <u>-3.5</u>	161+ <u>6</u>	0.77+ <u>.05</u>	-113+ <u>6</u>	138.8+ <u>4.0</u> , 2150K
US ¹	124.0+ <u>2.3</u>	181+ <u>8</u>	0.69+ <u>.05</u>		142.0+ <u>2.3</u> , 2020K
		181.1+ <u>3.5</u> (this work ⁶)			

C. Spectroscopic studies of high temperature molecules by matrix isolation techniques.

This work was aimed at obtaining molecular parameters and ground state degeneracies of high temperature molecules produced by the vaporization of refractory oxides and sulfides of the transition, rare-earth, and actinide metals, and certain other interesting materials. Such information enables accurate calculation of the thermodynamic properties of the molecules and force constants and gives some insight into their electronic energy levels and the nature of their chemical bonding. The work was supervised jointly by E. David Cater and H. Bruce Friedrich. The Ph.D. theses of Herbert J. Leary (1971) and of Terrance A. Rooney, resulted from this work, which was completed in the summer of 1972, following the termination of this contract. The technique consisted in vaporizing the molecules of interest from a Knudsen cell at an appropriate temperature and allowing them to impinge on an optical window cooled to a temperature near 10°K by liquid helium or near 20°K by liquid hydrogen. Simultaneously a large excess (mole ratio 100/1 to 10,000/1) of inert gas, argon or krypton, was sprayed onto the window. The result was a solid matrix of inert gas in which the high temperature molecules were held at separations sufficient to minimize any interactions, but at concentrations high enough to permit spectroscopic study. By this technique one can obtain fundamental information on molecules which cannot be isolated in any other way for spectroscopic study.

Two cryostats were used to provide for cooling the low temperature window, an Andonian Associates liquid helium cryostat and an Air Products Co. Cryotip hydrogen refrigerator. The former provided lower temperatures

but was expensive and less convenient to use because of the price of liquid helium trucked to Iowa City from Chicago and because each filling of the 3 liter helium dewar permitted a duration of only two hours per experiment. The Cryotip operates by the cooling effect of the Joule-Thompson expansion of gaseous hydrogen, which is inexpensive and conveniently permits experimental runs of many hours duration.

Our Knudsen cell assembly fit into a water-cooled, stainless steel housing attached to the tailpiece of the cryostat. The Knudsen cell was heated by radiation and electron bombardment from an adjacent filament (16).

As an example of typical operating conditions, for the studies of $\text{UO}(\text{g})$ mixtures of $\text{U}(\text{l}) + \text{UO}_{2-x}(\text{s})$ or pure $\text{UO}_2(\text{s})$ were vaporized at temperatures from 2200 to 2600°K, which correspond to partial pressures of $\text{UO}_2(\text{g})$ in the range 1×10^{-6} to 2×10^{-4} atm.

The Knudsen cell assembly could be attached either to the cryostat or to a Bendix time-of-flight mass spectrometer, so that both the mass spectrum and the optical spectrum could be obtained from the same sample in the Knudsen cell. Identification of the gaseous molecules in this way is a tremendous advantage in interpreting the optical data, and is unavailable to most workers in the field. However, one must be careful, as we found from experience, not to expect the same relative intensities of mass spectral and IR spectral peaks from various vapor species. For infrared spectroscopy, we used a Perkin-Elmer Model 421 spectrophotometer in the range 600 to 4000 cm^{-1} , and a Beckman Model IR-11 spectrophotometer in the range 33 to 800 cm^{-1} .

Work in this area in this laboratory through spring, 1971 on the molecules UO and UO_2 was summarized in a paper (16) published in 1971. Terrance A. Rooney continued work in this area on molecules in the uranium-oxygen and several transition metal-sulfur systems in the summer of 1971 and again during

the summer of 1972, at the end of which he completed his Ph.D. thesis (17). He was supported by this AEC contract during the summer of 1971 and by NSF grant GP-33457 during summer, 1972. The spectral interpretation of our work in 1971 was in agreement with that of other workers who independently published almost simultaneously (18). Subsequently, however, Gabelnick, et al. (19) and Carstens, et al. (20) at Argonne National Laboratory, using, respectively, Knudsen cell and hollow cathode discharge sources of molecules, and matrix isolation detection similar in nature to ours, presented new interpretations of the UO and UO₂ spectra.

