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# *Measurement and regulation of oxygen content in selected gases using solid electrolyte cells. IV. Accurate preparation of $CO_2$–CO and $H_2O$–$H_2$ mixtures*

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Mixtures of $CO_2$–CO, $H_2O$–$H_2$ and Ar–$H_2O$–$H_2$ of precise composition were prepared using a zirconia pump and analysed with a zirconia gauge. The $P_{CO_2}/P_{CO}$ ratio was varied from $5 \times 10^{-2}$ to $10^4$ and the $P_{H_2O}/P_{H_2}$ ratio from $3 \times 10^{-4}$ to $10^{-2}$. A 'Faraday's Law test' proved to be a simple and reliable procedure for checking the conditions of utilization of these gaseous mixtures and for verifying that no significant disproportionation of CO or leakage along the gas circuit altered the prepared composition. From a practical point of view the best methods of preparing mixtures with low oxygen activity are reduction of carbon dioxide in the range $5 \times 10^{-11}$ to $10^{-17}$atm and oxidation of inert gas–$H_2$ in the range $10^{-19}$ to $10^{-27}$atm at 800° C.

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## 1. Introduction

The three previous papers in this series [1–3] were essentially devoted to the improvement of zirconia gauges and pumps used for analysing and controlling the oxygen partial pressure in flowing, oxygen–inert gas mixtures. New designs were also proposed [2–4] which extended the use of the gauges to lower oxygen partial pressures. The results were confirmed in a thorough investigation of a static oxygen atmosphere controller [5] based on the improved gauge and pump. It was also shown [1] that small samples of $CO_2$–CO mixtures could be analysed to within a few per cent after an appropriate calibration of the gauge. In this paper, we describe a study of the performance of a zirconia pump gauge in the production of $CO_2$–CO and $H_2O$–$H_2$ mixtures.

Gaseous mixtures such as $CO_2$–CO and $H_2O$–$H_2$ have been extensively used with oxide systems in thermodynamic measurements [6–10], in conductivity experiments [11–12] and in phase diagram determination [13]. They are sometimes used as reference atmospheres in oxygen gauges [14–17]. Various methods have been proposed to control the composition of the mixtures. The conventional procedures are premixing in appropriate containers and mixing of flowing gases by calibrated flowmeters [18, 19] or titrating pumps [8, 20]. More recently, it has been proposed that mixtures circulating in a closed system could be controlled by coulometric titration using a zirconia pump and gauge [21, 22]. In the case of $H_2O$–$H_2$ mixtures, the partial pressure of water is often controlled by bubbling hydrogen through water at a controlled temperature [15, 23, 24]. Oxygen and hydrogen in appropriate proportions can also be passed over a platinum catalyst [8]. The control of the $P_{H_2O}/P_{H_2}$ ratio by a zirconia pump has already been proposed [20, 25]. Gas analysis is carried out by gas chromatography [18], infrared absorption of carbon monoxide [8] and zirconia or thoria gauges [1,7, 12, 14, 18, 26, 27].

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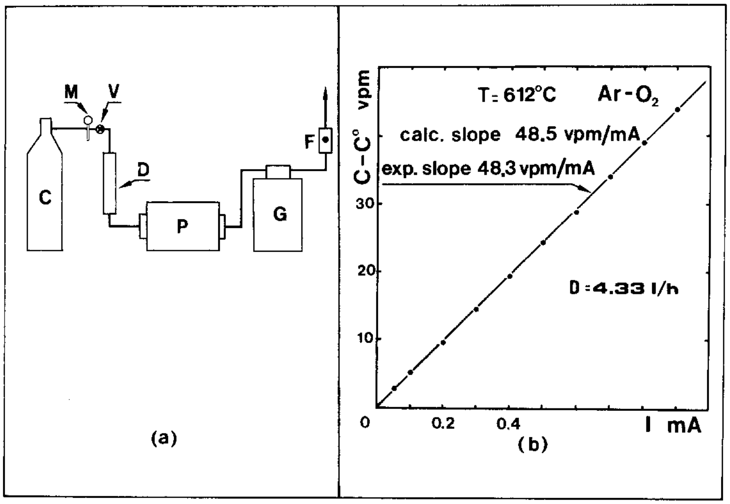

Fig. 1. (a) Experimental set-up. C, gas tank; M, manometer; V, valve; D, drying column; P, electrochemical pump; G, zirconia gauge; F, flowmeter. (b) Verification of Faraday's law with Ar–$O_2$ mixtures.

