HIGH TEMPERATURE ELECTROCHEMICAL RESEARCH IN METALLURGY

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The Ohio State University Research Foundation

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#### INTRODUCTION

During the first six months of this project, most of the specific research topics which were outlined in the original proposal have been initiated. The proposed research concerning a sulfur probe will begin soon. The initiation of research involving the coulometric kinetic apparatus will await some further testing and optimization of the coulometric oxygen control device.

As expected, the initial contract period was partly used to familiarize the graduate students with the literature, principles, relationships, calculations, apparatus, etc. pertinent to high temperature solid electrolyte research. However, as will be described in some detail, progress in the theoretical description of several of the systems, as well as the design and construction of devices and experimental arrangements, has already been made. The experimental apparatus for the several research topics is in various degrees of completion; obviously, the research with flowing liquid metals will involve more complex experimental problems than those for the control of oxygen in gas mixtures.

On March 30 and 31, our chemical metallurgy research group was visited by Professor Sven Eketorp and seven advanced graduate students from the Ferrous Metallurgy Division of the Royal Institute of Technology, Stockholm, Sweden. After a series of presentations describing the research activities of each group, individual discussions with inspection of apparatus and facilities brought about a mutual exchange of ideas and information which may lead to further interaction and cooperation between the research groups.

In the following pages, specific reference is made to the nature and the progress on the individual research topics. Associated with the title of each topic is the name of the graduate student who is active with that particular aspect of the research. Periodic "project meetings" involving the principal investigators and the graduate students have been used to accomplish an understanding of the total research area by those engaged in the research. The following research topics will be discussed:

- 1. A Device for the Control of Oxygen Activities in Gases
- 2. A Study of Characteristics of Coulometric Pumping and the Control of its Rate into High Temperature Gases

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3. The Coulometric Control of Oxygen in Liquid Metals

- 4. Kinetic Study of Oxygen Absorption by Molten Iron and Iron Alloys
- 5. The Design and Testing of an Electrocatalytic Afterburner for Automobile Exhaust Emissions

# 1. <u>A Device for the Contr 1 of Oxygen Activities</u> in Gases (Y. Agrawal)

As discussed in the contract proposal, a feed-back control circuit (potentiostat) is being designed to accomplish the electrochemical control of the oxygen activity in gas mixtures.\* The current status of this device is illustrated schematically in Fig. 1. A few important design improvements have been made. Firstly, contrary to the oxygen pumping cell of Yuan and Kroger,<sup>1</sup> it seems necessary to separate the inner "reading" electrode from the inner "pumping" electrode in the cell arrangement as shown in Fig. 1. The rationalization for this requirement follows.

The outer reference electrodes (Pt<sub>3</sub> and Pt<sub>2</sub> in Fig. 1) for the pumping and reading cell, respectively, should both equilibrate readily with the surrounding air at  $P_{O_2} = 0.21$  atm. If a voltage, E, were impressed across the pumping cell, with only a small flow of current, then for the pumping cell,

$$E \approx \frac{RT}{4F} \ln \frac{P_{02}(ref.)}{P'_{02}(gas)}$$

where  $P_{0_2}(\text{ref.}) = 0.21$ , and  $P'_{0_2}$  is the oxygen activity which is desired for the gas phase flowing past the inner pumping electrode. Depending upon the ionic resistance of the pumping cell, the amount of change in  $P_{0_2}$  required to reach  $P'_{0_2}$ , the rate of adsorption, desorption, or reaction on the pumping electrode, and the degree of mixing in the flowing gas, the desired  $P'_{0_2}$  may or may not be accomplished by the coulometric pumping. In all cases, the system will be used with  $P'_{0_2} < 0.21$ . The downstream reading cell with electrodes  $Pt_1$  and  $Pt_2$  is intended to measure the average  $P_{0_2}$  in the gas phase for comparison with the desired  $P'_{0_2}$ . However, if the inner electrodes of the pumping and reading cells are made common (as was done by Yuan and Kroger<sup>1</sup>), then they are necessarily at the same potential. Because the two outer reference electrodes are necessarily equilibrated with air and, therefore, at the same oxygen activity, it seems that the voltage of the reading cell

<sup>\*</sup> Prior to the initiation of the contract research, a U. S. patent application Serial No. 835,101 describing this control system was filed on June 20, 1969.



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would necessarily agree with that of the pumping cell (except for a small IA product in the pumping cell), but would not represent a measurement of  $P'_{0_2}$ , the average oxygen activity in the exit gas. In our control cell which is presently under evaluation, the inner electrodes have been separated and provided with separate Pt lead wires as shown in Fig. 1. To generalize the situation, when two gas electrodes of a given cell are required to set up a difference in  $P_{0_2}$  because of the application of an impressed voltage, the electrode at the higher  $P_{0_2}$  would be expected to remain reversible, while coulometric pumping would accomplish the required change in the oxygen activity in the electrode of lower  $P_{0_2}$ . For this reason the outer reference electrodes,  $Pt_2$  and  $Pt_3$ , may be made common (they are both equilibrated with  $P_{0_2} = 0.21$  anyway), but the inner electrodes at lower  $P_{0_2}$  may not be made common if the reading cell is indeed intended to measure the actual  $P'_{0_2}$  of the flowing gas phase. Experiments to test this hypothesis and the revised cell design will be made soon.

To ensure that the oxygen activity measured by the inner electrode of the downstream reading cell is indeed the average  $P_{O_2}$  of the gas mixture, and not some steady-state  $P_{O_2}$  resulting from laminar flow in the tube and the presence of a stagnant gas film on the wall, a constriction has been placed inside the tube between the pumping and the reading cell. This ceramic constriction is a hollow cylinder approximately 10 mm long and 3 mm I.D. which fits snugly into the 12-mm I.D. CaO-stabilized zirconia electrolyte tube and is positioned between electrolyte tube and is positioned between electrodes Pt<sub>4</sub> and Pt<sub>1</sub>. This venturi should create sufficient turbulence in the gas stream so that the reading cell will indicate the average  $P_{O_2}$  of the gas phase after pumping. The potentiostatic control circuit can then use the voltage based on the measured  $P_{O_2}$  for comparison with the desired  $P_{O_2}$ , so that the current to the pumping cell can be properly provided.

