

## VII. PHYSICAL ELECTRONICS AND SURFACE PHYSICS\*

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#### A. QUASI-EQUILIBRIUM TREATMENT OF THE REACTION OF A GAS WITH A SOLID TO FORM VOLATILE PRODUCTS: EROSION OF TUNGSTEN BY OXIDATION

##### 1. Introduction

Chemical reactions of gases with solid surfaces at high temperature and low pressure have been the subject of numerous investigations recently because such reactions frequently are encountered in power and propulsion systems, as well as in high-speed flight and re-entry.<sup>1</sup> The chemical reaction of gaseous oxygen with solid tungsten has received particular attention, not only because the O-W system seems well suited to controlled laboratory investigation but also because tungsten is a common material for high-temperature applications. Considerable effort has been devoted to measuring, either directly or indirectly, the rate of erosion of tungsten by oxidation.<sup>2-13</sup>

An interesting feature of the experimental data shown in Fig. VII-1 is that the erosion rate passes through a maximum as temperature increases. Perkins and Crooks<sup>9</sup> have suggested that this trend occurs because the formation of  $WO_3$  becomes thermodynamically unfavorable at high temperature. Anderson<sup>7</sup> has argued, however, that this view is not consistent with accepted thermodynamic data. Eisinger<sup>12</sup> had earlier attributed the observed decrease in erosion rate to a decrease in sticking probability. Becker et al.<sup>8</sup> attributed this behavior to changes in both the sticking probability and the heat of desorption of oxygen on tungsten, and they proposed a model in which oxygen is adsorbed in two distinct states. This two-state model has also been employed by Schissel and Trulson<sup>14</sup> in a kinetic treatment of the various steps occurring within the adsorbate phase.

By fitting the experimental data to Arrhenius-type equations, Perkins et al.<sup>6</sup> have obtained a useful correlation; however, the presence of the maximum in the data required the apparent desorption energy to decrease to zero and then become negative

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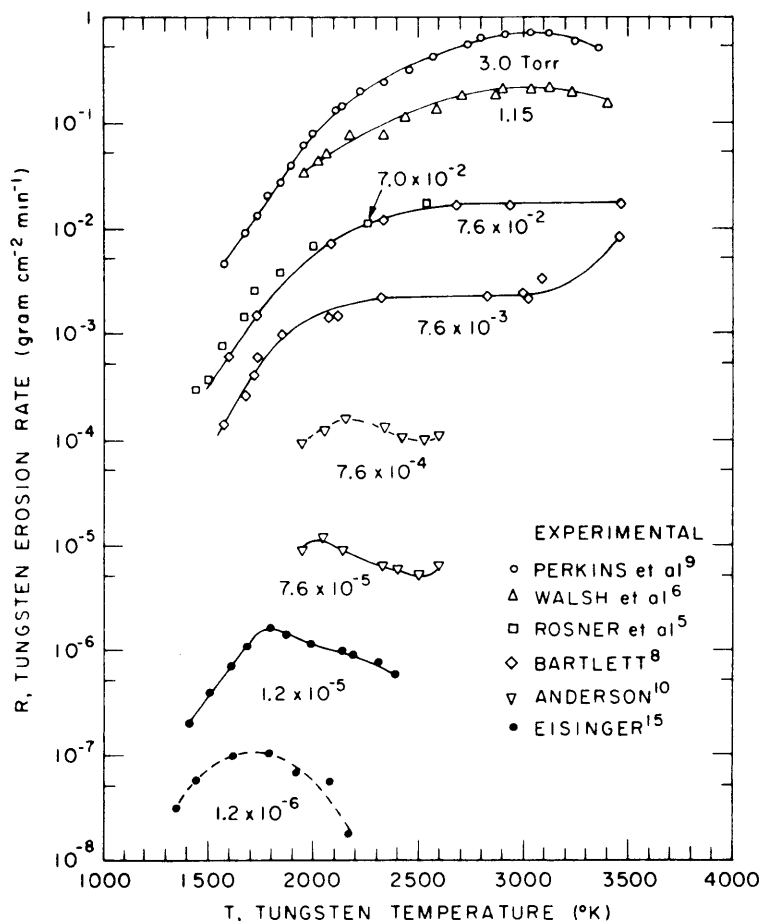


Fig. VII-1. Experimental data on the rate at which tungsten is eroded by oxygen for pressures in the range  $1.2 \times 10^{-6}$  to 3 Torr.

at the highest temperatures. A correlation based on the kinetic model of Schissel and Trulson<sup>14</sup> has been suggested by Walsh et al.,<sup>3</sup> but some adjustable parameters again appear in the form of rate constants.