Table 2

IR Spectra of UO and UO₂ Molecules Trapped in Argon at 20°K

Frequency (cm ⁻¹)	Assignment
819.1	U ¹⁶ O
775.2 (calc.)*	U ¹⁸ O
775.6 (Satellite at 778.6)	U ¹⁶ O ¹⁶ O ν_3 asym. stretch
770.6	U ¹⁶ O ¹⁸ O ν_3 " "
736.4 (Satellite at 739)	U ¹⁸ O ¹⁸ O ν_3 " "
728.1	U ¹⁶ O ¹⁸ O ν_1 sym. stretch

*This band could not be observed because it was hidden under the strong band at 775.6 due to U¹⁶O¹⁶O.

The bending mode ν_2 was not observed down to 100 cm⁻¹. The O-U-O angle, calculated from isotopic shifts and supported by relative intensities of the isotopic bands under the assumption of very low ν_2 , is $160 \pm 20^\circ$. Force constants calculated from the absorption frequencies are as follows. For UO, $f=5.92$ mdyn/ $\overset{\text{O}}{\text{A}}$, for UO₂, $f_{11}=5.25$ mdyn/ $\overset{\text{O}}{\text{A}}$ (stretching force constant) and $f_{12}=0.24$ mdyn/ $\overset{\text{O}}{\text{A}}$ (stretch-stretch interaction).

Rooney's most recent results, obtained from samples of UO_2 containing isotopic mixtures of oxygen-16 and -18, are summarized in Table 2. They are in excellent agreement with the results of Gabelnick and Carstens. An interesting feature of the spectra is that the isotopic splitting of ν_3 gives two bands close together and a third distant from them, rather than three bands more or less evenly spaced. This is due to the massive central uranium atom, which crudely can be thought of as uncoupling the vibrational modes of the two U-O bonds. The vibrational peak of UO turned out to be much weaker relative to those of UO_2 than was expected from mass spectrometric analysis of the vapor effusing from the Knudsen cell (8), and this led to our original incorrect interpretation.

Our studies of gaseous monosulfides were particularly frustrating because no bands were obtained in the infrared spectra from 100 to 4000 cm^{-1} which were attributable to the monosulfide species. Our mass spectra (1-7) showed that sublimation of US(s) , YS(s) , LaS(s) , GdS(s) , ScS(s) , and PrS(s) in the range 2000 to 2500°K gives vapor containing suitable concentrations of MS molecules.

Yet we were unsuccessful in obtaining their infrared spectra, even though we have operated in vapor pressure ranges similar to those successfully studied in the cases of UO and UO_2 , using the same techniques and apparatus, and materials from which the mass spectra show monosulfide vapor species, in concentrations of monosulfide molecules relative to the elemental metal atoms in the molecular beam from 9/1 to 1/3. Only in the case of YS was any absorption attributable to a monosulfide observed, namely a broad, totally absorbing band in one experiment, centered around 485 cm^{-1} . In the cases of $\text{La}_2\text{S}_3(\text{s})$ and $\text{Pr}_2\text{S}_3(\text{s})$ which yield a particularly high sulfur

partial pressure, a number of bands near 370, 490, 516, 550, and 650 to 670 cm^{-1} were observed. Very recently, Meyer and Stroyer-Hansen (21) attributed bands at 668, 483, 320, and 270 cm^{-1} to S_4 molecules formed by the irradiation with visible light of krypton matrices containing trapped S_2 molecules, so that sulfur polymers probably account for the bands we observed. Other workers (22) have recently been able to obtain ESR spectra of matrix isolated ScS, YS, and LaS, and the IR spectra of ScS (554 cm^{-1}) and of YS (483 cm^{-1}), the latter confirming our datum on YS. Attempts to obtain IR spectra of other sulfides were unsuccessful. A gas phase value of 457 cm^{-1} for the vibrational frequency of LaS was obtained by Marcano and Barrow (23), by analysis of the electronic spectrum from tube furnace containing La and ZnS and heated to 2000°C.

D. Electron Microscopic Studies of Nonstoichiometric Compounds.

The principal investigator spent the six month period March-August, 1971, in the Inorganic Chemistry Laboratory of Oxford University in the research group of J. S. Anderson, learning the techniques of electron microscopy and electron diffraction. Support was provided in the spring semester, 1971, by a Faculty Research Assignment from The University of Iowa and during the summer, 1971, by this AEC contract. Since the termination of this contract, May, 14, 1972, equipment has been obtained from NSF and University sources to enable the principal investigator to continue working in this area at the University of Iowa.

