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OXYGEN REDISTRIBUTION IN UO_{2+x}

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Rand and Markin[1] have proposed a mechanism, which appears to be campatible with available measurements[2], for the redistribution of oxygen in oxide fuel bodies subject to a temperature gradient. Their model assumes that a constant ratio of CO_2/CO, in conjunction with the known temperature field, determines the local oxygen partial pressures by the equilibrium constant of the reaction $CO(g) + \frac{1}{2}O_2(g) = CO_2(g)$ according to:

$$K = (p_{CO_2}/p_{CO})/\sqrt{p_{O_2}} \qquad (1)$$

With T and p_{O_2} known functions of position, the variation of x in UO_{2+x} with position is determined by the thermochemistry of hyper-stoichiometric uranium dioxide. The CO_2/CO ratio is adjusted until the average value of x is equal to the specified value.

We investigated the validity of assuming a constant CO_2/CO ratio in this situation. It has been suggested[3] that a constant ratio is maintained by convection currents within the gas. However, any circulatory processes which is vigorous enough to establish a constant CO_2/CO ratio would also tend to keep the oxygen partial pressure constant as well, which contradicts Eq(1). We have performed the Rank-Markin type computation without the arbitrary restraint that p_{CO_2}/p_{CO} is independent of position. In its place, the more general restriction which is based upon the closed nature of the system was utilized. In order to isolate the effects of constant as opposed to

variable CO_2/CO, the following simplifications were adopted:

1. The gaseous species CO_2, CO, and O_2 are all dilute in an inert carrier gas.

2. The only means of transport in the gas phase is molecular diffusion; turbulent mixing and thermal diffusion (the Soret effect) are not considered.

3. The diffusion coefficients of CO_2, CO, and O_2 in the inert gas are all equal.

4. Solid state diffusion of oxygen ions in the UO_{2+x} is neglected.

5. The thermochemical properties of hyperstoichiometric urania are approximated by:

$$\Delta \overline{H}_{O_2} = - 65 \text{ kcal/mole}$$

$$\Delta \overline{S}_{O_2} = - 120Rx \text{ entropy units}$$

(2)

where R is the gas constant. The enthalpy value has been utilized by Aitken[4] and the linear form of the entropy variation with O/M is taken from the plot of Perron (ref 5, Fig 10). It is valid for $2.025 < \frac{O}{M} < 2.10$. Assumptions 1, 3, and 5 are introduced for computational convenience only; they could be removed without altering the qualitative features of the results. The system analyzed is shown in Fig 1. A linear temperature profile is imposed along the z-axis. There is no transport of material across the boundaries at z = 0 and L. The system is at steady state.

Since the ends of the tube in Fig 1 are closed, mass conservation requires that there be no net mass flux of the inert species or of elemental carbon and elemental oxygen (irrespective of their molecular forms) across a plane such as A-A, or:

$$N_I = 0$$

$$N_{CO} + N_{CO_2} = 0 \tag{3}$$

$$N_{CO} + 2N_{CO_2} + 2N_{O_2} = 0$$

where N_i is the molar flux of component i relative to stationary coordinates. It can be shown that Eq(3) implies that the mass average velocity of the mixture is zero at all points[6]. As a consequence, the momentum equations require that the total pressure be independent of z. In accord with assumption 1, the species CO_2, CO, and O_2 behave as if they existed individually as binary mixtures with the inert diluent gas. Consequently, the fluxes may be expressed by the binary form of Fick's law:

$$N_i = -\frac{D_{iI}}{RT}\frac{dp_i}{dz} \qquad (i = CO_2, CO, O_2) \tag{4}$$

where D_{iI} is the diffusion coefficient of species i in the inert gas and p_i is the partial pressure of i. Eq(4) is valid to the extent that the average molecular weight of the mixture may be approximated by the molecular weight of the inert solvent[6]. Substituting Eq(4) into the last two equations of (2), and utilizing the equal diffusivity approximation results in:

$$p_{CO} + p_{CO_2} = p_c \tag{5}$$

$$p_{CO} + 2p_{CO_2} + 2p_{O_2} = (B + 1)p_c \tag{6}$$

where B and p_c are independent of z. p_c is the total pressure of CO_2 + CO in the gas phase and B is a constant to be determined. The manner in which the constancy of the left hand side of Eq(6) is expressed (i.e., as $(B+1)p_c$) is for convenience in subsequent analysis.

