

Measurement and regulation of oxygen content in selected gases using solid electrolyte cells. I. Discontinuous use of gauges

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Several points have been investigated which are of technological interest regarding cells involving zirconia-yttria solid solutions. The use of a metallic band coated on the electrolyte as a current lead to an electrode induces errors in the measurement of oxygen partial pressures due to local thermoelectric effects. The time dependences of platinum and silver electrodes have been measured as functions of oxygen partial pressure and temperature. A discontinuous use of gauges for analysing CO-CO₂ samples which gives the composition with an accuracy of 4% is described.

1. Introduction

Numerous solid electrolyte cells, giving voltages dependent upon the partial oxygen pressure in contact with an electrode, have been investigated since the start of the century. Haber *et al.* [1] in 1906 used porcelain as a solid electrolyte with gold and platinum as electrodes. However, the specific use of such cells as oxygen gauges has been developed more recently by Peters and Moebius [2] and Weissbart and Ruka [3].

Since these publications, numerous similar gauges have been designed, studied and patented [8–81]. An even greater number of papers exists dealing with gauges for measuring oxygen activity in metals or oxides; recent studies [4, 5] can be referred to for more details. Here we will only deal with gaseous-oxygen gauges and, in particular, with equilibrium conditions between the electrodes and the surrounding gases.

In general an oxygen gauge consists of a solid-electrolyte wall which conducts by O²⁻ ions and both sides of which are coated with an electronic conductor. This otherwise impervious wall separates the analysed gas with oxygen partial pressure P , from a reference gas where the oxygen

pressure is P_{ref} . The voltage measured between the two electronic conductors verifies the Nernst law:

$$E = \frac{RT}{4F} \ln (P/P_{ref}) \quad (1)$$

where R , T , and F have their usual meaning. When the parameters T and P_{ref} are known, the measurement of E is also a measurement of P , given the validity of the assumptions inherent in this equation. Solid electrolytes commonly used are based on the ZrO₂-Y₂O₃ and ZrO₂-CaO solid solutions.

Electrodes are usually made of platinum, sometimes silver [25, 47] or gold [74]. The cell size is small enough for the electrode temperature to be uniform. The electrodes consist either of metal wire or sheet affixed to the electrolyte during sintering [68] or of a porous metallic layer produced by evaporation under vacuum, sputtering, by chemical or thermal decomposition of chloroplatinic acid or from a metallic 'paint'. The deposition of this layer is sometimes preceded by sand-blasting [67].

The reference atmospheres are air, pure oxygen or gaseous buffer mixtures such as CO-CO₂ or H₂-H₂O [5, 27]. Occasionally solid reference electrodes are used instead. These electrodes are monovariant systems, such as Cu-Cu₂O, Ni-NiO, Fe-FeO, Cr-Cr₂O₃ [11, 17, 18, 27, 37, 43, 79, 81]. The article by Sato [6] gives details of the wide variety of arrangements which have been proposed.

This paper gives details of experimental results relevant to the technology of such gauges and their discontinuous use. A second article [107] describes the use and properties of a differential apparatus and a third [108] will describe the coupling of an electrochemical pump to a gauge.

2. Preparation of current leads

These frequently present technological difficulties. If the connections are made by metallic wires, these must be fastened to the electrodes. Frequently the lead wires are sintered to the electrodes by a metallic paint of the same nature as the electrode or with a slurry made of powdered stabilized zirconia and metal (generally platinum) [68].

To avoid the problems which arise in using this technique, several authors [55–57] have used a conducting metallic band deposited on the electrolyte. This is usually of the same composition as the electrode and acts as an electrical connection between the electrode proper and a colder location. The errors introduced by such an electrode are not at all negligible. The explanation put forward below for the origin of these errors can be applied to other inhomogeneous electrodes, for instance, those under an oxygen-concentration gradient. Goto and Pluschkell [87] stressed the importance of this case. It was also the subject of a controversy [88, 89] concerning the most appropriate set-up for measuring the oxygen diffusion coefficient in liquid metals by means of a zirconia cell.

