



Natural convection high temperature oxidation of iridium
by Hal Gene Kraus

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of
MASTER OF SCIENCE in Mechanical Engineering
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Abstract:

The experimental study of the natural convection oxidation of iridium was performed at temperatures of 1600, 1900, and 2200°C and pressures ranging- from 0.00132 to 1.32 atmospheres. A theoretical model describing the surface, recession rate was derived assuming that the rate was controlled by the diffusion of Ir, IrO₂, and IrO₃ through the gaseous boundary layer, adjacent to the iridium specimen. Average values for the standard state enthalpy and entropy changes for the formation of IrO_g and IrCh were calculated for the 1600 to 2200 °C temperature range. A value for the partial pressure of Ir at 22000C was found. Correlation between experiment and the theoretical model was good with the overall mean % error of experimental rates from theoretically predicted rates being 13.3% for the 1600 to 22000C range.

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A thesis submitted to the Graduate Faculty in partial
fulfillment of the requirements for the degree

of

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in

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NOMENCLATURE

Symbols

A, Effective equivalent weight equal to 192.2 gms of iridium consumed per gm mole of oxide formed divided by the density of the iridium

α , Accomodation coefficient

β , Coefficient of thermal expansion - $1/T_f$, $(^{\circ}\text{K})^{-1}$

C, Constant in diffusivity equation

CF, Correction factor for heat transfer coefficient due to cell enclosure

C_p , Constant pressure heat capacity of oxygen - cal/gm $^{\circ}\text{K}$

D, D_{av} , Average experimental wire diameter - cm

D_v , Molecular diffusivity - cm^2/sec

ΔF_f° , Standard state free energy change - kcal/mole

ΔH_f° , Standard state enthalpy of formation - kcal/mole

ΔS_f° , Standard state entropy of formation - eu (kcal/mole $^{\circ}\text{K}$)

ϵ_{12} , Energy of molecular interaction - ergs

ϵ_1/k , Force constant for oxygen - $^{\circ}\text{K}$

ϵ_2/k , Force constant for oxide specie - $^{\circ}\text{K}$

f, Friction factor

g, Gravitational acceleration - cm/sec^2

γ , Specific heat ratio of oxygen

G_M , Molal mass velocity - gm moles/sec cm^2

Gr, Grashof number - $g\rho^2\beta(T_s - T_a)D^3/\mu^2$

h, Film heat transfer coefficient - $\text{cal}/\text{cm}^2 \text{ sec } ^{\circ}\text{K}$

Symbols

I_D , Collision integral for diffusion - function of $\bar{k}T_f/\epsilon_{12}$

j_D, j_H , Chilton - Colburn factors

k , Thermal conductivity of oxygen - cal/cm sec $^{\circ}K$

$\bar{k}$, Boltzmann constant - 1.38×10^{-6} ergs/ $^{\circ}K$

k_c , Mass transfer coefficient - gm moles/(sec cm²)(gm mole/cm³)

k_G , Gas-film mass transfer coefficient for diffusion of oxide specie
through the boundary layer - gm mole/sec cm² atmos

K , Equilibrium constant

λ_m , Mean free path of oxygen molecules - cm

Le , Lewis number - Pr/Sc or $C_p \rho D_v/k$

M_1 , Molecular weight of oxygen

M_2 , Molecular weight of oxide specie

μ , Viscosity of oxygen - cp (centipoise or gm/cm sec)

μ_t , Viscosity of oxygen - p (poise)

n , Exponent of P_{O_2} where $x_e \propto (P_{O_2})^n$

Nu , Nusselt number - hD/k

Nu^* , Fictitious Nusselt number

P , Total pressure - atmos

P_{BM}, P_{O_2} , Partial pressure of oxygen - atmos

P_{Ir} , Partial pressure of iridium - atmos

P_t , Partial pressure of oxygen - torr

Pr , Prandtl number - $C_p \mu/k$

Symbols

$(r_o)_1, 1.18(V_o)_1^{1/3}$ - collision diameter for oxygen molecule/oxygen molecule collision - angstroms

$(r_o)_2, 1.18(V_o)_2^{1/3}$ - collision diameter for oxide molecule/oxide molecule collision - angstroms

$r_{12}, ((r_o)_1 + (r_o)_2)/2$ - collision diameter for oxygen molecule/oxide molecule collision - angstroms

ρ , Density of oxygen - gm/cm³

ρ_M , Density of iridium - gm/cm³

R , Universal Gas Law Constant - 81.7 cm³ atmos/gm mole °K or 1.987 cal/gm mole °K

Ra , Rayleigh number - GrPr

Sc , Schmidt number - $\mu/\rho D_v$

T_a , Ambient cell temperature - °C

T_f , Experimental film temperature - °K

T_k , Experimental wire temperature - °K

T_m , Melting temperature for oxides - °K

T_s , Experimental wire temperature - °C

U_{av} , Mean gas velocity - cm/sec

$(V_o)_1$, Molal volume of oxygen - cm³/gm mole

$(V_o)_2$, Molal volume of oxide specie - cm³/gm mole

$\dot{x}_e$, Experimental surface recession rate - cm/sec

$\dot{x}_{se}$, Standardized experimental surface recession rate at $D = 0.588$ cm - cm/sec

x

Symbols

$\dot{x}_{st}$, Standardized theoretical surface recession rate at $D = 0.588$ cm - cm/sec

$\dot{x}_t$, Theoretical surface recession rate - cm/sec

ABSTRACT

The experimental study of the natural convection oxidation of iridium was performed at temperatures of 1600, 1900, and 2200 °C and pressures ranging from 0.00132 to 1.32 atmospheres. A theoretical model describing the surface recession rate was derived assuming that the rate was controlled by the diffusion of Ir, IrO₂, and IrO₃ through the gaseous boundary layer, adjacent to the iridium specimen. Average values for the standard state enthalpy and entropy changes for the formation of IrO₂ and IrO₃ were calculated for the 1600 to 2200 °C temperature range. A value for the partial pressure of Ir at 2200 °C was found. Correlation between experiment and the theoretical model was good with the overall mean % error of experimental rates from theoretically predicted rates being 13.3% for the 1600 to 2200 °C range.

INTRODUCTION

Iridium is one of the platinum group metals. It is the only elemental metal known to man possessing a high enough melting point and a low enough oxidation rate to be used unprotected in air for an extended period of time in the 2000 to 2300 °C range. A thin oxide film is formed on its surface when iridium is subjected to temperatures from 600 to 1000 °C in an oxygen containing gas. When the temperature of the iridium exceeds 1000 °C it forms volatile oxides, and the oxidation rate becomes linear with time, leaving the surface shiny.

Iridium is considered to be the most corrosion resistant metal when it is compared with all other metals over a broad range of temperatures and environments. Numerous acids, salt solutions, fused salts, molten metals, and molten metal oxides are among the corrosive environments considered.

Iridium has been used for standardized high temperature thermocouples, for heating elements in high temperature furnaces, and for protective coatings for less expensive high temperature structural materials such as tungsten and tantalum base alloys. The most recent research on iridium oxidation has shown the potential applications for the leading edge of spacecraft, for components in nuclear reactors, and for parts in rocket and turbine engines.

Being a platinum group metal, iridium is expensive. This limits its use as a primary material in structural applications, even though iridium has reasonably good strength properties.

Among other properties, iridium has very low emittance and very high density. The low emittance causes problems when iridium is used to any extent on spacecraft because the primary means of heat dissipation on the nose of spacecraft re-entering the earth's atmosphere is by radiation. Where weight is a constraint, the 22.57 gm/cm^3 density of iridium (at room temperature) greatly restricts its application. In fact, iridium is either the most or the next to the most dense element known to man. (Controversy exists on whether iridium or osmium is the most dense due to the inconsistencies of density measurements based on the lattice structure and actual physical measurements. Actual measurements reveal iridium to be the most dense.)

REVIEW OF PAST WORK

A short review of the recent but relevant work done on the oxidation of iridium is in what follows. From this review, conclusions of a general nature were made which served as a starting basis for the work of this report.

The composition of the products of iridium oxidation and the thermodynamics involved have been investigated by several people. Cordfunke and Meyer¹ passed oxygen, or oxygen-nitrogen mixtures, over a boat shaped specimen containing iridium in the range of 1169 to 1462 °C. They concluded that the main volatile oxide formed was IrO_3 .