Combining Eqs(1), (5) and (6) yields:

$$\frac{2}{p_c K^2}\left[\left(\frac{p_{CO_2}}{p_{CO}}\right)^3 + \left(\frac{p_{CO_2}}{p_{CO}}\right)^2\right] + (1-B)\left(\frac{p_{CO_2}}{p_{CO}}\right) = B \tag{7}$$

which may be solved for the CO_2/CO ratio as a function of z if p_c is specified and B is known. (K is a function of T and T is a function of z)

Equilibrium between the gas phase and the solid UO_{2+x} at each point requires that:

$$\ell n\left(\frac{p_{CO_2}}{p_{CO}}\right) + \frac{\Delta H^\circ}{RT} - \frac{\Delta S^\circ}{R} = \frac{1}{2}\frac{\Delta \overline{H}_{O_2}}{RT} - \frac{1}{2}\frac{\Delta \overline{S}_{O_2}}{R} \tag{8}$$

where ΔH° and ΔS° are the standard state enthalpy and entropy of the reaction $CO(g) + \frac{1}{2}O_2(g) = CO_2(g)$. They have been taken as -67.5 kcal/mole and -20.75 eu, respectively. Inserting the approximations of Eq(2) into Eq(8) yields the profile of the non-stoichiometry parameter x:

$$x = \frac{1}{60}\left\{\left(\frac{1}{2}\frac{65}{R} + \frac{\Delta H^\circ}{R}\right)\frac{1}{T} + \ell n\left(\frac{p_{CO_2}}{p_{CO}}\right) - \frac{\Delta S^\circ}{R}\right\} \tag{9}$$

Conservation of total oxygen requires that the integral of Eq(9) over the length L be equal to the specified average value x_0 (the amount of oxygen in the gas phase is neglected by comparison with that in the solid). For a linear temperature profile, integration yields:

$$\int_0^1 \ell n\left(\frac{p_{CO_2}}{p_{CO}}\right) d\left(\frac{z}{L}\right) = 60\,x_0 - \left(\frac{1}{2}\frac{65}{R} + \frac{\Delta H^\circ}{R}\right)\frac{\ell n\left(T_0/T_L\right)}{\left(T_0 - T_L\right)} + \frac{\Delta S^\circ}{R} \tag{10}$$

In the case of the constant CO_2/CO assumption (the Rand-Markin model), the left hand side of Eq(10) is simply $\ell n(p_{CO_2}/p_{CO})$.

Substituting this constant into Eq(9) permits the stoichiometry profile to be determined directly. In the present analysis, however, the solution proceeds as follows: T_0, T_L, x_0 and p_c are specified; a value of B is guessed and the variation of the CO_2/CO ratio with z is determined by solution of Eq(7). The computed profile of p_{CO_2}/p_{CO} is integrated according to Eq(10). If Eq(10) is not satisfied, a new value of B is taken. Iteration ceases when Eq(10) is satisfied. The stoichiometric profile is then determined from Eq(9).

According to Eq(7), constancy of the CO_2/CO ratio is achieved only when the parameter $p_c K^2$ is large. This limit occurs if either the temperature is low or the total carbon pressure is high. Oxide fuel elements are designed to operate with centerline temperatures near the melting point, so that T_0 may approach 3000°K. It has been estimated at 2 ppm of carbon impurity in UO_2 will produce a CO + CO_2 pressure of 0.5 atm in a test capsule[3]. In a reactor fuel element, total carbon pressures between 0.1 and 1 atm appear plausible.

The preceeding analysis has been applied to a typical set of conditions with the results shown in Fig 2. The variation of the CO_2/CO ratio along the temperature gradient is sizeable; the ratio is a factor of nearly three greater at the cold end than at the hot end. The O/M ratio is not as drastically altered from the profile computed by the constant CO_2/CO assumption. Yet O/M - 2 is decreased by 20% at the hot end and increased by ~ 50% at the cold end as a result of relaxing the constant CO_2/CO restriction. The latter figure may be of some practical importance, since it corresponds to a change of ~ 4 kcal/mole in the oxygen potential of the fuel, in the direction of rendering the fuel better able to attack the cladding. (Although

the O/M ratios at the cold end are below the range of validity of Eq(2), similar behavior is found when the average O/M is large enough to yield a cold end stoichiometry > 2.025).

