

# Oxygen partial pressures; control, variation, and measurement in quench furnaces at one atmosphere total pressure

GORDON M. BIGGAR

Grant Institute of Geology, University of Edinburgh, West Mains Road, Edinburgh EH9 3JW

**SUMMARY.** Oxygen partial pressures in atmospheric-pressure quench furnaces were found to vary by as much as 0.5 in  $\log f_{O_2}$ , when changes were made in gas flow rate and direction suggesting that careful analysis of the gas mixture supplied to a furnace is *not* a guarantee of the oxygen pressure that a sample in the furnace will attain. The use of magnesiowüstite compositions, with variable oxygen contents, as indicators of oxygen pressure is described.

**INSTRUMENTAL** means of measurement of temperature and oxygen potential within a laboratory furnace often require the insertion of sensing devices such as thermocouples or oxygen cells. These suffer from the disadvantage that their presence may alter the distribution of the factors that they seek to measure. Sensors record values of temperature or  $f_{O_2}$  at their extremities. Experimental samples are usually slightly distant from the sensor. For accurate work a temperature calibration is made with reference to a standard. Calibration of  $f_{O_2}$  is generally neglected because it is assumed that a gas stream attains and maintains the thermodynamically calculated  $f_{O_2}$  at the sample temperature. A calibration of a gas flow meter is irrelevant to inter-laboratory systematic errors in  $f_{O_2}$ , due to furnace design, due to the design of sample containers, or due to arithmetical slips in the thermodynamic calculation.

In the present study changes in  $f_{O_2}$  were studied as a function of several changes in furnace design and operation. These led to the conclusion that systematic errors as large as 0.5 in  $\log f_{O_2}$  may be present in this and, by implication, in previous work. Changes in  $f_{O_2}$  were detected by examining quenched samples of magnesiowüstite that had been equilibrated in the furnace. Magnesiowüstite is a cation-deficient non-stoichiometric cubic oxide,  $(Mg_pFe_{1-p})_yO$  with  $p \leq 1$  and  $y \leq 1$ , the composition of which is sensitive to small changes in  $f_{O_2}$ . An increase in  $f_{O_2}$  oxidizes  $Fe^{2+}$  to  $Fe^{3+}$  resulting in a decrease in unit-cell size. This oxidation may be written as  $\langle 4FeO \rangle + O_2 \rightleftharpoons \langle 2Fe_2O_3 \rangle$ , in which the solids  $FeO$  and  $Fe_2O_3$  are in solution in  $(Mg_pFe_{1-p})_yO$ .  $\Delta G$  for this reaction is dependent on the magnesiowüstite composition but in practice the value is quite close to 75 000 cal. at 1065 °C. Since  $\Delta G = -RT \ln(f_{O_2})$  an error of 5.6 °C in  $T$ , the sample temperature, or of 0.12 in  $\log f_{O_2}$  will result in an error of 1 % (750 cal) in  $\Delta G$ . Furthermore for mixtures of  $H_2/CO_2$  a change of 7.5 °C in the gas temperature results in a change of 0.12 in  $\log f_{O_2}$ .

As oxygen pressure increases magnesiowüstite will fail as an indicator because it

disproportionates during quenching, and the practical limits are shown in fig. 4. Such products give diffuse X-ray diffraction peaks of magnesiowüstite and of magnesioferrite.

*The experimental equipment.* The furnaces, sample holder, and thermocouple calibration have been described (Biggar and O'Hara, 1969a). The original cemented assembly of twelve capsules has now been replaced by a platinum can, which holds twelve capsules of platinum, molybdenum, or other material. For the experiments shown in fig. 2D the modified sample holder was a small can suspended on a thin wire to avoid having a large bulk of ceramic sheathing in the furnace. The small bulk of this assembly closely approaches that employed by previous workers (Darken and Gurry, 1945; Taylor, 1964; Katsura and Kimura, 1965).