Holburn, Henning, and Austin² self resistance heated a piece of thin iridium foil to 1670 °C over which they passed oxygen, air, or nitrogen con-

taining 1.77% oxygen. They also concluded that IrO_3 was the main gaseous oxide specie formed.

Norman et al,⁴ performed a sequence of mass spectrometric studies of oxidizing iridium. This was done by introducing oxygen into a Knudsen Cell in which an iridium specimen was placed and heated in the range of 1557 to 1760°C. The exiting gaseous species were then "bombarded" with a stream of electrons. They detected the presence of Ir^+ , IrO^+ , IrO_2^+ and IrO_3^+ ions, but concluded that IrO_2 and IrO_3 were the main volatile oxide species present in their work.

Various related kinetic studies have also been performed. Norman et al also measured values of the standard state enthalpy and entropy changes for the formation of IrO_2 of 48.5 ± 0.5 kcal/mole and 3.9 ± 2.0 eu, and for IrO_3 5.5 ± 1.5 kcal/mole and -13.1 ± 2.5 eu in their respective orders.

Olivei⁵ performed some mass spectrometric studies also, in the range of 1627 to 2227°C, from which it was found that the standard state enthalpy and entropy of formation for IrO_3 were 6.0 kcal/mole and -9.0 eu respectively.

For the free entropy of formation of oxides of a general metal M, values of 20.6, 3.5 ± 2.1 , and -10 to -15 eu, as averages for volatile gaseous monoxide MO, dioxide MO_2 , and trioxide MO_3 species respectively, were indicated by Searcy.⁶

Phillips⁷ performed some kinetic studies of iridium oxidation in

air moved only by natural convection. The specimen was a 1/4 inch in diameter by 1/2 inch long iridium rod. The range of temperatures investigated was 650 to 1300 °C for which Phillips found an activation energy of 9.2 kcal/mole.

Krier and Jaffee⁸ heated an iridium specimen by means of a furnace through which slow moving air was passed in the range of 1000 to 1400 °C. They found a value of 16 kcal/mole for the activation energy.

Criscione⁹ passed oxygen or an oxygen-argon mixture parallel to a 1/2 inch diameter iridium rod having a hemispherically shaped end, in the range of 1150 to 1900 °C and at a pressure of 0.935 atmospheres. He measured surface recession rates for the hemispherical end and found an activation energy of 23 kcal/mole.

Work by Kuriakose and Margrave¹⁰ involved heating an iridium foil 0.002 inches thick suspended in a furnace for temperatures up to 1301 °C and resistance heating a 0.01 inch in diameter iridium wire inside a 1 inch diameter pyrex tube for higher temperatures. They passed oxygen or oxygen-helium mixtures through the tube parallel to the tube length at a total pressure of 1 atmosphere. For the iridium foil they found activation energies of 70 and 7.1 kcal/mole for temperatures below 1100 °C, and for temperatures between 1100 and 1300 °C respectively. Activation energies for the iridium wire were found to be 12.5 and 30-33 kcal/mole at 1150 to 1600 °C, and 1600 to 2217 °C respectively.

Among other dependencies, it has been found that the surface reces-

sion rate of a specimen depends upon the oxygen partial pressure to some power. Table I summarizes this dependency as found by various experimenters of which Tempero¹¹ is the only one not previously mentioned.

Except for the work recently done by Wimber and Tempero, no work has led to the characterization of the oxidation process which would allow taking into account the effects of varying temperature, oxygen partial pressure, flow rate past a specimen and specimen size. Wimber and Tempero resistance heated an iridium wire in the range of 1600 to 2200 °C. The wire was varied from 0.0635 to 0.0381 cm in diameter and oxygen was passed perpendicular to the wire. Among their investigations of describing the recession rate theoretically, they had some success in a model which considered the equilibrium diffusion of gaseous IrO_2 and IrO_3 through the boundary layer adjacent to the specimen.

In view of the mentioned past work on iridium oxidation, the following conclusions were arrived at.

1. IrO_2 and IrO_3 appear to be the main volatile oxide species formed above 1600 °C.
2. Values for the standard state enthalpy and entropy of these two major species are known at certain temperature levels, but are expected to vary with temperature.
3. Activation energies are expected to vary with specimen environment of oxygen, specimen configuration, and specimen temperature.
4. The surface recession rate, at least, depends upon the oxygen par-

Table I. DEPENDENCY OF RECESSION RATE ON P_{O_2}

$$x_e \propto (P_{O_2})^n$$

	Holburn et al	Criscione	Kuriakose & Margrave	Tempero
Iridium Specimen Environment	Foil - slow flowing	Rod - parallel flow	Foil & wire parallel flow	Wire - perpendicu- lar flow
Exponential Dependency - Temperature Range	$n = 1.5$ @ 1670°C	$n = 1.34$ @ 1900°C	Foil $n = 1.1$ @ 1181°C Wire $n = 1.2$ @ 1717°C	$n = 0.234$ @ 1600 to 2200°C
Oxygen Partial Pressure Range	$P_{O_2} = 0.017$ to 1.00 atmos	$P_{O_2} = 0.02$ to 0.93 atmos	$P_{O_2} = 0.02$ to 1.00 atmos	$P_{O_2} = 0.0046$ to 1.30 atmos

tial pressure, and the specimen configuration and temperature.

THEORY

When iridium is oxidized above 1000°C it forms volatile oxide species, for which the associated rate is expected to be controlled by one or more of the following steps in the process:

1. Bulk transport of the oxygen bearing gas from the source to the general vicinity of the metal being oxidized.
2. Diffusion of the oxygen through the gaseous boundary layer adjacent to the surface of the metal.
3. Adsorption of the oxygen from the gas phase onto the surface of the metal.
4. Reaction on the metal surface including possible rearrangement and migration processes.
5. Desorption of the oxide(s) from the surface of the metal.
6. Diffusion of the oxide(s) through the gaseous boundary layer with possible further chemical reaction(s) within the boundary layer of one of the oxide species with the same or different oxide species and/or oxygen.

A theoretical model was derived by Wimber¹², which takes into account the formation of IrO , IrO_2 , and IrO_3 at their equilibrium partial pressures on the inner surface of the boundary layer. The model also accounts for metal vaporization which occurs to an appreciable extent at high temperatures and low pressures. This model assumes that the surface recession

rate $\dot{x}_t$, is controlled by the rate of diffusion of these gaseous species through the gaseous boundary layer corresponding to the first part of step 6, and was expressed as,

$$\dot{x}_t = A(k_{G1}K_1P_{O_2}^{1/2} + k_{G2}K_2P_{O_2} + k_{G3}K_3P_{O_2}^{3/2} + k_{GM}K_M), \quad (1)$$

where the subscripts 1, 2, 3, and M refer to IrO , IrO_2 , IrO_3 , and Ir respectively, and:

A = Effective equivalent weight equal to 192.2 gms of iridium consumed per gm mole of oxide formed divided by the density of Ir ,

k_G = Gas-film mass transfer coefficient - gm mole/sec cm^2 atmos,

K = Equilibrium constant,

P_{O_2} = Partial pressure of oxygen - atmos.

Validity of equation (1) was tested by comparison of experimental data taken in the natural convection area, to results predicted by this model.

IRIDIUM ANALYSIS

The oxidation studies in natural convection were conducted using two different lots of commercially pure iridium, purchased from Engelhard Industries, Cateret, New Jersey. A spectrographic analysis of this iridium was requested of Engelhard Industries Division. These analyses are shown in Table II. The results of these two lots of iridium were compared experimentally.