In the potentiostatic control device, a divider circuit has been introduced so that the ratio (E/T) of Eq. (1) is controlled rather than E. Control of the ratio (E/T) allows the setting of a desired  $P_{O_{\mathcal{D}}}$  in the exit gas to be independent of small (or even large) fluctuations in the temperature of the reading cell. A computer program relating combinations of  $P'_{O_2}$  and various cell temperatures to the values of (E/T) has been run. However, it is now apparent that a small improvement in this part of the circuit can be made. Initially, the voltage from the reading cell thermocouple was used in the divider circuit to indicate T, and the room-temperature cold-junction correction, as well as the 273° required for absolute temperature, were added "manually" (by calculation) to convert the thermocouple voltage to °K. We are presently, however, revising the thermocouple input to the divider circuit such that the two corrections required to obtain °K are automatically added electrically into the control circuit. After experiments have demonstrated the reliability of the control device, schematic drawings of the electrical circuitry will be provided in a technical report.

The control cell has recently been revised and experiments are under way to investigate its effectiveness in controlling the oxygen activity in  $Ar-O_2$ ,  $CO-CO_2$ , and  $H_2-H_2O$  gas mixtures for various flow rates and cell temperatures. A demonstrated success for this device is required before the design and use of the coulometric kinetic apparatus can be initiated.

# 2. <u>A Study of the Characteristics of Coulometric</u> <u>Pumping and the Control of its Rate into High-</u> <u>Temperature Gases</u> (A. Mogollon)

To learn more about the interaction between a flowing gas an a surrounding, cylindrical pumping electrode, we are analyzing the composition change of the gas in terms of the three contributing and, perhaps, limiting factors:

- (a) assuming a reversible electrode on the outside of the electrolyte tube ( $P_{O_2} = 0.21$ ), the ionic conductivity of the electrolyte may limit the rate of passage of oxygen through the tube;
- (b) a surface reaction between adsorbed 0 or 0<sub>2</sub> and C0 or H<sub>2</sub>, or desorption of 0<sub>2</sub> at the inner pumping electrode may limit the rate of oxygen transfer to the gas stream;
- (c) mass transport between the flowing gas and the pumping electrode may limit the rate of reaction (or desorption).

We are beginning to analyze by calculation the rate of oxygen transfer under the assumption that only one of these steps is rate controlling while negligible gradients exist at the other two. Thus, three different calculations are foreseen. Each calculation should predict a certain dependence for the current density, j, as a function of x (distance along the electrode), and, therefore, a certain total composition change ( $I_{total}$ ) for a given applied E.

It is important to realize that the intended calculations and experiments do not involve the use of a potentiostatic control circuit, as was described in the preceding section. However, a cylindrical solid electrolyte tube with a pumping and a reading cell as illustrated in Fig. 1 is the pertinent experimental arrangement. The calculations assume that a given constant voltsge is applied to the pumping cell. With the passage of a given total current ( $I_{total}$ ) through the pumping cell, a change in the average oxygen activity of the gas phase will be accomplished. The resulting average P<sub>0</sub> will be indicated by the measuring cell and compared with the P<sub>02</sub> calculated from Eq. (1) to establish the efficiency of the pumping process in achieving a desired P<sub>00</sub>.

To analyze the pumping characteristics under rate control by step (a), i.e., that oxygen transfer through the tube is limited by the ionic conductivity of the tube, let us assume:

- (i) the electrode reactions are very fast and are, therefore, in local equilibrium,
- (ii) perfect mixing occurs in the gas stream so that no radial composition gradients exist in the gas as it flows through the pumping cell, and
- (iii) diffusion within the flowing gas phase in the longitudinal direction is negligible.

At steady-state, let an inert gas with oxygen partial pressure  $P_{O_2}(x=0)$  enter a pumping cell with internal radius,  $r_i$ , and external radius,  $r_0$ . For each stationary volume element within the pumping cell, the rate that oxygen leaves the element (moles/sec) equals the rate at which oxygen flows into the element (moles/sec) plus the rate at which oxygen is pumped into the element ( $(dn_{O_2}/dt)_I$  in moles/sec), or

$$\left(\frac{\mathrm{dn}_{O_2}}{\mathrm{dt}}\right)_{\mathbf{X}} + \left(\frac{\mathrm{dn}_{O_2}}{\mathrm{dt}}\right)_{\mathbf{I}} = \left(\frac{\mathrm{dn}_{O_2}}{\mathrm{dt}}\right)_{\mathbf{X} + \Delta \mathbf{X}}$$
(2)

From Faraday's law

$$\left(\frac{dn_{O_2}}{dt}\right)_{I} = \frac{j(x) \ 2\pi r_{i} \Delta x}{4F}$$
(3)

where j(x) is the local current density at the inner pumping electrode.

From the ideal gas law

$$\left(\frac{dn_{O_2}}{dt}\right)_{\mathbf{X}} = \frac{\left(\frac{P_{O_2}}{\mathbf{x}}\right)_{\mathbf{X}}}{\mathbf{RT}} \left(\frac{d\mathbf{V}}{dt}\right)_{\mathbf{X}} = \frac{\left(\frac{P_{O_2}}{\mathbf{x}}\right)_{\mathbf{X}}}{\mathbf{RT}} \quad \mathbf{G}_{\mathbf{X}}$$
(4)

where  $(dV/dt)_x = G_x$  is the total volumetric flow rate  $(cm^3/sec)$  through the tube at distance x. Then

$$\left(\frac{dn_{0_2}}{dt}\right)_{x+\Delta x} = \frac{\left(\frac{P_{0_2}}{x+\Delta x}\right)_{x+\Delta x}}{RT} G_{x+\Delta x}$$
(5)

For the addition of only a relatively small amount of oxygen, only a negligible change in flow rate occurs, so that,

$$(G)_{\mathbf{X}} \approx (G)_{\mathbf{X} + \Delta \mathbf{X}} = G \tag{6}$$

With the substitution of Eqs. (3) to (6) into Eq. (2),

$$\frac{G}{RT} \left[ \left( P_{O_2} \right)_{x+\Delta x} - \left( P_{O_2} \right)_x \right] = \frac{\pi r_1}{2F} j(x) \Delta x$$
(7)

Division of Eq. (7) by  $\Delta x$  and taking the limit as  $\Delta x \rightarrow 0$ :

$$j(x) = \frac{2FG}{RT_{\pi}r_{i}} \left(\frac{dP_{0_{2}}}{dx}\right)$$
(8)

