

SEALED GAS RECOMBINING LEAD-ACID BATTERIES PART I. A SIMPLE THEORETICAL APPROACH

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Summary

The solution of the differential equations expressing the gas material balance in a sealed lead-acid cell led us to propose a simple experimental method to evaluate the parameters controlling the cell behaviour both in dynamic and in steady state conditions.

Introduction

The gas recombining cell is not based on a recent idea: the principle, known since 1912, has been applied to the Ni-Cd system since 1938. In respect of lead-acid batteries, however, the applications are recent and have become more important during the past few years owing to their extensive utilization as power sources for electronic equipment, for telecommunication, and recently for automotive engine starting [1 - 3]. The methods of removing the oxygen and the hydrogen generated during the period of charge or storage of the batteries have been well defined. Ruetschi [4] described the oxygen and the hydrogen cycles and, taking into account conventional systems, he suggested the use of auxiliary electrodes to obtain a sufficiently high gas reaction rate. Mahato [5] studied the change of internal pressure in Pb-acid cells to determine the conditions under which the battery plates exhibit a good gas recombination efficiency. Recently, Thompson and Warrell [6], by means of the rotating disc electrode (RDE) technique, studied the kinetics of the electrochemical reaction of oxygen on lead, applying the results to aircraft batteries.

In their configuration gas recombining cells differ from conventional ones in that the separator is one which retains the electrolyte. The internal voids of the separator are only partially filled by the electrolyte, allowing the oxygen and hydrogen to diffuse both towards, and from, the plates. Some cells use gelled electrolyte, which also allows gas diffusion when suitable paths form in the mass of the gel. Generally, the sealed cells are considered to operate on the oxygen cycle basis.

The performance of sealed commercial batteries has been reported recently [1 - 3, 7 - 9] together with methods of evaluating the gas recombination efficiency [7, 8, 10, 11]. Some of these methods [7, 8] are based on the determination of the ratio between the theoretical water loss and that measured by weighing the cells. A review of the state-of-the-art of O₂ recombination technology has been presented recently [12].

Data derived from the analysis of the behaviour of a large number of batteries during their service life, have shown that these systems should not be hermetically sealed or placed in a closed environment [3], even if used as recommended by the manufacturer.

A constant emission of gas, particularly hydrogen [9, 11], has frequently been observed in systems working for long periods. This is evidenced by the fact that slow changes in the characteristics are different from those projected. In overcharge or during storage these systems have, in fact, sometimes vented, despite being supposedly sealed and recombining.

The aim of this work is to analyse the gas material balance and to define the parameters allowing different batteries, both in dynamic and in steady state conditions, to be compared. Such parameters would be very useful in evaluating batteries from various manufacturers, or studying the effect of additives, etc. In this first part of the work a simple theoretical approach to the problem is discussed; in the second part some experimental results will be reported.

Reaction kinetics

Oxygen reduction at the negative plate and hydrogen oxidation at the positive plate are coupled with lead oxidation and lead dioxide reduction to form lead sulphate and water, respectively. All reactions proceed by means of an electrochemical mechanism. The overall process includes various steps: the diffusion of the reagents and of the reaction products, respectively, into the gaseous and the liquid phases, the gas dissolution and diffusion into the electrolyte, and the charge transfer reactions.

It seems reasonable to suppose that gas diffusion in the liquid phase controls the overall process so that the reaction rate can be a simple function of the gas pressure. In practice, the potential values of the plates are either much higher, for H₂ oxidation, or much lower, for O₂ reduction, than the reversible values for the couples H₂/H⁺ and O₂/OH⁻. The rates of the electrochemical reactions therefore correspond to their limiting current values, proportional to the reagent concentrations in the liquid phase, *i.e.*, to the gas pressure.

For oxygen reduction this hypothesis is confirmed by numerous observations [13 - 16] according to which the reduction current is independent of the potential. The reaction rate is also diffusion controlled if the electrolyte layer wetting the active material becomes very thin, as in the case of the meniscus area of plates partially submerged [13]. To simplify the expression describing the system behaviour we suppose that:

- (a) the cell has a constant volume
- (b) the partial pressure of the non-reactive gas is constant
- (c) the gases are ideal
- (d) the spontaneous oxygen evolution on lead dioxide is negligible.