2.1 Errors induced by the thermoelectric e.m.f.

Fig. 1a is a schematic diagram of a gauge using a metallic coating and submitted to a temperature gradient as shown. Electrode A, element D, and the contacting electrolyte symbolized by the line ABCD, constitute a cell more conveniently

depicted in Fig. 1b. Under a temperature gradient this cell exhibits a thermoelectric e.m.f. which is short-circuited by the electric lead AD. A current therefore circulates around ABCDA and may cause an overpotential of electrode A and hence an error in the measuring of the oxygen pressure in contact with the electrode.

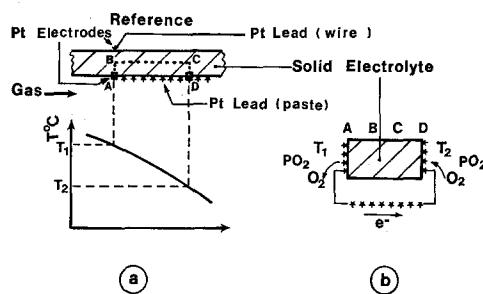
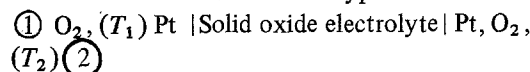


Fig. 1 Local cells formed by non-isothermal metallic coating of the electrolyte.

Non-isothermal cells of the type:



have already been studied by several authors [82–86]. Pizzini [7] has proposed their use as oxygen gauges without a reference atmosphere. Experimental results have shown that the e.m.f. of such cells can be split into two terms: a reversible e.m.f. originated in the difference of oxygen chemical potential μ_{O_2} between the two electrodes and another denoted ‘homogeneous e.m.f.’. This may be written as

$$E_1^2 = E_{\text{rev}} + E_{\text{hom}} \quad (2)$$

$$E_1^2 = \frac{1}{4F} \int_{\textcircled{1}}^{\textcircled{2}} t_0^{2-} d\mu_{\text{O}_2} + \alpha(T_2 - T_1) \quad (3)$$

t_0^{2-} is the O²⁻ ionic-transport number of the electrolyte and α a coefficient supposedly independent of temperature and oxygen pressure. With electrolytes used in oxygen gauges, t_0^{2-} is very close to 1 and the integral in Equation 3 is easily performed to yield

$$E_1^2 = \frac{1}{4F} \left[\mu_{\text{O}_2}^{\textcircled{2}} - \mu_{\text{O}_2}^{\textcircled{1}} \right] + \alpha(T_2 - T_1) \quad (4)$$

If we refer to the results of Goto [84], the value of α is close to 0.095 mV K⁻¹ for stabilized zirconia and μ_{O_2} is given by

$$\mu_{O_2} = -47.44 T - 0.00530 T^2 + 2075 + H: + RT \ln P \text{ (cal mol}^{-1}\text{)} \quad (5)$$

where $H:$ is a constant and P the oxygen pressure as before. The corresponding reversible e.m.f. is equal to

$$E_{rev} = \{-5.14 \times 10^{-4} + 5.75 \times 10^{-8} (T_1 + T_2) + 4.96 \times 10^{-5} \log_{10} P\} (T_2 - T_1) \text{ (V)} \quad (6)$$

Taking into account the two numerical values of α and E_{rev} , the thermoelectric e.m.f. at a temperature around 700°C can be calculated

$$E_1^2 = (-5.25 \times 10^{-4} + 4.96 \times 10^{-5} \log_{10} P) (T_2 - T_1) \text{ (V)} \quad (7)$$

From this equation it may be deduced that:

(a) under the usual conditions, the negative electrode of the cell depicted in Fig. 1b appears in A. Hence the short-circuit current circulates in such a direction that oxygen evolves at electrode A. This induces an error in the detection of an excessive oxygen pressure with the gauge described in Fig. 1a.

(b) the thermoelectric e.m.f. and hence the short-circuit current increases as the oxygen pressure decreases. Moreover as the electrode polarizability increases also as the oxygen pressure decreases [90], the error correspondingly increases.