The local driving force for the passage of oxygen ions through the electrolyte is  $E_{net}$ , the difference between the applied voltage,  $E_{appl.}$ , and the local chemical voltage,  $E_{chem.}(x)$ , of the pumping cell, where

$$E_{\text{chem.}}(x) = \frac{RT}{4F} \ln \frac{P_{O_2}(\text{ref})}{P_{O_2}(x)} = \frac{RT}{4F} \left[ \ln P_{O_2}(\text{ref}) - \ln P_{O_2}(x) \right]$$
(9)

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$$\mathbf{E}_{\text{net}} = |\mathbf{E}_{\text{appl.}}| - |\mathbf{E}_{\text{chem.}}| \tag{10}$$

Over the incremental electrode length  $\triangle x$ ,

$$\mathbf{E}_{\text{net}} = \mathbf{j}(\mathbf{x}) 2\pi \mathbf{r}_{\mathbf{i}} \Delta \mathbf{x} \Omega \tag{11}$$

where the ionic resistance  $\Omega$  through the wall of the hollow, cylindrical electrolyte tube is given by

$$\Omega = \frac{1}{2\pi\sigma_{ion}\Delta x} \ln \frac{\mathbf{r}_{o}}{\mathbf{r}_{i}}$$
(12)

Substitution of Er. (12) into Eq. (11) gives

$$\mathbf{E}(\mathbf{x})_{net} = \frac{\mathbf{j}(\mathbf{x})\mathbf{r}_{\mathbf{i}}}{\sigma_{\mathbf{ion}}} \ln \frac{\mathbf{r}_{\mathbf{o}}}{\mathbf{r}_{\mathbf{i}}}$$
(13)

Substitution of Eqs. (8), (9) and (13) into Eq. (10) gives

$$F_{appl.} - \frac{RT}{4F} \ln P_{O_2}(ref) = \left[\frac{2FG}{RT\pi r_i \sigma_{ion}} \ln \frac{r_o}{r_i}\right] \left(\frac{dP_{O_2}}{dx}\right) + \frac{RT}{4F} \ln P_{O_2}$$
(14)

Equation (14) is of the form

$$A = B\left(\frac{dP_{0_2}}{dx}\right) + C \ln P_{0_2}$$
(15)

Rewriting Eq. (15), with further substitution of variables

$$\frac{dP_{0_2}}{dx} = \ln\beta - \frac{C}{B}\ln P_{0_2} = \ln\beta P_{0_2}^{-\frac{C}{B}}$$
(16)

Integration of Eq. (16) gives

$$x = \int_{P_{O_2}}^{P_{O_2}(x)} \frac{dP_{O_2}}{\ln \beta P_{O_2} C/B}$$
(17)

$$C/B = \left(\frac{RT}{F}\right)^2 \frac{\pi r_i \sigma_{ion}}{8G}$$
(18)

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and

$$\beta = \exp\left[\left(\frac{RT_{\pi}r_{i}\sigma_{ion}}{2FG}\right)\left(\ell_{n}\frac{r_{o}}{r_{i}}\right)\left(E_{appl.} - \frac{RT}{4F}\ell_{n}P_{O_{2}}(ref)\right)\right] \quad (19)$$

Evaluation of Eq. (17) by numerical methods with the use of the computer will be accomplished to yield the function  $P_{O_2}(x)$  so that j(x) from Eq. (8) and the integrated  $I_{total}$  over the entire pumping electrode can be calculated.

In experiments involving various values of applied E (not using the potentiostatic control circuit), we shall attempt to measure j(x)(by using various lengths of pumping electrodes). We shall further measure I<sub>total</sub> vs. E<sub>appl</sub> to compare calculation and experiment. Of course, the theoretical analysis of the two other possible limiting steps must yet be accomplished. Ultimately, flowing Ar + O<sub>2</sub>, CO + CO<sub>2</sub>, and H<sub>2</sub> + H<sub>2</sub>O will be investigated at a couple of temperatures for a couple of electrodes (say Pt and Ag). The construction of the experimental apparatus is progressing.

### 3. The Coulometric Control of Oxygen in Liquid Metals (L. Friedman)

Oxygen is the principal refining agent used in modern metallurgical practice. Refining of the molten metal is accomplished by the formation of insoluble oxides through reaction of dissolved oxygen with impurity elements. The final composition and, therefore, to a great extent, the final properties of the metal are determined by the oxygen content of the bath, both during the refining period and when the refined metal is poured. The presence of nonmetallic oxide inclusions or porosity created by the evolution of gaseous oxide compounds during solidification can be extremely deleterious. This phase of the project deals with the application of high temperature, solid electrolyte electrochemical cells to control the oxygen content of liquid metals during their various stages of processing.

A. Feasibility Studies on the Use of Electrochemical Cells for the Continuous Coulometric Deoxidation of Flowing Liquid Metals

It has been proposed to remove oxygen from liquid metals by flowing them through or around cylindrical electrolyte tubes while inducing (through application of an external voltage) the transport of oxygen across the electrolyte, from the metal on one side to an oxygen sink (e.g., the atmosphere) on the other.

Analysis of the results of subsequent laboratory experimentation depends upon the development of theoretical models which treat the possible rate-limiting kinetic mechanism involved in transporting oxygen from the following bulk liquid across the electrolyte to a reference gas (sink).

a) Rate Limited by Transport of Oxygen Ions through Electrolyte

For a process limited by the rate of transport of oxygen through the solid electrolyte by ionic conduction, the theoretical rate of oxygen removal from a liquid by coulometric titration can be computed from relationships analogous to those derived and presented in the preceding section for oxygen removal from well-mixed flowing gases.

b) Rate Limited by Diffusion of Oxygen from the Bulk Liquid to the Metal/Electrolyte Interface

It is conceivable that in the absence of any appreciable turbulence within the flowing metal stream the rate of oxygen removal could be limited by atomic diffusion of dissolved oxygen in the liquid to the electrolyte interface. This situation has been treated mathematically. The analysis is outlined below.