The application of electron optical techniques to the study of thin crystal sections is the most powerful tool available for studying short range lattice ordering in "nonstoichiometric" compounds. X-ray and neutron diffraction determine an average structure over the entire crystal or powder studied, and only by detailed analysis of diffusely scattered radiation can one obtain information on short range ordering (24). The chief advantages of the electron microscopic technique as compared to x-ray or neutron

diffraction are four.

First, the transmission or dark field images and diffraction patterns can be examined visually on the fluorescent screen so that interesting crystals and interesting areas of crystals can be chosen and oriented for photographic recording with great convenience.

Second, dark field techniques show up domains in the crystal, which have different structures or orientations, with striking clarity.

Third, diffraction patterns from different domains only a few hundred Angstroms in dimension can be obtained by the "selected area" technique, so that one can obtain structural data on smaller samples than by any other technique.

Fourth, lattice fringe-imaging is a technique which superimposes on the micrograph image a sequence of alternating dark and light bands, blocks, or patterns, whose spacings and geometry give directly the spacings and geometry of major structural features in the crystal lattice.

The combination of lattice fringe-imaging with selected area diffraction has had its most spectacular success in the elucidation of the crystallographic shear structures by which changing stoichiometry is accommodated in lattices which are made up of repeated layers of metal-oxygen octahedra, so that the unit cell dimensions are large in the 2-dimensional layers and short in the direction normal to them. For example, in slightly reduced rutile ($\text{TiO}_{1.90}$ - $\text{TiO}_{1.999}$) and rutile doped with various M^{+3} cations, the oxygen vacancies are segregated into shear planes rather than isolated defects (25,26). Effectively the result is at least two structural homologous series of formula $\text{Ti}_n\text{O}_{2n-1}$ ($n=10-100$ or so) in a composition region where x-ray studies had only revealed a single, "nonstoichiometric" phase region (27).

A large number of series of block structures based on the ReO_3 -type structure of WO_3 and MoO_3 , and the related Nb_2O_5 structure has similarly been elucidated by these techniques (28,29). Iijima and Cowley (30) have obtained lattice images of some of these Nb-O structures of such high resolution that a prejudiced observer can convince himself that he is looking at a picture of the actual octahedra in the blocks of octahedra in a given lattice sheet. These and other studies on crystallographic shear in oxides are reviewed by Tilley (31). An example of the application of electron diffraction and dark field techniques is the discovery by Watanabe, et al. (32) of ordering of Ti and O vacancies in TiO (basically the NaCl-type structure) to give a monoclinic phase at $\text{TiO}_{1.00}$ and a new tetragonal phase at $\text{TiO}_{1.25}$, previously not found in x-ray work because of their existing as intergrown regions in single crystals.

A study was begun in Oxford of a series of samples with the formula $\text{Ba}_x(\text{Ti}_{8-x}\text{Mg}_x)\text{O}_{16}$ (where $1.2 \leq x \leq 7$) and some progress was made after returning to Iowa toward interpretation of micrographs and electron diffraction patterns brought back from Oxford. These synthetic compounds are isostructural with several manganese and titanium minerals (33), including hollandite $[\text{A}\text{Mn}_8\text{O}_{16}]$, where A is one of the ions Ba^{+2} , K^+ or Pb^{+2} , cryptomelane $[(\text{K},\text{Ba})_{1.1}\text{Mn}_{7.0}(\text{Mn}^{+2}, \text{Al}, \text{Mg}, \text{Na})_{1.0}\text{O}_{16}]$ and priderite $[(\text{K},\text{Ba},\text{Na})_{1.3}(\text{Ti}_{6.5}(\text{Fe},\text{Al})_{1.5})\text{O}_{16}]$. The structure, shown in Figure 1, consists of columns of edge-shared MO_6 octahedra arranged in a framework penetrated by tunnels which contain the alkali and alkaline earth ions. These ions presumably occupy sites along the axes of the tunnel walls. It is not known with certainty whether the sites are occupied randomly throughout all the tunnels, whether there is local ordering involving adjacent tunnels, or whether some tunnels are empty and others are filled, and in this last case, whether the filled

Figure 1

Structure of $\text{Ba}_x(\text{Ti}_{8-x}\text{Mg}_x)\text{O}_{16}$ [the Hollandite Structure] Projected Along the Tunnel Axis.

