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Results of a Collaborative Study on ZIRCONIA-BASED OXYGEN GAUGES

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RESULTS OF A COLLABORATIVE STUDY ON ZIRCONIA-BASED OXYGEN GAUGES

Abstract Stabilized zirconia tubes which were specially manufactured from five different types of commercially available materials for this project have been studied in the ten collaborating laboratories. The microstructures of these electrolyte materials have been examined in detail and characterized and the techniques used in the incorporation of the tubes into oxygen gauges have been evaluated. The performance of these gauges in a series of standard electrochemical tests has also been determined. In addition, the devices have been tested at very low oxygen potentials and at higher temperatures to assess the effects of electronic conductivity in the electrolytes and of their partial permeability to oxygen. The experimental data have been analysed centrally and the study has made it possible to lay down the basic principles to be followed in the fabrication of such gauges and to quantify the level of accuracy which can be expected when such gauges function correctly.

I. INTRODUCTION

I.1 Oxygen Gauges based on Stabilized Zirconia

Since its introduction as an oxygen fast-ion conductor stabilized zirconia has found many applications. Systems based on this high-temperature electrolyte have been used as gas sensors, as components in fuel cells, as oxygen pumps and as oxygen recyclers in closed systems. Perhaps their most important application is as oxygen gauges which are now used extensively to measure oxygen activity in processes involving gaseous, liquid or solid phases. These gauges are used in high temperature processes such as steel manufacture but more recently have been applied in two areas of immediate importance. The first is in the analysis of exhaust gages in internal combustion engines with obvious implication for environmental protection and energy conservation. The second use is in large furnaces where the devices provide instant analysis of the combustion process and continuous tuning to ensure the most efficient energy conversion rates. Solid state cells using stabilized zirconia are also important in basic research studies which seek to determine the basic thermodynamic parameters in oxide materials.

Despite this widespread use no detailed or standard procedure has yet been defined for the construction and operation of zirconia-based oxygen gauges. Neither are there any practical recommendations for the non-expert who wishes to build and use such a device. To these difficulties we may add the problems which arise because the proper functioning of these cells is possible only at high temperatures (typically > 900 K): this makes them particularly susceptible to errors which may arise from the relatively severe environmental conditions under which they operate. Until now there has been little effort made to assess the magnitude and importance of the various complex factors which influence the performance of gauges fabricated from a variety of commercially available electrolyte materials. Thus it is difficult to make a reliable estimate of the accuracy which can be expected with conventional oxygen gauges.

These are the basic reasons why the Commission on High Temperature and Solid State Chemistry of the International Union of Pure and Applied Chemistry initiated a Collaborative Group Study on these gauges. Workers in the participating laboratories have carried out wide-ranging tests on a number of stabilized zirconia materials which have been supplied by the manufacturers expressly for this purpose. They have also examined the performances of gauges in which these materials have been incorporated and this report is a summary of the principal results of their investigations. In the following sub-section (I.2) we outline the working procedure adopted in this project and indicate where more detailed reports on certain aspects of the study may be found. We then discuss the fundamental principles of the operation of the cells (Section II), analyse the main sources of error in their use (Section III) and describe the preparation of the gauges and the experimental procedure followed in the laboratories (Section IV). The remaining sections provide a critical analysis of the results obtained as well as an indication of the performance which can be expected from gauges of this kind. Section V is concerned with electrochemical tests performed under conditions where sources of error arising from departures from true electrolytic behaviour by zirconia are expected to have negligible effects. Section VI emphasises the limitations imposed by the onset of electronic conductivity in the electrolytic materials. These become more severe as the chemical potential of oxygen is lowered by dilution with an inert gas.

I.2 Procedure

The project has as a principal objective the evaluation of commercially available materials as used in working laboratories. The tubes were therefore requested centrally in a standard size from a number of manufacturers around the world and then distributed to the participating laboratories. In each laboratory the tubes were incorporated into oxygen gauges and their performances were examined in detail. No formal instructions were given beyond the request to use the tubes to verify the Nernst relationship for cells involving air versus pure oxygen and to investigate the voltages given by these devices when they were operated with the same gas (air or pure oxygen) on both sides of the electrolyte. A large part of this report will be concerned with data measured in these standard experiments and which have now been collected and evaluated. However in addition to the standard procedures two of the laboratories have carried out extensive and most valuable complementary investigations of the same materials which have already been published (refs. 1, 2). We shall also summarize their conclusions.

In the first of these complementary studies (ref. 1), the microstructures of the electrolyte materials were examined using a variety of characterization techniques with particular reference to silicate-containing grain boundary phases detected by electron microscopy. In the second (ref. 2), the tests were based on the coupling of gauges with an electrochemical oxygen pump to determine a domain of ideal response. The reliability of the devices within this domain was also investigated with respect to the effect of electronic conductivity in the materials at high temperature.

II GENERAL BACKGROUND

II.1 Electrochemical Basis of Cell

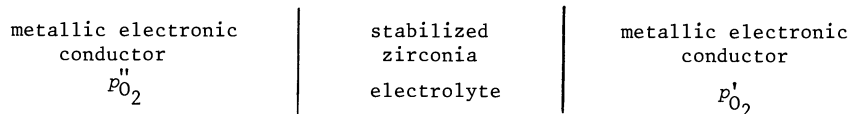
To consider the factors which can influence the performance of zirconia-based oxygen sensors we shall first describe the ideal situation and then introduce the complications which can arise during the practical operation of the devices. In general an oxygen gauge consists of a solid electrolyte, conducting by O^{2-} ions in the case of stabilized zirconia, both sides of which are coated with a metallic conductor. Under isothermal conditions and when oxygen partial pressures differ at the two electrodes an emf is developed across the cell. Provided that no significant current is driven into the voltage measuring system, the voltage produced is given by (refs. 3,4).

$$E = \frac{RT}{4F} \int_{p_{O_2}'}^{p_{O_2}''} t_i d(\ln p_{O_2}) \quad (1)$$

where T is the Kelvin temperature of the cell assembly, R is the gas constant and F is the Faraday constant. If we assume that the electrolyte is operating within the ionic domain in which the ionic transport number t_i departs only negligibly from unity then equation (1) may be reduced to a simple Nernst relationship

$$E = (RT/4F) \ln(p_{O_2}''/p_{O_2}') \quad (2)$$

Insertion of the standard values (ref. 5) for R ($= 8.31441 \pm 26 \text{ K} \cdot \text{p}^{-1} \text{ K}^{-1}$) and F ($= 9.648456 \pm 27 \cdot 10^4 \text{ C mol}^{-1}$) into this expression shows that any uncertainties in these numbers will have a negligible effect on the results. The basic principle for the operation of an oxygen gauge lies in the determination of the emf developed in an isothermal concentration cell



If one of the oxygen partial pressures, let us say p_{O_2}' is known to a good accuracy and acts as a reference oxygen pressure, then measurements of the emf of the cell, E , and its temperature, T , when taken with equation (2) allows p_{O_2}'' to be determined

II.2 Choice of the Reference Atmosphere

It is evident from equation (2) that the relative uncertainty in the knowledge of P_{O_2} (P_{ref} in the following) introduces an equivalent uncertainty in the determination of P_{CO} . For gauges with which we wish to measure accurately oxygen partial pressures in the range from 10^{-2} Pa to several hundred kPa it is now widely accepted (ref. 6) that the best reference gas is air which has a partial pressure of oxygen of 21.222 kPa (ref. 7). However, depending on the nature and objective of the measurements required other reference materials can be used. These may involve gaseous buffer mixtures such as CO-CO₂ (ref. 8) or metal-metal oxide monovariant systems such as Cu-Cu₂O, Ni-NiO, Fe-FeO, Cr-Cr₂O₃ and others (ref. 9). In the case of the former it should, however, be realized that discrepancies exist in the free energy data, ΔG° , for the reaction



from which oxygen partial pressures are calculated by means of the equation

$$\ln P_{O_2} = 2\Delta G^\circ/RT + 2\ln\{P_{CO_2}/P_{CO}\} \quad (4)$$

several values of the expected standard emf derived from equation (4) for the cell

$P_{CO}/P_{CO_2} = 1$	solid electrolyte	pure oxygen
$P_{CO} + P_{CO_2} = 1.01325 \text{ bar}$	$T = 1173 \text{ K}$	$P_{O_2} = 1.01325 \text{ bar}$

are listed in Table 1. The discrepancies in E_o amount to about 10 mV, an uncertainty which, as we shall see, is quite large when compared to the accuracy expected from a properly constructed and correctly operated device. Another difficulty arises in the

Table 1 Values of E° at 1173 K for the reaction $CO + \frac{1}{2} O_2 \rightleftharpoons CO_2$ derived as described in the text. The sources of these data are given in ref. 9

E°/V	Authors
0.9369	Richardson and Jeffes
0.9302	Peters and Moebius
0.9339	Elliott and Gleiser
0.9403	Kubaschewski and Alcock
0.9363	Etsell and Flengas
0.9382	Fouletier

failure to achieve thermodynamic equilibrium, particularly below 900 K and at higher flow rates. Finally CO-CO₂ mixtures are susceptible to composition gradients due to thermal diffusion and to overall composition changes due to carbon deposition in the colder parts of the gas path.

The use of metal-metal oxide couples is often convenient from the experimental point of view since a sintered pellet of the mixture with the corresponding metallic electrode and lead may be sealed inside a closed tube (refs. 10, 11). The size of the gauge may then be considerably reduced (ref. 10) as it is no longer necessary to pass a reference gas from cold to hot parts of the cell. Furthermore, the choice of

a metal-metal oxide couple that fixes the reference oxygen pressure close to the value to be measured can significantly reduce errors which may arise in measurements at low oxygen potentials since oxygen semipermeability through the electrolyte will lower the voltage produced by the cell (see later). However, the free energies of formation of the metal oxides are not always accurately known. Furthermore the formation of a thin layer of metal oxide near the surface of the electrolyte due to inefficient sealing and/or oxygen semipermeability may disturb the proper functioning of this type of reference electrode (ref. 8)

As there are many applications for zirconia-based gauges which require their operation in oxidizing or only mildly reducing environments pure oxygen and air were chosen as the main gases in the present materials evaluation program. Furthermore these gases are readily available and because they can provide precisely known oxygen partial pressures on either side of the gauge their use eliminates otherwise uncontrollable sources of error.