> Oxygen Flux to and from a Stationary Volume Element Within the Electrolyte Tube

Conditions Imposed:

- (i) Cylindrical geometry
- (ii) Electrolyte tube completely filled with metal
- (iii) Steady-state conditions
- (iv) Laminar flow of metal stream
- (v) Oxygen diffusion coefficient independent of concentration

To obtain the concentration distribution of oxygen,  $e_0(r, t)$ , within the flowing metal stream, an oxygen flux balance must be made over a ring-shaped element of space inside the electrolyte tube as shown. This type of analysis is chosen because  $e_0$  is a function of r, the tube radius, and t, the longitudinal distance from the cell entrance, but not a function of time. Oxygen enters and leaves this ring because of diffusion in the liquid in both the r and t directions. In addition, oxygen will enter and leave the element because of metal flow in the tdirection. By noting also that steady-state conditions require the met oxygen flux be equal to zero, the flux balance

$$\left| \left( \frac{\partial e_0}{\partial t} \right)_{t=0,t} - \left( \frac{\partial e_0}{\partial t} \right)_t \right| b_0 + 2\pi \pi t d t = 0$$

$$\left| \left( \frac{\partial e_0}{\partial t} \right)_{t=0,t} - \left( \frac{\partial e_0}{\partial t} \right)_t \right| b_0 + 2\pi \pi t d t = 0$$

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$$\left| \left( \frac{\partial e_0}{\partial t} \right)_{t=0,t} - \left( \frac{\partial e_0}{\partial t} \right)_t \right| d t = 0$$

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$$\left| \left( \frac{\partial e_0}{\partial t} \right)_{t=0,t} - \left( \frac{\partial e_0}{\partial t} \right)_t \right| d t = 0$$

is obtained.  $D_0$  is the diffusion coefficient of oxygen in the liquid metal and  $v_p$  is the linear velocity of the liquid metal streamline at a distance r from the center of the tube.

In the limit as  $\Delta r$  and  $\Delta l$  approach zero, Eq. (20) becomes

$$\frac{\partial \mathbf{e}_{0}}{\partial t} \cdot \mathbf{v}_{\mathbf{r}} \cdot \mathbf{r} = \mathbf{b}_{0}\mathbf{r} \frac{\partial}{\partial t} \left(\frac{\partial \mathbf{e}_{0}}{\partial t}\right) \cdot \mathbf{b}_{0} \frac{\partial}{\partial \mathbf{r}} \left(\mathbf{r} \frac{\partial \mathbf{e}_{0}}{\partial \mathbf{r}}\right)$$
(21)

which is a specific second-order partial differential equation whose solution relates  $c_0$  to r and t under the assumed conditions of mass transport control and fluid flow behavior.

For laminar flow the radial velocity distribution within the liquid metal stream can be given as

$$v_{\rm F} = v_{\rm SMAX} \left( 1 - \frac{{\rm F}^2}{{\rm R}^2} \right)$$
 (22)

where R is the inner radius of the electrolyte tube (i.e., the outer radius of the metal stream) and  $v_{max}$  is the maximum linear velocity of a streamline at the center of flow. Under these conditions  $v_{max}$  is equal to twice the <u>average</u> linear velocity,  $\bar{v}$ , which is readily computed from the mass flow rate and the system geometry and which is the quantity most often directly measured. Substituting Eq. (22) into Eq. (21) and noting that oxygen transfer in the longitudinal direction by diffusion is very small in comparison to the transfer by forced connection, i.e., that the longitudinal diffusion term

$$b_0 \mathbf{r} \frac{\partial}{\partial t} \left( \frac{\partial \mathbf{e}_q}{\partial t} \right)$$

in Eq. (21) can be neglected, we arrive at the relationship

$$\mathbf{v}_{\mathbf{MAX}}\left[1-\frac{\mathbf{r}^2}{\mathbf{R}^2}\right]\left(\frac{\partial \mathbf{e}_0}{\partial t}\right) = \mathbf{D}_0\left[\frac{\partial^2 \mathbf{e}_0}{\partial \mathbf{r}^2} + \frac{1}{\mathbf{r}}\frac{\partial \mathbf{e}_0}{\partial \mathbf{r}}\right]$$
(23)

This partial differential equation, when solved for the appropriate boundary conditions

- (i)  $l \leq 0$ ,  $e_0 = e_0^2$  for all r
- (ii) & ≥ 0, e<sub>0</sub> = cg (constant) for r = R (potentiostatic gamping)
- (iii) r = 0, de\_/dr = 0 for all #
   (semi-infinite diffusion)

yields the theoretical concentration distribution of oxygen in the metal as it flows through the electrolytic oxygen removal cell.

To facilitate solution, Eq. (23) can be rewritten in the slightly modified form

$$2\overline{\mathbf{v}} \left[ \mathbf{1} - \frac{\mathbf{r}^2}{\mathbf{s}^2} \right] \frac{\partial \phi}{\partial t} = b_0 \left[ \frac{\partial^2 \phi}{\partial \mathbf{r}^2} + \frac{\mathbf{1}}{\mathbf{r}} \frac{\partial \phi}{\partial \mathbf{r}} \right]$$
(24)

where

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 $\theta = e_0 - e_0^{\rm H}$ 

a.m.t

 $c_{0}^{\infty}$  - concentration of oxygen in the metal at the wall of the electrolyte tube, assumed to be constant for  $j \ge 0$  as a direct result of the uniform potential difference applied through the wall of the electrolyte tube along the length of the pumping cell and the hypothesis of transport control by diffusion in the metal stream.

The separation of variables technique can be employed if it is assumed that

$$\theta(\mathbf{r},t) = \mathbf{L}(t) \cdot \mathbf{P}(\mathbf{r}) \tag{25}$$

Substituting this into Eq. (24) and separating variables,

$$\frac{\overline{dr}}{D_0 L} \frac{dL}{dg} = \frac{\frac{d^2 P}{dr^2} \cdot \frac{1}{r} \frac{dP}{dr}}{\left[1 - \frac{r^2}{R^2}\right] P}$$
(26)

Since the right-hand side of Eq. (26) is a function of r alone and the left-hand side a function of l alone, the value of the quantity to which each side is equal is dependent on neither l nor r; that is, it is a constant. If both sides are arbitrarily set equal to  $-1/b^2$ , then

$$\frac{dL}{ds} = -\frac{LD_0}{2m^2} \qquad (7.1)$$

and

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$$\frac{d^{0}P}{dr^{2}} = \frac{1}{r}\frac{dP}{dr} + \frac{1}{b^{0}}\left[1 - \frac{r^{2}}{R^{0}}\right]P = 0$$
(28)

The integral of Eq. (27) is

$$L = L_{0}e^{-(2\pi)^{2}}$$
(29)

where L is the constant of integration.