The apparatus used for mixing gases is described in fig. 1 and its legend. All flow rates are quoted as linear flow rates or velocities of gas at room temperature in the furnace tube. At working temperatures the gas will be flowing four or five times faster. When mixtures of  $\text{CO}_2$  and  $\text{H}_2$  were used some of the water produced condensed on the water cooler at the entrance to the furnace and this would contribute water vapour to the furnace atmospheres but its effect on  $f_{\text{O}_2}$  is very small (Biggar, 1969). Purification of gases was not undertaken since even if oxygen were an impurity in parts per thousand it is 'neutralized' by the buffering action of the  $\text{H}_2$  and  $\text{CO}_2$ .

Starting materials were made by a gel technique (Biggar and O'Hara, 1969b). Irregular pellets were used to ensure only point contacts with the platinum containers. Loss of iron from the bulk of the pellets was considered negligible. Negligible iron loss has been proved when pellets are suspended by thin platinum wires (Taylor, 1964; Katsura and Kimura, 1965). After equilibration under reducing conditions the pellets were quenched into water, removed quickly, and dried at  $100^\circ\text{C}$ . Values of  $d_{220}$  were determined using  $\text{Cr-K}\alpha$  radiation with silicon ( $d_{311} = 1.6374 \text{ \AA}$ ) as internal standard. Magnesiowüstites with  $d_{220}$  values that differed by  $0.0004 \text{ \AA}$  were considered distinguishable.

The starting materials were initially in an oxidized state. Samples held for 2 hours and for 5 hours under reducing conditions gave magnesiowüstite with the same value of  $d_{220}$  but when held for 20 hours  $d_{220}$  consistently decreased by  $0.0004 \text{ \AA}$ , which is just at the limit of resolution. A test sample taken to a lower  $f_{\text{O}_2}$  for 2 hours and then allowed to approach the final  $f_{\text{O}_2}$  from this reduced state gave, after 20 hours, the same value of  $d_{220}$  for magnesiowüstite as had been obtained by approach from oxidizing conditions.

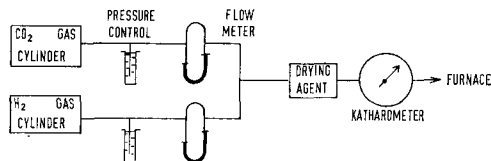


FIG. 1. The gas-mixing apparatus used was considerably modified from that described by Ulmer (1971). Gas pressure was controlled by dip tubes in water, and flow rate was known ( $\pm 10$  cc per min) from approximately calibrated capillary flow meters. The gas mixture was monitored by a katharometer, which was periodically checked by volumetric analyses with an Orsat's apparatus. Final calibration of the furnace conditions was based on oxygen-sensitive reactions in the furnace.

*Experimental results.* It was assumed that, for a given furnace, probe design, and sample holder, the  $f_{O_2}$  actually realized at the sample will depend on the temperature of the sample, the initial gas composition and the flow rate of the gas, and the temperature of the gas, particularly if this was different from the sample temperature. Some of these variables are interdependent but as far as possible each was checked whilst keeping the others constant. Then the design of the sample holder was modified to a thin wire and the effect of flow rate reinvestigated.

The temperature of the sample was checked by placing next to it in a similar capsule a piece of gold wire, and by small ( $\pm 2^\circ\text{C}$ ) adjustments to the controller an attempt was made to get solid gold or melted gold in alternate experiments. The results are presented in figs. 2A–E and from these and a few other experiments the following features were noted.

Two ostensibly identical furnaces gave different results (figs. 2C, 2E). A change in sample position of  $\pm 1$  cm had no effect (not shown in figures). Slow flow rates gave more oxidizing conditions (smaller values of  $d_{220}$ ). Downflow of gas gave slightly more oxidizing conditions than upflow (figs. 2C, 2E). The modified sample holder gave smaller changes of  $d_{220}$  for a given change of flow rate (figs. 2C, 2D). At a flow rate of  $\frac{1}{3}$  cm per sec both assemblies and both flow directions gave the same magnesiowüstite. At this low flow rate thermal diffusion probably controlled the  $f_{O_2}$  attained (Darken and Gurry, 1945).