## 2. Experimental set-up

The gas circuit is represented schematically in Fig. 1a. It consists of a gas supply, an electrochemical zirconia pump, a zirconia gauge and an accurate flowmeter. Nominally pure gases (CO, $CO_2$, Ar) and a premixed gas (Ar–5% $H_2$) (Air Liquide) were used. Due to the important buffer effect of the $CO_2$–CO and $H_2O$–$H_2$ mixtures, the semipermeability effect was found to be negligible and the zirconia tip electrode was not required [4]. The oxygen gauge was of conventional type [1], consisting of a closed-end, yttria-doped (9 mol%) zirconia tube. It was prepared in our laboratory by slip casting and firing at 1800° C for 2 h. The raw materials were pure oxides [$ZrO_2$ (Merck) and $Y_2O_3$ (Pechiney)]. The external reference electrode was formed from a platinum paste (Degussa 308 A). Air was used as a reference gas. The inner surface of the flat bottom was platinized to form the measuring electrode. A Pt–Pt-10%Rh thermocouple measured the temperature at the surface of this electrode. Measurements were performed at temperatures in the range 800–1000° C. The gauge voltage was measured using a high-impedance voltmeter (Tacussel, Aries 20 000).

The oxygen pump consists of an yttria-stabilized zirconia tube (Zircoa), 2.5 cm in diameter, with metal coatings deposited on the inner and outer surfaces. Vitrifiable paint (Degussa M 8005) was used to increase the adherence of the electrodes on the surface of the tube. The gas whose composition was to be controlled flowed inside the tube. The outside electrode was exposed to ambient air. The control of the gaseous mixtures required a wide range of current intensities from a few microamperes to several amperes. To avoid current densities higher than 50 mA $cm^{-2}$, the inner and outer electrodes were 12 cm in length. The homogeneous temperature zone of the furnace was approximately 5 cm long. The maximum temperature was selected in the range 850–1000° C. Four platinum wires were used as current collectors to avoid excessive heating of the leads. The power supply (0–2.5 A, 0–60 V, Lambda) had a stability of $10^{-4}$ for the operating conditions. The intensity was measured by an ammeter with a 0.5% accuracy (Tacussel MAL-U). The gas flowrate (1–10 l $h^{-1}$) was monitored by rotameters and accurately measured to within 1% using a laboratory-made liquid displacement flowmeter [28]. The connecting tubes were of stainless steel and all O-ring sealings were of Viton.

To make sure that the set-up worked properly, we first carried out a 'Faraday's Law test' [2, 29] with an argon–oxygen mixture. We verified, using a previously established procedure, that the oxygen mole fraction $C$ in the gas streaming in the pump obeyed the following equation as a function of the pump current $I$ [25]

$$C - C^0 = 0.209 I/D \tag{1}$$

where $C^0$ is the oxygen mole fraction upstream in the gas carrier and $D$ is the gas flowrate (in l $h^{-1}$

NTP). The total pressure is 1 atm. The oxygen content in the gas was measured using the downstream zirconia gauge.

The most noticeable perturbation in oxide electrolyte cells is due to the small electronic conductivity of stabilized zirconia. The resulting oxygen flux increases the oxygen partial pressure of the gas in the pump and the gauge and disturbs the electrode equilibrium in the gauge [4]. All these perturbations lead to an absolute value of the gauge voltage that is too low with respect to the ideal value; the sources of error in the pump and gauge are cumulative. Therefore, this test allows the correct functioning of the zirconia gauge and the pump to be checked simultaneously. A further advantage is that the current density passing through the pump may be varied over a broad range, from a few microamperes up to several amperes, therefore Equation 1 may be verified over a range of several orders of magnitude. Moreover, the slope can also be determined accurately from the measured flowrate. This value will be designated *calculated*. It can be compared to that deduced from the plot, called *experimental*.

A typical result from such an experiment is shown in Fig. 1b. Nominally pure argon (Air Liquide) circulated at a measured flowrate of 4.33 l h$^{-1}$ NTP. The experimental points lie on a straight line with a correlation coefficient of 0.9998. The agreement between the calculated slope (48.3 vpm mA$^{-1}$) deduced from Equation 1 and the experimental slope (48.5 vpm mA$^{-1}$) verifies the accuracy of the set-up.