Substituting r/b = u and R/b = 0 into Eq. (28), one can show that a particular integral of this equation is

$$F(U) = \sum_{p=0}^{n} B_{2n} U^{2n} + B_0 - B_0 U^0 + B_4 U^4 + B_6 U^6 + \cdots$$
(30)

where

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 $B_{2n} = \frac{1}{(2n)^2} \left[ \frac{1}{\beta^2} B_{2n-4n} B_{2n-2} \right]$ 

 $B_0 = 1$ 

 $B_2 = -\frac{1}{2^2}$ 

so that

$$B_{4} = \frac{1}{16} \left[ \frac{1}{\beta^{2}} \cdot 1 + \frac{1}{4} \right] = \frac{1}{16\beta^{2}} + \frac{1}{64}$$
$$B_{6} = \frac{1}{36} \left[ -\frac{1}{4\beta^{2}} - \frac{1}{16\beta^{2}} - \frac{1}{64} \right] = -\frac{1}{144\beta^{2}} - \frac{1}{576\beta^{2}} - \frac{1}{2304} + \cdots$$

then,

$$P(U) = 1 - \frac{U^2}{4} + \frac{U^4}{16\beta^2} + \frac{U^4}{64} - \frac{U^6}{144\beta^2} - \frac{U^6}{576\beta^2} - \frac{U^6}{2304} + \cdots$$

This series is convergent for any value of U where  $\beta > 1$ . For r = R, by definition U =  $\beta$  and  $\theta = 0$ . Therefore, according to Eqs. (25) and (29), P = 0. In other words, the constants  $\beta$  are the roots of the equation

$$P(\beta) = 0 \tag{31}$$

The n<sup>th</sup> root may be denoted by  $\beta_n$ .

The general solution to the differential equation becomes

$$\theta = \sum_{n=0}^{n=\infty} L_{n} e^{-\left[\frac{\beta_{n}^{2}}{2} \cdot \frac{D_{0}}{R^{2} \overline{v}}\right] \ell} P_{n}\left(\frac{r}{R}\right)$$
(32)

where the substitution  $b = R/\beta$  has been made.

Nusselt<sup>2</sup> was able to calculate the n = 0, n = 1, and n = 2 values of  $\beta$ . These are:

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$$\beta_0 = 2.705$$
  
 $\beta_1 = 6.66$   
 $\beta_2 = 10.3$ 

He also determined values of  $P_n$  as a function of r/R noting that  $P_n(r/R)$  must satisfy Eq. (28). The values of  $P_0$ ,  $P_1$ , and  $P_2$  are given in the following table.

r/R	Po	P1	P <sub>2</sub>		
0	1	1	1		
0.1	0.9818	0.8923	0.753		
0.2	0.9290	0.6067	0.206		
0.3	0.8456	0.2367	-0.290		
0.4	0.7382	-0.1062	-0.407		
0.5	0.6147	-0.3399	-0.204		
0.6	0.4833	-0.4317	0.104		
0.7	0.3506	-0.3985	0.278		
0.8	0.2244	-0.3051	0.278		
0.9	0.1069	-0.1637	0.144		
1.0	0	0	0		

Introducing the boundary condition  $\theta = \theta_0$  at  $\ell = 0$ , so that

$$\theta_{0} = \sum_{n=0}^{n=\infty} L_{n}R_{n}$$
(33)

according to Eq. (32), where  $\theta_0 = c_0^1 - c_0^W$ , and proving mathematically that

$$L_{n} = -\frac{2\theta_{0}}{\beta_{n} \left(\frac{\partial P}{\partial \beta}\right)_{n,r/R=1}}$$
(34)

Graetz<sup>3</sup> was able to calculate values of  $N_n/\theta_0$ . He found for the first three terms (n = 0, 1, and 2) that

$$\frac{L_0}{\theta_0} = 1.477$$
$$\frac{L_1}{\theta_0} = 0.810$$
$$\frac{L_2}{\theta_0} = 0.385$$

Substituting the values of  $\beta_{n}$  and  $L_{n}/\theta_{0}$  in Eq. (32) we get

$$\frac{\theta}{\theta_0} = 1.477e^{-\left[\frac{3.658D_0}{\bar{v}R^2}\right]\ell} P_0(r/R) = 0.810e^{-\left[\frac{22.178D_0}{\bar{v}R^2}\right]\ell} P_1(r/R) + 0.385e^{-\left[\frac{53.050D_0}{\bar{v}R^2}\right]\ell} P_2(r/R) = \cdots$$

It can be seen that the concentration profile

$$\frac{\theta}{\theta_0} = \frac{c_0 - c_0^{\vee}}{c_0^1 - c_0^{\vee}}$$

depends only on the ratio r/R (i.e., P(r/R)) and the dimensionless group  $\frac{\beta_n^2 D_0}{2vR^2} \ell$ .

Since the imposed voltage in the intended experiments will drop the concentration at the wall to essentially zero, the final expression for concentration can be written as

$$\frac{c_0}{c_0^1} = 1.477 e^{-m_0 t} P_0(r/R) - 0.810 e^{-m_1 t} P_1(r/R) + 0.385 e^{-m_p t} P_2(r/R) - \cdots$$

where  $m = \frac{\beta_n^2 D_0}{2 \bar{v} R^2}$ .

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Although the sum of this series is not always oscillating, the exponents are rapidly decreasing so that three terms are sufficient for good accuracy.

#### c) Rate Limited by Reaction at the Electrolyte Interfaces

Analyses based on the assumption that the rate of oxygen removal is controlled by the rate of adsorption or desorption of oxygen at the inner and outer surfaces of the electrolyte are presently under consideration.

Considerable attention has been directed to the design of the experimental apparatus, in particular the establishment on a laboratory scale of a continuous, laminar flow of molton metal through a coulometric deoxidation cell. Initial designs incorporating a large reservoir of molten metal above the deoxidation tube were seen to be impractical. The experimental arrangement now under consideration is diagraned in Fig. 2. Nolten metal is electromagnetically pumped up from an inductively heated chamber positioned above the reservoir. The metal then drains back down to the lower reservoir by passing through an electrolyte tube which is the electrolytic oxygen removal cell. The metal should be well mixed and of uniform oxygen concentration as it enters the pumping cell. The metal flow rate through the electrolyte tube can be controlled by controlling the height of the metal above it; flows can be adjusted from strictly laminar into the turbulent regime. The surface of the molten metal would be protected from extraneous oxygen absorption by a layer of molten glass.

The analysis of this system would be based on the mean exygen concentration of the outlet stream of the pumping cell. It can be shown<sup>5</sup> that the mean concentration  $\theta_n$  is given by the relationship

$$\theta_{n} = \sum_{n=0}^{n} N_{n} e^{-\theta_{n} t}$$
(35)

where

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$$H_{n} = \frac{\theta \theta_{0}}{\theta_{n}^{2}} \left[ \frac{dP_{n}}{dr} \frac{\partial P_{n}}{\partial \theta_{n}} \right]_{r/R} = 1$$

 $M_{0}$  can be obtained from  $\beta_{n}$  and Eq. (40).