Unit cell is outlined with dashed line. Each octahedron contains one Ti^{+4} or Mg^{+2} ion at its center and 6 O^{2-} ions at the vertices. Octahedra are connected by sharing either two oxygens (edge in common) or one oxygen (vertex in common). Heavily outlined octahedra are centered one half unit cell higher than lightly outlined ones. The Ba^{+2} ions occupy positions along the tunnels, presumably equidistant from eight oxygens in the octahedra forming the tunnel walls. Ordering of the Ba^{+2} ions in the tunnels is not completely understood. Lattice parameters from Guinier x-ray patterns are monoclinic, $a=10.19$, $b=2.972$, $c=10.04 \text{ \AA}$, $\beta=90.41^\circ$. Natural priderite ($\text{Na}_{.14}\text{K}_{.87}\text{Ba}_{.32})(\text{Ti}_{6.48}\text{Fe}_{1.14}\text{Al}_{.33})\text{O}_{16}$ is tetragonal with $a=10.148 \pm 0.005$ and $c=2.965 \pm 0.003 \text{ \AA}$. Dryden and Wadsley (33) prepared $\text{Ba}_x(\text{Ti}_{8-x}\text{Mg}_x)\text{O}_{16}$ in a tetragonal form with $a=10.110$ and $c=2.986 \pm 0.005 \text{ \AA}$.

Figure 1

and empty tunnels are ordered or random. Hopefully, the answers will be forthcoming from the electron microscope data.

Dryden and Wadsley, (34) prepared $\text{Ba}_x(\text{Ti}_{8-x}\text{Mg}_x)\text{O}_{16}$ ($1.14 > x > 0.67$) by a flame fusion technique from mixed, powdered oxides, obtaining large aggregates of oriented crystals which were annealed in oxygen at 1000°C . X-ray data gave the same structure for all compositions with diffuse features which were thought to indicate possible short range ordering of ions in adjacent tunnels. Measurement of dielectric absorption in directions parallel and perpendicular to the tunnels were interpreted in terms of movement of Ba^{+2} ions from eight-coordinated sites to adjacent unoccupied sites of a similar kind along the tunnels. However, the measurements could not distinguish between like population of all tunnels or partial population of some tunnels with other tunnels either full or empty.

The question of occupancy of the tunnels can best be answered by electron microscopy/electron diffraction. Ideally one might hope to obtain lattice fringe-images projected along the tunnel direction which might show some filled and some empty tunnels. Indeed, such lattice images have been obtained by Iijima for some tungsten bronzes (30). To date, however, Iijima's lattice images surpass all others, and the present data do not permit of such elegantly simple interpretation. Evidence has been found in various crystals of superlattice formation with the new unit cell of twice the dimensions of the fundamental cell (see the legend of fig. 1 for lattice parameters). Other crystals have a more complex ordering with a superlattice of lower symmetry, which still has to be worked out.

Other studies to be pursued are related to the structures and ordering of solid state electrolyte materials (see next section) and oxide contaminated monosulfides.

E. High Temperature EMF Measurements in the Titanium-Oxygen and Other Systems

The use of solid state galvanic cells of the type $\text{Pt, M, MO}_x \mid \text{solid electrolyte} \mid \text{N, NO}_y, \text{Pt}$ for the determination of the difference in partial pressure (or chemical potential) of oxygen in two metal-oxygen systems at elevated temperatures is by now well known. Extensive reviews by Etsell and Flengas (34) have given particular attention to the role and limitations of the electrolyte, and one by Rapp (35) emphasizes experimental aspects of the technique. In the above generalized cell M and N represent different metals or different oxidation states of the same metal, and x and y are stoichiometric numbers denoting the oxide formulas. The solid electrolyte is one which conducts solely by ionic, usually $\text{O}^{=}$, migration. The most commonly used oxide electrolytes are ZrO_2 containing 10 to 20 mole percent CaO , and ThO_2 containing 5 to 8 mole percent Y_2O_3 or La_2O_3 . Numerous other oxide solid solutions have been employed. However, stabilized zirconia, $\text{ZrO}_2(\text{CaO})$, and doped thoria, $\text{ThO}_2(\text{Y}_2\text{O}_3)$, are the most used because of their own extremely low oxygen partial pressures and very high melting points, because of their commercial availability in the form of flat-bottomed tubes and other shapes, and because together they provide essentially pure conduction by $\text{O}^{=}$ ion migration over the range in P_{O_2} from 1 atm to perhaps 10^{-25} to 10^{-34} atm at 1000°C (34,35).