We have attempted to predict the erosion rates of tungsten by oxidation, using the simple quasi-equilibrium model<sup>15</sup> which has provided a satisfactory description of mass spectrometric data<sup>16</sup> on the rates of evaporation of volatile products from a tungsten surface exposed to  $O_2$ . The results are compared with experimental data obtained in different laboratories.

## 2. Theoretical Analysis

Since the quasi-equilibrium model as it applies to the O-W reaction has been described in detail previously,<sup>17</sup> only the basic features are reviewed here.

1. Oxygen molecules impinge upon the tungsten surface at a rate  $Z'_{O_2}$ , and the

impingement rates for other species are assumed to be negligible.

2. We assume that the impinging oxygen molecules may be divided into two classes, one comprising the molecules that become equilibrated to both the solid and the adsorbate, and the other those that are reflected as  $O_2$  without undergoing chemical reaction. The symbol  $\zeta'_{O_2}$  will be used to designate that fraction of the incident molecules that are equilibrated, and it will be referred to as the equilibration probability.

3.  $R_{W_x O_y}$ , the rate of evaporation of each of the assumed product species, is assumed to be equal to the rate that would exist if the  $O_2$  gas were replaced by an oxygen and tungsten oxide mixture that is in equilibrium with the solid tungsten and for which the conservation of oxygen condition,

$$2\zeta'_{O_2} Z'_{O_2} = R_O + 2R_{O_2} + R_{WO} + 2R_{WO_2} + 3R_{WO_3} + 6R_{W_2O_6} + 8R_{W_3O_8} + 9R_{W_3O_9} + 12R_{W_4O_{12}}, \quad (1)$$

is satisfied.

The equilibrium desorption rates,  $R_{W_x O_y}$ , are further related through the expression<sup>17</sup>

$$K_{W_x O_y} = (2\pi RT)^{1/2(1-y/2)} \left( \frac{M_{W_x O_y}}{M_{O_2}^{y/2}} \right)^{1/2} \frac{R_{W_x O_y}}{R_{O_2}^{y/2}}, \quad (2)$$

where  $T$  is the tungsten temperature,  $M_{W_x O_y}$  is the molecular weight of species  $W_x O_y$ , and  $K_{W_x O_y}$  represents the equilibrium constant for the general reaction



The desorption rate of each of the individual species may be computed from Eqs. 1 and 2, provided  $\zeta'_{O_2}$ ,  $Z'_{O_2}$ , and  $K_{W_x O_y}$  are known. The determination of  $\zeta'_{O_2}$  remains a major difficulty, in that, at present, it cannot be determined on the basis of theory alone.<sup>18</sup> For  $Z'_{O_2}$  we turn to kinetic theory which gives

$$Z'_{O_2} = p'_{O_2} / \left( 2\pi m_{O_2} kT' \right)^{1/2}, \quad (4)$$

where  $p'_{O_2}$  and  $T'$  are the pressure and temperature of the incident oxygen.

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We shall use Eq. 4, with  $T'$  taken as  $300^\circ\text{K}$ , to calculate  $Z'_{\text{O}_2}$  for the entire range of pressures considered in Fig. VII-1. This assumption is justifiable if the oxygen molecules incident upon the reaction surface are in equilibrium with the room-temperature walls of the reaction chamber. At sufficiently high pressures the collision rate between approaching  $\text{O}_2$  molecules and particles leaving the hot surface becomes significant and other assumptions may be desirable. For example, Walsh et al.,<sup>3</sup> in using Eq. 4 to calculate  $Z'_{\text{O}_2}$ , have taken  $T'$  to be a computed temperature of the gas one mean-free path from the surface, while Rosner and Allendorf<sup>1</sup> have taken  $T'$  to be the temperature of the reaction surface itself. We have not included such refinements in our present calculations.