The difference between oxygen redistribution computed with the mass balance condition compared to calculations based upon constant CO_2/CO can be appreciable under conditions that render the oxygen partial pressure comparable to the total carbon pressure (e.g., high temperature, large deviation of average O/M from stoichiometry, and low total carbon pressure).

O/M profiles computed by the present method show a less pronounced variation along the temperature gradient than predicted by requiring constant CO_2/CO. This feature is in accord with the recent results of experiments on oxygen redistribution, in which the Rand-Markin model overestimated the extent of the effect[7].
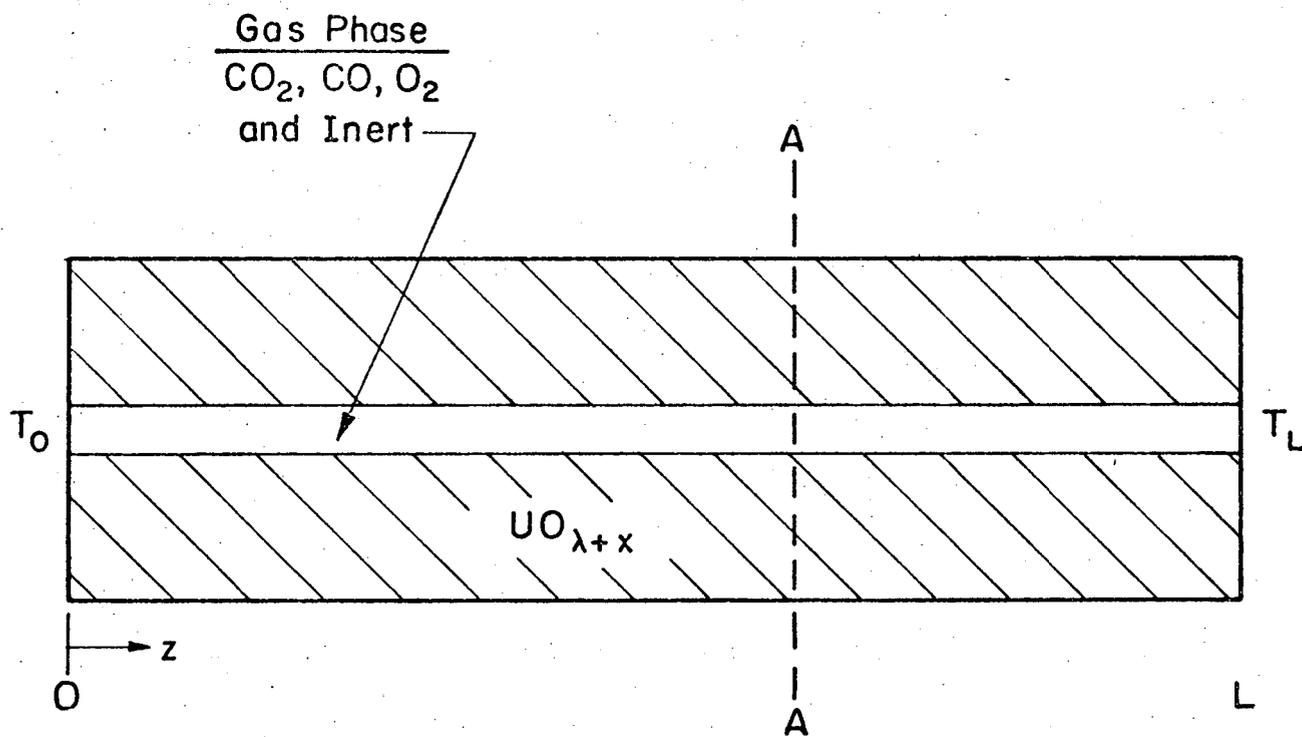
The present calculation shows a smooth transition between the limiting cases of constant p_{CO_2}/p_{CO} and constant p_{O_2}. The former occurs as $p_c \rightarrow \infty$, while the latter is approached as $p_c \rightarrow 0$. The dependence of the O/M profile upon the total carbon pressure is shown in Fig 3.