III SOURCES OF ERROR

There are several sources of error which can disturb the performance of zirconia-based oxygen gauges. These are described in the literature (ref. 8) and it is not intended here to discuss at length the problems which have been identified. However it is useful to summarize present knowledge as the errors can result from unsuitable experimental arrangements in the apparatus or from departures from the ideal conditions upon which the derivation of the value of the cell voltage is based. Among the former we may expect:

(i) physical permeability of the ceramic materials to gases due to microcracks or open porosity and leading to leakage of gases between the cell compartments; (ii) experimental uncertainties in the determination of the cell temperature, in the measurement of the cell voltage or in the evaluation of the reference oxygen partial pressure $p_{O_2}^{\text{ref}}$; and (iii) non uniformity of the cell temperature. With respect to the last of these a temperature gradient is expected to produce two effects. First a thermoelectric voltage will be induced along and/or between the electrodes and will interfere with the voltage developed by the cell. Secondly because the cell temperature is often measured at a specific point in the cell using a thermocouple the gradient will introduce some uncertainty into this datum. On the other hand the most common sources of error intrinsic to the material arise from a small electronic contribution to the conductivity of the stabilized zirconia electrolyte. Under an external open circuit this effect can produce ionic and electronic currents which are mutually self-cancelling but which correspond to a net transfer of oxygen across the electrolyte.

III.1 Physical Permeability of the Electrolyte to Gases

Before assembling a gauge the zirconia tube should be tested for gas tightness, at least at room temperature, by using helium leak detectors or conventional vacuum systems and pressure gauges. In the present study there have been no reports that any of the tubes failed to meet this requirement.

III.2 Uncertainties in Measurements of Cell Voltage, Temperature and Reference Oxygen Pressure

The influence of a lack of precision in the characteristic parameters of equation (2) may be estimated once the basic relationship has been differentiated as

$$\frac{\Delta p_{O_2}''}{p_{O_2}''} = \frac{4F\Delta E}{RT} - \frac{4FE}{R} \frac{\Delta T}{T^2} \quad (5)$$

Close to 1000 K an uncertainty of 0.1 mV in the measurement of the cell voltage corresponds to an uncertainty of $\sim 0.5\%$ in p_{O_2}'' . We shall describe the precautions necessary in the measurement of E in section IV.2. The effect of an uncertainty in the measurement of the temperature depends more specifically on the voltage itself. For air versus pure oxygen systems an error of 3 K is equivalent to an error of 0.1 mV which itself is equivalent to a possible error of 0.5% in p_{O_2}'' . As we have already mentioned uncertainties in the known value of the reference oxygen² partial pressure depend on the specific reference system. When air is used very accurate results are *a priori* possible.

III.3 Non-Uniform Cell Temperatures

The existence of thermal gradients within the space which contains the active part of the electrochemical cell must be carefully considered as they may give rise to substantial errors due to thermoelectric effects. This situation has been discussed in detail by Fouletier (ref. 8) both for gradients occurring along the electrodes or through the solid electrolyte: only the latter case is considered here.

The emf of a slightly non-isothermal cell with $p_{O_2}'(T_1)$ vs $p_{O_2}''(T_2)$ may be split into two terms. The first of these, as for the analogous² isothermal cell, has its origin in the difference in the oxygen chemical potential, μ_{O_2} at the two electrodes: the second is due to a simple thermoelectric effect (ref. 12).

$$E = \frac{1}{4F} \int_1^2 d\mu_{O_2} + \alpha(T_2 - T_1) \quad (6)$$

where the Seebeck coefficient α is assumed to be independent of temperature and oxygen partial pressure (ref. 8). This yields

$$E = \frac{\Delta\mu^0}{4F} + \frac{RT_2}{4F} \ln p_{O_2}'' - \frac{RT_1}{4F} \ln p_{O_2}' + \alpha(T_2 - T_1) \quad (7)$$

where $\Delta\mu^0$ is the difference in the standard chemical potential of oxygen at each of the temperatures. If the cell temperature is measured at the reference electrode and

denoting $T_2 - T_1$ by ΔT equation (7) becomes

$$E = \frac{RT}{4F} \ln \frac{p_{O_2}''}{p_{O_2}^{\text{ref}}} + \frac{\Delta \mu^O}{4F} + \alpha \Delta T + \frac{R \Delta T}{4F} \ln p_{O_2}' \quad (8)$$

If the temperature is measured at the other electrode then we have:

$$E = \frac{RT}{4F} \ln \frac{p_{O_2}''}{p_{O_2}^{\text{ref}}} + \frac{\Delta \mu^O}{4F} + \alpha \Delta T + \frac{R \Delta T}{4F} \ln p_{O_2}^{\text{ref}} \quad (9)$$

and for temperatures close to 1000 K, and neglecting the small term, $\alpha \Delta T$, the errors calculated from these basic equations are respectively in mV

$$\Delta E = (0.52 + 5.0 \times 10^{-2} \log_{10} p_{O_2}'') \Delta T \quad (10)$$

$$\text{and } \Delta E = (0.52 + 5.0 \times 10^{-2} \log_{10} p_{O_2}^{\text{ref}}) \Delta T \quad (11)$$

The advantage of determining the temperature at the measuring electrode is generally to make the error depend only on the temperature difference. Note that as far as oxygen versus air measurements are concerned the precise location of the thermocouple with respect to either electrode is not so important as the pressure dependent terms in both equations (10) and (11) will be small in comparison with 0.52 mV K^{-1} .

It should be evident from the above analysis that the temperature gradients in zirconia-based oxygen gauges should be eliminated or at least reduced to a minimum. This can be achieved by utilizing a furnace in which the temperature profile is sufficiently flat in the region which contains the active part of the device. In addition the flow rates of the gases should be restrained so that they do not alter the homogeneity of the system.

III.4 Electronic Leakage in the Electrolyte

The existence of even a small electronic conductivity in the electrolyte is known to be a serious limitation to the practical use of these gauges (ref. 8). In terms of an error analysis there are three effects. First the voltage of the gauge is lowered by an amount $\bar{\tau}_e E_{th}$ where $\bar{\tau}_e$ denotes an average electronic transport number with respect to the theoretical voltage E_{th} expected from equation (2): this is analogous to an ohmic drop due to a slight partial short circuit of the cell. Next a small ionic current counterbalances the flow of electronic charge carriers and induces an electrochemical permeability of the material to oxygen which gas is then injected into the atmosphere with the smaller oxygen chemical potential. This will generally be the gas which is being analysed, with air or oxygen as the reference environment, and the injection of even small amounts of oxygen can therefore significantly alter its composition. Finally the diffusive process may polarize the measuring electrode (and under certain circumstances the reference electrode). This is especially so when the oxygen content of the gas phase to be analysed is low and may occur even if the quantities of oxygen which are pumped are too small to noticeably alter the gas compositions. As a consequence of the polarization the voltage delivered by the gauge is lowered by the electrode overpotential.

We note that of these three effects only the second can be circumvented, and that probably only partially, by increasing the gas flow rates so that compositional changes in the gases are negligible. On the other hand the overpotentials will always be included in the voltage produced unless special arrangements, for instance the use of a tip electrode, prevent the oxygen flux from reaching the surface of the electrolyte close to the measuring electrode (ref. 6).

In general, the errors arising from these various sources may combine and contribute together to the overall voltage delivered by the cell. Analyses of departures from the expected ideal behaviour will then be complicated unless conditions are specified which allow each source of error, or a small set of these sources, to be investigated independently. Results at present in the literature (ref. 8) indicate that, under the oxidizing conditions provided by air or oxygen gases in the range of temperature used in this study, the reliability of the devices should not be significantly influenced by the onset of electronic conductivity. We shall see later that this view is largely confirmed by the conclusions of section VI. Thus it was possible to design tests involving air/oxygen systems where the effects of the factors described in sections III.2 and III.3 could be analysed independently (section V) of those due to a departure from pure electrolytic behaviour in the stabilized zirconia electrolytes used in the cells. Finally, special experiments were developed to determine separately the consequences of non-negligible

electronic conductivity.

IV THE GAUGES

IV.1 Fabrication

To form the electrochemical cell electrodes and leads must be applied to the tube which acts as the electrolyte. Electrodes are usually made from noble metals such as platinum or sometimes from silver (refs. 13, 14). Although it has been reported that silver electrodes exhibit smaller overpotentials and timelags than are observed when platinum is used (ref. 8), the vapour pressure of silver prevents its use at temperatures much above 1000 K as the lifetime of the cell may be considerably reduced. Moreover the temperature range is finally limited by the relatively low melting point of silver at 1235 K. These limitations, combined with the fact that platinum (and platinum-rhodium alloy) wires are commonly used in the thermocouples used to determine the temperature of the cell, imply that platinum remains the most common choice for electrodes and leads.

The cell size must be sufficiently small so that the electrodes-electrolyte system can be maintained at a uniform temperature within the flat region of the temperature profile of the furnace. Preparation of the voltage leads may present some technical difficulties as the metallic wires must be fastened to ceramic porous electrodes. Frequently, in laboratory studies such as in the present project, the electrodes are first applied to the tube as a platinum paste or paint. The inner coating is applied using a capillary to drop a small quantity of the paint, which is diluted to a suitable consistency with a pure solvent, down inside the tube and onto its closed end. The outer electrode is applied by brushing a small area with the platinum-bearing fluid. These coatings are then baked in air for several hours to eliminate volatile material and obtain good mechanical and electrical properties of the coatings. The stabilized zirconia tubes should not, in general, be cooled at rates in excess of 150 K/hour as the material may be subject to thermal shock. Several laboratories have reported that the electrode material had to be applied and fired for a second time before the cells functioned satisfactorily. Contact with the outer electrode is generally made by wrapping a platinum wire around the tube and it may be improved by coating the wire by a layer of the platinum paint which is

subsequently fired. Contact by a platinum wire with the inner electrode is frequently effected by a spring-loaded arrangement using multiple-bore alumina tubing through which the gas stream to the inner electrode may also be carried. Such an assembly, shown schematically in Figure 1, was used by most of the participants: more extensive experimental details of the design and mode of operation used in each laboratory are given in Table 2.