2.2 Experimental verification

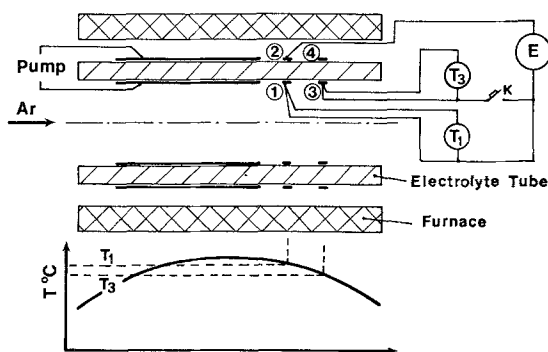


Fig. 2. Arrangement for estimating the errors induced by the thermoelectric e.m.f. along a non-isothermal metallic coating.

The phenomenon was demonstrated on the arrangement depicted in Fig. 2.

This comprised an electrochemical pump and

two gauges on the same electrolyte tube* (ID = 9 mm, OD = 12.6 mm) whose composition was $(ZrO_2)_{0.91} (Y_2O_3)_{0.09}$. The electrodes were prepared by painting †. The electrical leads were insulated platinum wires. The second gauge was composed of metallic rings ③ and ④ located at about 2 cm from the first gauge. The oxygen content of the argon circulated inside the tube was regulated by an upstream electrochemical pump. The outside of the tube was in contact with the ambient atmosphere.

Thermocouples of Pt-Pt 10% Rh measured the temperature at the surfaces of electrodes ① and ③ as 669 and 659°C respectively. Measurements were performed as follows. Under given oxygen pressure, the voltage E of the first gauge (formed by metallic rings ① and ②) was measured with a high impedance millivoltmeter ‡. This system is assumed to be free of errors because of the insulation of the electric lead. This voltage constitutes a measurement of the oxygen pressure inside the electrolyte tube. To simulate the behaviour of an electric lead formed by a metallic coating in contact with the electrolyte, electrodes ① and ③ were then short-circuited by means of K, and the voltage of the first gauge again measured, giving the error, ΔP_{O_2} , in the measurement of the oxygen pressure caused by the short-circuit.

Fig. 3 summarizes the results obtained under different oxygen pressures.

As deduced from published data, the error is an excess oxygen and is larger the smaller the oxygen pressure. In terms of potential difference, the variation of E resulting from the short-circuit is 4.4 mV at 0.2 p.p.m. of oxygen and 1 mV at 400 p.p.m. Significantly, even for an atmosphere of air, the error is not zero.

3. Electrode time-lag

Oxygen gauges are frequently used as probes in regulation systems. Numerous examples can be quoted: the adjustment of combustible mixtures [15, 26, 33, 91, 92, 93], the control of furnace atmospheres in metallurgy [29, 30, 33, 45, 46], the regulation of oxygen contents in gases by electrochemical pump-gauges which has been

* Supplied by Zircoa. † Platinum Degussa 308A.

‡ Tacussel AS70/AS

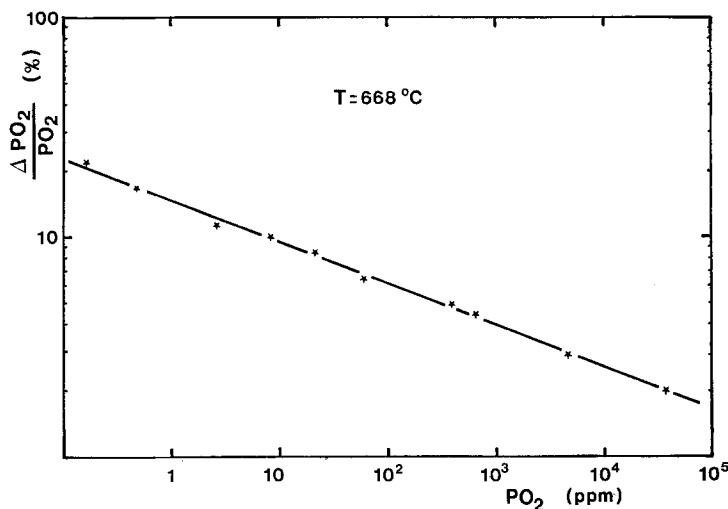


Fig. 3. Errors observed in the measurement of oxygen pressures by means of the cells depicted in Fig. 2 after short-circuiting electrodes ① and ③.