EXPERIMENTAL EQUIPMENT AND PROCEDURE

Figure 1 is a schematic representation of the equipment used. An iridium specimen was placed horizontally between two electrodes in a cell

Table II. SPECTROGRAPHIC ANALYSIS OF IRIDIUM*

Impurity	Lot #1 diameter 25 mils	Lot #2 diameter 20 mils
Pt	99	<0.5
Rh	20	38.0
Pd	10	11.0
Ru	166	1.5
Au	<1	<0.5
Ag	50	-
Pb	<5	<0.5
Sn	5	<0.5
Zn	<10	0.41
Fe	170	64
Cu	96	17
Si	43	6.1
Mg	41	1.1
Ca	78	0.61
Al	14	35
Ni	10	1.1
Cr	31	0.84
Mn	10	0.69
Sb	<10	<0.5
B	<50	0.0032
Co	100	1.8
As	<10	0.066
Bi	<1	-
Cd	<1	-
W	0.6%	710
N	50	0.24
H	4	-
O	70	8.3
Ta	-	46
In	-	0.26
Zr	-	1.1
Ga	-	0.20
V	-	0.096
Ti	-	0.49
K	-	0.67
Cl	-	0.59
S	-	0.57

Table II. (Continued)

P	-	0.81
Na	-	2.2
F	-	0.27
C	-	15.0
Li	-	0.00072

* Impurities are given in parts per million unless otherwise specified.

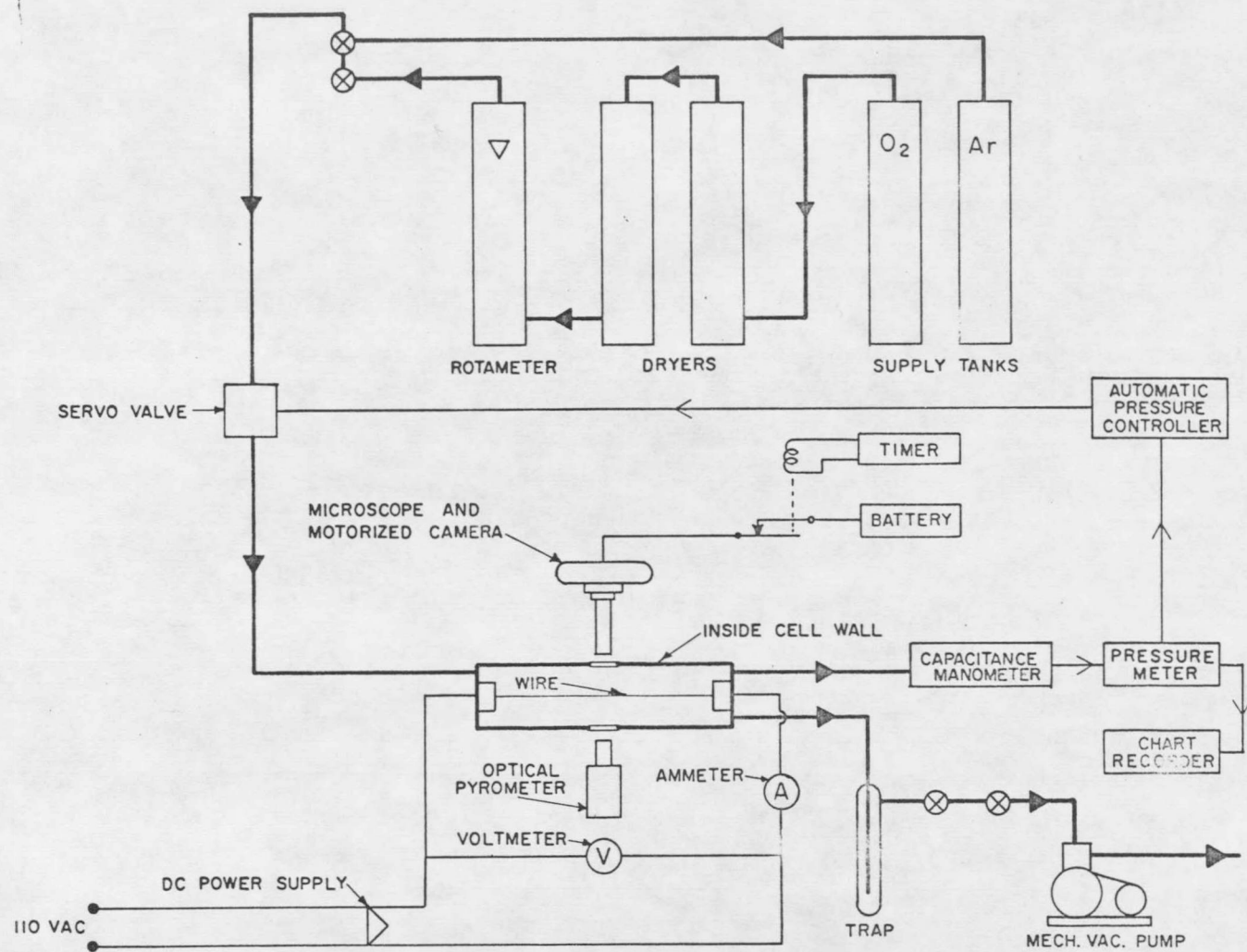


Figure 1. EXPERIMENTAL EQUIPMENT SCHEMATIC

1 inch wide by 3 inches long by 3 inches deep. The electrodes were used to deliver the current to resistance heat the wire. To accomodate the thermal expansion of the wire and thus prevent its bending, a leaf spring type mount was used on one end. This enabled the wire to be loaded tensilely to a pre-determined level such that when the wire was heated to the desired level, the leaf spring would no longer be deflected and thus leave the wire in a near zero stress level.

On the underside of the cell was centered a 4 inch to 1 inch reduction copper plumbing "T", such that the 4 inch diameter main portion of the "T" was centered about a vertical axis through the center of the cell. A 4 inch diameter circular plate was then soldered on the bottom of the "T" to close it off. To the remaining horizontal one inch outlet, was a line leading to the trap and eventually to the mechanical pump. On the opposite side and same elevation as the 1 inch outlet, was located the oxygen gas inlet.

The power to heat the wire was supplied by a Hewlett Packard DC Power Supply, LVR Series, Model 6260B which has the capability of maintaining a constant voltage across or a constant current through whatever it is connected to. In this work the power supply was used so that the voltage drop across the electrodes was constant, which minimized the power change during a run. The current was measured by a DC Ammeter and the voltage was measured by a Honeywell Digital Multimeter, Digitest Model 333R.

Either oxygen or argon was introduced into the cell. The argon was directly connected to the cell through valves, whereas the oxygen was passed through a Drierite Drying Column (to remove any moisture in the oxygen), a #74 Matheson Tube Flowmeter, a manual valve, the servo valve and eventually to the cell. A Granville-Phillips Automatic Pressure Controller No. 0-00-216006 (which included the servo valve), was used in conjunction with a MKS Baratron TM Type 77 Pressure Meter. The MKS unit sensed pressure by means of a MKS Capacitance Manometer 77H-1000. The line tap for the capacitance manometer was located about 2 inches lower and rotated 90 degrees from the inlet for the oxygen, in the wall of the plumbing "T", thus preventing any possible pressure head from the oxygen flow which might cause an incorrect pressure reading.

Gas exiting the cell during a run was passed through a trap designed to condense the oxides present. Liquid nitrogen was used in the trap when the run pressure P_{O_2} , was less than 0.25 atmospheres. When P_{O_2} was greater than 0.25 atmospheres, dry ice was used, since at the temperature of liquid nitrogen and high pressures, P_{O_2} , the boiling point of oxygen is greater than the temperature of the liquid nitrogen. Because of this, if liquid nitrogen were used, the oxygen condensed in the trap. Thus, since the boiling point of the oxygen at the temperature of dry ice and pressure P_{O_2} greater than 0.25 atmospheres is less than the temperature of dry ice, the dry ice was used for P_{O_2} greater than 0.25 atmospheres. From atmospheric, pressure decrease in the cell was achieved by use of a mechan-

ical pump.

All parts of the cell were cooled by cold water circulation through tubes on its surface.

Sight ports were located on opposite sides of the cell at the vertical elevation of a mounted specimen. Shadowgraph quality pyrex windows were used to provide visible access to the cell. These windows were cleaned and polished periodically due to accumulation of oxides on their surfaces. To measure the temperature of the specimen, a Leeds and Northrup 6836-C Optical Pyrometer was used, which was aligned to enable sight through one of the sight port windows. The optical pyrometer was calibrated to take into account the effects of the pyrex windows and thus enable a true temperature reading. This calibration was done as part of the work by Halvorson and Wimber¹³ on the thermal expansion of iridium. Aligned for sight through the other window was a Beseler Topcorn Super D Camera and Electric Motor Drive fitted with a Topcorn Microscope Attachment Model III, which in conjunction with a Lafayette Model 51012T Timer, enabled the taking of a sequence of pictures at a predetermined interval and 20X magnification. For many of the runs, a Lafayette Model 58033, 5-IN-1 Timer was used. The latter timer enabled longer intervals between pictures.