## 3. Control of the $P_{CO_2}/P_{CO}$ ratio

### 3.1. *Theoretical considerations*

The direct reduction of carbon dioxide molecules in zirconia cells has been studied for regenerating respiratory atmospheres [30, 31], for the removal of oxygen from gases [20, 32] and for the control of oxygen activity in $CO_2$–CO mixtures circulating in a closed system [21, 22]. The theoretical relationship between the current $I$ passing through the pump of our experimental circuit and the gauge voltage $E$ has been previously described [3]. To recall the principle of the derivation let us consider the situation where pure $CO_2$ is supplied to the gas circuit. After the electrochemical reduction, the $CO_2$–CO mixture will be assumed to reach a rapid equilibrium with a small appropriate quantity of oxygen in any part of the gas circuit. The electrode reactions in the pump can be written as

Cathode

$$CO_2(\text{gas}) + 2e(\text{metal}) \rightarrow CO(\text{gas}) + O^{2-}(\text{electrolyte})$$

Anode (in contact with air)

$$O^{2-}(\text{electrolyte}) \rightarrow \tfrac{1}{2}O_2(\text{gas}) + 2e(\text{metal}).$$

The balanced reaction is

$$CO_2 = CO + \tfrac{1}{2}O_2. \qquad (2)$$

This can be viewed as a simple transfer of oxygen through the pump wall from the controlled atmosphere into the ambient air. According to Faraday's law, the flux $J$ of oxygen extracted from $CO_2$ molecules is proportional to the pumping current $I$

$$J = \tfrac{1}{2}(I/F) \qquad (3)$$

where $J$ is in atom s$^{-1}$. The flux of $CO_2$ molecules supplied to the pump can be expressed as

$$J' = D/V \qquad (4)$$

where $D$ is the gas flowrate (in l h$^{-1}$ NTP), $V$ is the molar volume of a perfect gas and $J'$ is in mole s$^{-1}$. Using these two equations we can, for instance, calculate the ratio of the quantity of oxygen present in the gas after pumping to the quantity of carbon

$$\frac{P_{CO} + 2P_{CO_2} + 2P_{O_2}}{P_{CO} + P_{CO_2}} = \frac{2J' - J}{J'} \qquad (5)$$

$$\frac{P_{CO} + 2P_{CO_2} + 2P_{O_2}}{P_{CO} + P_{CO_2}} = 2 - \frac{V}{2FD}I = 2 - kI. \qquad (6)$$

The partial pressures can be calculated from this equation and the following two basic equations

$$P_{CO} + P_{CO_2} + P_{O_2} = P_t \qquad (7)$$

$$\frac{P_{CO_2}}{P_{CO}P_{O_2}^{1/2}} = K_c(T) = \exp\left(-\frac{\Delta G^0(T)}{RT}\right) \qquad (8)$$

where $P_t$ is the total pressure (in atm), $K_c(T)$ and $\Delta G^0(T)$ are the equilibrium constant and the standard Gibbs energy change of Reaction 2 at $T_K$. The partial pressure of oxygen can be neglected with respect to the CO and $CO_2$ pressures in Equation 7. Under these conditions, we get

$$P_{O_2} = \frac{1}{K_c^2(T)}\left(\frac{1-kI}{kI}\right)^2 \qquad (9)$$

$$P_{CO} = kP_tI \qquad (10)$$

and

$$P_{CO_2} = P_t(1-kI). \qquad (11)$$

Numerically

$$P_{O_2} = \frac{1}{K_c^2(T)}\left(2.392\frac{D}{I}-1\right)^2 \qquad (12)$$

$$P_{CO} = 0.418P_t(I/D) \qquad (13)$$

and

$$P_{CO_2} = P_t[1-0.418(I/D)] \qquad (14)$$

with $D$ in $1\,h^{-1}$ NTP and $I$ in amperes.