recently proposed [94]. To be able to determine the optimal conditions of regulation, the time-lags of the electrodes used in the gauges must obviously be adequate. No useful data seem to be currently available and some measurements have therefore been made using the set-up depicted in Fig. 4. This is composed simply of a regular oxygen gauge and a container of about 3 litres capacity connected by a high conductance pipe which could be rapidly obturated by a valve. The air pressure in the container was measured by a manometer and could be set in the range 10^{-2} to 1 atm.

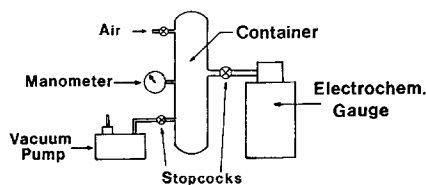


Fig. 4. Experimental set-up for measuring the electrode time-lags.

The electrolyte was in the form of a closed-end tube* (ID = 9 mm, OD = 12.6 mm) whose composition is $(\text{ZrO}_2)_{0.91} \cdot (\text{Y}_2\text{O}_3)_{0.09}$. Electrodes were

prepared by 'painting' the inner and outer surfaces of the flat bottom of the tube with platinum or silver† and the cell is rendered gas tight by O-rings between stainless-steel components.

A measurement is simply performed by introducing air under a pressure P_{initial} into the gauge, and air at a different pressure into the container. When the gauge voltage is stable, the gauge and the container are rapidly connected by opening the valve. The pressure in the gauge then reaches the pressure P_{final} . The gauge voltage variations are recorded continuously after this operation.

Table 1. Time-lag of a platinum electrode at different temperatures for two reverse variations of pressure

Pressure (Torr)		Time-lag(s) at	
P_{initial}	P_{final}	550°C	650°C
760	40	120	10
40	760	75	5

At sufficiently low temperatures the plots are characteristic of the electrode properties and not of the hydrodynamic characteristics of the system. It also appears that the time-lags are generally longer after a decrease in pressure than for an

* ZIRCOA. † DEGUSSA Platinum n.308A and Silver n. 202 N.

increase as shown in Table 1. The time-lag is defined as corresponding to a voltage variation equal to 99% of the total. Only the longer time-lags, corresponding to pressure decreases have been studied. The voltage variations measured as described, follow an exponential law:

$$\Delta E = \Delta E_0 \{1 - \exp - (t/\tau)^{\frac{1}{2}}\} \quad (8)$$

to reasonable accuracy (Fig. 5).

$$t_r = A (P_m)^{-1/2} \exp - \frac{E}{RT} \quad (10)$$

at least for small variations in pressure. Qualitatively, platinum and silver electrodes follow the same laws (Equations 8 and 10).

The numerical values for activation energies and the variation have been compared with previously published data. No obvious correlations

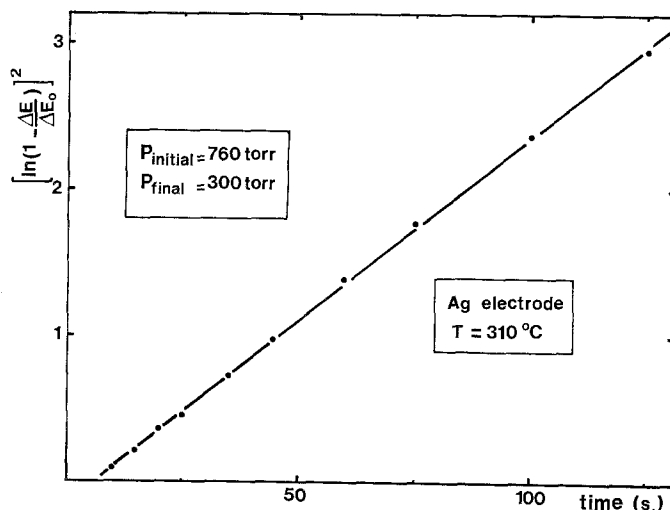


Fig. 5. Voltage variation after a rapid change in oxygen pressure.