As for grid corrosion, a corrosion current ranging between 5 and 10 μA per A h of plate capacity is forecast at 300 K [17].

Material balance

The number of gas moles in the cell depends on the rates of gas production and consumption. The former, expressed as current intensity, is equal to the difference between the current, I , flowing through the cell and that needed to maintain the plates in a stable condition of charge. The latter depends on the gas pressure.

Let:

I_1 represent the hydrogen evolution current as a consequence of spontaneous lead sulphation,

I_c the grid corrosion current,

N_H and N_O , the number of H_2 and O_2 moles present at time t in the free volume V of a cell,

\bar{N}_H and \bar{N}_O the corresponding moles at time zero,

K_H and K_O the rate constants for the H_2 and the O_2 reactions.

Applying the ideal gas law the molar fraction of:

H_2 is $Y_H = N_H RT/PV$

and of O_2 is $Y_O = N_O RT/PV$,

where T is the temperature of the cell and P the internal pressure.

As a consequence of the gas reactions the plates are discharged at a rate, expressed as current, equal to:

$2FK_H N_H$ for the positives

$4FK_O N_O + I_1$ for the negatives.

Three cases must be considered depending on the values of I and of the differences $D_H = (I - 4FK_O \bar{N}_O - I_1)$ and $D_O = (I - 2FK_H \bar{N}_H - I_c)$:

“High-Current” — when both D_H and D_O are greater than zero; “Open-Circuit” — when the external current I is zero; “Low-Current” — when D_H or D_O have negative values which, having no physical meaning, must be set to zero. The transition between the “High-” and the “Low-current” cases corresponds approximately to the so-called “critical floating voltage” of Berndt [10].

In subsequent calculations we define:

$f = \exp(-Kt)$ where $K = K_H + K_O$

$f_O = \exp(-K_O t)$

$f_H = \exp(-K_H t)$

(a) High-current conditions

In this case, corresponding to overcharge, the corrosion current, I_c , can be neglected, and the current relative to H_2 and O_2 evolution: I_H and I_O , respectively, Fig. 1 has the values:

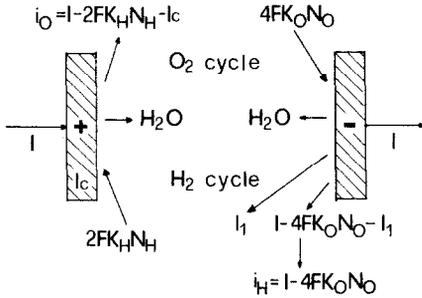


Fig. 1. Scheme of the gas material balance in a sealed lead-acid cell expressed in terms of the current.

$$I_H = I - 4FK_O N_O \quad \text{for H}_2 \quad (1a)$$

$$I_O = I - 2FK_H N_H \quad \text{for O}_2 \quad (1b)$$

and the material balance equations for the gases in the cell are:

$$dN_H/dt = I_H/2F - K_H N_H \quad (2a)$$

$$dN_O/dt = I_O/4F - K_O N_O \quad (2b)$$

Thus, eliminating I_H and I_O we get:

$$dN_H/dt = I/2F - 2K_O N_O - K_H N_H \quad (3a)$$

$$dN_O/dt = I/4F - K_O N_O - K_H N_H/2 \quad (3b)$$

These simultaneous differential equations can be solved by calculating the second order derivatives and considering, from eqns. (3a) and (3b), that, at constant current, $2dN_O/dt$ is equal to dN_H/dt . The resulting second order equation, taking into account the boundary conditions expressed above gives:

$$N_H = \bar{N}_H + (I/2F - 2K_O \bar{N}_O - K_H \bar{N}_H) * (1 - f)/K \quad (4a)$$

$$N_O = \bar{N}_O + (I/4F - K_O \bar{N}_O - K_H \bar{N}_H/2) * (1 - f)/K \quad (4b)$$

Setting the internal pressure of the cells at time 0 and t as \bar{P} and P , respectively, it follows that:

$$P = \bar{P} + (3I/4F - 3K_O \bar{N}_O - 3K_H \bar{N}_H/2) * (1 - f) * RT/KV \quad (5)$$

and

$$d \ln(|dP/dt|)/dt = K \quad (6)$$

This last expression can be used to calculate K from $P(t)$ curves. Expressions (4) and (5), calculated for $t = \infty$ give the stationary conditions reached by the system in overcharge. In addition, at time $t = 0$, the gas pressure increase is given by:

$$(dP/dt)_{t=0} = (3I/4F - 3K_O \bar{N}_O - 3K_H \bar{N}_H/2) * RT/V \quad (7)$$

which can be used to evaluate K_H or K_O :