It should be borne in mind that platinum paints may contain mineral binders. These products cannot be used in the preparation of electrodes if any of their constituents exhibit variable valencies in the temperature and oxygen pressure ranges of interest or if they are likely to form a glassy phase that would hamper oxygen exchange between the electrode-electrolyte interface and the gas phase.

IV.2 Electrical Circuitry

Zirconia cells behave as moderate to high impedance voltage sources. Although the electrical conductivity of the electrolyte material increases rapidly with temperature, with activation energies of the order of 100 kJ/mol (ref. 15) the internal impedance of the cell remains generally high. In the temperature range of interest (800 to 1300 K) the typical internal impedance of the cells measured under a.c. conditions* lay between 10 and $10^5 \Omega$. In agreement with earlier

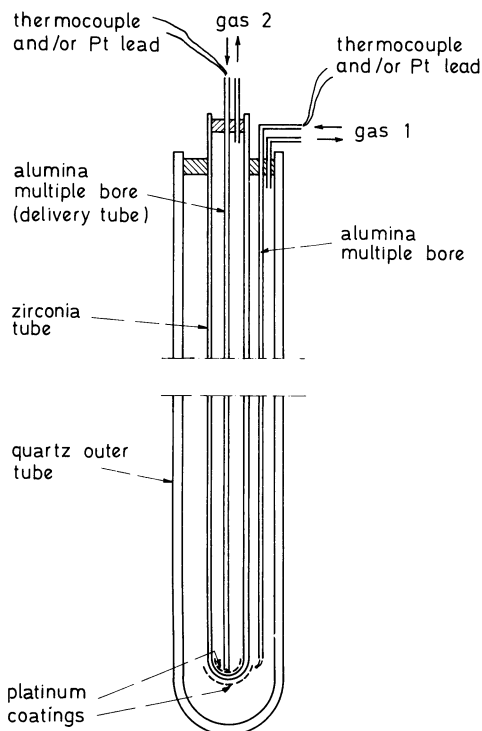


Fig. 1 Schematic diagram of a cell assembly

*The measurements were made at 1592 Hz: this should be considered only as an approximate value as the conductivity is frequency dependent (ref. 16).

Table 2. Experimental details of the oxygen gauges used in the participating laboratories.

Cell Arrangement	Laboratory 1	Laboratory 2	Laboratory 3	Laboratory 4	Laboratory 5 ^e	Laboratory 6
O ₂ electrode	inner/outer	inner/outer	outer ^a	inner	inner/outer ^f	inner/outer
thermocouple	Pt/Pt 13% Rh	Pt/Pt 13% Rh	Pt/Pt 10% Rh	Pt/Pt 10% Rh ^b	-	Pt/Pt 10% Rh
location of thermocouple	inside and outside	inside and outside	inside or outside	outside	inside and outside	inside
direct contact between thermocouple and cell	inner yes outer no	inner yes outer no	no	no	-	yes
inner potential lead	Pt thermo-couple lead	Pt thermo-couple lead	separate	separate	separate	Pt thermo-couple lead
gas flow cm ³ /min inside	4 - 70	4 - 50	15 - 70	30 ^c	5 - 150	15 - 100
gas flow cm ³ /min shielding	600 yes	10 - 220 partly	30 - 600 yes	d	10 - 300 yes	15 - 120 yes

- a. except for 1 measurement per tube. d. 200 cm³/min in the complementary study
- b. Pt/Pt 13% Rh in a complementary study on IUPAC 1. e. different cell configuration.
- c. 50 cm³/min in the complementary study. f. except tube 1.

conductance measurements (ref. 15) the internal impedances of the cells made with calcia doped tubes were consistently higher than those containing yttria doped materials.

There are two important practical consequences of this large cell impedance. First the voltage delivered must be measured with a high impedance ($> 10^{12}\Omega$) instrument: to keep full precision the sensitivity should be 1 to 10 μV . Even for a modest source impedance this prevents any d.c. current in the external circuitry and avoids parasitic polarization and the semipermeability effects to which we have referred previously. If the cell emf is continuously monitored with a recorder then the latter should be isolated from the cell by the voltmeter itself or have a large impedance unity gain buffer. The second consequence arises because high impedance circuitry is known to be susceptible to electrical (capacitive and inductive) pick-up. This problem will be avoided if the a.c. common mode rejection ratio of the voltmeter is large to reject any a.c. component of the voltage. It is nonetheless generally advisable to reduce pick-up by shielding both the gauge and all external leads within an earthed circuit.

IV.3 Materials.

The suppliers who provided tubes especially for this collaborative study are listed in Appendix A. Material from one additional source was examined in the complementary microstructural study (ref. 1). The laboratories which participated in the work associated with the project are given in Appendix B: results from six of these groups will be discussed and analysed here. We should emphasise that the results to be described for tubes numbered IUPAC 1 to IUPAC 5 respectively refer to a group of tubes in each case, and not to a single tube, since tubes of each kind provided by the suppliers were sent simultaneously to each participating laboratory.

All the samples were subjected to a range of modern materials characterization techniques so that the relevant structural information would be available for correlation with the behaviour of the gauges incorporating the tubes. A report on this aspect of the project has been published (ref. 1) and the results are summarized in Table 3.

All X-ray diffraction patterns from powdered samples could be indexed on the basis of a face-centered cubic unit cell of approximate lattice parameter of 0.5 nm. Microstructural details and especially compositional modifications at grain boundaries were revealed by scanning transmission electron microscopy combined with energy dispersive X-ray analysis. While no impurities were detected in significant quantities at the grain-boundaries of the yttria doped samples the calcia stabilized materials investigated were shown to contain various grain-boundary phases. Two crystalline phases, one containing Mg, Al, Si and Ca and the other Si and Ca, and amorphous phases containing Si, Al and Ca were detected with a Ca content generally higher than in the bulk surrounding grains. All the calcia doped samples exhibited diffraction patterns with diffuse scattering attributable to microdomains of CaZr_4O_9 (ref. 18). The composition of IUPAC 1 puts it into the diphasic field of a recent phase diagram (ref. 19) consisting of tetragonal and fluorite-type zirconia. This is in agreement with the observation of tetragonal superstructure dots in the electron diffraction patterns. Composition of IUPAC 5 puts it close to the edge of the diphasic region when referred to the same phase diagram: it has, however, also been shown to be diphasic by the electron diffraction pattern

V ELECTROCHEMICAL TESTS WITH OXYGEN-AIR ATMOSPHERES

One of the most straightforward ways to assess gauge performance is to measure the emfs produced by the cells when operated under accurately known oxygen partial pressures and to examine differences between the measured values and those derived from the basic relationship of equation (2). For reasons already given, these measurements were made using air and oxygen and the procedure was to vary the temperature of the system over a broad range, at least 900 to 1300 K, so that the variation in the measured emf could be compared to that given by the theoretical relationship. In addition to these measurements it was suggested that each participating laboratory should measure the cell voltage over the same range with air on both sides of the electrolyte: clearly the resulting emfs would be expected to be zero or close to zero. Finally the symmetry of the response of the cells when the gases flowing over the electrodes were reversed should also be investigated.

A considerable number of data concerning the influence of gas flow rates in each compartment of the cells has been given in their individual reports by the participants: we shall comment on some of these later.

V.1 Verification of the Nernst Relationship for Air and Oxygen*

Results representative of those supplied by the participating laboratories are presented in two different ways. In Figure 2 the emfs observed experimentally on tube 1 in each of the participating laboratories have been plotted without correction with the exception of those from Laboratory 1 (see section V.4). This plot therefore contains data measured on tubes made from that particular material, IUPAC 1. Figure 3 shows the data obtained in one of the participating laboratories for the set of tubes supplied and also the theoretical line expected on the basis of the Nernst relationship. Similar data for the other tubes and for the other participating laboratories are available from the authors**.

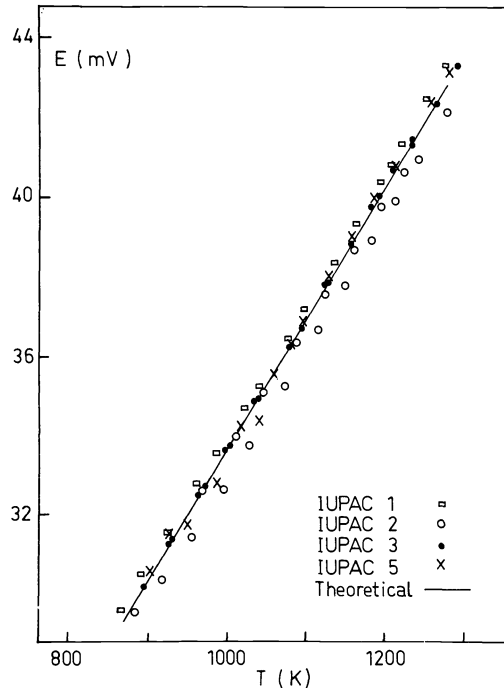
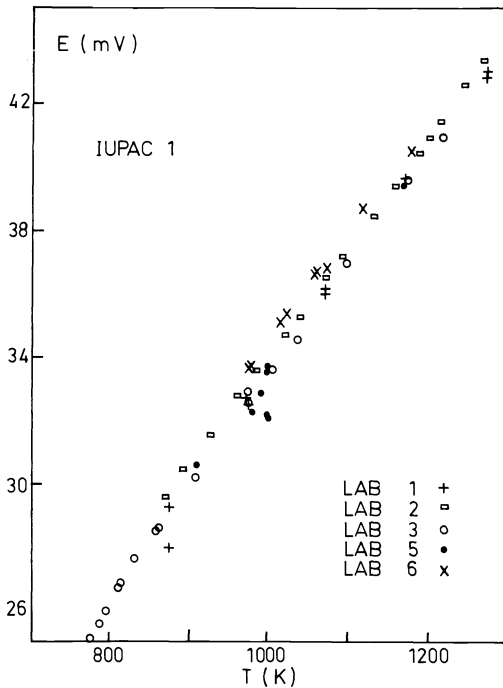