The parameter τ follows the Arrhenius law. To determine the activation energy the time-lags t_r were measured corresponding to voltages variation equal to 99% of the total variation. They are proportional to τ and give a more straightforward idea of the electrode time-lags. Fig. 6 shows the variation in t_r as a function of temperature for silver and platinum and for a pressure variation of 760 to 300 Torr with corresponding activation energies of 0.6 and 1 eV.

We have also studied the influence of oxygen pressure on t_r by maintaining the ratio $P_{\text{initial}}/P_{\text{final}}$ constant at 1.25. The results indicate that t_r is proportional to the square-root of the average pressure P_m :

$$P_m = (P_{\text{initial}} + P_{\text{final}}/2) \quad (9)$$

Fig. 7 shows four examples of the proportionality for silver and platinum for which, the time-lag t_r (and τ) seems to follow the general law

of activation energies have been thereby revealed. In the case of silver it seems reasonable to assume that changes in equilibrium conditions of the electrode involve evolution of oxygen from the bulk of the metal. Eichenauer [95] and Ramanarayanan and Rapp [96] have demonstrated that the permeation of oxygen in silver occurs with an overall activation energy of 1 eV, a value very different from that which we obtained. It is possible that the limiting step of the investigated time-lags is the oxygen desorption from the surface of the metal. Here comparison with published data is not easy because of the large discrepancies and the lack of correspondence with our experimental conditions.

Generally, adsorption studies have been carried out at low temperatures and much lower oxygen pressures. In the cases closest to our experiments, the proposed activation energies for oxygen desorption from a silver surface are 1.8 eV [97]

and 1.4 eV [98] compared with our value of 0.6 eV.

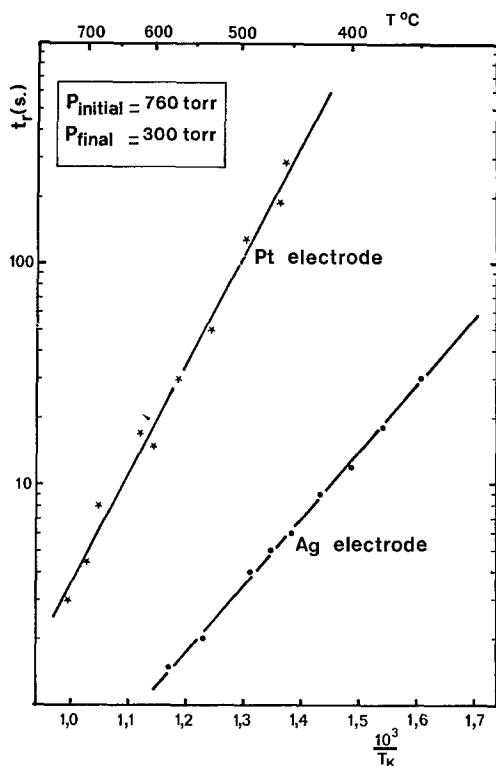


Fig. 6. Variation of the time-lags of a silver and a platinum electrode as functions of temperature.

With platinum, the results by Norton [99], Velho and Bartlett [100] clearly demonstrate that oxygen must be considered as essentially insoluble in the metal at the temperatures of our measurements whose possible contribution must be limited to its capability of absorbing oxygen. Unfortunately, here again, there are few points of comparison among published data, which were obtained under much lower oxygen pressures. The recent results of Schouler *et al.*, [101] suggest that platinum is covered by a superficial oxide layer under our conditions upon which oxygen adsorption is likely to occur.

The proportionality of t_t to $\sqrt{P_m}$ is noteworthy, such a dependence is in good agreement with results for point electrodes [102] which have shown that the oxygen exchange rate between the electrode triple contact and the surrounding atmosphere is proportional to the square-root of the oxygen pressure. These results, like our own, did not show any qualitative difference between silver and platinum electrodes although oxygen is very soluble in one and essentially insoluble in the other.