Because of the possibility of power or water loss, the system was fitted with a network of relays which acted as protection devices if water or power supply should be lost during a run.

To perform a run, a 2 7/32 inch section of iridium wire was cut,

cleaned with acetone, ground flat on one end for reference and mounted in the cell. (In the first few runs, rotational pictures were taken of the wire before and after the run. From these it was determined that the eccentricity of the wire was less than 1.2% and thus this procedure was discontinued at that point.) A reference picture was then taken of a drill rod of known diameter (0.0655 cm) in order to provide a reference for the size of the pictures of the iridium wire. An argon atmosphere of 0.92 atmospheres was then introduced into the cell in which the wire was annealed for 30 minutes at 2200 °C. (The anneal was performed upon the use of each new section of wire for the purpose of achieving a grain size and electrical resistivity that would be essentially invariant with time for the runs.) The argon was then removed and the cell filled with oxygen. Then the oxygen was pumped out and a pressure leak test taken to insure a near pure oxygen environment in the cell. The pressure and temperature at which a run was to be made were then set on the equipment. The wire was then oxidized for a short period of time to characteristically texturize its surface. The cycle timer was then activated at its pre-determined cycle interval. A run consisted of ten exposures of the wire, which in total length, corresponded with changing the wire diameter by 0.0015 to 0.0035 cm. (The "0.0015 to 0.0035 cm" range was arrived at because approximately a one mil diameter change was necessary to obtain reasonable data, but if the diameter changed much more than one mil, too much variation in the oxidation rate occurred due to its dependency on the diameter of the wire.)

Because of the tendency of the pyrex windows to slowly receive a coating of oxide during a run, they were rotated periodically to insure good pictures and correct readings on the optical pyrometer. (Also a habit was made of changing these windows between every run.)

The temperature of the wire and the oxygen pressure in the cell were continuously monitored throughout a run. Flow of the oxygen gas was maintained through the "T" section beneath the cell where the wire was mounted, in order to keep a continuously fresh supply of oxygen to the cell, thus keeping the oxygen concentration essentially 100% and preventing depletion of the oxygen.

Upon completion of the desired number of film exposures, the system was shut down, the film removed from the camera and developed. This film was allowed to dry for at least a 2 hour period to minimize shrinkage during the process of reading the wire diameter. The film was then placed between two disks of optical quality fused quartz 3/16 inch thick mounted in a metal frame. The light of a lamp was passed through the disk-film combination, directly into a Gaertner Microscope Attachment-Cathetometer arrangement. A Gossen Luna-Pro Exposure Meter was placed on the viewing end of the microscope attachment. This cathetometer provided measurement of the film negatives by light intensity measurements and eventual conversion to their equivalent wire diameter through use of the drill rod reference picture on each film. This unit was calibrated to read accurate to ± 1 micron, but the actual repeatability when reading the film was near

± 10 microns. Each negative was measured in the middle and at each end, and these values averaged in order to achieve better data statistically. A plot of diameter versus time was then made and a linear average recession rate determined. Figure 2 represents a typical run, showing the relative deviation of the data points from an approximately linear relationship and thus illustrates the validity of assuming $\dot{x}_e$ was essentially constant for each run. The value of D_{av} was also determined from this plot.

EXPERIMENTAL RESULTS AND THEORETICAL RATE CALCULATIONS

The experimental data obtained for the natural convection oxidation of iridium are tabulated in Table III, in order of increasing temperature and increasing oxygen pressure.

It was also found that the experimental surface recession rate $\dot{x}_e$, was dependent upon the wire diameter. As a result, this dependency in the Rayleigh number range from 8.65×10^{-12} to 2.06×10^{-1} , was investigated experimentally. It was found that this dependency could be described by the diameter of the wire raised to the -1.11 power. This dependency resulted in a maximum deviation of 2.76% from experiment. Then, to facilitate comparison of experimental and theoretical surface recession rates, they were converted to equivalent values at a diameter of 0.0588 cm. The subscript "s" on $\dot{x}$, thus indicates this standardization of recession rates to a diameter of 0.0588 cm.

It was seen, through examination of the values of $\dot{x}_{se}$ in Table III, that the surface recession rates varied only within experimental repeata-