Fig. 2 The variation of the emf with the cell temperature as measured in the participating laboratories for tubes IUPAC 1

Fig. 3 Emf versus temperature data from Laboratory 2: the line gives the theoretical values from equation (2)

The measurements were made under the specifications listed in Table 2. In some laboratories only O_2 /air or air/ O_2 runs were made while others reported data for both modes of operation of the cells. Also in a number of laboratories several measurements were made at the same temperature while the flow rates of the gases were varied. In general it was found that the dispersion of data for such a set of experiments, performed at a fixed temperature while the gas-flow rates were varied, was relatively small compared to the difference between the mean value and the expected theoretical value, whenever this difference exceeded ~ 0.3 mV. Thus it was decided to choose the mean value as representative of the results obtained and this procedure does not affect the conclusions derived within the framework of the Nernst Law test using air and oxygen gases. As shown below, the conclusions also remain essentially the same whether data from one or both (O_2 /air and air/ O_2) symmetries are considered in the numerical analyses. Generally speaking emf measurements taken when gas was not flowing at both electrodes have been omitted from these analyses.

*Unless otherwise stated air/ O_2 (O_2 /air) means air (O_2) inside the tube (respectively) and vice versa.

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The parameters which result from the fitting of the experimental data to straightlines after a standard least square regression are given in Table 4. They are the slope of the fitted straight line, the intercept at 0 K, the correlation factor of the linear regression and the mean absolute value of the departure from the theoretical voltage assuming that the temperature measurements were free of error. Most of the participating laboratories reported their data only to the nearest 10 μV . The results of the statistical analyses of these data in Tables 4, 5 and 6 are shown to 1 μV .

In the strict sense errors in temperature readings should also be considered. For Pt/Pt-10% Rh and Pt/Pt-13% Rh thermocouples the usual maximum deviation from standard is ± 1 K in the range 273 to 1273 K. If we now assume an error in reading of 1 K the temperature uncertainty amounts to ± 2 K which corresponds to an uncertainty of ~ 0.07 mV in the emf. If we refer to Figures 2 and 3 it is evident that any uncertainty in the measurement of the temperature is not the main source of error to be considered.

After consideration of the parameters derived from the fitting and listed in Table 4 we may conclude that for most of the runs the experimental data lie along or very close to straight lines. In almost all cases the values of the correlation factors for the linear regressions do not depart significantly from unity. Of the 28 runs 5 have correlation factors > 0.999 , 14 > 0.9995 , 20 > 0.99 and 23 > 0.98 . The data from some experiments do, however, exhibit very poor correlation: in particular those for Laboratory 5 on IUPAC 3, and Laboratories 3 and 5 on IUPAC 5. It was considered here that a correlation factor below an arbitrary value of 0.9 corresponded to a dispersion of data which could hardly be reconciled with representation as a straight line. We also observed that very poor correlation was found where there are serious departures from the ideal Nernst law line. We have therefore concluded that the cells have not functioned properly for the three experiments in question and the results of all runs with correlation factor values < 0.9 have been disregarded.

Another conclusion which may be drawn from the fitting of the electrochemical data is that runs which contain data for both O_2/air and air/O_2 modes of operation, perhaps unexpectedly, do not exhibit significantly larger dispersions of data points about the theoretical curve than those shown by runs whose data refer to a single configuration of the cell. We shall comment further on this point later. It is also clear that a correlation factor very close to unity, observed in a number of runs, does not mean that Nernst relationship is accurately obeyed. It was not possible to find a correspondence between the departure of the value of the correlation factor from unity and the deviations observed from the theoretical slope or intercept at 0 K. These latter deviations are shown schematically in Figure 4 where the results from the best fitting achieved for each laboratory have been plotted. It is noteworthy that the results for two laboratories are reasonably well distributed about the expected theoretical values. A third participant found relatively high slopes with negative intercepts and the data from a fourth showed the converse behaviour. Overall it is evident that higher slopes gave rise to negative intercepts and conversely.

An examination of all the data received showed that measurements made at temperatures below 880 K generally yielded cell potentials lower than their expected theoretical values. To check this point all the fitting was redone but this time using only data taken at temperatures above 880 K: the resulting parameters are given in Table 5. For some runs the results are not different from those given in Table 4 since all the measurements had been made above 880 K. Where there are differences and with the exception of Laboratory 4, the results in Table 5 show a strong tendency to move towards the theoretical slope, to yield smaller intercepts at 0 K and to give correlation factors closer to unity. Although there were some differences evident between data from different laboratories, perhaps due to variations in the materials and procedures for the fabrication of the cells, it seems that a minimum operating temperature of 880 K should be recommended for devices of this kind.

Mean absolute values of the departure from the emf as given by the Nernst relationship are shown in Figure 5(a). Most of these lie in the range 0.1 to 0.5 mV which would correspond to errors of 0.5 to 2.5% in the measured oxygen pressure with respect to pure oxygen.

It is important at this point to state clearly the level of accuracy that is attainable with these gauges. In one probably quite careful study (Laboratory 4 on IUPAC 1) the value of the slope for data taken > 880 K was $3.360 \times 10^{-2} \text{ mV K}^{-1}$ which represents an error of 0.21% on the theoretical value of $3.367 \times 10^{-2} \text{ mV K}^{-1}$. The zero Kelvin intercept was 0.025 mV, the correlation factor was 0.9999 and the mean departure from the Nernst relationship was 0.059 mV. This last figure represents a typical error $< 0.3\%$ in the measurement of an unknown partial pressure of oxygen and the overall quality of the fitting is a clear demonstration of the performance which can be achieved with a carefully constructed and operated gauge.

Table 4. Parameters from the fitting of Nernst Law data to straight lines. The parameters in each case are as follows: (i) 10^2 slope in mV K^{-1} ; (ii) intercept at 0 K in mV; (iii) correlation factor and (iv) mean absolute value of the departure from the theoretical voltage in mV assuming no error in the temperature measurements.

TUBE MATERIAL	Laboratory 1	Laboratory 2	Laboratory 3	Laboratory 4	Laboratory 5	Laboratory 6
IUPAC 1 (i)	3.512	3.374	3.524	3.179	3.480	3.323
(ii)	-1.754	0.314	-1.815	0.978	-1.664	1.357
(iii)	0.995	1.000	0.998	0.999	0.935	0.997
(iv)	0.223	0.403	0.357	0.225	0.545	0.901
IUPAC 2 (i)	3.560	3.296	3.503	3.471	3.229	-
(ii)	-2.318	0.298	-1.819	-2.562	1.694	-
(iii)	0.994	0.994	0.984	0.988	0.990	-
(iv)	0.314	0.352	0.545	0.701	0.450	-
IUPAC 3 (i)	3.501	3.355	3.140	3.203	(2.936	-
(ii)	-1.692	0.167	1.745	0.290	(4.485	-
(iii)	0.979	1.000	0.988	0.994	0.705)	-
(iv)	0.474	0.059	0.837	0.634	1.733)	-
IUPAC 4 (i)	3.407	-	3.198	3.416	2.933	3.336
(ii)	-0.521	-	2.155	-2.000	4.716	1.114
(iii)	0.998	-	0.996	0.992	0.992	0.995
(iv)	0.167	-	0.396	0.671	0.534	0.785
IUPAC 5 (i)	3.375	3.431	(2.534	2.996	(3.900	3.163
(ii)	-0.191	-0.620	(5.904	2.514	(-7.064	3.226
(iii)	0.999	0.996	0.573)	0.998	0.897)	0.997
(iv)	0.125	0.213	3.999)	0.635	1.640)	1.090
IUPAC 1 (i)				3.357		
(ii)				0.069		
(iii)				*		
(iv)				1.000		
Mode of Operation	Air/O ₂ and O ₂ /Air	IUPAC 2,3: Air/O ₂ and O ₂ /Air IUPAC 1,5: O ₂ /Air	Air/O ₂ 1 measurement O ₂ /Air	*Air/O ₂ and O ₂ /Air otherwise Air/O ₂	IUPAC 1: O ₂ /Air IUPAC 2,3,4,5 Air/O ₂ and O ₂ /Air	O ₂ /Air

Measurements made using synthetic air with a nominal composition of 0.217% Oxygen: all other data refer to natural air.