In Equation 12, the equilibrium constant of Reaction 2, $K_c(T)$, is the only unknown parameter and can therefore be determined using a least-squares fit. Details of such a determination of the corresponding Gibbs energy variation $\Delta G^0(T)$ and its accuracy are presented in another paper. The equation obtained is

$$\Delta G^0(T) = -67\,664 + 20.90T_K \qquad (\text{cal mol}^{-1}) \qquad (15)$$

with a standard deviation of

$$\sigma = 20\,\text{cal mol}^{-1}. \qquad (16)$$

This value agrees with our previous determination of the standard potential of Reaction 2 using premixed $CO_2$–CO mixtures [1]. As an example, at 900° C, $\Delta G^0 = -43.15$ kcal mol$^{-1}$ according to the previous investigation and $\Delta G^0 = -43.27$ kcal mol$^{-1}$ according to Equation 15.

The above derivation is valid assuming an electrolysis efficiency equal to unity. Kleitz *et al.* [25] have shown that the electrolysis efficiency equals unity under nonreducing conditions. Deviations are observed when the current $I$ is greater than a limiting value $I_l$; in this case an electrochemical reduction of the electrolyte occurs. Deviation from the ideal value will obviously also be observed when a disproportionation of CO occurs.

When free oxygen is also present in the carbon dioxide gas supplied, Equations 3–14 are still valid, provided $I$ is replaced by $(I - I_0)$, where $I_0$ is the current intensity needed to pump out the oxygen content (see Section 3.3). The equations corresponding to the reduction of a gas mixture initially containing some carbon monoxide can be derived as previously, for instance by defining the flux of $CO_2$ molecules as

$$J' = \alpha D/V \qquad (17)$$

and the flux of CO molecules as

$$J'' = (1-\alpha)D/V \qquad (18)$$

where $\alpha$ is the carbon dioxide mole fraction in the upstream gas. The pump can also be used to oxidize pure CO or $CO_2$–CO mixtures. Here again the equations relating the partial pressures to the pumping current can be calculated according to a similar procedure by changing the sign of $I$.

### 3.2. *Experimental conditions*

Nominally pure carbon dioxide was used ($CO_2$, 'N 45', Air Liquide). The composition by volume was: $CO_2 > 99.995\%$, $O_2 < 5$ vpm, $H_2O < 10$ vpm, $N_2 < 30$ vpm, $CO < 5$ vpm and $H_2 < 0.1$ vpm. The gas was purified by passing it through a column of dehydrating compound (Zeolite 4 X). In the following, the total pressure $P_t$ was always equal to 1 atm.

The equilibrium oxygen pressure was measured using the oxygen gauge, according to Nernst's law

$$E = 4.958 \times 10^{-5}T \log\frac{P_{O_2}}{0.209p_{atm}} \qquad (19)$$

(with $T$ in degrees K, $P_{O_2}$ in atmospheres, $E$ in volts and $p_{atm}$ (ambient atmospheric pressure) in atmospheres). The response time of the gauge after a rapid modification of the current passing through the pump depended on the $P_{CO_2}/P_{CO}$ ratio and the gas flowrate. With buffered mixtures ($10^{-2} <$ ratio $< 10^2$) the response time is of the order of a few minutes, probably determined by the hydrodynamic characteristics of the circuit. With weakly buffered mixtures (ratio smaller than $10^{-3}$ or higher than $10^3$), it is of the order of one hour (with a $5\,1\,h^{-1}$ flowrate and at 900° C). Under steady-state conditions, with a constant current passing through the pump, the erratic voltage variations of the gauge were of the order of 0.1 mV, corresponding to a relative inaccuracy of about 0.4% on the equilibrium oxygen pressure.

### 3.3. *Results*

As with an argon–oxygen mixture, 'Faraday's Law test' is a reliable method for checking the electrochemical reduction of $CO_2$. We have, more precisely,

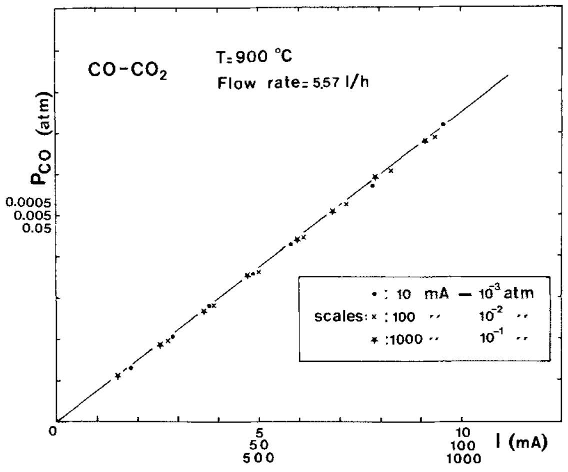

Fig. 2. Verification of Faraday's law for the reduction of pure carbon dioxide.