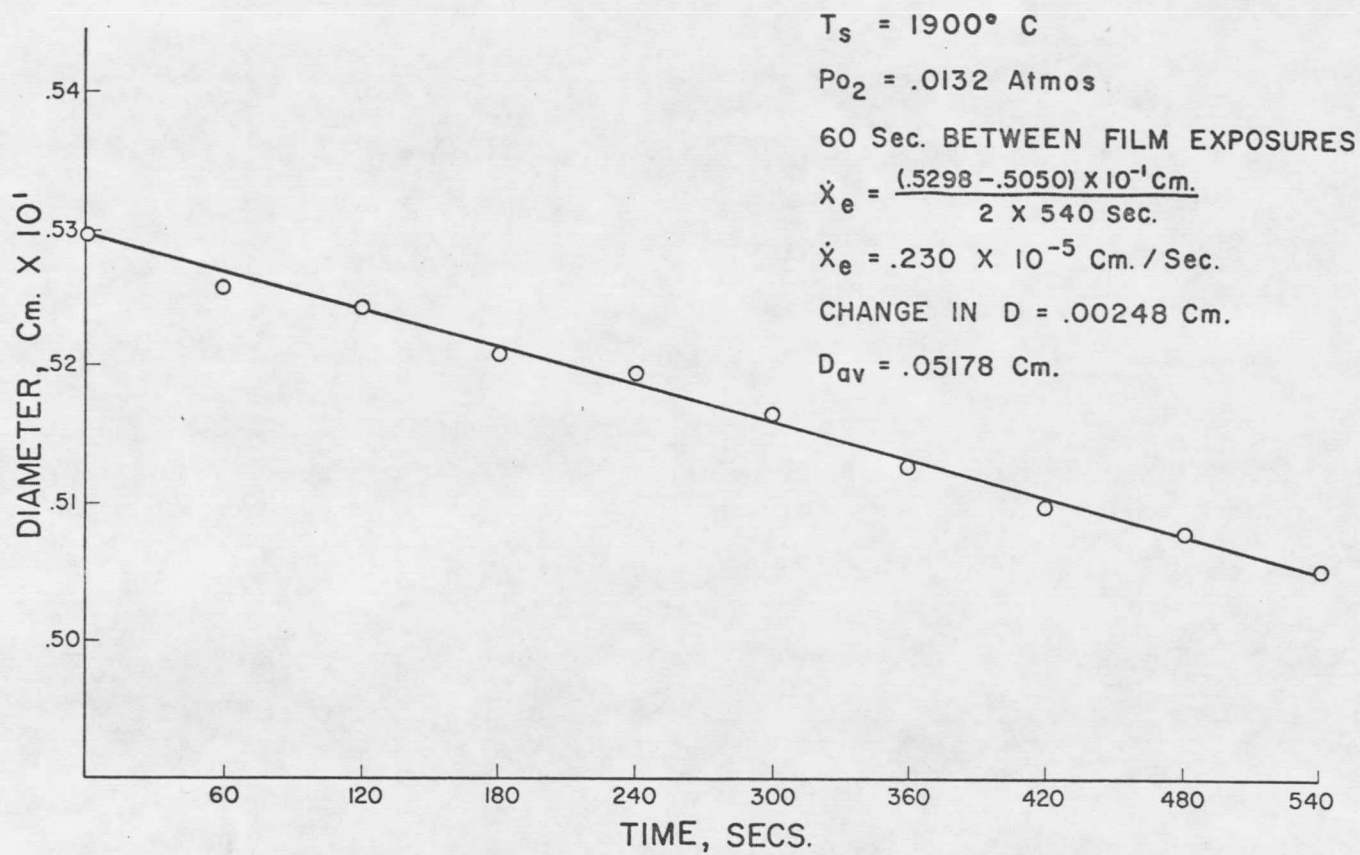


Figure 2. SAMPLE PLOT FOR DETERMINATION OF EXPERIMENTAL SURFACE RECESSION RATES

Table III. EXPERIMENTAL DATA

$T_s - ^\circ C$	P_{O_2} - atmos	$\bar{x}_e \times 10^6$ cm/sec	$\bar{x}_{se} \times 10^6$ cm/sec	$D_{av} - cm$	Rayleigh Number
1600	0.00132	0.352	0.249	0.040707	6.05×10^{-8}
1600*	0.00132	0.244	0.269	0.0610	2.01×10^{-7}
1600	0.00132	0.250	0.217	0.0492	1.06×10^{-7}
1600	0.0132	0.570	0.635	0.0616	2.07×10^{-5}
1600	0.0132	0.535	0.632	0.0640	2.32×10^{-5}
1600	0.132	1.46	1.53	0.0582	1.74×10^{-3}
1600	0.132	1.50	1.67	0.0614	2.05×10^{-3}
1600	1.32	6.34	5.88	0.0522	1.26×10^{-1}
1600	1.32	5.89	6.56	0.0615	2.06×10^{-1}
1600	1.32	6.51	6.62	0.0567	1.61×10^{-1}
1600	1.32	7.28	6.68	0.0516	1.22×10^{-1}
1600	1.32	8.15	6.63	0.0463	8.81×10^{-1}
1600	1.32	9.38	6.49	0.0401	5.69×10^{-1}
1600*	1.32	7.84	8.09	0.0574	1.68×10^{-1}
1600*	1.32	7.07	6.34	0.0506	1.15×10^{-1}
1900	0.00132	0.805	0.679	0.0479	6.63×10^{-8}
1900	0.00132	0.546	0.501	0.0517	8.33×10^{-8}
1900	0.00132	0.680	0.665	0.0547	9.90×10^{-8}
1900	0.0132	2.61	2.08	0.0455	5.68×10^{-6}
1900	0.0132	2.15	2.12	0.0552	1.02×10^{-5}
1900	0.0132	1.62	1.88	0.0638	1.57×10^{-5}
1900	0.0132	1.76	1.90	0.0600	1.30×10^{-5}
1900	0.0132	1.97	1.95	0.0553	1.02×10^{-5}
1900	0.0132	2.13	1.96	0.0519	8.42×10^{-6}
1900*	0.0132	2.57	2.22	0.0489	7.08×10^{-6}
1900*	0.0132	2.30	2.12	0.0518	8.39×10^{-6}
1900	0.132	5.11	3.59	0.0406	4.05×10^{-4}
1900	0.132	3.68	3.49	0.0532	9.11×10^{-4}
1900	1.32	10.7	11.7	0.0604	1.33×10^{-2}
1900	1.32	9.48	10.9	0.0634	1.54×10^{-2}
2200	0.00132	1.49	1.45	0.0544	6.88×10^{-8}
2200	0.00132	1.67	1.68	0.0561	7.55×10^{-8}
2200	0.00132	1.93	2.26	0.0644	1.14×10^{-7}
2200*	0.00132	1.83	1.92	0.0584	8.52×10^{-8}
2200*	0.00132	1.96	1.66	0.0481	4.76×10^{-8}
2200	0.0132	5.83	6.95	0.0564	1.20×10^{-5}
2200	0.0132	5.33	5.42	0.0567	7.81×10^{-6}

Table III. (Continued)

2200	0.132	13.2	11.4	0.0489	5.00×10^{-4}
2200	0.132	6.84	5.97	0.0494	5.17×10^{-4}
2200	0.132	6.52	7.02	0.0597	9.09×10^{-4}
2200	1.32	35.9	30.0	0.0475	4.58×10^{-2}
2200*	1.32	22.0	25.6	0.0639	1.12×10^{-1}
2200	1.32	28.2	24.8	0.0498	5.28×10^{-2}

* Designates runs done using lot #2 Ir wire

† Is the run shown on Figure 2.

bility, between the two lots of iridium. In fact, for any run using the second lot of iridium, the % deviation of $\dot{x}_{se}$ from the mean of $\dot{x}_{se}$ for the group having the same temperature and pressure, was less than 13% in all cases, although the mean experimental deviation for all the runs was 8.5%. (See Table VIII, the column headed "% Exper. Dev.") Thus the 0.6% tungsten in lot 1 had no perceptible effect on the oxidation rate.

In calculating theoretical surface recession rates from equation (1) it is necessary to have values of the unknowns involved. P_{O_2} is known from the experimental conditions and in the present case is the total pressure of the system. Several properties of oxygen were needed and because they varied with pressure and/or temperature, they were least squares curve fit in the range of 1000 °K to 1400 °K from original data.^{14,15} (1083 to 1383 °K was the range of film temperatures T_f encountered experimentally.) The resulting relations for these properties are shown in Table IV.

In order to obtain values for the mass transfer coefficients k_G , the following Chilton-Colburn relations were employed.¹⁶

$$j_H = (h/C_p C_{av}^U)(C_p \mu/k)^{2/3} = f/2 \quad (2)$$

$$j_D = (k_c P_{BM}/U_{av} P)(\mu/\rho D_v)^{2/3} = (k_G P_{BM}/G_M)(\mu/\rho D_v)^{2/3} = f/2 \quad (3)$$

By equating the expressions for j_H and j_D and solving for k_G , where $k_c = k_G RT_f$ and for this case $P_{BM} = P$,

$$k_G = (h/C_p \rho^{RT_f})(C_p \mu/k)^{2/3}/(\mu/\rho D_v)^{2/3}$$

$$k_G = (h/C_p T_f R)(Le)^{2/3} \quad (4)$$

where:

Table IV. OXYGEN PROPERTIES

$$1000^{\circ}\text{K} \leq T_f \leq 1400^{\circ}\text{K}$$

O ₂ Property	Relation	% Variation from data
Density	$\rho = 0.3899 P_{O_2} / T_f$	0.04
Specific Heat	$C_p = 0.116 T_f^{0.117}$	0.21
Viscosity	$\mu = 5.374 \times 10^{-6} T_f^{0.650}$	0.44
Thermal conductivity	$k = 9.48 \times 10^{-7} T_f^{0.758}$	0.31
Specific Heat Ratio	$\gamma = 1.682 T_f^{0.0359}$	0.08

C_P = Specific heat ratio of oxygen - cal/gm $^{\circ}$ K,

D_v = Molecular diffusivity - cm²/sec,

f = Friction factor,

G_M = Molal mass velocity - gm moles/sec cm²,

h = Film heat transfer coefficient - cal/cm² sec $^{\circ}$ K,

j_D, j_H = Chilton-Colburn factors,

k = Thermal conductivity of oxygen - cal/cm sec $^{\circ}$ K,

k_c = Mass transfer coefficient - gm moles/(sec cm²)(gm mole/cm³),

Le = Lewis number - Pr/Sc or $C_P \rho D_v / k$,

μ = Viscosity of oxygen - cp (centipoise or gm/cm sec),

P = Total pressure,

P_{BM} = Partial pressure - atmos,

Pr = Prandtl number - $C_P \mu / k$,

ρ = Density of oxygen - gm/cm³,

R = Universal Gas Law Constant - 81.7 cm³ atmos/gm mole $^{\circ}$ K,

Sc = Schmidt number - $\mu / \rho D_v$,

T_f = Experimental film temperature - $^{\circ}$ K,

U_{av} = Mean gas velocity - cm/sec.

In equation (4) all parameters are known at this point at any given temperature and pressure except h and D_v which were found as follows.

To find the value of h , the value of the Nusselt number, Nu , was first found from the expression below developed by Madden and Piret.¹⁷

This is for natural convection from heated horizontal wires of 0.00701

and 0.0251 cm in diameter in air or helium and pressures from 0.00658 to 1.0 atmospheres.

$$Nu = \frac{2}{2/Nu^* + 8\lambda_m/\alpha \text{Pr}(\mathcal{J} + 1)D - \ln(1 + 2\lambda_m/D)} \quad (5)$$

where the fictitious Nusselt number Nu^* is,

$$Nu^* = 2/\ln(6.82/Ra^{1/3}), \quad (6)$$

and for the work of this report α , the accommodation coefficient, was initially assumed equal to 0.8. The other parameters in equations (5) and (6) are:

β = Coefficient of thermal expansion - $1/T_F (^{\circ}K)^{-1}$,

D = Average experimental wire diameter - cm,

$\mathcal{J}$ = Specific heat ratio for oxygen,

g = Gravitational acceleration - cm/sec^2 ,

Gr = Grashof number - $g\beta(T_s - T_a)D^3/\mu^2$,

λ_m = Mean free path of oxygen molecules - cm,

Ra = Rayleigh number - PrGr ,

T_s = Experimental wire temperature - $^{\circ}C$,

T_a = Ambient temperature inside the cell - $^{\circ}C$.