The emf of the generalized cell above is related to the oxygen potentials by $E = \Delta G/2F = -(RT/2F) \ln [P_{\text{O}_2}(\text{N, NO}_y)]^{1/2} / [P_{\text{O}_2}(\text{M, MO}_x)]^{1/2}$. Compositions of single phase electrode pellets can be changed by coulometric titration of oxygen from the reference electrode through the electrolyte. From the known oxygen potentials and partial pressures of one electrode system (the reference electrode) as a function of temperature, one can then calculate the partial molar free energies of metal and oxygen in the other electrode phases.

at a given composition, and can integrate over a range of compositions to obtain the integral molar free energies and other desired thermochemical information.

In this laboratory Yuill and Cater (36) measured oxygen potentials in solid mixtures of US, UOS, and UO_2 by means of high temperature emf cells and studied some cells involving Ta, Ta_2O_5 and Nb, NbO_2 electrodes. In the summer of 1971, Mr. Ronald Sommer took up the problem of a study of the titanium oxides Ti_3O_5 , Ti_2O_3 , and TiO_{1+x} . After some experiments with Yuill's apparatus, he decided to abandon it and designed an entirely new high vacuum furnace for emf studies. The design is somewhat like those which Fender and Riley used in studying the three sub-regions of the "FeO" (Wustite) phase (37) and those in the "MnO" phase (38).

During the present contract period, Mr. Sommer completed the design and began construction of the vacuum furnace, which is shown in Figure 2. The apparatus has since the end of the contract been completed and tested. A six-inch diffusion pump, using polyphenylether pump fluid and equipped with a chevron-type baffle, cooled by liquid nitrogen, evacuates a water-cooled brass chamber, within which the emf cell is supported and heated by radiation from a hot tantalum sleeve of 2 in. diameter and 12 in. length. The sleeve is heated by high frequency induction, with power supplied by a Thermonic 25 KW generator. Appropriate grounding and shielding are necessary to eliminate deleterious effects of the high frequency field on the measurement of the emf of the cell. The electrolyte is in the form of a commercially available tube with a flat bottom. Both calcia-stabilized zirconia and yttria-doped thoria tubes 1/2 in. O.D. by 18 in. length, obtained from Zirconia Corp. have been used.

One of the electrodes, in the form of mixed powders, loose or pressed into thin wafers, rests on a platinum disk in a recrystallized alumina cup.

Figure 2
High Temperature Solid State
EMF Apparatus

Figure 2

The Other electrode is contained inside the flat-bottomed electrolyte tube, which dips into or presses down on the first electrode powder or wafer. The bottom of the stabilized zirconia or doped-thoria tube serves as the solid electrolyte which transmits the oxygen potential. To avoid problems due to diffusion of the metal from the lower electrode into the electrolyte, a separate disk of electrolyte material can be placed between the bottom of the tube and the lower electrode powder or wafer. Such disks are fabricated by mixing the powdered oxides, pressing them at 40,000 psi and firing the disk at 1200°C in air followed by 2000°C in vacuum. Emf's are currently measured by a Cary vibrating reed electrometer at lower temperatures where cell resistance is high or a Rubicon potentiometer at higher temperatures. An electrometer with fast response and digital readout would greatly facilitate measurements particularly when it is desired to check response of the cell when the high frequency heating power is alternately turned on and off.

Because no one has previously reported successful emf studies in induction heated furnaces several experiments were performed to study possible effects of the high frequency field (250 khz) on the measurements. It appears that with additional shielding (not shown in Figure 2) the effects of the high frequency field is nullified. It appears then, that temperature and emf measurements at relatively high oxygen potentials are acceptable.