Jakob<sup>6</sup> computed the following three values:



Fig. 2 - Conception of Experimental Arrangement for Deoxidation of Continuously Flowing Liquid Metals

$$\frac{M_2}{\theta_0} = 0.0135$$

By substitution of these values in Eq. (35), we obtain the converging series

$$\frac{d_{m}}{d_{0}} = 0.820e^{-m_{0}\ell} + 0.0972e^{-m_{1}\ell} + 0.0135e^{-m_{2}\ell} \cdots$$
(36)

where again  $m_n = \frac{\beta_n^2 D_0}{2 \bar{v} R^2}$ .

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The metal in the lower reservior would be treated as if it were in a stirred pot and the average oxygen activity of this reservoir would be determined periodically by an auxiliary solid electrolyte probe cell.

#### Experiments on the Removal of Oxygen from Non-flowing Metals

Preliminary to working with flowing metals, coulometric deoxidation of stationary liquid copper is being investigated not only to ascertain the effects of variation of electrolyte materials, metal temperature, oxygen concentration, system geometry, degree of agitation, and applied cell voltage on the rate of oxygen removal for reference in the later work, but to gain some degree of expertise on experimental technique and procedure as well.

The experimental apparatus which has been set up for this purpose is depicted schematically in Fig. 3. The molten copper and its containing crucible, a closed-end cylindrical tube (6" high, 2-1/2" I.D., and 3/16" wall), are held in a constant temperature zone of a molybdenumwound resistance furnace. The crucible, composed of ZrO2-10 mole % Y2O3, serves a dual role as the solid electrolye in the oxygen pumping circuit. Initially, the molten copper has dissolved in it a known amount of oxygen; a one-inch deep molten silica glass cover is provided at the copper surface to prevent leakage of additional oxygen into the metal from external sources. A conventional ceramic cover is also used both to support the thermocouple and the cell electrode lead which protrude down into the melt and to prevent foreign matter from falling into the bath. Electrical contact is established with the molten copper through a chronium cernet rod (72% Cr - 28% Alo03) to alleviate contamination of the metal by the lead material. Contact on the outside of the electrolyte crucible is achieved by platinization of the crucible wall as previously described. Argon gas of constantly monitored oxygen concentration is passed around the outer walls of the crucible to serve as a referince gas and oxygen sink.



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A potential difference, applied across the electrolyte by means of a potentiostat as shown in Fig. 3 is used to force the oxygen concentration at the liquid copper/electrolyte interface (inner crucible wall) to a very low level. This results in the establishment of a radial oxygen concentration gradient within the copper if oxygen transport in the metal is the mechanism which governs the rate of oxygen removal from the bath. The current, I, flowing in the cell circuit is measured with the aid of a milliammeter and represents the rate at which oxygen is being removed from the metal.

For the case of a completely quiescent melt, Fick's second law of diffusion can be employed to obtain an expression for the theoretical cell current as a function of time. Expressed in cylindrical coordinates this is written as

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$$\frac{\partial \mathbf{c}_{0}}{\partial \mathbf{t}} = \frac{1}{\mathbf{r}} \frac{\partial}{\partial \mathbf{r}} \left[ \mathbf{r} \mathbf{D}_{0} \frac{\partial \mathbf{c}_{0}}{\partial \mathbf{r}} \right]$$
(37)

where any axial diffusion of oxygen is assumed to be very small and is therefore neglected.

The boundary conditions for this experimental arrangement are

(i) At t = 0, 
$$c_0(r, 0) = c_0^1$$
 for  $0 \le r < R$   
(ii) At t > 0,  $c_0(R, t) \approx 0$  for  $r = R$ 

Assuming that  $D_0 \neq f(r,c_0)$  and applying the boundary conditions yields a solution to Eq. (37) of the form<sup>4</sup>

$$\frac{\overline{c}_{o}}{c_{o}} = \sum_{n=1}^{n=\infty} \frac{\mu}{\lambda_{n}^{2}} \exp \frac{-\lambda_{n}^{2} D_{o} t}{R^{2}}$$
(38)

where  $c_0$  is the average concentration of oxygen in the melt at time t, and R is the inner radius of the containing crucible.

The total amount of oxygen that has been removed from the metal at time t, expressed as  $M_t$ , and the amount which is diffused out in infinite time,  $M_{\omega}$ , which represents the total amount of oxygen initially dissolved (a constant), can be found from Eq. (38) as

$$\frac{M_{t}}{M_{w}} = 1 - \frac{4}{\lambda_{i}^{2}} \exp - \frac{-\lambda_{n}^{2}D_{o}t}{\pi^{2}}$$
(39)

where ), is the first root of the Bessel function of sero order (2,402).

Now the rate at which oxygen leaves the melt is given by the first time derivative of My which, seconding to Eq. (39) is

$$\frac{\mathrm{d} \mathbf{x}_{\mathrm{t}}}{\mathrm{d} \mathbf{t}} = \frac{\mathrm{k} D_0 \mathbf{y}_{\mathrm{s}}}{\mathrm{k}^2} \exp\left[\frac{-\lambda_{\mathrm{t}}^2 D_0 \mathbf{t}}{\mathrm{k}^2}\right] \tag{40}$$

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$$H_{\rm E} = \frac{1}{2T} \int_0^{\rm E} I \, dt \tag{41}$$

so that

$$2T \frac{\Phi t_0}{dt} = I \tag{42}$$

where F is the Faraday equivalent and I is the electric current in the cell circuit. Therefore, combining Eqs. (40) and (42), we arrive at the relationship

$$I = \frac{8D_0 N_m F}{R^2} \exp\left[\frac{-2.402D_0 t}{R^2}\right]$$
(43)

which represents the exponential decay of the cell current with time as oxygen is removed from the metal.

The experimental data for completely stagmant melts will be analyzed on the basis of Eq. (43). A relationship between cell current and time has also been derived for a well agitated melt on the basis of boundary layer theory. This relationship, by necessity, contains one adjustable parameter and consequently is not an exact expression. The derivation is not presented here. Experimentation is to begin presently on this phase of the project.

## 4. <u>Kinetic Study of Oxygen Absorption by</u> Molten Iron and Iron Alloys (S. Won)

In order to understand more completely the mechanism of oxygen solution and reaction in liquid iron, phenomena which are of prime importance to the refining operation, a study has been undertaken to determine the factors which affect the rate at which oxygen enters and undergoes reactions with impurity elements in molten iron.