Since the properties of oxygen are very near that of air, this expression was assumed valid for pure oxygen also. This heat transfer correlation is valid in the range of $10^{-8} \leq Ra \leq 10^{-1}$. Valid use of equation (5) is indicated by the listing of the corresponding Rayleigh numbers of each experimental run in Table III.

The value for λ_m in equation (5) was calculated from the Dushman

equation ¹⁸,

$$\lambda_m = (8.589\mu_t/P_t)(T_f/M_1)^{1/2}$$

where;

μ_t = Viscosity of oxygen - p (poise)

M_1 = Molecular weight of oxygen

P_t = Partial pressure of oxygen - torr

By converting μ_t and P_t to μ and P , substituting for μ from Table IV, and using M_1 for oxygen as 32.0, the above expression became,

$$\lambda_m = 1.074 \times 10^{-8} T_f^{1.15} / P \quad (7)$$

From equation (7), λ_m could then be readily calculated for any condition of temperature T_f and pressure P corresponding to experiment. At this point Nu was calculated, and h was found from equation (8).

$$h = CF(Nu k / D) \quad (8)$$

The CF was a correction factor for the heat transfer coefficient due to the presence of the lid on top of the cell and connecting chamber of "T" below the cell. The value of CF was found to be 1.0 within the $\pm 1\%$ accuracy of the experimental equipment used. Because the investigations of the value of CF couldn't take into account the effects of the side-walls on the heat transfer, (the experiments to determine CF were performed with the cell open on top and bottom as opposed to the fully assembled apparatus) this was also investigated. According to Jones and Masson¹⁹, if the ratio of the distance from the wall to the center of the cylinder to the cylinder diameter is greater than 0.7, the heat transfer is not affected.

In the present case this ratio was approximately 20, so that this possibility was ruled out.

It was also shown in the experimental studies that there was no effect on the heat transfer, and thus the oxidation rate, due to the oxygen flow through the "T" section beneath the cell.

The values for D_v were calculated from the Wilke and Lee modification of the Hirshfelder, Bird, and Spotz²⁰ equation which is,

$$D_v = \frac{CT_f (1/M_1 + 1/M_2)^{1/2}}{P_{BM}^2 I_D} \quad (9)$$

where:

$$C = 10.7 - 2.46(1/M_1 + 1/M_2)^{1/2} \times 10^{-4},$$

I_D = Collision integral for diffusion,

M_2 = Molecular weight of oxide specie,

$(r_o)_1 = 1.18(V_o)_1^{1/3}$, collision diameter for oxygen molecule/oxygen molecule collision - angstroms,

$(r_o)_2 = 1.18(V_o)_2^{1/2}$, collision diameter for oxide molecule/oxide molecule collision - angstroms,

$r_{12} = \frac{(r_o)_1 + (r_o)_2}{2}$, collision diameter for oxygen molecule/oxide molecule collision - angstroms,

$(V_o)_1$ = Molal volume of oxygen - $\text{cm}^3/\text{gm mole}$,

$(V_o)_2$ = Molal volume of oxide specie - $\text{cm}^3/\text{gm mole}$.

As noted in the NOMENCLATURE, I_D is a function of the parameter $(\bar{k}T_f/\epsilon_{12})$.

From data tabulated in reference 20, I_D was least squares curve fit as a

function of $(\bar{k}T_f/\epsilon_{12})$ for $1.8 \leq (\bar{k}T_f/\epsilon_{12}) \leq 2.8$, the range encountered experimentally. The maximum % deviation from data was 0.30% for the relation,

$$I_D = 0.673(\bar{k}T_f/\epsilon_{12})^{-0.324},$$

where,

ϵ_{12} = Energy of molecular interaction - ergs

$\bar{k}$ = Boltamann constant - 1.38×10^{-6} ergs/ $^{\circ}$ K.

The value of $\epsilon_{12}/\bar{k}$ was determined from the relation,

$$\epsilon_{12}/\bar{k} = ((\epsilon_1/\bar{k})(\epsilon_2/\bar{k}))^{1/2}$$

where the force constant $\epsilon_1/\bar{k}$ is known for oxygen as 113.2° K and the force constant $\epsilon_2/\bar{k}$ was determined for the various oxide species from the relation,

$$\epsilon_2/\bar{k} = 1.92T_m.$$

The value of T_m , the melting temperatures of the oxides in the above expression, is unknown. For IrO , IrO_2 , and IrO_3 , T_m was assumed to be 1500° K initially, whereas the known value of the melting temperature, 2727° K for Ir was used. Using equation (9) then, with the appropriate constants substituted in for each specie, D_v was calculated for each experimental condition of wire temperature and oxygen pressure. The k_G values were then calculated using equation (4).

The equilibrium constants for IrO , IrO_2 and IrO_3 were initially estimated by use of the corresponding ΔH_f° and ΔS_f° of previous experiments as summarized in Table V. The equilibrium constant, K_M , for Ir was

Table V. SUMMARY OF ΔH_f° & ΔS_f° VALUES BY PAST EXPERIMENTERS

Specie	Experimenter	ΔH_f° kcal/mole	ΔS_f° eu (kcal/mole·K)	Temp. Range °C
IrO*	Margrave	105.	---	1010-2217
MO*	Searcy	---	20.6	25
IrO ₂ **	Norman <u>et al</u>	48.5 $\pm$ 0.8	3.9 $\pm$ 2.0	1557-1760
MO ₂	Searcy	---	3.5 $\pm$ 2.1	25
IrO ₃ *	Norman <u>et al</u>	5.5 $\pm$ 1.5	-13.2 $\pm$ 2.5	1557-1760
IrO ₃	Olievi	6.0	-9.0	1627-2227
MO ₃	Searcy	---	-10 to -15	25

* These values were used to initially estimate the values of the equilibrium constants for IrO, IrO₂, and IrO₃.

Table VI. INITIALLY PREDICTED EQUILIBRIUM CONSTANTS

Wire Temperature	K_{LM}	K_1	K_2	K_3
1600 °C	2.19x10 ⁻¹¹	1.78x10 ⁻⁸	1.56x10 ⁻⁵	1.67x10 ⁻³
1900 °C	6.27x10 ⁻⁹	8.73x10 ⁻⁷	9.42x10 ⁻⁵	2.09x10 ⁻³
2200 °C	4.56x10 ⁻⁷	1.67x10 ⁻⁵	3.68x10 ⁻⁴	2.47x10 ⁻³

seen to be equal to the partial pressure of the iridium or its vapor pressure. The vapor pressure of Ir, P_{Ir} , was initially estimated from the vapor pressure equation resulting from the work of Hampson and Walker²¹. This relation is,

$$\ln(P_{Ir}) = 7.139 - 33,337/T_s = K_M \quad (10)$$

The values of all the equilibrium constants at 1600, 1900, and 2200 °C as initially estimated, are shown in Table VI.