selected the linear relationship between $P_{CO}$ and $I$ (Equation 13). Carbon monoxide pressure was determined using Equations 7, 8 and 19

$$P_{CO} = \left[1 + 0.457 p_{\text{atm}}^{1/2} \exp\left(\frac{2FE - \Delta G^0(T)}{RT}\right)\right]^{-1}. \qquad (20)$$

An example of such a verification is shown in Fig. 2. The gas flowrate was $5.57\,\text{l}\,\text{h}^{-1}$. Actually, the original experimental straight line obtained did not pass through the origin. To correct this effect we plotted $P_{CO}$ as a function of $(I - I_0)$, where $I_0$ corresponds to the small current needed for the extraction of the traces of oxygen present in the carbon dioxide gas ($I_0 = 4.2$ mA in the present results). Using this presentation, a multiple scale can be used and the linear relationship can be visualized and checked over several powers of ten. In the example presented in Fig. 2, the experimental results lie on a straight line over three powers of ten from 2 mA up to 1 A, with a correlation coefficient of 0.99997. Moreover, the calculated slope determined using the measured flowrate of the gas agrees with the experimental slope to within 1%.

The linear relationship was not obeyed for high CO contents. This experimental limitation was also investigated as a function of the carbon dioxide flowrate (from $0.94–5.71\,\text{l}\,\text{h}^{-1}$). As shown in Fig. 3, the linear relationship was good for relatively high gas flowrates but not for low flowrates. At a flowrate of $0.94\,\text{l}\,\text{h}^{-1}$, a noticeable deviation appeared for a current higher than 1.7 A (i.e. carbon monoxide content higher than 78%). This deviation corresponds to an apparent diminution

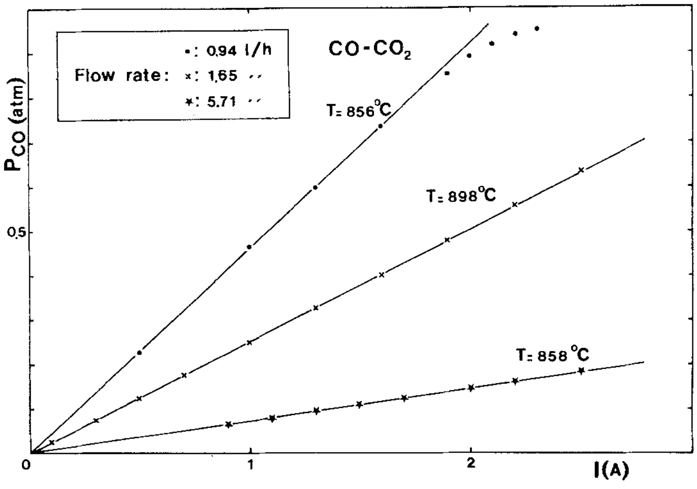

Fig. 3. Variation of CO content as a function of the current passing through the pump.

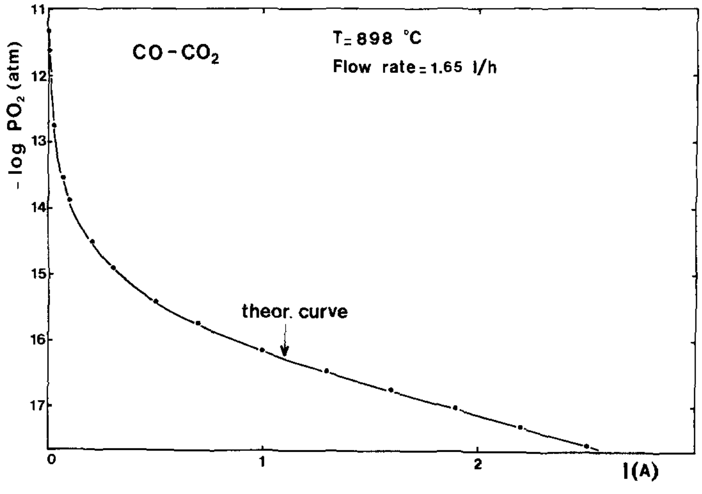

Fig. 4. Variation of the equilibrium oxygen pressure as a function of the current passing through the pump.