(b) Open-circuit conditions

In this case hydrogen evolves at a rate corresponding to a current I_1 , due to the lead reaction with sulphuric acid. Writing again the material balance of the gases it follows that:

$$N_H = N_H f_H + I_1(1 - f_H)/2FK_H \quad (8a)$$

$$N_O = N_O f_O \quad (8b)$$

Thus we obtain:

$$P = (\bar{N}_H f_H + \bar{N}_O f_O + I_1(1 - f_H)/2FK_H) * RT/V$$

and

$$d \ln(|dP/dt|)/dt = f(t) \quad (9)$$

The function $f(t)$ becomes equal to the constant K_H if, at $t = 0$ $\bar{N}_O = 0$, and equal to the constant K_O if, at $t = 0$ $\bar{N}_H = 0$ and I_1 is negligible. This expression can be used to determine the values of K_H and K_O by analysing the gas pressure decay in cells maintained sealed at open circuit and filled, respectively, with hydrogen or with oxygen. Expression (9) can also be used to evaluate the approximate value of current I_1 .

(c) Low current conditions

If the current is too low for overcharge to occur the differences $(I - 4FK_O \bar{N}_O + I_1)$ and $(I - 2FK_H \bar{N}_H - I_c)$ can become zero or negative; in this case the plates discharge and the differential equations must be rewritten setting I_H equal to I_1 or I_O equal to zero.

It is easy to show that if $I_H = I_1$ the solutions are:

$$N_H = \bar{N}_H f_H + I_1(1 - f_H t)/2FK_H \quad (10a)$$

$$N_O = \bar{N}_O f_O + (I - I_1) * (1 - f_O)/4FK_O + (2K_H \bar{N}_H - I_1/F) * (f_O - f_H)/4(K_O - K_H) \quad (10b)$$

or if $i_O = 0$, they are

$$N_O = \bar{N}_O f_O \quad (11a)$$

$$N_H = \bar{N}_H f_H + I(1 - f_H)/2FK_H + 2K_O \bar{N}_O (f_H - f_O)/(K_O - K_H) \quad (11b)$$

Stable conditions are reached after a continuous discharge and decreased N_H and N_O until, if $I_H = I_1$:

$$N_H = I_1/2FK_H$$

$$N_O = (I - I_1 - I_c)/4FK_O$$

or if $I_O = 0$:

$$N_H = I/2FK_H$$

$$N_O = 0$$

If I_H and I_O are zero, N_H and N_O decrease until both $4FK_O N_O + I_1$ and $2FK_H N_H + I_c$ become equal to the current intensity, I . At this point the plates recharge and the system tends to a steady state depending on the boundary conditions, the geometry of the cells, and the capacity of the plates.

Results

The theoretical behaviour of a lead-acid cell has been evaluated, using the above expressions, for suitable values of K_H and K_O and at various boundary conditions. The results obtained are reported in Figs. 2 - 8 where Y_H and Y_O are molar fractions of H_2 and of O_2 , respectively.

The effects of the parameter K_O and of the spontaneous hydrogen evolution current, I_1 , are illustrated in Figs. 2 and 3 where theoretical decay curves of the oxygen pressure in a Pb-acid cell, Fig. 2, and in a glass vessel containing a group of negative plates wetted with sulphuric acid, Fig. 3, are shown.

Figure 4 shows the internal pressure of a cell initially filled with oxygen at 100 kPa *versus* time, for various currents. It is apparent that there is a value of current at which the internal pressure is constant with time. According to eqn. (7) this value is given by:

$$I = 4FK_O \bar{N}_O + 2FK_H \bar{N}_H \quad (12)$$

At this current the gases evolve without internal pressure increase. In Fig. 5 the hydrogen molar fractions corresponding to the conditions of