Table 5 Parameters from the fitting of Nernst Law data taken at temperatures higher than 880 K to straight lines where these differ from the results shown in Table 4: all designations and symbols have the same meaning as in Table 4						
TUBE MATERIAL	Laboratory 1	Laboratory 2	Laboratory 3	Laboratory 4	Laboratory 5	Laboratory 6
IUPAC 1 (i) (ii) (iii) (iv)	3.382 -0.228 0.999 0.093	3.371 0.353 1.000 0.406	3.400 -0.489 0.998 0.161	as table 4 a	as table 4	as table 4
IUPAC 2 (i) (ii) (iii) (iv)	3.441 -0.940 0.998 0.201	as table 4	3.142 2.311 0.995 0.251	3.215 a 0.409 0.992 0.276	3.413 -0.419 0.991 0.331	--
IUPAC 3 (i) (ii) (iii) (iv)	3.401 -0.530 0.994 0.245	as table 4	3.078 2.464 0.985 0.864	2.986 a 2.791 1.000 0.250	deleted	--
IUPAC 4 (i) (ii) (iii) (iv)	3.341 0.261 0.999 0.118	--	3.223 1.864 0.993 0.315	a as table 4	3.372 -0.300 0.993 0.252	as table 4
IUPAC 5 (i) (ii) (iii) (iv)	3.384 -0.291 0.999 0.133	as table 4	deleted	2.916 a 3.459 0.998 0.323	deleted	as table 4
IUPAC 1 (i) (ii) (iii) (iv)				3.360 0.025 1.000 0.059		

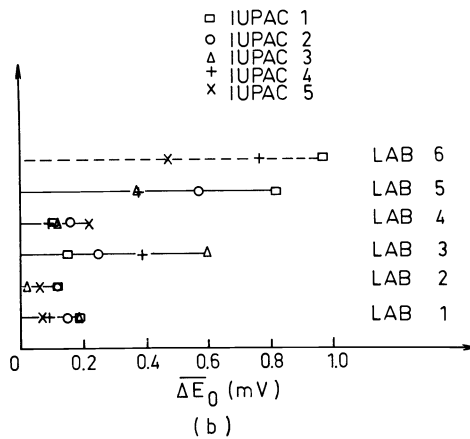
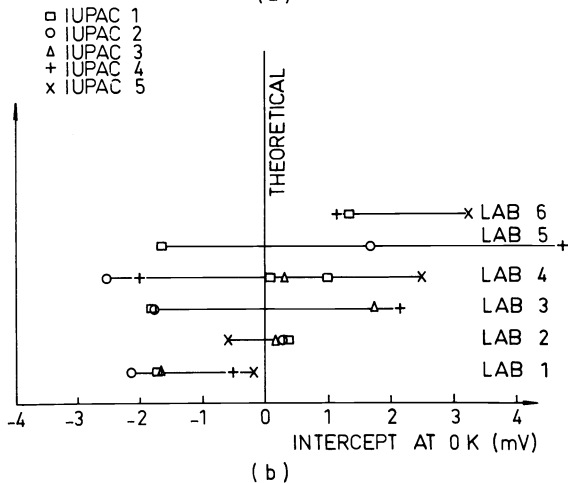
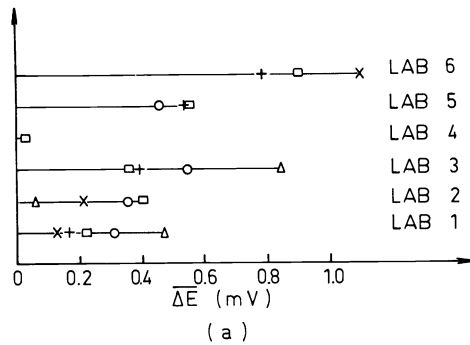
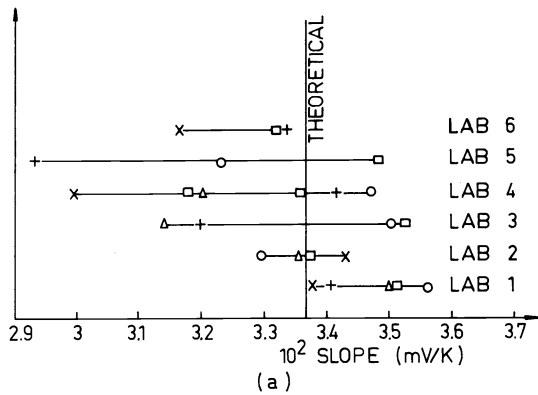


Fig. 4 (a) Deviations from the theoretical slope shown schematically for each laboratory
(b) deviations from the theoretical intercept at 0 K

Fig. 5 (a) Absolute values of the mean departures from the theoretical emf
(b) the average absolute values of the zero emf for cells in the air/air condition

V.2 Zero emf test under air/air Conditions

The mean zero emfs were measured by the participants for the cells operating with air on both sides and over a temperature range similar to that through which the Nernst relationship had been investigated. From their reported data the average zero emf, the standard deviation from this value and the average absolute value of zero emf have been calculated and are reported in Table 6: the average absolute values of zero emf, $\overline{\Delta E_0}$ are plotted in Figure 5(b). For three laboratories the values of $\overline{\Delta E_0}$, which is probably the most significant parameter here, lie within the range 0.1 to 0.2 mV: for the others it is significantly larger.

The reason for the observed non-zero emf in the symmetrical air/air cells is not clear. Several explanations, such as the existence of some unknown 'chemical' asymmetry in the gas|electrode|electrolyte systems or the effect of a temperature gradient in the active parts of the gauge, may be advanced. A potential of 0.1 to 0.2 mV corresponds approximately to a temperature difference of 0.2 to 0.4 K through the electrolyte in the absence of a longitudinal gradient. This emphasizes the necessity to achieve a uniform thermal profile within the cell. Several of the participants reported temperatures measured at both inner and outer electrodes and on some occasions observed a systematic temperature difference between the parts of the cell. However both thermocouples were not in direct contact with the electrodes and the measured temperature difference, which was confirmed by interchanging the thermocouples, was much higher than 0.2 to 0.4 K. Thus these observations almost certainly reflected factors external to the electrolyte rather than a genuine temperature gradient through the material. We shall comment below on variations due to total gas pressure differences.

Table 6 Analysis of data measured with air on both sides of the cells: under these conditions the emf should ideally be zero. (i) is the average zero emf in mV; (ii) is the standard deviation from this average value and (iii) is the average absolute value of the zero emf.						
TUBE MATERIAL	Laboratory 1	Laboratory 2	Laboratory 3	Laboratory 4	Laboratory 5	Laboratory 6
IUPAC 1 (i) (ii) (iii)	-0.197 0.173 0.197	0.013 0.110 0.060	0.145 0.121 0.145	0.055 0.117 0.115	-0.817 0.557 0.817	-0.975 -- 0.975
IUPAC 2 (i) (ii) (iii)	-0.152 0.069 0.152	0.066 0.149 0.118	0.253 0.485 0.253	-0.153 0.121 0.163	0.478 0.404 0.566	--
IUPAC 3 (i) (ii) (iii)	-0.197 0.092 0.197	0.023 0.044 0.043	0.611 0.121 0.611	-0.063 0.130 0.120	-0.320 a 0.287 0.354	--
IUPAC 4 (i) (ii) (iii)	-0.044 0.092 0.090	--	0.395 0.275 0.395	0.058 0.088 0.098	-0.356 0.533 0.373	-0.765 0.016 0.765
IUPAC 5 (i) (ii) (iii)	-0.076 0.016 0.076	0.071 0.131 0.072	2.715 a 0.583 2.715	-0.195 0.249 0.218	-0.360 a 0.603 0.369	-0.474 b -- 0.474
IUPAC 1 (i) (ii) (iii)				-0.17 -- 0.17		

a. the data from this run has been deleted from the general analysis

b. refers to a single measured value

The zero emf test would be most valuable to assess the performance of a gauge if the observed trends could be correlated with those observed during the investigation of the Nernst relationship. We have explored this possibility by plotting in Figure 6 the average absolute departure from the theoretical emf, as given by equation (2), against the average absolute departure from zero emf. Although some correlation is evident it is not so sufficiently well established that the zero emf test can replace that based on the Nernst relationship.

V.3 The Symmetry of the Cells

Ideally the response of the cell should be symmetrical with respect to the gas flows, i.e. O₂/air data would be exactly similar to those measured in an air/O₂ configuration. That this ideal behaviour is not always observed was evidenced by a large number of data provided by the participants in the vicinity of 970 K. Rather than confining our attention to data taken at a single temperature we shall refer here to a number of curves measured over the complete temperature range as the analysis of these is finally more revealing.

The data in question are plotted in Figure 7. For tubes IUPAC 1 and IUPAC 3 there is hardly any difference between O₂/air and air/O₂ measurements: furthermore all the data lie quite close to the theoretical line. For IUPAC 2 on the other hand, the observed emfs in both data sets are somewhat lower. A more convenient representation is given in Figure 8 where the relative departures from the theoretical

$$\frac{\Delta E}{E} = \frac{\text{observed emf} - \text{theoretical emf}}{\text{theoretical emf}} \quad (12)$$

are plotted against the temperature. For IUPAC 1 and IUPAC 3 the data are for the most part distributed statistically within an interval of 0.0015 to 0.002 about the zero value. For IUPAC 2, which is representative of several other results, the trend is quite different. In the cases where a significant departure from the theoretical line is observed, there is a tendency for the symmetry of the response to improve at higher temperatures. This does not mean however that the accuracy of the cell is also improved: for the data illustrated for IUPAC 2 the air/O₂ configuration yields the 'best' results at lower temperatures. This type of behaviour explains why results obtained using either one or both modes of operation with O₂/air and air/O₂ symmetries, generally led to the same conclusion in the Nernst law test. Although strictly speaking the results are quantitatively different in each mode of operation, data points in each case are distributed so that departure from the Nernst law values retains the same sign and magnitude.

We should emphasise at this point that the particular gauges which gave the best performance as judged on the basis of the slopes and intercepts measured while verifying the Nernst relationship performed equally well in the other tests. Indeed the complete series of measurements made with the gauges served to emphasise the reproducibility and quality of their performances.

V.4 Effect of Flow Rates

It has often been reported in the literature that changes in the gas flow rates may lead to small variations in the cell voltages. This effect has been described in several of the individual reports and a possible explanation has been proposed in that from Laboratory 1. It is not realistic to attribute the variations observed under oxidising conditions to a leakage arising from a partial electronic conductivity as the effect of the latter is expected to be quite small (refs. 2,6). It has been suggested that a change in the gas flow rate in one compartment could generate a change in the total local pressure at this electrode thus implying a small difference in the oxygen partial pressure. For a pressure difference Δp between the gases at the two electrodes, relative to an overall pressure p the additional term ΔE_p in the cell emf is given as

$$\Delta E_p (\text{mV}) = 2.154 \times 10^{-2} T \Delta p / p \quad (13)$$

To examine the validity of equation (13) one cell was exposed to a constant rate of flow of air outside while variable oxygen flow rates inside the tube induced variable total pressure differences between the cell compartments. The results are shown in Figure 9. The dependence of the emf on the rate of flow was removed by the correction for pressure differences given by equation (13). All the data from Laboratory 1 could then be corrected systematically for variations in the flow rate, and used throughout section V.