Further experiments since the close of the contract have attempted to explore the low oxygen potential regimes with Ni, NiO/Nb, NbO and Nb, NbO/Ta, Ta₂O₅ electrode systems. Polarization effects and some high frequency effects were traced to a gray coating which developed on electrode and electrolyte surfaces. This apparently was silicon (or Si + SiO or SiO₂)

which resulted from pyrolysis of silicone diffusion pump vapor at the tantalum heating sleeve. A twelve inch, liquid-nitrogen-cooled, chevron-type baffle was obtained from government surplus and installed between the diffusion pump and the furnace housing, and the silicone pump fluid originally used was replaced with Santovac polyphenyl ether fluid. At this writing, we are preparing to renew the experiments, beginning with a re-run of the Ta, $\text{Ta}_2\text{O}_5/\text{ThO}_2(\text{Y}_2\text{O}_3)/\text{Ta}, \text{Ta}_2\text{O}_5$ cell to check for temperature gradients and high frequency effects.

It should be quite possible for us to determine oxygen potentials in the two phase regions $\text{Ti}_2\text{O}_3\text{-Ti}_3\text{O}_5$, $\text{Ti}_3\text{O}_5\text{-Ti}_4\text{O}_7$, and $\text{Ti}_4\text{O}_7\text{-Ti}_5\text{O}_9$; we shall attempt $\text{Ti}_2\text{O}_3\text{-TiO}_{1+x}$ and the single phase region TiO_{1+x} , in order to establish experimentally the lower limit of usefulness of ThO_2 -based electrolytes. A Ta, Ta_2O_5 reference electrode will be used for $\text{Ti}_2\text{O}_3\text{-Ti}_3\text{O}_5$ and $\text{Ti}_3\text{O}_5\text{-Ti}_4\text{O}_7$, and the latter will be tried as reference electrode for TiO_{1+x} . The lower P_{O_2} limit of usefulness of ThO_2 -based electrolytes is not really known, and no successful attempts to use it at this low a value of P_{O_2} have been reported. Experimental materials will be examined both by x-ray diffraction (Debye-Scherrer and Guinier techniques) and by electron microscopy to determine the phases present on the scales of both long-range and short range ordering.

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II. Training of Graduate Students

Eleven scientists have received graduate degrees in physical chemistry in part as a result of work done under this contract. Several of these scientists are currently employed either directly in AEC-sponsored research or in the nuclear energy field.

1. Ernest W. Johnson, Ph.D., January, 1965, is employed at the Mound Chemical Laboratory of the Monsanto Chemical Company, Miamisburg, Ohio, which is primarily an AEC contractor. His section was involved in the SNAP program and is responsible for developing radiosotope heat sources for specific uses.

2. Thomas E. Lee, M.S., June, 1964, is presently employed by the Ethel Corp. in Detroit, and is doing research in foamed metals.

3. William A. Yuill, Jr., Ph.D., February, 1967, employed by Phillips Petroleum Co. at the National Reactor Test Station, Arco, Idaho.

4. Barbara Ann Holler, M.S., February, 1967, (now Mrs. Marvin M. Mueller) is currently doing high temperature chemical research at Los Alamos Scientific Laboratory.

5. Roger A. Steiger, Ph.D., June, 1967, is employed in research in ceramic materials by PPG Industries, Chemical Division, Barberton, Ohio.

6. Ronald P. Steiger, Ph.D., June, 1968, was formerly employed at the Mound Laboratory, Monsanto Research Corp., Miamisburg, Ohio, where he was working in high temperature mass spectrometry on AEC-sponsored projects, is now a research associate at Rice University.

7. Thomas A. Gregory, M.S., February, 1967, subsequently was a graduate assistant in the AECS radiation laboratory at Notre Dame University, South Bend, Indiana, where he received a Ph.D. degree.

8. James A. Fries, Ph.D., August, 1969, is now Associate Professor of Chemistry at Northern State College, Aberdeen, South Dakota.

9. Herbert J. Leary, Jr., Ph.D., January, 1971, is now employed by General Electric Corp. and is involved in studies of gas-surface reactions of fluorescent lamp materials.

10. Terrance A. Rooney, Ph.D., August, 1972, is seeking scientific employment in the Philadelphia area, where in the meantime he is teaching at the high school level.

11. Ronald G. Sommer, B.S., University of Wisconsin at Milwaukee, 1967, received the M.S. in May, 1971 and is currently completing Ph.D. research which was begun with support of this contract.

III. Publications and Reports

The following published papers summarize work performed at least in part with the support of the present contract.