of the electrolysis efficiency. Similar non-ideal behaviour was observed in attempts to prepare mixtures enriched in carbon dioxide by electrochemical oxidation of pure carbon monoxide. The deviation from linearity decreased with increasing gas flowrate. Furthermore it decreased with increasing temperature of the pump and the gauge. This apparent decrease of the electrolysis efficiency cannot be accounted for by an oxygen flux through the tube due to an electronic conductivity of stabilized zirconia. These results are quite consistent with carbon deposition at high carbon monoxide content. Boudouard's reaction

$$2CO = CO_2 + C \qquad (21)$$

is then no longer negligible. This reaction was observed in various investigations using electrochemical cells [18, 29]. The thermodynamic properties of this reaction are reported in the literature [18, 19, 33]. Reaction 21 is catalyzed by platinum. We found insulation of the hot current leads to be a technical solution which partially limits this perturbation.

Provided appropriate care is taken to avoid this phenomenon, the equilibrium oxygen pressure can be varied over a wide range. An example of the variation of oxygen pressure as a function of the current $I$ passing through the pump is shown in Fig. 4 (temperature of the gauge, 898° C; gas flowrate, $1.65\,\mathrm{l\,h^{-1}}$). The current was modified from 5 mA (corresponding to $P_{CO} = 1.2 \times 10^{-3}$ atm and $P_{O_2} = 5 \times 10^{-11}$ atm) up to 2.5 A (corresponding to $P_{CO} = 0.635$ atm and $P_{O_2} = 2.65 \times 10^{-17}$ atm).

## 4. Control of the $P_{H_2O}/P_{H_2}$ ratio

The control of the partial pressure ratio in $H_2O$–$H_2$ mixtures by oxidation of hydrogen in a flowing gas with an electrochemical pump has been proposed by various investigators [20, 25, 32]. The dissociation of water vapour by electrochemical reduction was aimed at producing pure hydrogen rather than at controlling an atmosphere [24, 34].

The use of ternary mixtures of Ar–$H_2O$–$H_2$ enabled us to prepare mixtures with high $P_{H_2O}/P_{H_2}$ ratios and prevented the dew point being reached: in this way, condensation along the gas circuit was avoided. The drawback of this solution is a decrease in the buffer capacity of the gaseous mixture and a consequent increased sensitivity to leakages and especially to the oxygen semipermeability flux through the electrolytes [4].

The calculation of the theoretical equilibrium pressures of the components as a function of the current intensity passing through the pump can be achieved in the same way as for $CO_2$–CO mixtures. When an Ar–$H_2$ mixture (hydrogen mole fraction $q$) is supplied to the pump, we have, assuming that the amount of free oxygen is negligible with repsect to the quantity of $H_2O$ and $H_2$,

$$P_{H_2O} + P_{H_2} = qP_t \qquad (22)$$

$$P_{H_2O}/P_{H_2}P_{O_2}^{1/2} = K_H(T) \qquad (23)$$

$$\frac{P_{H_2O}}{P_{H_2} + P_{H_2O}} = \frac{V}{2FqD}I = \frac{k}{q}I. \qquad (24)$$

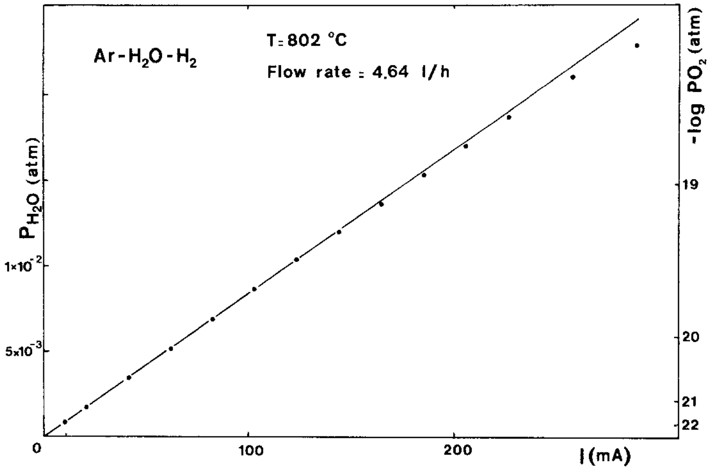

Fig. 5. Variation of water vapour partial pressure in an Ar–$H_2$ mixture as a function of the current density passing through the pump.