Another parameter which should be considered is the electrode microstructure. This could influence the electrode time-lag principally by slowing down gaseous diffusion to the electrode triple contact through the pores of the metal. However,

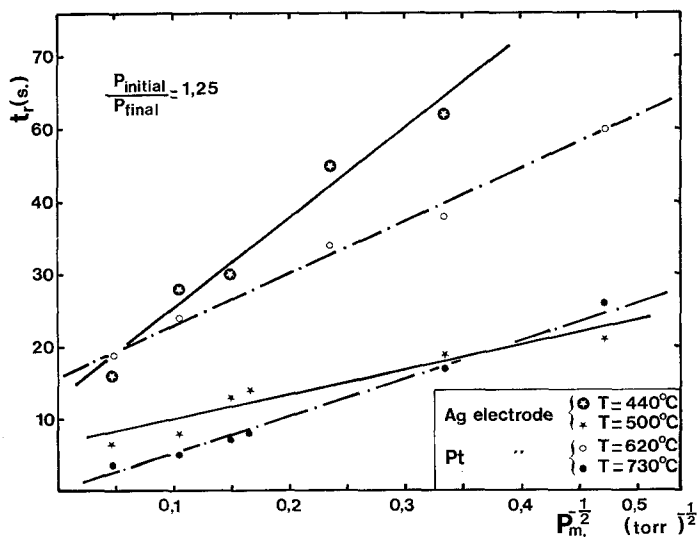


Fig. 7. Variation of the time-lags of a silver and a platinum electrode as functions of the average oxygen pressure.

the $\sqrt{P_m}$ law mentioned above seems to indicate this is not the case. The results analysed show that under low oxygen pressures, electrode time-lags may be considerable. If extrapolation is legitimate, the estimated time-lag of about 10^{-6} atm at 700°C is of the order of 2 h with platinum. Under these conditions temperature obviously plays an important part. An increase from 600 to 800°C reduces the time-lag by about 10 with platinum. The results also indicate that silver should form better electrodes. Under the previously selected conditions (10^{-6} atm, 700°C) the time-lag calculated by extrapolation is only 1 min. However the results obtained with differential gauges [107] show that silver induces errors much larger than platinum in the measurement of low oxygen pressures, and hence the advantages of the lowered time-lag with the former are principally realized only when the oxygen pressures are not low.

Two further comments must be made. The first concerns the case of gaseous-buffer mixtures. The conclusions reached above are obviously relevant only to free oxygen molecules. However if the oxygen pressure is determined, for instance, by a CO-CO₂ mixture, the electrode time-lag may be short although the oxygen pressure is very low. Overpotential measurements at electrodes surrounded by such mixtures have shown that the exchange rate of oxygen is determined by the exchange of CO and CO₂ molecules between electrode and gas and not by a straightforward exchange of oxygen molecules.

The second point which should be made is with regard to the presence of a solid-buffer system in contact with the electrodes. By virtue of its buffer properties such a system needs to exchange a large amount of oxygen to shift from an equilibrium with a given oxygen activity to another. If the oxygen exchange rate is low, as at low oxygen pressures, such a process may take an extended time. Under these circumstances the time-lags may be much longer than mentioned above. For instance with platinum electrodes prepared from 'paint'* containing mineral binders especially bismuth oxide, the time-lag is greater than a week under about 10^{-5} atm and at a temperature close to 700°C . The time-lags are so long that changes around 10^{-6} atm in oxygen pressure are no longer

revealed by the gauge on an hour scale and a rapid increase in temperature does not lead to the expected increase of the voltage but to a decrease, as is usually observed when the electrode is in contact with a solid redox system. For practical applications, it is therefore essential to avoid the presence near the electrode of impurities which change valence in the oxygen pressure range under examination.