1. H. J. Leary, R. J. T. A. Rooney, E. D. Cater, and H. B. Friedrich, "The Infrared Spectra of Matrix Isolated UO and UO_2 ", High Temperature Science, 3, (1971).
2. Ronald P. Steiger and E. David Cater, "The Preparation and Identification of the ZrS Phase in the Zirconium-Sulfur System", High Temperature Science, 2, 398 (1970).
3. D. Bonderman, E. D. Cater, and W. E. Bennett, "Vapor Pressures, Mass Spectra, Magnetic Susceptibilities, and Thermodynamics of Some Phthalocyanine Compounds", J. Chem. Engin. Data, 15, 396 (1970).
4. E. D. Cater, "Vapor Pressure Methods; Measurement of the Gross Equilibrium Vaporization Rate (Knudsen Methods)," Chapter 2A in R. A. Rapp, ed., Physiochemical Measurements in Metals Research (Vol. IV; part 1 of the series Techniques in Metals Research), Wiley-Interscience, New York (1970).
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6. E. D. Cater and R. P. Steiger, "Vaporization, Thermodynamics, and Dissociation Energy of Lanthanum Monosulfide. II", J. Phys. Chem., 72, 2231 (1968).
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The following reports are now being revised and will be submitted for publication at an early date.

1. R. A. Steiger and E. D. Cater, USAEC Report COO-1182-16, Feb. 10, 1967, "Vaporization, Thermodynamics, and Dissociation Energy of Yttrium Monosulfide".
2. R. P. Steiger and E. D. Cater, USAEC Report COO-1182-23, April 1, 1968, "Mass Spectrometric Determination of Dissociation Energies of High Temperature Molecules: ScS, YS, LaS, ZrS, UO".
3. J. A. Fries and E. D. Cater, USAEC Report COO-1182-27, April 3, 1969, "Mass Spectrometric Determination of the Dissociation Energies of PrS, GdS, and PrO".

IV. Financial Report for Final Contract Year May 15, 1972-May 14, 1973

This section is copied directly from Appendix C, Statement of Actual Costs, submitted to AEC in September, 1972.

1. Name and Address of Contractor:

University of Iowa
Iowa City, Iowa 52240

2. Contract Number: AT(11-1)-1182

3. Beginning and ending date of pertinent contract period:

May 15, 1971 through May 14, 1972

4. Support Ceiling for pertinent contract period: \$21,100.00

5. Article A-II (a) costs:

Cost Categories

a) Salaries and Wages:

Principal Investigator - Dr. E. D. Cater		
100% time for 2½ months		\$3,890.00
Senior Investigator - H. Bruce Friedrich		
20% time for 2½ months		772.00
Two Graduate Assistants:		
T. A. Rooney	\$1,405.00	
R. G. Sommer	<u>3,853.13</u>	5,258.13

b) Supplies and Materials including Liquid Helium, Hydrogen Gas, Refractory Metals, and Chemicals		1,722.40
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c) Equipment:

1 CRYO-TIP Model AC-2L Refrigerator		2,635.00
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d) Publications	- 0	- 0 -
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e) Travel:

Domestic	556.23	
Foreign	<u>- 0 -</u>	556.23

f) Other:

Office Expense	147.19	
Machine Shop Services	621.49	
Repairs	78.45	
Fringe Benefits	<u>466.20</u>	1,313.33

g) Total Direct Costs		<u>16,147.09</u>
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h) Indirect Costs

38.5% x \$3,890.00	1,497.65	
57.3% x \$6,030.13	<u>3,455.26</u>	<u>4,952.91</u>

i) Total Project Costs		<u>\$21,100.00</u>
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APPENDIX C (continued)

5.	j) Total Costs Chargeable to AEC:		
	100% of (i) - Same as Support Ceiling		<u>\$21,100.00</u>
6.	A-II (b) Items to be Furnished by University:		
	Liquid Nitrogen	\$ 300.00	
	Glass Shop Services, Electronic		
	Parts, Supplies	<u>150.00</u>	<u>\$ 450.00</u>

Oral Presentations of work done under this contract have been given at:

Iowa State University, Ames

Illinois Institute of Technology, Chicago

Argonne National Laboratory

National Bureau of Standards

PPG Industries, Chemical Division, Barberton, Ohio

American Chemical Society National Meetings

Gordon Conferences on High Temperature Chemistry

Midwest High Temperature Chemistry Conferences

Northern State College, Aberdeen, South Dakota

Dordt College, Sioux Center, Iowa

Central College, Pella, Iowa

Wisconsin State University, Platteville

Sioux Valley Section, American Chemical Society

Iowa Academy of Science Annual Meetings