In finding the value for A, the only other parameter in equation (1), the density of the iridium had to be found as a function of temperature. Data were taken from the results of work done by Halvorson and Wimber¹³ on the thermal expansion of iridium and least squares curve fit in the range of 1873 to 2473 °K, which is the range of T_k encountered experimentally. This resulted in a maximum % deviation of 0.035% for the relation as shown below.

$$DL = 6.144 \times 10^{-6} T_k^{1.632} \quad (11)$$

where DL is the % change in length of iridium from 298 °K to T_k , and T_k is the experimental wire temperature in °K. Using the expression,

$$\rho_M = \frac{\rho_M @ 298^\circ K}{(1 + (DL @ T_k)/100)^3}, \quad (12)$$

the density of the iridium at any particular experimental value of wire temperature T_k , was found. Then the value of A was found for each run, where,

$$A = \frac{192.2 \text{ gm iridium consumed/mole oxide formed}}{\rho_M @ T_k} \quad (13)$$

At this point the theoretical recession rate, $\dot{x}_t$, was calculated from equation (1) for each of the experimental conditions of the runs made. Comparison of experiment with theory revealed a difference of about one order of magnitude in the recessions rates of theory and experiment. It was also noted that the best correlation resulted when K_1 of equation (1) was essentially zero. It was then concluded that if IrO is present at all, it is so in relatively small quantities. Thus the term corresponding to IrO participation was excluded from further consideration, changing equation (1) to,

$$\dot{x}_t = A(k_{G2} K_2^{\alpha} P_{O_2} + k_{G3} K_3 P_{O_2}^{3/2} + k_{GM} K_M) \quad (14)$$

Because of the fact that the ΔH_f° and ΔS_f° values have considerable uncertainty associated with them, as may be seen by close examination of Table V, it was deemed reasonable to then treat the equilibrium constants K_2 and K_3 as unknowns. The equilibrium constant K_M , the accommodation coefficient α , and the melting temperature T_m of the IrO_2 and IrO_3 were the only other uncertain parameters involved in the calculation of $\dot{x}_t$, and thus were also treated as unknowns. The results of employing an optimization process to find the best values of the unknowns K_2 , K_3 , K_M and α for different values of T_m are listed in Table VII. The column headed "Mean % Error" is the average of the difference between $\dot{x}_t$ and $\dot{x}_e$ divided by $\dot{x}_t$ for the runs at that particular level of T_s . It was noted that the total of the mean % error of the three T_s levels, or the quality of the fit of the theoretical model, was best at the 1400 and 1500 K values for T_m .

Table VII. OPTIMIZATION RESULTS - FINAL VALUES FOR EQUILIBRIUM
CONSTANTS AND ACCOMODATION COEFFICIENT

T_m °K	T_s °C	K_2	$\Delta F_f^\circ - \text{IrO}_2$ kcal/mole	K_3	$\Delta F_f^\circ - \text{IrO}_3$ kcal/mole	K_M	α	Mean % Error
1400	1600	8.81×10^{-4}	26.2	2.67×10^{-3}	22.1	$< 10^{-12}$	0.389	13.5
1500*	1600	8.80	26.2	2.70	22.0	$< 10^{-12}$	0.395	13.4
1600	1600	9.05	26.1	2.70	22.0	$< 10^{-12}$	0.400	14.1
1700	1600	9.30	26.0	2.70	22.0	$< 10^{-12}$	0.406	14.7
1800	1600	9.54	25.9	2.70	22.0	$< 10^{-12}$	0.410	15.3
1400	1900	2.17×10^{-3}	26.5	3.63	24.3	$< 10^{-12}$	0.645	11.8
1500*	1900	2.19	26.5	3.66	24.2	$< 10^{-12}$	0.645	11.8
1600	1900	2.20	26.4	3.68	24.2	$< 10^{-12}$	0.643	11.8
1700	1900	2.20	26.4	3.71	24.2	$< 10^{-12}$	0.690	12.1
1800	1900	2.20	26.4	3.75	24.1	$< 10^{-12}$	0.754	12.5
1400	2200	8.63	23.4	4.68	26.4	2.46×10^{-8}	0.219	14.9
1500*	2200	8.68	23.3	4.73	26.3	2.46	0.221	15.0
1600	2200	8.72	23.3	4.78	26.3	2.46	0.223	15.2
1700	2200	8.77	23.3	4.82	26.2	2.46	0.224	15.2
1800	2200	8.81	23.2	4.86	26.2	2.46	0.227	15.3

* These values were used in the final correlation of $\bar{x}_t$ with $\bar{x}_e$.

Because the value of T_m must then be between 1400 and 1500 °K, and the quality of the fit is very insensitive in this range, the value of $T_m = 1500$ °K for IrO_2 and IrO_3 was retained. The final correlation was based on the standardized surface recession rates $\dot{x}_{st}$ and $\dot{x}_{se}$ as arrived at using the values of K_2 , K_3 , K_M , and α as indicated in Table VII to calculate $\dot{x}_{st}$.

Figure 3 shows the results graphically of $\dot{x}_{se}$ and $\dot{x}_{st}$ versus P_{O_2} , while Table VIII indicates the numerical results. In Table VIII, the column headed "% Error" is the % difference between $\dot{x}_{st}$ and $\dot{x}_{se}$, based on $\dot{x}_{st}$. The theoretical model described by equation (14) fit the experimental results with a mean % error per run, of 13.4% at 1600 °C, 11.8% at 1900 °C, and 15.0% at 2200 °C, or 13.3% for an overall mean % error in the 1600 to 2200 range. Also, the column headed "% Exper. Dev." is the difference between $\dot{x}_{se}$ and the mean value of $\dot{x}_{se}$ divided by the mean $\dot{x}_{se}$ for a particular set of runs at the same temperature and pressure, i.e. the % experimental deviation. The mean % experimental deviation for all the runs was 8.5%.

To enable a comparison of ΔH_f° and ΔS_f° with previous experimenters, the values of ΔF_f° for IrO_2 and IrO_3 in Table VII, were least squares curve fit to the linear relation $\Delta F_f^\circ = \Delta H_f - T_K \Delta S_f^\circ$. This calculation of the values of ΔH_f° and ΔS_f° "filters" out the small dependence of these parameters on temperature in the 1600 to 2200 °C range, as can be seen by inspection of Table VII. The results obtained were, for IrO_2 , $\Delta H_f = 35.7 \text{ kcal/}$