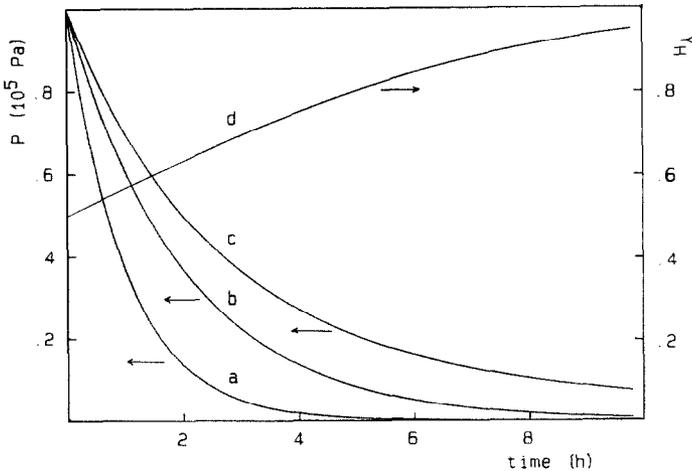


Fig. 2. Gas pressure *vs.* time (curves a, b, c) and H_2 molar fraction (curve d) in a Pb-acid cell, calculated for $V = 500$ ml, $T = 300$ K, $K_H = 0.25$ h^{-1} . a: $I_1 = 0$ mA, starting $Y_O = 1$, $K_O = 1$ h^{-1} ; b: $I_1 = 0$ mA, starting $Y_O = 1$, $K_O = 0.5$ h^{-1} ; c, d: $I_1 = 8$ mA, initial $Y_O = 0.5$, $K_O = 0.5$ h^{-1} .

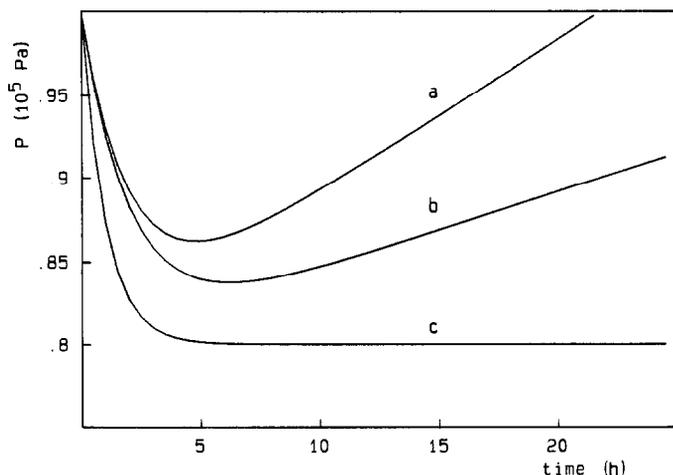


Fig. 3. Gas pressure vs. time in a vessel containing negative plates, calculated for $V = 500$ ml, $T = 300$ K, $K_H = 0.25$ h $^{-1}$ and starting $Y_O = 0.2$. a: $I_1 = 10$ mA, $K_O = 0.5$ h $^{-1}$; b: $I_1 = 5$ mA, $K_O = 0.5$ h $^{-1}$; c: $I_1 = 0$ mA, $K_O = 1$ h $^{-1}$.

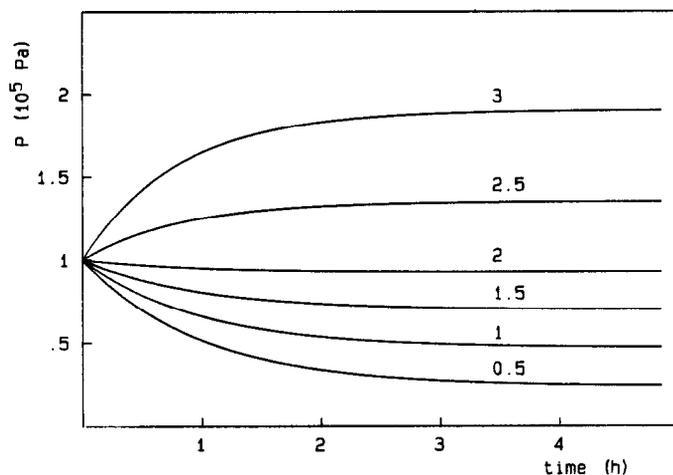


Fig. 4. Influence of the current I (in A) on the cell pressure vs. time curves. $V = 500$ ml, $T = 300$ K, $K_H = 0.25$ h $^{-1}$, $K_O = 1$ h $^{-1}$, $I_1 = 5$ mA, starting $Y_O = 1$. Dynamic conditions.