Considerable caution must be exercised, however, before extending these ideas to other gas flow rates. In many of the runs the temperature readings from the thermocouples were also affected by variations in the flow rates. At higher linear rates thermal equilibrium of the gases may not be attained before they reach the electrodes and the temperature profile

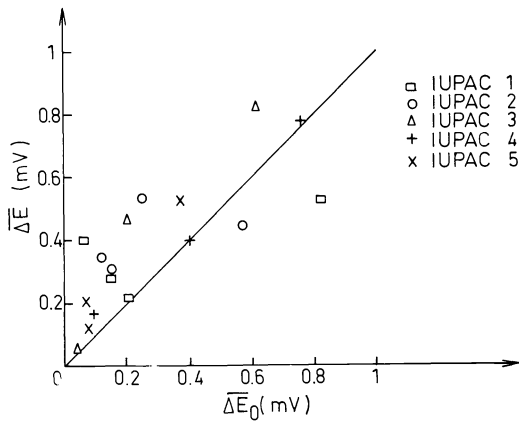


Fig. 6 Correlation between the average absolute departure from the theoretical emf, ΔE , and the average absolute departure from zero emf ΔE_0 .

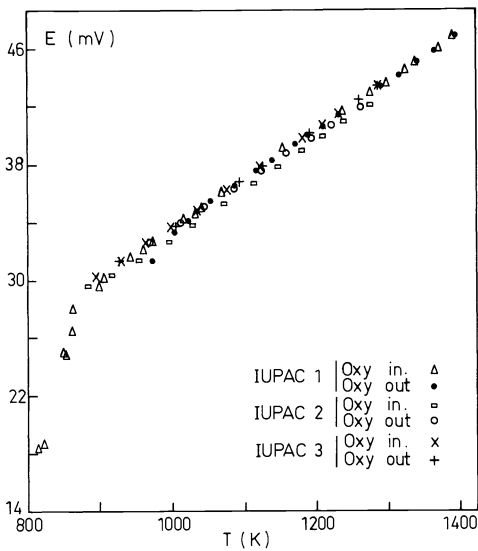


Fig. 7 Representative emf versus temperature data for symmetry tests during which the gas flows were interchanged.

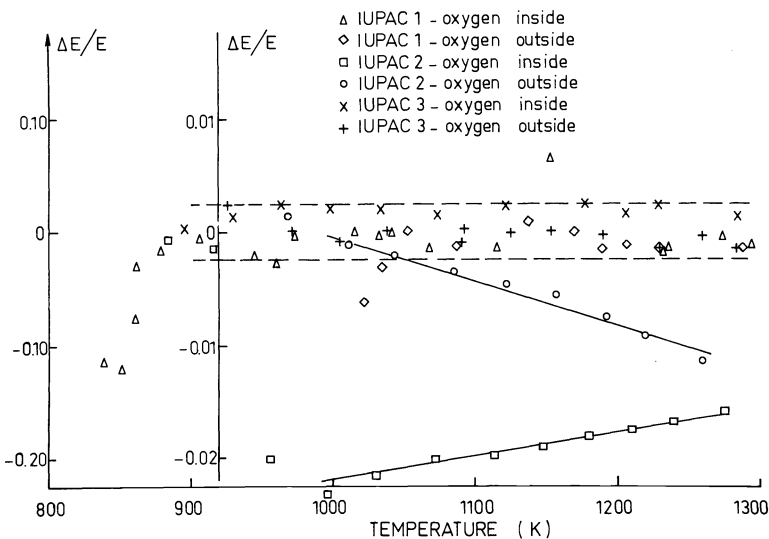


Fig. 8 The symmetry test data of Figure 7 displayed as relative departures from the theoretical emf. $\Delta E/E$ is defined by equation (12).

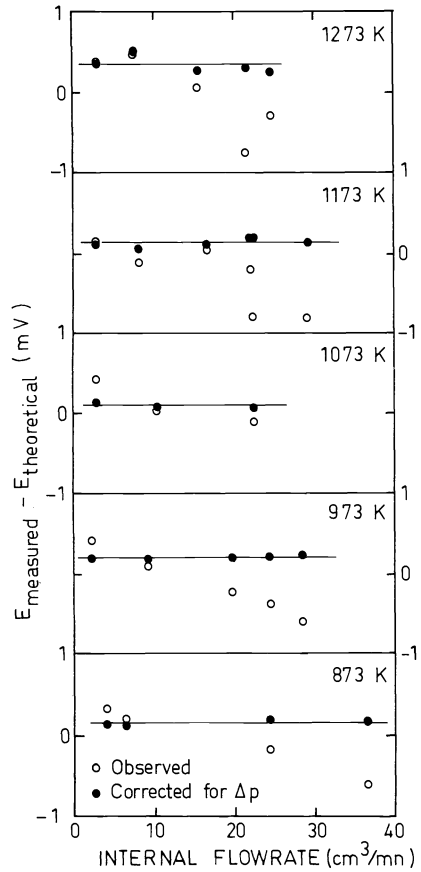


Fig. 9 Dependence of emf on internal flowrate. The data refer to IUPAC 3 with air outside and O_2 inside the cell: they are corrected for Δp using equation (13).

of the assembly may be modified. For the tubes used in the present study (about 5 mm in external diameter) inner and outer flow rates of 20-50 cm³/min and 500-700 cm³/min respectively seemed to yield acceptable results.

VI. ELECTROCHEMICAL TESTS AT LOWER OXYGEN POTENTIALS - EFFECTS OF ELECTRONIC CONDUCTIVITY

To take account of the three detrimental effects of electronic conductivity mentioned in section III.4, the voltage produced by the gauge is rewritten as (see equation (2))

$$E = (1 - \bar{t}_e) \frac{RT}{4F} \ln \left[\frac{\beta(P_{O_2}'' + \Delta p_{O_2}'')}{\beta_{ref}(p_{O_2}^{ref} + \Delta p_{O_2}^{ref})} \right] \quad (14)$$

\bar{t}_e is the average electronic transport number of the electrolyte ($\bar{t}_e = 1 - \bar{t}_i$), $\Delta p_{O_2}''$ and $\Delta p_{O_2}^{ref}$ the alterations of the corresponding pressures due to oxygen permeation and β and β_{ref} the coefficients expressing the polarizations of the electrodes. Under the conditions selected for the experiments described below the outer reference electrode is kept in contact with air so that this electrode may be considered as being non-polarized ($\beta_{ref} = 1, \Delta p_{O_2}^{ref} = 0$).

VI.1 The gas line used for tests at lower oxygen potentials

The gas supply and control line for use at low oxygen potentials is shown schematically in Figure 10: all connections were made of stainless steel tubing and sealed with Viton 'O' rings. Argon flowed from the gas tank A first through an electrochemical oxygen pump, EP, and then through the oxygen gauge which was under test, OG1. The rate of gas flow was accurately controlled by the flow meter FM and could be measured to 1% accuracy by a displacement flowmeter DFM. A second oxygen gauge, OG2, which incorporated either a laboratory-made zirconia tube or a IUPAC tube which had already been tested, and operating at a temperature at which it was known to obey the Nernst law correctly was also placed in the gas line. When placed upstream of the gauge under test this was used to ensure that the gas supplied had a constant composition. While in a position downstream of OG1 (as in Figure 10) it measured the alteration of the gas composition due to the permeation of oxygen at high temperature through the tube wall in the cell which was being tested.

The oxygen pump is shown in Figure 11 and was fabricated from a 300 mm long laboratory-made yttria-stabilized zirconia tube (9 mole% Y₂O₃), with outer and inner diameters of 12 and 8 mm, respectively. It was operated at a fixed temperature in the range 873 - 1073 K where it had been definitely established (refs. 20, 21) that Faraday's law is accurately obeyed. The passage of a direct current between the platinum electrodes deposited on both sides of the tube wall causes oxygen to be reduced at one electrode and the oxide ions to be oxidized at the other. The overall result is that oxygen is pumped from outside the tube into the gas flowing inside it or vice versa. The flow of pumped oxygen, J , is related to the current intensity I by the Faraday equation

$$J = I/4F \quad (15)$$

where J is in mol s⁻¹, I in A, and F is the Faraday constant. When this passage of oxygen remains small compared to the rate of flow of argon through the tube, the mol fraction of oxygen, χ , in this gas after its passage through the pump varies with the current intensity as

$$\chi = \chi^0 + 0.209 I/D \quad (16)$$

where χ^0 is the mol fraction of oxygen in the gas supplied to the pump and D is the rate of flow of the gas in l h⁻¹ NTP.

VI.2 Electrochemical tests at intermediate temperatures (773 - 1773 K)

The conventional Nernst law test based on the use of a circulating oxygen-inert gas mixture of constant composition may also be employed for lower oxygen potentials. To evaluate the gauge performance the mixture, in which the oxygen content need not be known with a high accuracy, must only be kept at constant composition while the temperature is varied. The variation in cell voltage is then compared with the straight line predicted by the Nernst equation (equation (2)). At relatively high oxygen pressures a straight line is in fact observed over a rather broad temperature interval but with low pressures two difficulties make the test less reliable. First, equilibration in the gauge after each change in temperature becomes relatively sluggish and the plotting of the voltage-temperature diagram is excessively time consuming. Under these conditions it is usually difficult to maintain

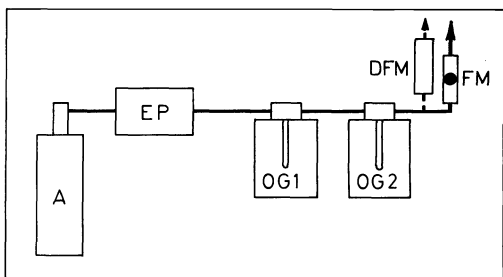


Fig. 10 Gas line used for electrochemical tests at lower oxygen potentials. A is the argon gas tank; EP the electrochemical oxygen pump; OG1 the gauge under test and OG2 another gauge; FM the control flowmeter and DFM the displacement measuring flowmeter.