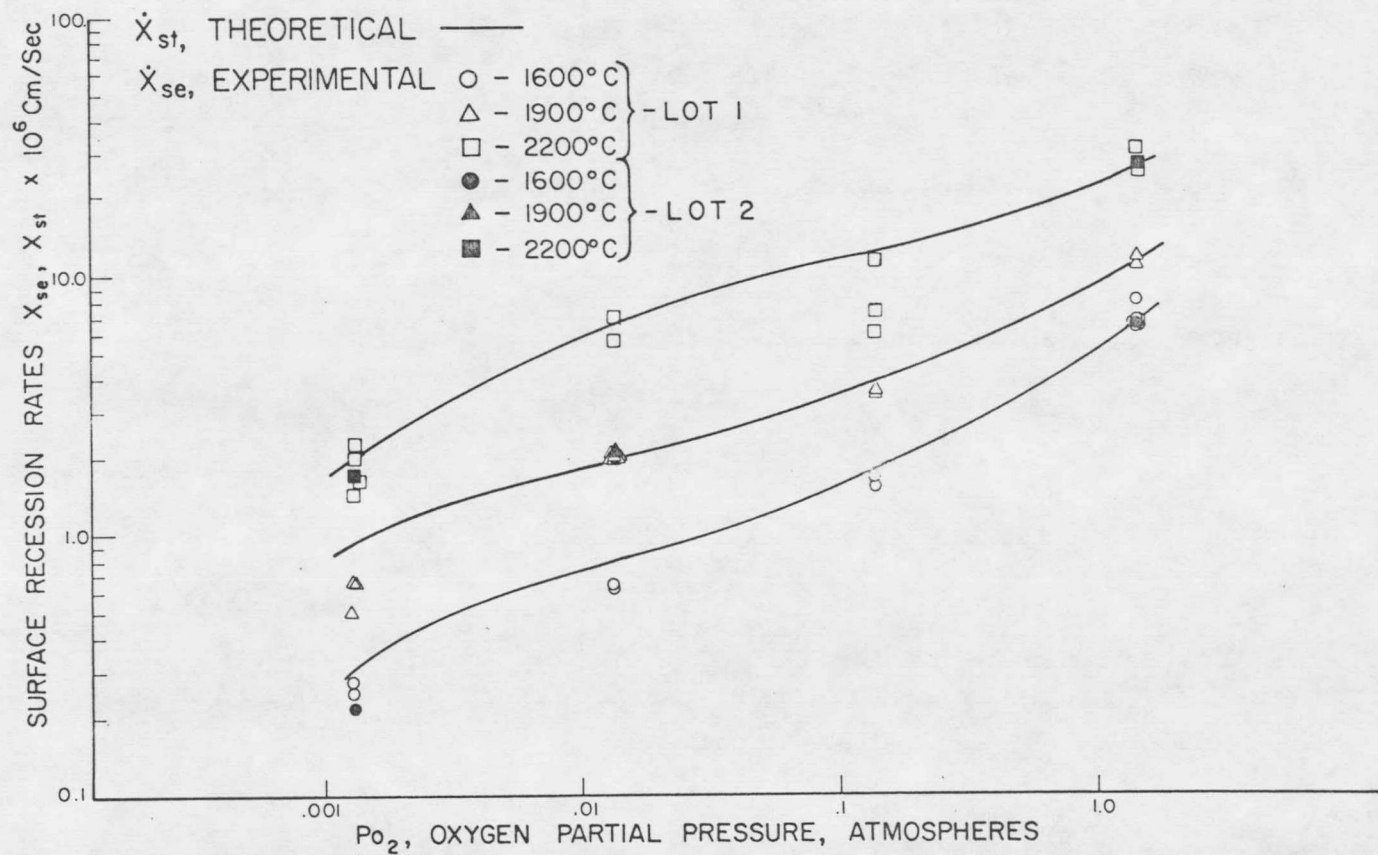


Figure 3. PLOT OF EXPERIMENTAL AND THEORETICAL RECESSION RATES VERSUS OXYGEN PARTIAL PRESSURE

Table VIII. FINAL CORRELATION DATA

 $\dot{x}_{st}$ & $\dot{x}_{se}$ @ $D = 0.0588$ cm

$T_s, ^\circ C$	$\dot{x}_{se} \times 10^6$ cm/sec	$\dot{x}_{st} \times 10^6$ cm/sec	% Error	% Exper. Dev.
1600	0.249	0.304	-18.2	1.6
1600*	0.269	0.304	-11.6	8.9
1600	0.217	0.304	-28.6	-12.9
1600	0.635	0.802	-20.8	0.2
1600	0.632	0.802	-22.4	-0.2
1600	1.53	1.87	-18.2	-4.6
1600	1.67	1.87	-10.8	4.2
1600	5.88	6.45	-8.9	-13.3
1600	6.56	6.45	1.7	-1.5
1600	6.62	6.45	2.6	-0.6
1600	6.68	6.45	3.5	0.3
1600	6.63	6.45	2.7	-0.5
1600	6.49	6.45	0.6	-2.6
1600	8.09	6.45	25.4	17.7
1600*	6.34	6.45	-1.8	-5.0
1900	0.679	0.929	-26.9	9.0
1900	0.501	0.929	-46.1	-22.8
1900	0.665	0.929	-28.4	8.1
1900	2.08	1.96	5.9	2.4
1900	2.12	1.96	8.1	4.2
1900	1.88	1.96	-4.3	-8.0
1900	1.90	1.96	-3.0	-6.8
1900	1.95	1.96	-0.7	-4.1
1900	1.96	1.96	0.0	-5.7
1900*	2.22	1.96	13.0	8.6
1900	2.12	1.96	7.8	4.2
1900	3.59	3.80	-5.6	1.4
1900	3.49	3.80	-8.2	-1.4
1900	11.7	10.9	7.3	3.4
1900	10.9	10.9	0.3	-3.7
2200	1.45	1.93	-24.9	-23.7
2200	1.68	1.93	-13.0	-6.9
2200	2.26	1.93	17.3	20.6
2200*	1.92	1.93	-0.2	6.6
2200	1.66	1.93	-13.9	-8.1
2200	6.95	6.31	10.3	11.0

Table VIII. (Continued)

2200	5.42	6.31	-14.0	-14.1
2200	11.4	11.8	-3.1	28.7
2200	5.97	11.8	-49.1	-36.2
2200	7.02	11.8	-40.3	-15.8
2200	30.0	25.3	18.4	-10.7
2200	25.6	25.3	0.8	-4.7
2200*	24.8	25.3	-2.0	-8.1

* Has same meaning as in Table III.

mole and $\Delta S_f^\circ = 4.77$ eu and for IrO_3 , $\Delta H_f^\circ = 8.63$ kcal/mole and $\Delta S_f^\circ = -7.16$ eu.

DISCUSSION OF RESULTS

The overall mean % error of the surface recession rates predicted theoretically was 13.3% as compared to a mean % experimental deviation of 8.5%. When considering the type of work involved in the present study, and the inherent experimental error or experimental data scatter, this was seen to be an excellent degree of correlation.

Because ΔH_f° and ΔS_f° are temperature dependent parameters, direct comparison of these values for IrO_2 and IrO_3 in the present report, to those summarized in Table V, is not fully possible. Table IX shows some typical trends in the ΔH_f° and ΔS_f° values for one volatile dioxide specie and two volatile trioxide species, showing the temperature dependence involved.^{22,23} It was seen that the ΔH_f° for MoO_2 tends to decrease with temperature, and thus ΔH_f° for IrO_2 might also be expected to decrease with temperature. Making a comparison, the ΔH_f° of 35.7 kcal/mole for the 1600 to 2200 °C range of the present work is indeed less than the value of 48.5 kcal/mole reported by Norman et al, for the 1557 to 1760 °C range, as might be expected. When examining the ΔS_f° of MoO_2 , a slight decrease is seen with temperature, whereas the $\Delta S_f^\circ = 4.77$ eu for IrO_2 in the 1600 to 2200 °C of the present work falls within the range of both Norman et al's value of 3.9 ± 2.0 eu in the 1557 to 1760 °C range for IrO_2 and Searcy's value of 3.5 ± 2.1 eu for MO_2 at 25 °C. From this, results of the present work,

Table IX. TYPICAL TRENDS FOR VOLATILE DIOXIDE AND TRIOXIDE SPECIES
AS A FUNCTION OF TEMPERATURE

Oxide Specie	ΔH_f° kcal/mole	ΔS_f° eu	Temp. ° K
MoO_2^{23}	-4.33	8.45	1000
	-5.39	7.53	1500
	-6.99	6.65	2000
MoO_3^{22}	-120.	-40.3	1068
	-107.	-28.1	1530
	-82.9	-1.24	2500
WO_3^{22}	-133.0	-37.9	1743
	-115.8	-28.0	2100
	-83.2	-12.5	2500

Norman et al's work, and Searcy's work seem to indicate that ΔS_f° for IrO_2 is relatively temperature insensitive in the 25 to 2200 °C range.

By using Tables V and IX again, an increasing trend with temperature was seen for ΔH_f° of MoO_3 , WO_3 and IrO_3 . This tended to be true for the present work for which ΔH_f° for IrO_3 was 8.63 kcal/mole in the 1600 to 2200 °C range when compared to the 5.5 ± 1.5 kcal/mole in the 1557 to 1760 °C range of Norman et al's work. But the 8.63 kcal/mole was a little higher than the 6.0 kcal/mole for IrO_3 in the 1627 to 2227 °C range reported by Olievi. The ΔS_f° values show a similar increasing trend with temperature for MoO_3 , WO_3 , and IrO_3 . This was mostly the case, for ΔS_f° for IrO_3 of -7.16 eu of the present work in the 1600 to 2200 °C range when comparing the ΔS_f° values of -10 to -15 eu for MO_3 at 25 °C reported by Searcy, the -13.1 ± 2.5 eu for IrO_3 in the 1557 to 1760 °C range by Norman et al, and the -9.0 eu for IrO_3 in the 1627 to 2227 °C range reported by Olievi. The ΔS_f° for IrO_3 of -7.16 eu is most directly comparable to, and was seen to be somewhat lower than the -9.0 eu because of the similar temperature ranges of 1600 to 2200 °C and 1627 to 2227 °C respectively.

SUMMARY AND CONCLUSIONS

It was seen that the main species present in the oxidation of iridium are IrO_2 , IrO_3 , and Ir with the latter being important only at the 2200 °C level. Except for the inclusion of Ir at 2200 °C these results coincide with the limited theoretical success of Tempero's work in the forced convection oxidation of iridium area. The theoretically predicted recession

rates, by use of equation (14), yielded a mean % error from experiment of 13.4, 11.8, and 15.0% at 1600, 1900, and 2200 °C respectively, or an overall mean % error of 13.3% for the 1600 to 2200 °C range. Values were found for ΔH_f° and ΔS_f° for IrO_2 and IrO_3 for the temperature range 1600 to 2200 °C and are; 35.7 kcal/mole and 4.77 eu and; 8.63 kcal/mole and -7.16 eu, in their respective orders.

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