The equilibrium constants may be computed from

$$K_{\text{W}_x\text{O}_y} = \exp\left[-\left(\Delta H_{\text{W}_x\text{O}_y} - T\Delta S_{\text{W}_x\text{O}_y}\right) / RT\right], \quad (5)$$

where  $\Delta H_{\text{W}_x\text{O}_y}$  and  $\Delta S_{\text{W}_x\text{O}_y}$  are the enthalpy and the entropy of the reaction described by Eq. 3.<sup>19,20</sup>

The oxygen conservation relation, Eq. 1, with the addition of  $R_{\text{W}}$ , the sublimation rate of pure tungsten,<sup>21</sup> provides a list of those species assumed to be present. The value of  $R_{\text{W}}$  is independent of  $Z'_{\text{O}_2}$  and is obtained directly from Eq. 2, with  $y$  taken as zero and  $x$  taken as one. The tungsten erosion rate  $R$  is simply the summation of the evaporation rates of the individual species:

$$R = R_{\text{W}} + R_{\text{WO}} + R_{\text{WO}_2} + R_{\text{WO}_3} + 2R_{\text{W}_2\text{O}_6} + 3R_{\text{W}_3\text{O}_8} + 3R_{\text{W}_3\text{O}_9} + 4R_{\text{W}_4\text{O}_{12}}. \quad (6)$$

The erosion rate may be expressed in any desired units by multiplying Eq. 6 (atoms  $\text{cm}^{-2} \text{sec}^{-1}$ ) by the appropriate conversion factors. We choose to express our results in  $\text{g cm}^{-2} \text{min}^{-1}$ .

### 3. Comparison of Theoretical and Experimental Results

Presented in Fig. VII-2 are the theoretical erosion rates based on the simplifying assumption that  $\zeta'_{\text{O}_2} = 1$  over the entire range of temperature and pressure. Note that in general the theoretical values of Fig. VII-2 differ from the experimental values of Fig. VII-1 by several orders of magnitude. Even more disturbing is the observation that while the experimental data clearly pass through a maximum, the theoretical curves do just the opposite; that is, they pass through a minimum. The prediction of a minimum by the model is of particular interest. The model agrees with experiment with respect

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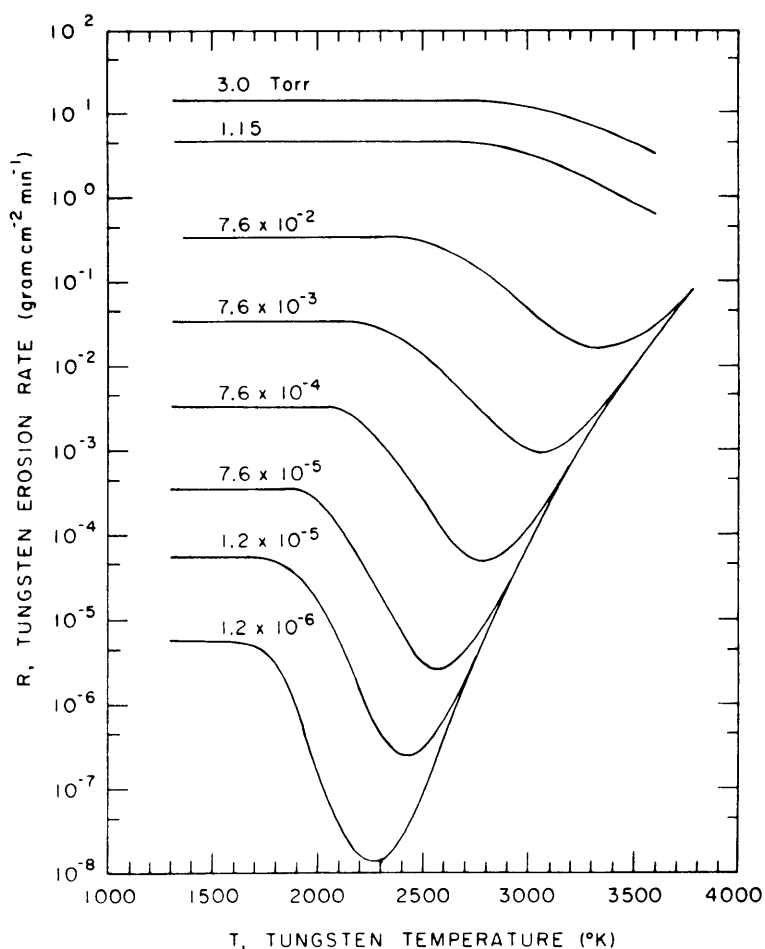