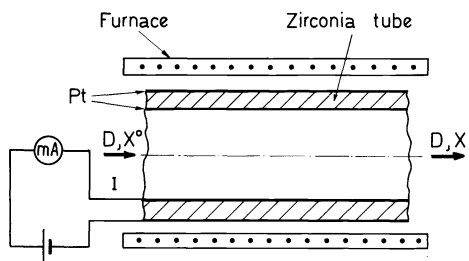


Fig. 11 Schematic representation of electrochemical oxygen pump

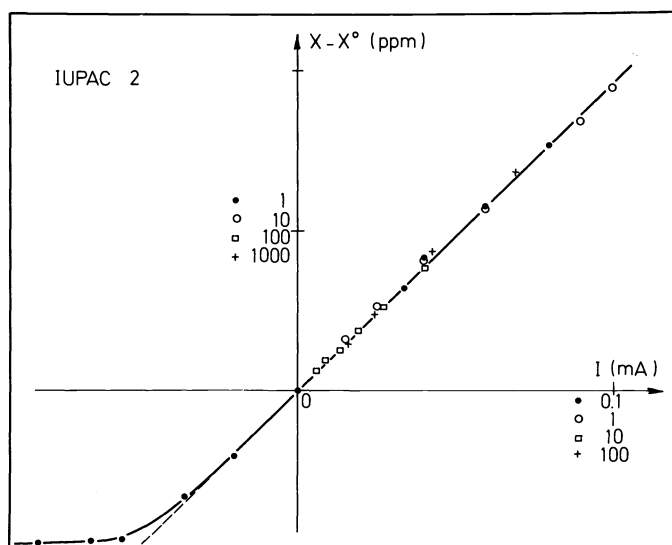


Fig. 12 Faraday law test IUPAC 2

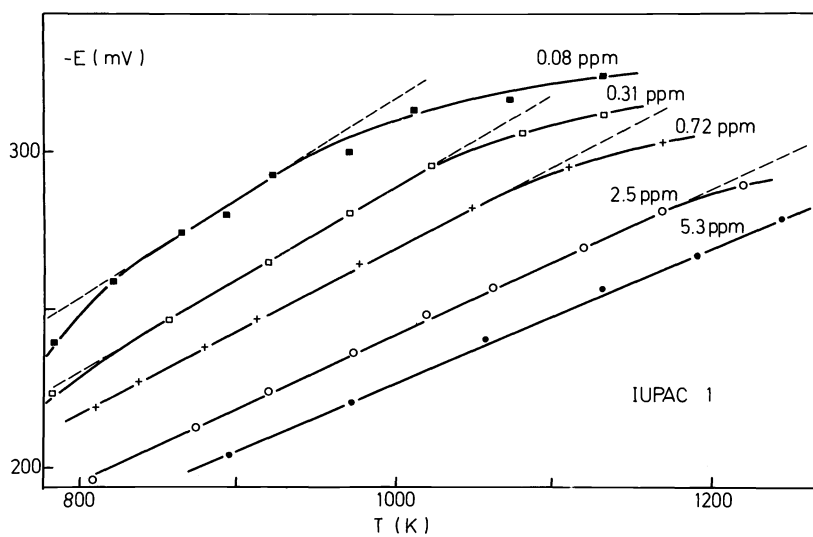


Fig. 13 Improved Nernst law test IUPAC 1

the gas composition constant within 1%. Secondly, the temperature range in which the Nernst equation is obeyed is shortened and the straight line averaging the experimental points cannot be accurately determined.

An alternative method to evaluate the correct functioning of the gauge is called the Faraday law test and relies on using the gauge in conjunction with an oxygen pump in a gas line such as that shown in Figure 10 (refs. 20, 22). The oxygen content of the circulating gas is measured by the gauge under test for various current intensities I passing through the oxygen pump and the basis for the test is the verification of Faraday's law as represented by equation (16). This test has two advantages. First, the current intensity in the pump and therefore the oxygen content in the gas, can be varied over a broad range (typically 4 or 5 orders of magnitude) independently of the gauge temperature so that the straight line averaging the experimental points $\chi = f(I)$ can be defined with excellent precision. Secondly, the parameters I and D in equation (16) can be measured accurately and therefore the slope of the experimental line can be compared with a value calculated from independent data.

As will be evident the use of this test yields an accurate determination of the oxygen content of the gas and this value can be further checked by the second gauge in the gas line. Thus the experimental configuration described and, in particular, the use of the electrochemical oxygen pump enables gases with a broad range of accurately known compositions to be prepared. Under these circumstances an improved Nernst law test can be implemented for these gases. Because the oxygen content of the gas to be analyzed is accurately known a theoretical straight line for the expected cell voltage as a function of temperature can be calculated and compared to the experimental measurements.

It has been frequently observed that the gauge voltage obeys the Nernst equation within a certain range of oxygen pressure and temperature and this will be referred to as the domain of ideal response. As one moves away from the limits of this domain the deviation from the Nernst equation increases rapidly. In the experiments described below the evaluation of the accuracy of the oxygen measurement within the domain of ideal response relied in the main on the use of the Faraday law test. The improved Nernst law test was used to determine the limits of this domain although the Faraday law test could also have been used for this purpose.

VI.3 Accuracy of the measurement: the Faraday law test

Results typical of those obtained are shown in Figure 12 for a IUPAC 2 tube. So that these results can be represented with the maximum accuracy ($\chi - \chi^0$) is plotted instead of χ (cf. equation (16)). Successive parts of the plots are also superposed on each diagram using appropriate scales since a single scale would need to cover 5 orders of magnitude.

The parameter χ^0 and the slope of the straight line m , were calculated using the theory of adjustment. Traditional least-squares fitting is not convenient here since an error of 1 ppm in the oxygen content does not have the same meaning in a gas containing 1000 ppm as in a gas which contains only 0.1 ppm. The function used was

$$L = \sum_{i=1}^n p_i \{ \chi_i - (mI_i + \chi^0) \}^2 \quad (17)$$

where (χ_i, I_i) pairs are the experimental values and p_i are appropriate weightings. The weighting was chosen as the reciprocal of the mol fraction of oxygen in the gas so that

$$L = \sum_{i=1}^n \frac{\{ \chi_i - (mI_i + \chi^0) \}^2}{\chi_i} \quad (18)$$

The coefficients m and χ^0 were the solutions of the equations

$$\frac{\partial L}{\partial m} = \frac{\partial L}{\partial \chi^0} = 0 \quad (19)$$

and the results from tubes IUPAC 1 to IUPAC 4 are given in Table 7.

The agreement between the slopes of the straight lines and the values calculated using the rates of flow of the gas, D , is within 4%. Table 7 also gives the average value and the maximum deviation of the experimental points from the average straight line. Within the domain of ideal response, which in these experiments was found to extend down to ~ 0.1 ppm, the average deviation from the line is of the order of 1% and the maximum deviation is $\sim 5\%$.

Figure 12 also shows the behaviour observed outside the limits of the domain of ideal response. The voltage of the gauge appears to saturate and to imply a constant oxygen pressure. At still lower oxygen potentials a sharp jump towards more cathodic voltages is observed indicating that the reduction of traces of CO_2 and H_2O may be involved in the gas equilibrium.

VI.4 Limits of the domain of ideal response: the Nernst law test.

The oxygen content in argon was set at a fixed value using the oxygen pump, as was done for the Faraday law test. This was then continuously monitored by the second oxygen gauge (OG2 of Figure 10) and kept constant throughout the test. Then the temperature of the gauge under test (OG1) was varied in the range 773 to 1253 K. At each of the chosen temperatures the cell voltage was measured when its erratic variations were < 0.1 mV over one hour. The results were plotted on a voltage versus temperature plot and compared to the theoretical straight line corresponding to the known oxygen partial pressure. An example, for tube 1, is shown in Figure 13 where deviations, due mainly to polarization of the measuring electrode, are evident at low and high temperatures. On the low temperature side the polarization results from a large increase in the impedance of the electrode, while, on the high temperature side, it is due to the increase in the polarizing flux of oxygen permeating through the zirconia wall by electrochemical semipermeability. The low and high temperature limits beyond which deviations exceed a selected threshold delineate the temperature interval of ideal response at that oxygen partial pressure. The threshold was selected so that it corresponds to an error on the measured oxygen mol fraction of 10% i.e.

$$\frac{\Delta\chi}{\chi} = 0.1 \quad (20)$$

The voltage error for this oxygen mol fraction error is ~ 2.5 mV. For additional information the temperature limits corresponding to an oxygen mol fraction error of 50% were also determined in some cases.

Figure 14, also for tube 1, shows how these limits vary with the measured oxygen mol fraction. Figure 15 compares the results for all tubes measured using the 10% error limits.

VI.5 High temperature (1173 - 1773 K) electrochemical tests

Measurements were also made at high temperatures to quantify the importance of the two sources of error described in equation (14), i.e. the $\bar{t}_e E_{th}$ term and the alteration, $\Delta\chi$ in the oxygen content of the gas which is being analyzed due to electronic conductivity in the zirconia electrolyte. These measurements are made possible by the use of a zirconia tip electrode (ref. 23), such as is shown in Figure 16, which eliminates the corresponding electrode polarization effects. Under such conditions equation (16) is modified as

$$E = (1 - \bar{t}_e) \frac{RT}{4F} \ln \left\{ \frac{p_{\text{O}_2}'' + \Delta p_{\text{O}_2}''}{p_{\text{O}_2}^{\text{ref}}} \right\} \quad (21)$$

where $\Delta p_{\text{O}_2}''$ is the alteration in oxygen partial pressure due to the passage of oxygen through the tube wall.