Literature Cited

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6. R. B. Bird, W. E. Stewart, and E. N. Lightfoot, Transport Phenomena, Chap. 16, Wiley, New York (1960).

7. A. T. Jeffs, Atomic Energy of Canada Ltd. Report AECL-3690 (1970).

Figure Captions

1. UO_{2+x} in contact with a gas containing a CO_2/CO mixture and subject to a temperature gradient.

2. Variation of O/M and CO_2/CO along the temperature gradient. $T_0 = 2500°K$, $T_L = 1500°K$, $p_c = 0.1$ atm, $x_0 = 0.05$.

3. Effect of total carbon pressure on oxygen redistribution. $T_0 = 2500°K$, $T_L = 1500°K$, average O/M = 2.05
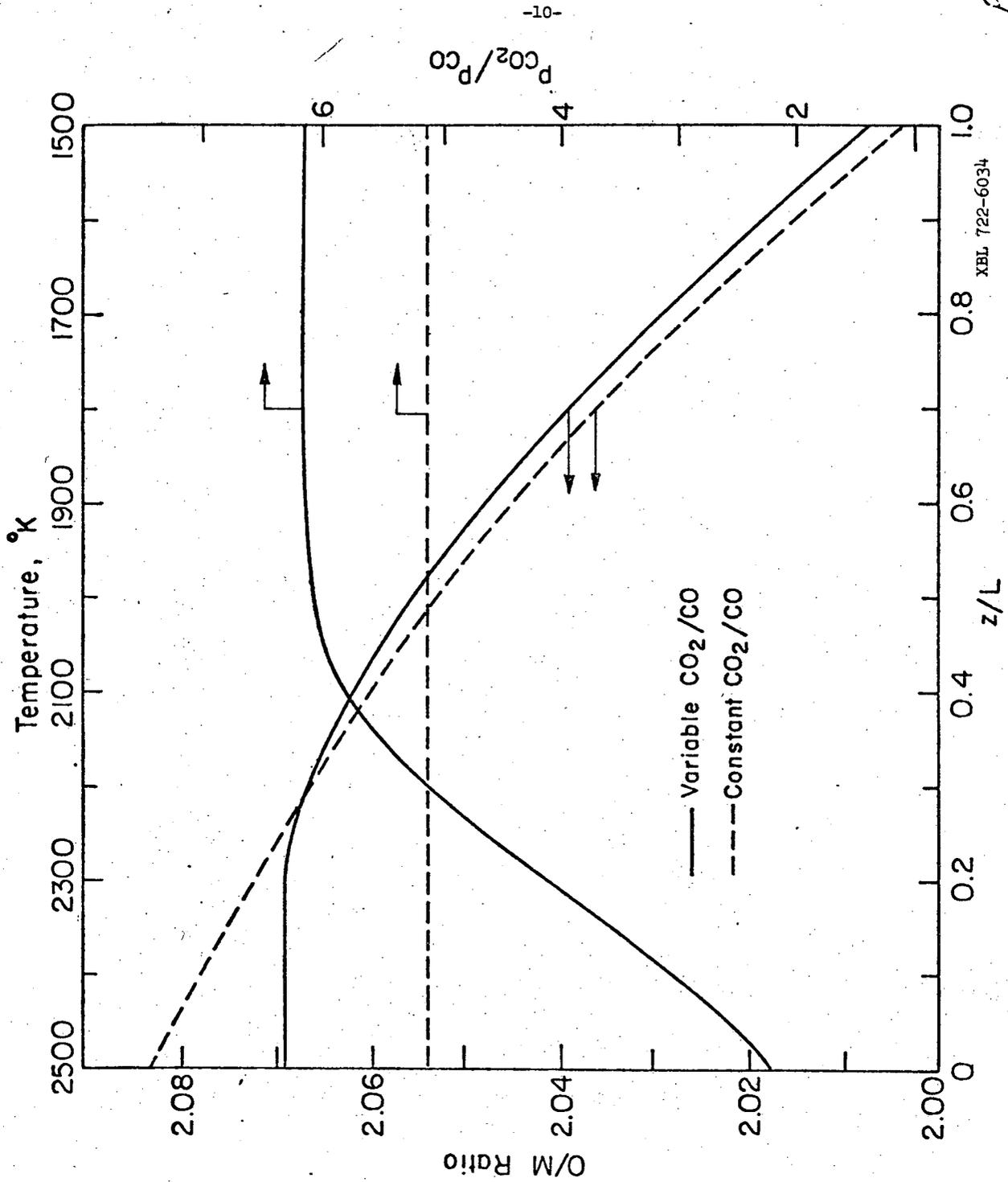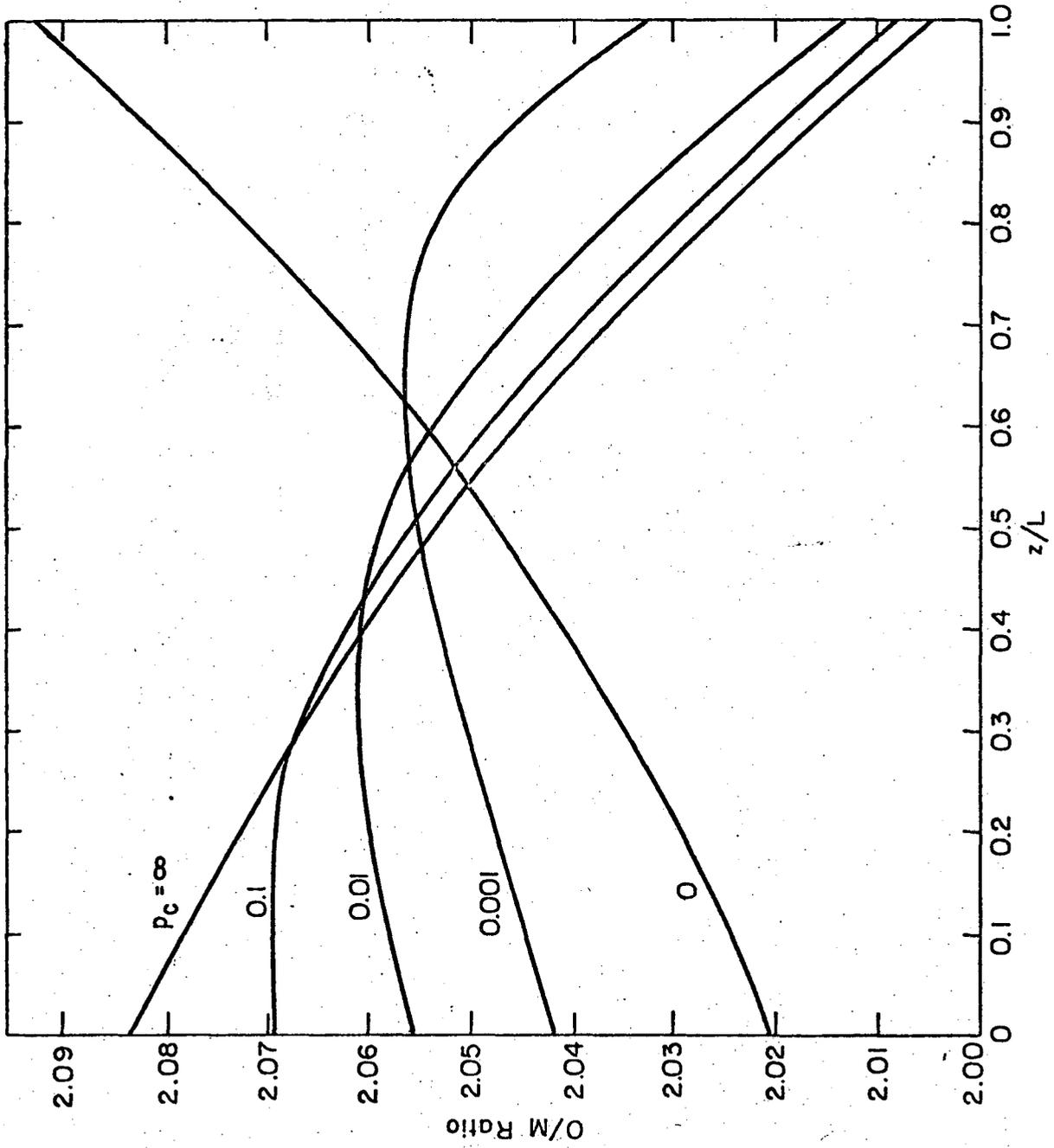
Fig. 1

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Fig. 2

Fig. 3

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