Fig. VII-2. Erosion rates predicted by the quasi-equilibrium model based on the assumption that  $\zeta'_{O_2} = 1$  over the entire range of oxygen pressure and tungsten temperature. Oxygen pressures correspond to those of the experimental results presented in Fig. VII-1.

to the suggestion that an increase in tungsten temperature may be accompanied by a sharp decrease in erosion rate, particularly at the lower pressures. This feature may be explained by considering the theoretical evaporation rates of the individual species as shown in Fig. VII-3 for an oxygen pressure of  $1.2 \times 10^{-6}$  Torr and in Fig. VII-4 for a pressure of 3.0 Torr. The minimum in the erosion rate occurs at that temperature when the equilibrated oxygen molecules thermodynamically prefer to dissociate rather than chemically combine with the tungsten. At lower temperatures  $WO_3$ , or its polymers, tends to dominate, while at the higher temperatures the erosion rate is increased not only by the increase in  $WO$  production but also by the sublimation rate  $R_W$  achieving relative importance. Comparison of Figs. VII-3 and VII-4 reveals why the erosion-rate curves are flatter at the higher pressures and the minimum is less pronounced. In

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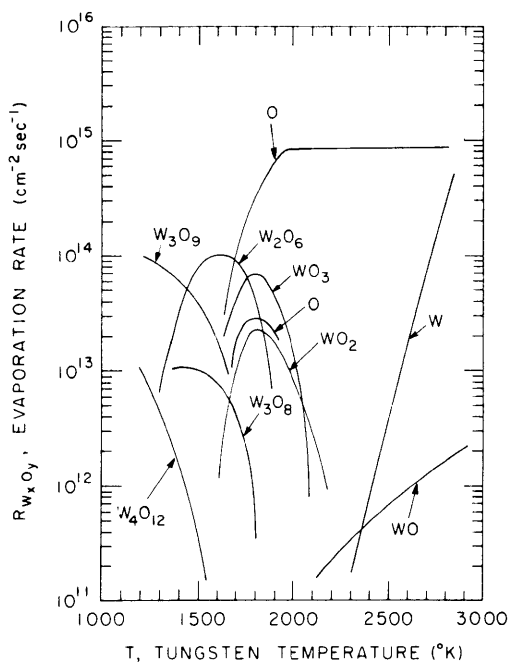


Fig. VII-3.

Evaporation rates of the individual products of the reaction of gaseous oxygen with solid tungsten as predicted by the quasi-equilibrium model, under the assumption that  $p'_{O_2} = 1.2 \times 10^{-6}$  Torr and  $\zeta'_{O_2} = 1$ .

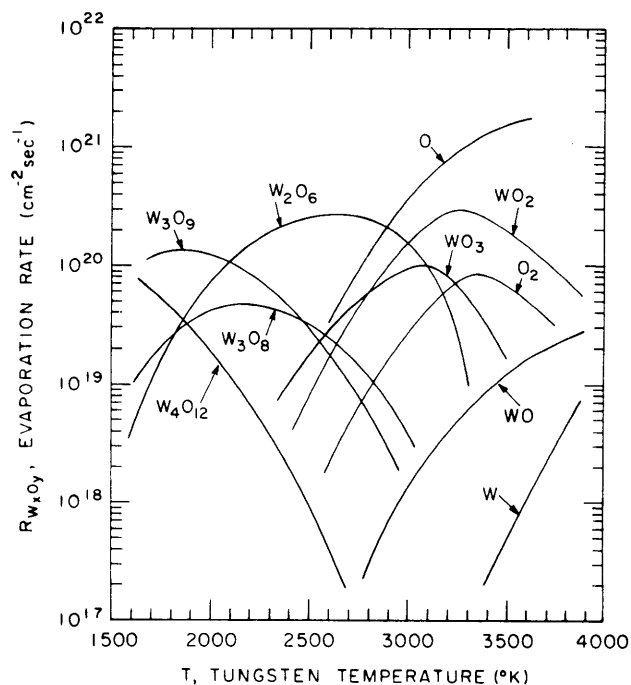


Fig. VII-4.