Fig. 4 are reported; the data show the influence of the external current intensity. As the value of I is lowered, the hydrogen molar fraction decreases in the "High-current" case (on the left) while it increases in the "Low-current" case (on the right).

The remaining Figures refer to a cell under static conditions, initially filled with O_2 , Fig. 6, or with H_2 , Fig. 7. The values of the hydrogen molar fraction demonstrate the transition from the "High-current" to the "Low-current" case. As the external current intensity is increased the hydrogen molar fraction tends to $2/3$. By contrast, if the cell is initially filled with

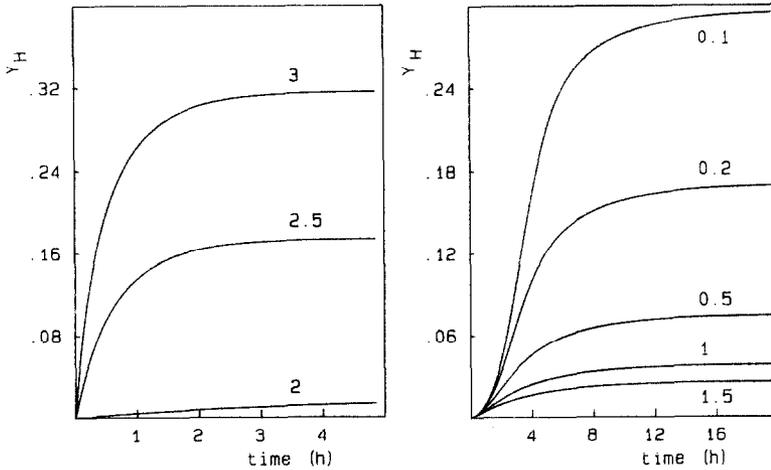


Fig. 5. Gas composition vs. time in a Pb-acid cell, calculated for $V = 500$ ml, $T = 300$ K, $K_H = 0.25$ h⁻¹, $K_O = 1$ h⁻¹, $I_1 = 5$ mA and various I values (in A). Dynamic conditions.

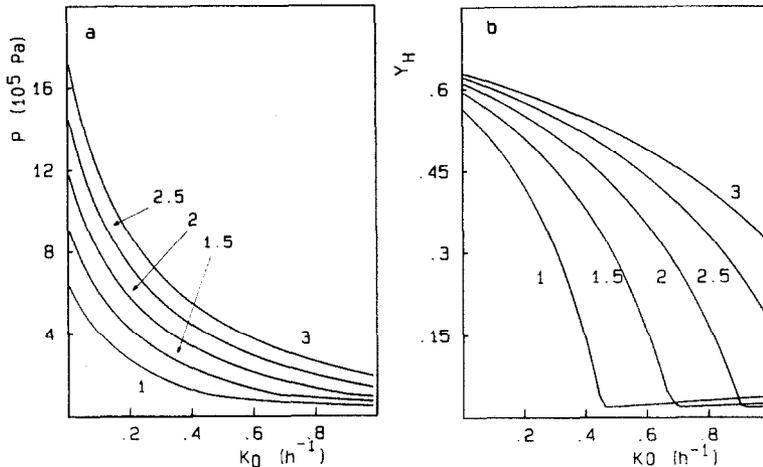


Fig. 6. Gas pressure (a) and composition (b) vs. K_O in a Pb-acid cell. Starting conditions: $Y_O = 1$ and $P = 100$ kPa. Data calculated for $V = 500$ ml, $T = 300$ K, $K_H = 0.25$ h⁻¹, $I_1 = 5$ mA and various I values (in A). Steady state conditions.

hydrogen (Fig. 7), its molar fraction remains close to 1 if K_O is high and the current value is low.

From the fact that K_O is greater than K_H [5, 6] it follows that a battery, originally containing air and left at rest after overcharge, can become filled with hydrogen.

The calculations given in Fig. 8 show that, as a consequence of successive openings of the pressure relief valve during overcharge, all the nitrogen is eliminated from inside the battery and the hydrogen molar fraction becomes equal to $2/3$. At rest oxygen is rapidly consumed so that Y_H quickly acquires values greater than 0.95.