*Discussion.* Between furnaces and between extremes of slow and fast flow (fig. 2C) there is a variation of  $0.0040 \text{ \AA}$  in  $d_{220}$ , which by interpretation from fig. 2B suggests a variation of 0.5 in  $\log f_{O_2}$ . This does not conform to the constancy of results for flow rates between 0.5 and 1.7 cm per sec claimed by Darken and Gurry (1945) for an experiment at  $1600^\circ\text{C}$ , on the basis of which the majority of subsequent experiments have used an upflow at a rate of 1 cm per sec, except, perhaps significantly, Katsura and Kimura (1965), who used 0.25 cm per sec *in order to get in their furnaces agreement with the data of Darken and Gurry.*

In our furnaces there seems no good reason to choose one set of conditions rather than another. When upflow at 1 cm per sec is used and the assumption made that gas and sample temperatures are equal at  $1065^\circ\text{C}$  the value of  $\Delta G$  found for  $2\text{Fe} + \text{O}_2 = 2\text{FeO}$  is in the range  $-83\,570$  cal. to  $-84\,180$  cal. (slight variations between furnaces), which is at the high end of the range of values from the literature,  $-84\,100$  to  $-84\,800$  cals.

Differences in  $f_{O_2}$  as a function of flow rate are usually ascribed to thermal diffusion. There is also the possibility that gas and sample temperatures are different. A difference of about  $30^\circ\text{C}$  is required to account for the maximum differences of  $f_{O_2}$  observed in fig. 2. There is no easy way of distinguishing the effects of thermal diffusion from the effects of variation in gas temperature and both probably contribute to the observed variation. Our particular furnace design (the winding is a coiled coil with few turns in the centre) may be more sensitive to changes in flow rate than the simple spirally wound furnaces usually employed.

So that the conditions of our experiments can be accurately known, and if necessary repeated in the future, each furnace is calibrated for  $f_{O_2}$  and temperature using the