Typical results, measured on tube 4 with a gas flow rate of 11 l h^{-1} NTP, are summarized in Figure 17 in terms of \bar{t}_e and the increase, $\Delta\chi$, in the oxygen content of the gas which is being analyzed. The scatter evident in \bar{t}_e around 1273 K is due to the very small value of the voltage deviation measured at these temperatures. It is evident from these results that there is a marked increase in the oxygen semipermeability of the zirconia above 1373 K. Because of this, the reliability of measurements of oxygen contents less than 0.1% cannot be guaranteed at temperatures above 1473 K under the experimental conditions described here. As a further complication the average electronic transport number also becomes significant and under the experimental conditions relating to Figure 17 a resulting error of 50% in the measured oxygen pressure is exceeded at 1393 K. With higher measured oxygen pressures or lower reference oxygen pressures this limit occurs at a higher temperature. The extrapolation of the results to intermediate temperatures confirms that the $\bar{t}_e E_{th}$ error term is very small. At 1173 K this term is ~ 2 mV which must be compared with experimentally observed deviations of 9 mV and 18.3 mV under 7.6×10^{-7} bar and 2.5×10^{-7} bar of oxygen, respectively.

VII CONCLUSIONS

This Collaborative Group Project has provided a very large number of data relating to the fabrication and operation of zirconia-based oxygen gauges and extending to the characterization of their electrolyte materials. While the detailed data are set down in the

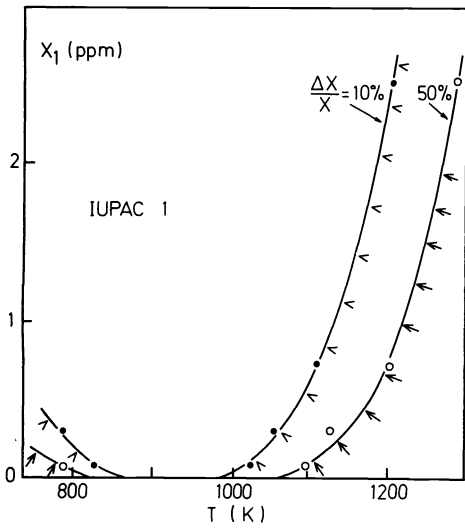


Fig. 14 Domain of ideal response for IUPAC 1: limits fixed at 10% or 50% error on the measured oxygen content.

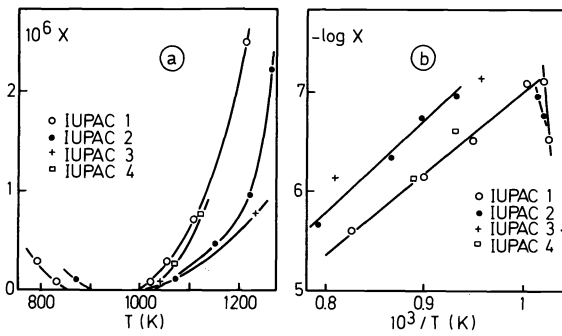


Fig. 15 Comparison of the domains of ideal response with limits at 10% error: oxygen mol fraction as a function of temperature.

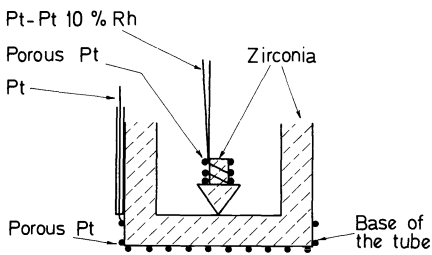


Fig. 16 Zirconia tip electrode used at high temperature to prevent electrode polarization.

Table 7 : Results of the Faraday's law tests

Tube	T (K)	Oxygen mole fraction interval (ppm)	Number of measurements	X ⁰ (ppm)	m _{calc} (A ⁻¹)	m _{exp} (A ⁻¹)	Δm/m (%)	Average deviation ΔX/X (%)	Maximum deviation ΔX/X (%)
1	966	0.2 - 1100	22	0.46	1.65 10 ⁻²	1.69 10 ⁻²	2.4	0.8	3.7
2	1173	0.5 - 2350	22	0.91	1.88 10 ⁻²	1.96 10 ⁻²	4.0	1.1	8.1
3	1175	0.14 - 1400	16	0.67	1.76 10 ⁻²	1.76 10 ⁻²	0	1.2	5.6
4	973	4 - 1600	13	0.75	1.80 10 ⁻²	1.77 10 ⁻²	1.7	0.5	3.4

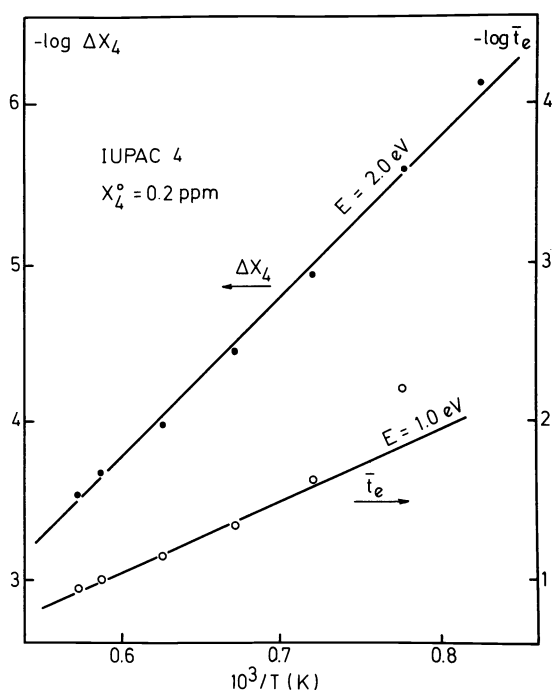


Fig. 17 The sources of error at high temperature for IUPAC 4. is the alteration of the oxygen content due to oxygen permeation (electrochemical semipermeation) through the tube wall and \bar{E}_e is the average electronic transport number of the zirconia

reports from the individual laboratories it is not possible in a paper of this size to cover every aspect of the work. Rather we have sought to isolate those factors, relating to both the preparation and operation of the gauges, which are particularly important to their proper functioning. This has made it possible to lay down the basic principles which should be followed when a gauge is being made. The combining of the data from the standard test procedures, as measured in each of the participating laboratories, and their central analysis allows an assessment of the level of accuracy that can be expected when the gauges function correctly.

The successful determination of an unknown oxygen pressure by a gauge of the type described here first requires the careful choice of a well-defined and reliable reference partial pressure of oxygen and a precise measurement of the operating temperature. We have also discussed the detrimental effects of the presence of a temperature gradient within the cell and stressed the importance of keeping the active parts of the gauge within a uniform region of the temperature profile of its furnace. The rates of flow of the gases over the electrodes must also be carefully regulated so that they do not influence the cell potential either by causing temperature gradients or inducing pressure differentials between the cell compartments. The very large influence of geometrical factors within the cell on these last effects means that it is not possible to give recommendations which are universally reliable.

The vast majority of the tubes sent to the participating laboratories were made into oxygen gauges which worked very well. Yet despite standard procedures within individual laboratories the gauges made from three tubes failed to give acceptable results. It would clearly be of great interest to determine why these failures occurred and to identify whether they were due to some intrinsic properties of the particular tubes or perhaps to the electrodes. Another result for which we cannot offer an explanation is that while some of the tubes were almost perfectly symmetrical with respect to the gas configuration several of the gauges, under apparently identical conditions, were quite unsymmetrical when the gas flows in the compartments were interchanged. Because of these various difficulties it is clear that one cannot be assured of a 100% success rate and that cells, even when made under identical conditions, may not exhibit a standard behaviour.

The present cooperative study has established that, in the domain of high chemical potentials of oxygen, departures of 0.2 to 0.3 mV from the ideal Nernst law cell potential would represent a fair estimate of gauge performance. This corresponds to errors of 1-2% in the determination of an unknown oxygen partial pressure. This estimate of the error, derived from the Nernst law test in the domain of ideal response, is in good agreement with the value provided by the independent investigation based on the Faraday law test. However, it is clear that when a gauge is fabricated and operated carefully it is possible to obtain results within 0.2% of the theoretical emf. It is also evident that within the domain of ideal response, from the point of view of reliability and accuracy, there are no

essential differences between the performances of tubes made from the different materials.

The results analyzed here represent the current practice in working laboratories which can provide and manage moderately high temperatures. Because there are no experimental techniques immediately available with which to determine the exact temperature distribution within the active components of the cell or to monitor the changes in these temperatures brought about by gas flow or other perturbations it is difficult to envisage how the level of performance reported here can be significantly improved. Consideration of the limits determined for the domain of ideal response show that these limits vary significantly with the tubes but that no simple correlations can be found with the physical characteristics of the tubes nor, in particular, with their compositions. For gases with extremely low oxygen content operating temperatures of 923 - 973 K are most appropriate since the extrapolation of the results show that oxygen contents of 10^{-2} ppm can be measured to within a few percent (such accuracy was checked only down to 8×10^{-2} ppm). With good quality tubes oxygen contents of ~ 1 ppm can be determined accurately at temperatures up to 1173 K. This range is of special interest for transient measurement since response times decrease significantly as the temperature is raised. At temperatures greater than 1273 K serious limitations reduce the accuracy of the measurement at all oxygen pressures even when a zirconia tip electrode is used. This deterioration in the gauge performance is caused by partial short-circuiting of the cell by the electronic conductivity of the electrolyte and by the contamination of gases by oxygen permeation. The short-circuit error may be corrected by an evaluation of the average electronic transport number. The error resulting from permeation of the tube wall by oxygen can be reduced by increasing the gas flow rate but the error due to an overpotential at the measuring electrode cannot be eliminated in this way.

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APPENDIX A

Manufacturers who supplied tubes especially for this study

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