It had been proposed to measure the rate of oxygen absorption into liquid iron by measuring the rate of change of oxygen activity at various struta within a metal pool. To accomplish these measurements a solid electrolyte tube would be used as the containing crucible for the molten charge. A series of oxygen activity measuring cells would be formed at intervals from the top of the crucible to the bottom by tightly wrapping platinum bands and lead wires around the exterior of the electrolyte crucible. One electrode of these cells would be a stratum of the molten iron containing dissolved oxygen; the reference electrode would be the gas phase surrounding the crucible.

Soon after initiating this program, it was realized that the transport of oxygen into the molten iron from the gas-liquid interface by atomic diffusion could possibly be short-circuited by the rapid transport of oxygen from regions of the melt high in oxygen concentration to regions lower in oxygen concentration by ionic conduction down the electrolytic crucible wall due to local cell action.

If this local cell action can indeed occur, then the experimental regults analyzed without taking this into account would have little significance. It was, therefore, decided to investigate the local cell phenomenon in more detail before proceeding further with the experimental program.

> Calculations on the Effect of Local-Cell Transport of Oxygen Ions Within an Electrolyte Wall on the Bate of Change of Oxygen Concentration in the Melt

Calculations are in progress which attempt to prodict theoretically the magnitude of a local-cell transport of oxygen into the metal. In the primary analysis, a slab geometry, as shown below, is assumed.



Constitues esement:

- (1) At  $\gamma = 0$ ,  $t \ge 0$ ,  $T_{D_{\alpha}}(gas) = T_{D_{\alpha}}(gata)$
- (11) At  $x = 0, y \ge 0, P_{D_y}(\text{metal}) = P_{D_y}(\text{alsb})$
- (111) At t = 0, for all x and all y,  $e_0^{11q} = e_0^{11q}(init.)$ 
  - (iv) so lateral gradients in oxygen activity exist within the electrolyte slab.

Conditions (i) and (ii) imply that local equilibrium is established rapidly at the phase interfaces. Therefore, we can write

$$e_{1}^{21}$$
 (x = 0, y, t) =  $\lambda_{x} \, y_{21}^{-\alpha}$  (x < 0, y, t) (10 slab) (44)

for the slab/metal interface where he is dieverts' inv constant, and

$$e_{0}^{12q}(x,y=0,t)=x_{q}T_{0q}^{2q}(qns)$$
 (45)

for the gus/owth) interface.

The local ionic current I down the electrolyte slab represents the passage of orygen loss and can be given as

$$I(y) = \frac{a_{10}}{27} \frac{\partial u_{0}}{\partial y}$$
(46)

where

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$$u_0 + u_0 + 2fg$$
 (47)

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me - chemical potential of anyon in electrolyte, and o - electrical potential.

However, no electrical potential gradient can exist down the slab because each segment of the slab is in contact with the same highly conducting metal (e.g., moltes iron).

therefore, since on is zero, Eq. (46) reduces to

$$\Sigma(\mathbf{y}) = -\frac{\partial \omega \delta}{\partial \mathbf{y}} \frac{\partial \omega_{\phi}}{\partial \mathbf{y}}$$
(46)

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$$u_0(0,y,t) - u_0(0,0,t) = 87 \ln \frac{P_{0,2}(0,y,t)}{P_{0,2}(0,0,t)}$$
(49)

Sputton (46) can be written as

$$\Gamma(\mathbf{y}, \mathbf{t}) = -\frac{\mathbf{y} \nabla_{\mathbf{0}} \mathbf{x} \mathbf{b}}{2\mathbf{y}} \frac{\mathbf{d} \ln \mathbf{y}_{\mathbf{0}} \mathbf{x}_{\mathbf{0}}^{\mathbf{x}}(\mathbf{0}, \mathbf{y}, \mathbf{t})}{\mathbf{d} \mathbf{y}}$$
(50)

substitution of Eq. (44) into (50) gives

$$I(\mathbf{y},\mathbf{t}) = -\frac{\mathbf{HTeut}}{2\mathbf{y}\mathbf{e}_{0}^{\mathbf{1}\mathbf{1}\mathbf{q}}(\mathbf{0},\mathbf{y},\mathbf{t})} \left(\frac{\partial \mathbf{e}_{0}^{\mathbf{1}\mathbf{1}\mathbf{q}}(\mathbf{0},\mathbf{y},\mathbf{t})}{\partial \mathbf{y}}\right) \tag{51}$$

Differentiating with respect to y.

$$\frac{\partial I}{\partial y} = \frac{-iT_{\text{BM}}}{2\pi} \left[ \frac{-1}{\left(\frac{1}{e_0^{11}q}\right)^2} \left( \frac{\partial e_0^{11}q}{\partial y} \right)^2 + \frac{1}{e_0^{11}q} \left( \frac{\partial^2 e_0^{11}q}{\partial y^2} \right) \right]$$
(52)

The oxygen current passing down the electrolyte will decrease with increasing y, because oxygen is entering the liquid metal at the electrolyte/metal interface. Considering the loss of oxygen to the liquid from both faces of the slab, at any y we have

$$\frac{\Delta I}{\partial y} = 2 \cdot 2 f_{\psi} J_{\phi}(y) \tag{53}$$

where  $J_{0}(y)$  is the local flux of anygen leaving the slab and u is the length of the slab (and effects are neglected).

Then, applying Flick's first law to Eq. (53)

$$\frac{\partial \mathbf{I}(\mathbf{y})}{\partial \mathbf{y}} = -4\mathbf{F}\omega D_{\mathbf{0}}^{\mathbf{1}\mathbf{i}\mathbf{q}} \left(\frac{\partial \mathbf{c}_{\mathbf{0}}^{\mathbf{1}\mathbf{i}\mathbf{q}}}{\partial \mathbf{x}}\right)_{\mathbf{x}=\mathbf{0}}$$
(54)

Comparing Eq. (54) with Eq. (52) we see that

$$\left(\frac{\partial \mathbf{c_o^{liq}}}{\partial \mathbf{x}}\right)_{\mathbf{x}=\mathbf{0}} = \frac{\mathrm{RT}_{\sigma b}}{\mathrm{8F^2}_{\mathbf{D}}^{\mathrm{liq}}} \left[\frac{1}{\mathbf{c_o^{liq}}} \left(\frac{\partial^2 \mathbf{c_o^{liq}}}{\partial \mathbf{y}^2}\right) - \frac{1}{(\mathbf{c_o^{liq}})^2} \left(\frac{\partial \mathbf{c_o^{liq}}}{\partial \mathbf{y}}\right)^2\right]$$
(55)

Equation (45) relates the oxygen gradient in the melt in the x - direction (down the slab) at the metal/electrolyte interface.