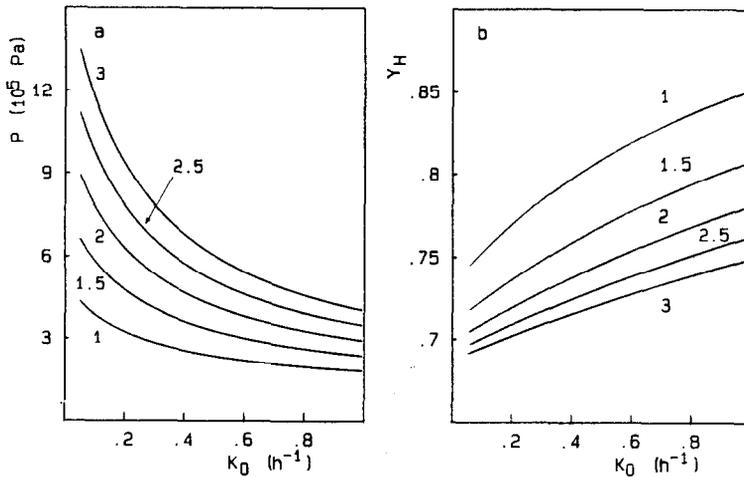


Fig. 7. Gas pressure (a) and composition (b) vs. K_O in a Pb-acid cell. Starting conditions: $Y_H = 1$ and $P = 100$ kPa. Data calculated for $V = 500$ ml, $T = 300$ K, $K_H = 0.25$ h^{-1} , $I_1 = 5$ mA and various I values (in A). Steady state conditions.

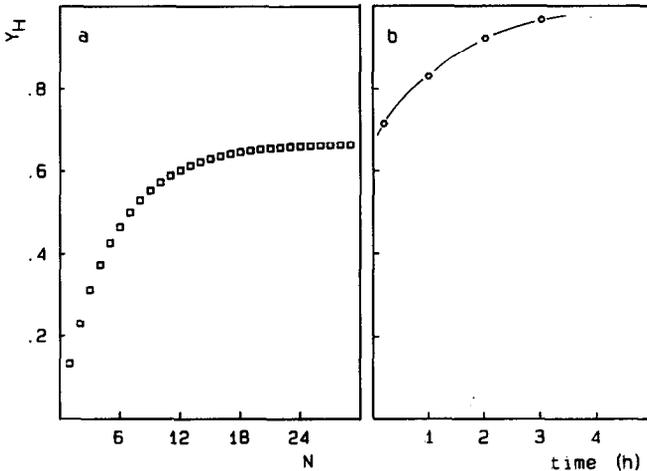


Fig. 8. Hydrogen molar fraction Y_H in a cell of a battery. (a) In overcharging conditions as a function of the number of safety valve openings, N ; (b) at rest after overcharge as a function of time. The battery was initially filled with air.

Conclusions

By measuring the decay of internal pressure of recombination in lead-acid cells initially filled with either hydrogen or with oxygen, the rate constants of the reactions between these gases and the active materials have been deduced. These parameters were used in conjunction with a theory developed in this paper to determine the pressure and composition of gases in the cells during charge, floating, or storage, both in dynamic and in steady state conditions.

List of symbols

D_H	$= I - 4FK_O\bar{N}_O - I_1$
D_O	$= I - 2FK_H\bar{N}_H - I_c$
F	Faraday's constant
f	$= \exp(-Kt)$
f_H	$= \exp(-K_H t)$
f_O	$= \exp(-K_O t)$
$f(t)$	$= d \ln(dP/dt)/dt$
I	Charge current
I_c	Positive grid corrosion current
I_H, I_O	Current intensities for H ₂ and O ₂ evolution
I_1	Current intensity for spontaneous H ₂ evolution
K	$= K_H + K_O$
K_H, K_O	Kinetic constants for the reactions of H ₂ and O ₂ with the active materials
N_H, N_O	Number of H ₂ and O ₂ moles present in the free volume of the cell
\bar{N}_H, \bar{N}_O	Number of H ₂ and O ₂ moles present in the free volume of the cell at time zero
P	Cell internal pressure
\bar{P}	Cell internal pressure at time zero
R	Gas constant
t	Time
T	Temperature
V	Free volume of the cell
Y_H, Y_O	H ₂ and O ₂ molar fractions

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