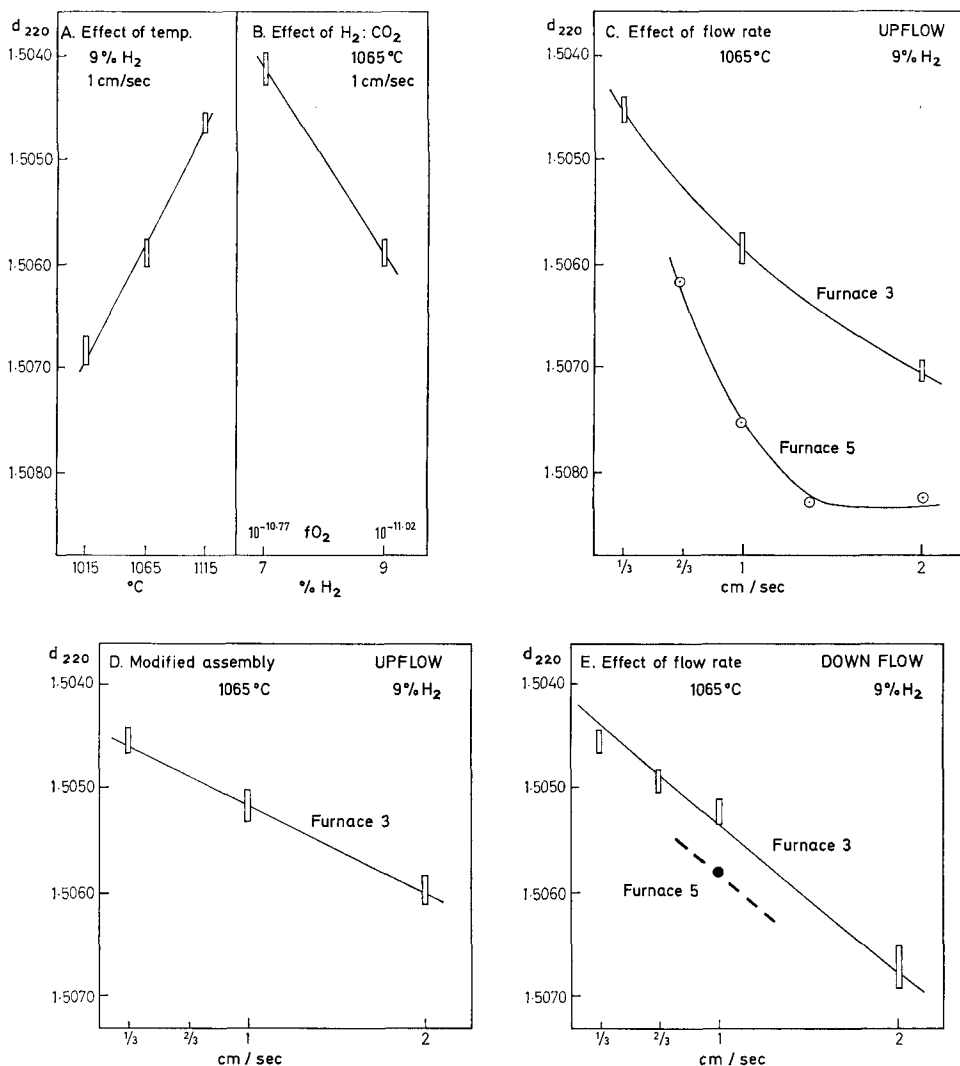


Fig. 2. Results using  $H_2$  and  $CO_2$  mixtures. Experimental values of  $d_{220}$  for  $(Mg_{0.4}Fe_{0.6})_yO$  for various changes in experimental conditions with gas upflow except in fig. E. In fig. B the values of  $f_{O_2}$  are calculated assuming the gas temperature was  $1065^\circ C$ . Fig. D presents results for experiments in which a thin wire was used to suspend the samples.

same assembly and same flow rate as is used for equilibrium experiments. As far as possible equilibrium experiments are made at an  $f_{O_2}$  fixed by a calibrant (usually a 'buffer' or univariant reaction as described below). No value is attached to analyses of the gas stream supplied to the furnace.

*A proposal for  $f_{O_2}$  calibrations*

It will be surprising if interlaboratory discrepancies as large as 0.5 in  $\log f_{O_2}$  are not found. Precise research requires that the  $f_{O_2}$  of a particular furnace design is investigated and some form of calibration undertaken other than analyses of the gas supplied.

Practical temperature scales are defined by fixed points at constant pressure. A practical  $f_{O_2}$  scale could be likewise defined ideally using invariant points such as tridymite-fayalite-magnetite-liquid, but more conveniently by a univariant reaction combined