Additional work is being done to solve Eq. (55) to find an analytical expression for  $c_0^{jiq}(x,y,t)$  which is the quantity desired in order to evaluate the severity and consequences of a short-circuit path for oxygen transport into the melt. The available mathematical solutions treating short-circuit grain boundary diffusion into metals are being examined for assistance in this analysis.

### 5. <u>The Design and Testing of an Electrocatalytic</u> <u>Afterburner for Automobile Exhaust Emissions</u> (J. Burt, J. Kauffmann)

Consistent with the statement of our contract purpose, to control oxygen activities in flowing fluids, we are considering an electrocatalytic "afterburner" for the exhaust of automobiles. In principle, the afterburner would simply consist of a hot solid electrolyte tube with a long pumping cell whose inner platinum (for the initial experiments) electrode would be set at some positive potential (higher  $P_{O_2}$ ) relative to the external air reference electrode. The purpose of the cell would be to oxidize to completion any CO and hydrocarbons in the exhaust.

In considering this system, many difficulties arise, but then, exhaust pollution is a major problem. Some new and helpful design considerations are being suggested by the auto manufacturers:

(a) leaded fuels are likely to be discontinued (the Pb fouls catalysts),

- (b) the maximum horsepower of engines may be reduced (therefore, only lower exhaust rates need be treated),
- (c) a "leaner" air-to-fuel mixture will be used (more  $O_2$  to fuel will give lower  $CO/CO_2$  in exhaust and less unburned hydrocarbons.

Some obvious problems involved with using an electrolytic "afterburner" of a  $ZrO_2$ -base electrolyte are:

- (a) possible fracture of the electrolyte tube resulting from thermal fluctuations and mechanical vibrations,
- (b) limited coulometric pumping capacity of the solid electrolyte because of limited ionic conductivity,
- (c) necessity to heat the tube much hotter than the exhaust gases to provide a reasonable ionic conductivity,
- (d) fouling of the pumping electrode because of deleterious residuals in exhaust,
- (e) possible unavailability of sufficiently cheap, reliable, and durable (no evaporation) electrodes.

Consider for the moment, a <u>simple catalytic</u> automobile afterburner. Oxygen from air of half an atmosphere pressure is mixed with the exhaust and passed over a hot catalyst. The maximum possible oxygen activity of the catalyst is 0.5 atm. The rate of reaction would probably be reaction controlled, and for fast exhaust rates, it seems unlikely that highly efficient burning of CO,  $H_2$ , and hydrocarbons would be achieved.

Now, in a <u>simple electrolytic</u>  $2rO_2$ -tube afterburner with an air  $(P_{O_2} = 0.21 \text{ atm})$  external reference electrode and the application of only a few hundred millivolts, an oxygen activity of  $10^3$ ,  $10^4$  or  $10^5$  atm at the inner electrode is conceivable. The rate of oxidation at an electrode temperature of,  $1000^{\circ}C$ , might otherwise be quite rapid, except that, even for a slow rate, the ionic transport in the electrolyte tube would become rate controlling. In other words, while the electrolytic afterburner can potentially provide a fantastically high oxygen activity, it cannot provide the necessary flux.

Consider, now, a <u>combination of the two processes</u>, i.e., an electrolytic afterburner for which excess air is also injected upstream. Conceivably, a cell voltage could maintain at the inner electrode  $P_{O_2} = 10^3$  to  $10^5$  atm but most of the oxygen used for reaction would be provided from the  $O_2$  injected into the exhaust. This latter system, call it an "electrocatalytic" afterburner, could not be inferior in reaction rate to either of the simple types, although it would be somewhat more costly, complex, etc. If the "electrocatalytic" afterburner is going to provide a significant increase in exidation rate compared to the two simple parents, then the following requirements seem essential.

- (a) The rate of oxidation must depend critically upon the activity of oxygen in the pumping electrode. This condition would be met if the rate controlling step were a reaction step between adsorbed oxygen atoms and CO, or 2H, or  $C_XH_Y$ . Reactant adsorption or product desorption control would not be satisfactory. However, at sufficiently high temperatures, perhaps reaction control would be achieved.)
- (b) (Partially, a restatement of (a)). The concentration of adsorbed oxygen must depend critically upon the activity of oxygen, even at extremely high oxygen estivities. (According to the Langmuir Adsorption Isotherm, the electrode should not be close to saturation. Again, high temperatures should favor the "electrocatalytic" afterburner.)
- ( ) The oxygen adsorbed on the electrode at the very high activity must react with the combustion gases, and not simply desorb.

The equilibrium exchange rates for the two possible events, surface reaction and desorption, will determine which event succeeds in the competition for oxygen. In turn, the two exchange rates are likely to differ greatly in both absolute and relative magnitudes for different catalytic electrodes. From fuel cell studies, the platimum electrode is known to be very reversible to oxygen molecules in a gas phase (which may be unfavorable), but readily desorbs CO<sub>2</sub> (favorable), and is an excellent substrate for the oxidation of hydrocarbons (very favorable). Silver, on the other hand, is not very reversible with an oxygen gas (which may be favorable), does not catalyze well the oxidation of hydrocarbons (unfavorable), and may have too high a vapor pressure at the temperatures of interest (unfavorable). Oxide electrodes would also be worthy of consideration.

Research into the design and combustion characteristics of automobile engines has been in progress for many years in the Department of Mechanical Engineering at The Ohio State University. Operational engine test cells are, therefore, immediately available for use. Also available is quantitative analysis equipment to sample exhaust gases for CO, CO<sub>2</sub>, NO<sub>2</sub>, and unburned hydrocarbons. Within a couple months we expect to have set up a stabilized-zinconia-tube-afterburner with platinum electrodes so that we may test whether the application of a voltage to the cell will influence the rate of oxidation reactions on the electrode-catalyst.

#### ST. BOKLEY

In the first six months of the contract period some progress has been made in the theoretical analysis and the experimental design and construction of apparatus for the five related research topics which have been outlined. When justified by successful experiments and analysis in the laboratory, attempts to apply the high-temperature electrochemical methods to industrial problems will be undertaken.

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