4. Utilization of gauges for discontinuous analysis of CO-CO₂ mixtures

When an electrode of a gauge is in equilibrium with a CO-CO₂ mixture, the gauge voltage is given by the following equation:

$$E = E^0 + \frac{RT}{4F} \ln(P_{\text{CO}_2}/P_{\text{CO}}) \quad (11)$$

such that the voltage is independent of proportional variations of the pressures. The voltage should therefore not depend on the total pressure of the gas mixture or on dilution of the mixture by an inert gas (assuming ideal behaviour at the working temperatures). This property allows us to consider a discontinuous analysis of such a buffered gas mixture. Samples can be taken in containers and then carried to a gauge by an inert gas without the ratio of the pressures P_{CO_2} and P_{CO} being affected. The results obtained have confirmed this possibility. The ratio of the pressures P_{CO_2} and P_{CO} is given below as r .

4.1. Experimental set-up

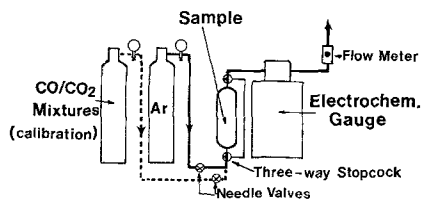


Fig. 8. Experimental gas circuit for the discontinuous analysis of CO-CO₂ mixtures.

The apparatus depicted diagrammatically in Fig. 8 consists of a regular gauge similar to the one pre-

*Degussa N. 414 for example.

viously described (Section 2) and a container for sampling a capacity of about 1 litre. A gas circuit formed by stainless steel pipes connects the gauge and the container to a cylinder containing a CO-CO₂ mixture and to another containing nominally pure argon*. The container is short-circuited by a by-pass which allows rinsing of the gauge and the gas circuit by argon.

4.2. Experimental verification

It was first verified that a discontinuous analysis and the regular continuous analysis of a CO-CO₂ mixture yield the same result. This was performed as follows. A CO-CO₂ mixture contained in a cylinder was continuously circulated through the gauge under a total pressure of 1 atm until the voltage reached a steady value named E_{sf} . The container was then filled under 1 atm by the same mixture and isolated by turning off its input and output valves. The whole gas circuit, container excepted, was rinsed with argon. When traces of the CO-CO₂ mixture were no longer detectable in the gauge, the valves were turned on in such a way that argon penetrated the container and carried along the mixture from the container to the gauge. The gauge voltage, E , was recorded throughout this step. Measurements were made as follows:

- (a) several times on the same CO-CO₂ mixtures:
- (b) with mixtures of different compositions (approximately 0.1, 1, 5 and 50% CO);

- (c) with different argon flow-rates (in the range 1–15 lh⁻¹)
- (d) at different gauge temperatures.

Fig. 9 shows an example of the recorded variation. Initially the curve was recorded on a 0–1500 mV scale; when the steady state value E_{ac} was approximately reached the voltage was measured on a 0–15 mV scale, with a corresponding shift of the zero. In this case, the sensitivity is about 0.05 mV. The results obtained indicate that:

(a) the temperature of the gauge does not play an important role in the measurement conditions which seem to be determined mostly by the hydrodynamic properties of the gas circuit and the mixture of the gases. However, the temperature must not be much lower than the Boudouard equilibrium temperature [52].

(b) the method described can be utilized with mixtures containing more than approximately 0.5% CO. With $r = 99$ a plateau is readily observed on the E/t curve. On the other hand, with mixtures containing only 0.1% CO ($r = 99$) no plateau was obtained. At high CO levels the method is likely to be useful up to $r = 0.01$ by analogy with the results obtained with low CO contents.