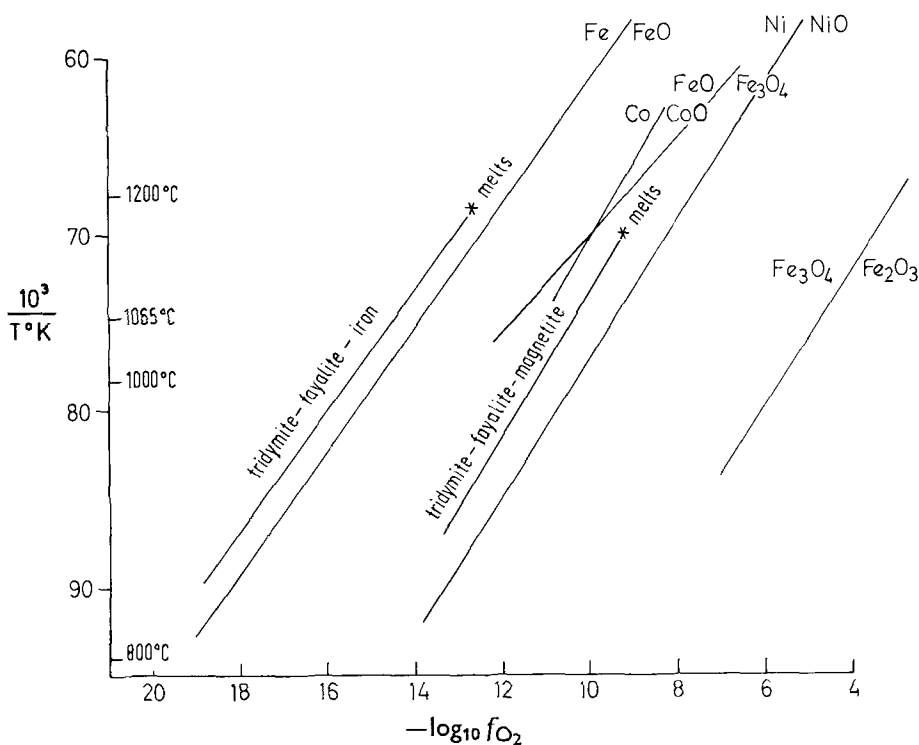


FIG. 3. Some possible  $f_{O_2}$  calibrants. Equations for many of these appear in Ulmer (1971).

with a precise temperature measurement, for example tridymite-fayalite-magnetite at the melting-point of gold. Intermediate points can be interpolated by using an oxygen-sensitive cell or by using an oxygen-sensitive material such as magnesiowüstite. There are countless possible univariant systems and a conveniently spaced selection is shown in fig. 3. Most of the compositions are commercially available or are easily made by mixing  $Fe_2O_3$  and  $MgO$ , which is as easy to do as it is to prepare diopside as a temperature calibrant. Most of the univariant curves are parallel but the wüstite-magnetite curve is of different slope because of the increased solubility of ferric iron in wüstite at higher temperatures. There results an interesting crossover of the wüstite-magnetite and Co-CoO equilibria such that at 1065 °C cobalt metal and magnetite are stable,

in the same atmosphere, in the  $\log f_{O_2}$  range  $-11.1$  to  $11.45$ , and CoO and wüstite are stable, in the same atmosphere, in the  $\log f_{O_2}$  range  $-9.1$  to  $-9.4$  at  $1200^\circ\text{C}$ . These rather limited  $f_{O_2}$  ranges were aimed for and encountered in the following preliminary results, which use various magnesiowüstite compositions as  $f_{O_2}$  indicators (fig. 4). Fig. 4 illustrates the range of usefulness of some of the magnesiowüstites studied.