The calculated equilibrium partial pressures are

$$P_{O_2} = \frac{1}{K_H^2(T)}\left(\frac{kI}{q-kI}\right)^2 \qquad (25)$$

$$P_{H_2O} = kP_tI \qquad (26)$$

and

$$P_{H_2} = P_t(q-kI). \qquad (27)$$

Numerically

$$P_{O_2} = \frac{1}{K_H^2(T)}\left(2.392\frac{qD}{I}-1\right)^{-2} \qquad (28)$$

$$P_{H_2O} = 0.418P_t\frac{I}{D} \qquad (29)$$

$$P_{H_2} = P_t\left(q-0.418\frac{I}{D}\right) \qquad (30)$$

with $D$ in $\mathrm{l\,h^{-1}}$ and $I$ in amperes.

These theoretical relationships were verified using a premixed Ar–$H_2$ gas ($q = 0.05$). An example of the variation of $P_{H_2O}$ as a function of the current intensity passing through the pump is represented in Fig. 5. The water vapour partial pressure was calculated from the gauge voltage, using thermodynamic data published in [35]. Without any current in the pump, $P_{H_2O}$ equalled $8 \times 10^{-5}$ atm. This small oxidation of hydrogen was probably due to the semipermeability flux through the pump and the gauge tubes. The linear relationship between $P_{H_2O}$ and $I$ is well verified up to a pressure of $1.2 \times 10^{-2}$ atm which corresponds to the dew point of water at the temperature of the coldest parts of the set-up. In this way, the equilibrium oxygen pressure was varied from $10^{-24}$ up to $3 \times 10^{-19}$ atm at 800° C.

Mixtures with a greater reducing effect can be prepared from pure hydrogen instead of an Ar–$H_2$ mixture. However, the possible appearance of a noticeable n-type electronic conductivity in stabilized zirconia could then lead to errors in the measurement of the equilibrium oxygen pressure [14, 26]. We evaluated the possibility of such a preparation of $H_2O$–$H_2$ mixtures by using nominally pure hydrogen in the set-up at constant flowrate. The metallic parts of the set-up were heated using wound resistors to avoid water vapour condensation. Results at two temperatures of the zirconia gauge are given in Fig. 6. In both cases, straight lines were obtained. At 805° C the

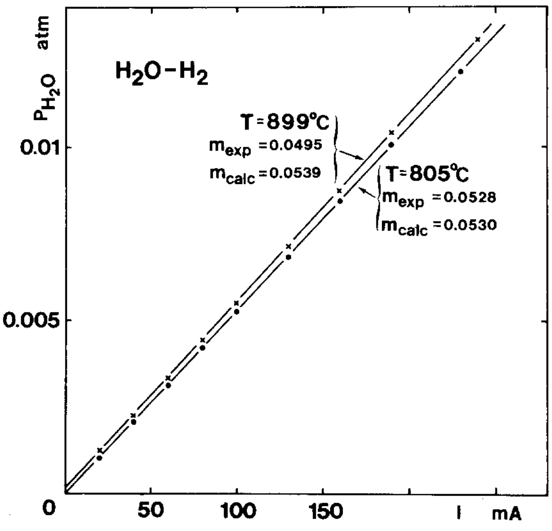

Fig. 6. Variation of the water vapour partial pressure prepared from pure hydrogen as a function of the current density passing through the pump, at two temperatures of the zirconia gauge ($m$: slope in atm $A^{-1}$).

agreement between the calculated slope deduced from the measured flowrate and the experimental slope was within 1%. However, at 899° C there was a noticeable disagreement (about 9%). An experimental slope that is too low is characteristic of the existence of an electronic conductivity in the electrolyte. Such a result clearly shows that accurate control of $H_2O$–$H_2$ mixtures with low $H_2O$–$H_2$ ratios is not possible at temperatures higher than 800° C with zirconia gauges. Below this temperature, the utilization of pure $H_2O$–$H_2$ mixtures enables us to prepare and control atmospheres with low oxygen activity; for instance, we were able to prepare an atmosphere with $P_{O_2} = 10^{-27}$ atm at 805° C.

The results of this study illustrate well the efficiency of Faraday's law as a test of the reliability of a pump gauge device for controlling $CO_2$–$CO$ or $H_2O$–$H_2$ mixtures.

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