(c) The argon flow rate must be sufficiently small. As an example, with a mixture containing 5% CO, no plateau was observed with an argon flow rate of 12 lh⁻¹. With a 5 lh⁻¹ flow rate, a plateau was observed and the measured E_{ac} value

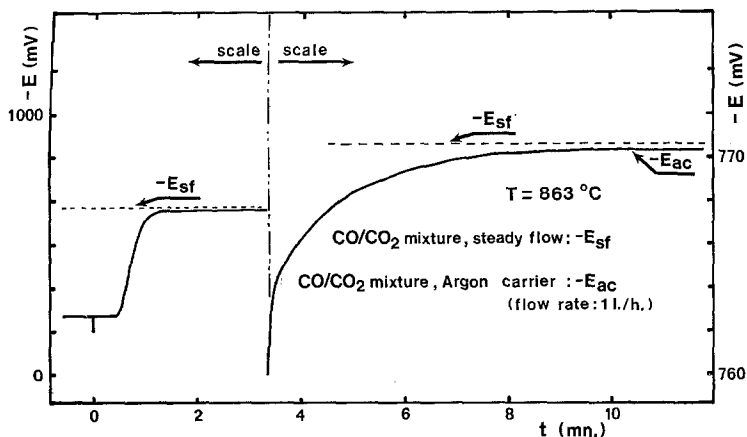


Fig. 9. Voltage variations during a discontinuous analysis of a CO-CO₂ mixture.

* Argon U, Air liquide.

Table 2. Standard potential of a gauge electrode in contact with a CO-CO₂ mixture

Authors	Year	Reference	-E ⁰ at 900° C
F. D. Richardson J. H. E. Jeffes	1949	103	0.9369
H. Peters H. H. Moebius	1958	104	0.9302
J. F. Elliot M. C. Gleiser V. Ramakrishna	1960	105	0.9339
O. Kubaschewski E. Ll. Evans C. B. Alcock	1967	106	0.9403
T. H. Etsell S. N. Flengas	1972	52	0.9363

Table 3. Calibrating a gauge. Experimental standard potential of a given gauge electrode in contact with calibrated CO-CO₂ mixtures

% CO	T (K)	-E ⁰ (V)
49.8 ± 0.2	1075	0.9843
	1127	0.9605
	1168	0.9407
	1123	0.9155
	1280	0.8888
5.06 ± 0.25	1136	0.9537
	1230	0.9107
	1089	0.9765
4.71 ± 0.15	1184	0.9351
	1225	0.9169
	1266	0.8953
	1318	0.8725
	1037	0.9987
1.02 ± 0.03	1089	0.9781
	1115	0.9642
	1183	0.9324
	1197	0.9276
	1227	0.9132
	1268	0.8932
	1277	0.8896
	1318	0.8721
0.093 ± 0.003	1226	0.9157
	1269	0.8948
	1314	0.8727

was 1 mV smaller than E_{sf} . With a 1 lh flow rate, the deviation was only 0.5 mV.

(d) Under the favourable conditions previously described, several discontinuous analyses of the same CO-CO₂ mixture yielded values of E_{ac} differing by no more than 0.5 mV. Moreover, these values were equal to the continuous measurement voltage E_{sf} to within ±0.5 mV. A scatter of 0.5 mV in the value of E corresponds to a relative inaccuracy of about 1% on r . The sensitivity and the reproducibility of the proposed discontinuous analysis allow measurement of relative variations of the ratio r to 1%.

4.3. Analysis of a CO-CO₂ mixture

The measured values E_{ac} are linked to the ratio r by the relationship shown in Equation (11). The utilization of this relation for calculating r from E_{ac} requires a knowledge of E^0 . Table 2 lists literature values of E^0 at 900°C. In the worst case, these values differ by 10 mV. Such a scatter induces an uncertainty of about 18% for the determination of an r value without taking the inaccuracy of the E^0 values into account when the reproducibility is about 1%. To remedy this we have estimated what could be the advantages of calibrating the utilized gauge. Voltages, E_{sf} , were measured with different calibrated CO-CO₂ mixtures* and at different temperatures. The values of E^0 obtained are shown in Table 3. The calculation of the straight line $E^0 = f(T)$ from these values by the least-squares method yields:

$$E^0 = 1.4769 + 4.592 \cdot 10^{-4} T_k \text{ (V)} \quad (12)$$

with a standard deviation

$$\sigma = 1.2 \times 10^{-3} \text{ V.} \quad (13)$$

By such calibration the inaccuracy in r by the proposed discontinuous method is smaller than 4%.

Acknowledgement

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* Air Liquide.

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