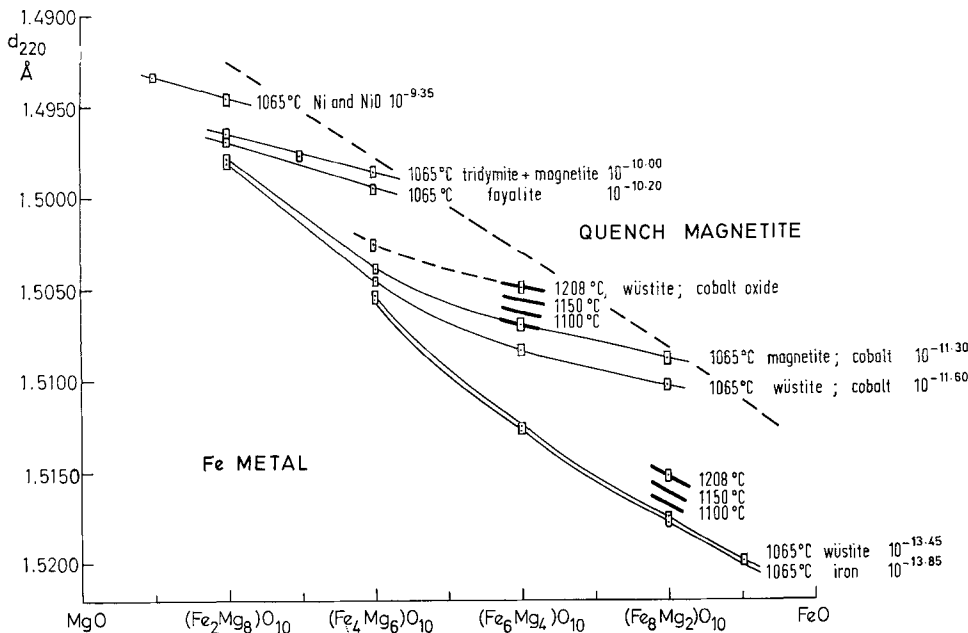


FIG. 4. Experimental relationship between  $f_{O_2}$  calibrants and values of  $d_{220}$  of various magnesiowüstite compositions at  $1065^\circ\text{C}$  (and a few results at  $1208^\circ\text{C}$ ). In a typical experiment four or five magnesiowüstite compositions were held side by side with a calibrant (such as tridymite–fayalite–magnetite) such that in one run fayalite was obtained and in the next tridymite and magnetite. The  $f_{O_2}$  interval between these preliminary bracketing runs could well be decreased. The values of  $f_{O_2}$  shown are for guidance since they have been calculated from the composition of the gases supplied. Values of  $d_{220}$  change with temperature as shown by contours interpolated between results at  $1065^\circ\text{C}$  and  $1208^\circ\text{C}$  at the Co–CoO and at the Fe– $\text{Fe}_y\text{O}$  calibrations.

A magnesiowüstite such as  $(\text{Fe}_{0.2}\text{Mg}_{0.8})_y\text{O}$  is acceptably sensitive to changes in  $f_{O_2}$  in the range between the Ni–NiO and tridymite–fayalite–magnetite calibrants:  $(\text{Fe}_{0.4}\text{Mg}_{0.6})_y\text{O}$  is acceptable between the tridymite–fayalite–magnetite and Co–CoO calibrants; and either  $(\text{Fe}_{0.6}\text{Mg}_{0.4})_y\text{O}$  or  $(\text{Fe}_{0.8}\text{Mg}_{0.2})_y\text{O}$  between the Co–CoO and Fe– $\text{Fe}_y\text{O}$  calibrants.

The use of magnesiowüstite as an indicator has the advantage that a  $0.1\text{ g}$  pellet is sufficient for X-ray work and its presence next to or between samples is unlikely to distort the oxygen pressure profile in a furnace. The oxygen pressure is fairly accurately described by the value of  $d_{220}$  of an appropriate magnesiowüstite and more importantly can be compared for relative  $f_{O_2}$  with results from other furnaces and from other laboratories.

## REFERENCES

- BIGGAR (G. M.), 1969. *Progress in Experimental Petrology, First Report*, 105-8.  
— and O'HARA (M. J.), 1969a. *Min. Mag.* **37**, 1-15.  
— — 1969b. *Ibid.* 198-205.  
DARKEN (L. S.) and GURRY (R. W.), 1945. *Journ. Amer. Chem. Soc.* **67**, 1398-1412.  
KATSURA (T.) and KIMURA (S.), 1965. *Bull. Chem. Soc. Japan*, **38**, 1664-70.  
TAYLOR (R. W.), 1964. *Amer. Min.* **49**, 1016-30.  
ULMER (G. C.), Editor, 1971. *Research techniques for high pressure and high temperature*. New York (Springer-Verlag).

[Manuscript received 29 March 1973]