Evaporation rates of the individual products of the reaction of gaseous oxygen with solid tungsten as predicted by the quasi-equilibrium model, under the assumption that  $p'_{O_2} = 3$  Torr and  $\zeta'_{O_2} = 1$ .

Fig. VII-3 there is a region (near 2300°K) where the evaporation rate of oxides is relatively much less than at substantially lower or higher temperatures where the sublimation rate  $R_W$  has not yet become significant. At a pressure of 3.0 Torr, as shown in Fig. VII-4, this region of relatively low oxide evaporation rates does not occur until the tungsten temperature is above the melting point (~3650°K).

Returning to the comparison with the experimental results and the feature that the experimental results possess a maximum, we consider further  $\zeta'_{O_2}$ , the apparent equilibration probability. In an earlier report<sup>17</sup> we have shown that Schissel and Trulson's<sup>14</sup> mass-spectrometer data for the O-W reaction may be used to estimate  $\zeta'_{O_2}$  as a function of the tungsten temperature  $T$  for a constant value of  $p'_{O_2}$ . We now propose to approximate the apparent equilibration probability by the empirical expression<sup>18</sup>

$$\zeta'_{O_2} = 360 p'_{O_2}{}^{-.36} \exp(-23,000/T), \quad (7)$$

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where  $p'_{O_2}$  is measured in Torr and  $T$  in  $^{\circ}K$ .  $\zeta'_{O_2}$  is taken to be one if Eq. 7 yields a value greater than unity.

Using this expression for  $\zeta'_{O_2}$ , we have recalculated the erosion rates, and the results are compared with experimental data in Fig. VII-5. The correlation over the entire range of pressure is surprisingly close, in view of the fact that Eq. 7 represents what was intended to be only a first approximation of  $\zeta'_{O_2}$ . At the lower temperatures an increase in temperature is accompanied by an increase in erosion rate as a result of the increasing equilibration probability. The maximum occurs when the effect of increasing  $\zeta'_{O_2}$  is exactly counterbalanced by the increased thermodynamic preference for the incident oxygen to dissociate rather than combine with tungsten. Just as in Figs. VII-3 and VII-4, when the temperature becomes sufficiently great  $R_W$  and  $R_{WO}$  become relatively significant and the erosion rate climbs rapidly.

In the low-temperature region the temperature dependence of the erosion rates is in excellent agreement with that observed by Perkins et al.<sup>6</sup> Note that in this region the oxidation rate is limited by  $\zeta'_{O_2}$ , the equilibration probability. By rewriting in Eq. 7 the term providing the temperature dependence as  $\exp(-E/RT)$ , we have an apparent activation energy of 45,600 cal/gmol. Perkins et al.<sup>6</sup> used a value of 43,900 for the activation energy in their Arrhenius-type expression for the erosion rates in this temperature range.

We note also that in Fig. VII-5 the theoretical curves are generally lower than the corresponding experimental curves, so that better agreement could be obtained simply by increasing the constant coefficient in Eq. 7 from 360 to, say,  $\sim 720$ ; however, we have chosen not to resort to "adjusting" parameters to obtain a better fit of the data. Also, the reported experimental values may be too large because faceting causes the actual reaction surface area to be larger than the measured area.

In considering the results of Perkins et al.<sup>6</sup> covering the pressure range from 0.11 to 3.0 Torr, Kofstad<sup>22</sup> has pointed out that the erosion rate is proportional to  $p'^{.59}_{O_2}$  at 1670 $^{\circ}K$ , to  $p'^{.82}_{O_2}$  at 2230 $^{\circ}K$ , and to  $p'_{O_2}$  above the maximum. It may be observed from Fig. VII-5 that the theoretical curves exhibit similar pressure dependencies, the erosion rate being approximately proportional to  $p'^{.64}_{O_2}$  at  $\sim 1600^{\circ}K$ , to  $p'^{.85}_{O_2}$  at  $\sim 2200^{\circ}K$ , and to  $p'^{1.15}_{O_2}$  at  $\sim 2600^{\circ}K$ . That the erosion rate in certain temperature ranges may be proportional to the oxygen pressure raised to a power greater than one is a consequence of the increase in pressure causing the temperature range in which oxide production is thermodynamically preferred to be shifted upward, as demonstrated by comparing Figs. VII-3 and VII-4. Close inspection of the data of Perkins et al.<sup>6</sup> verifies that above the

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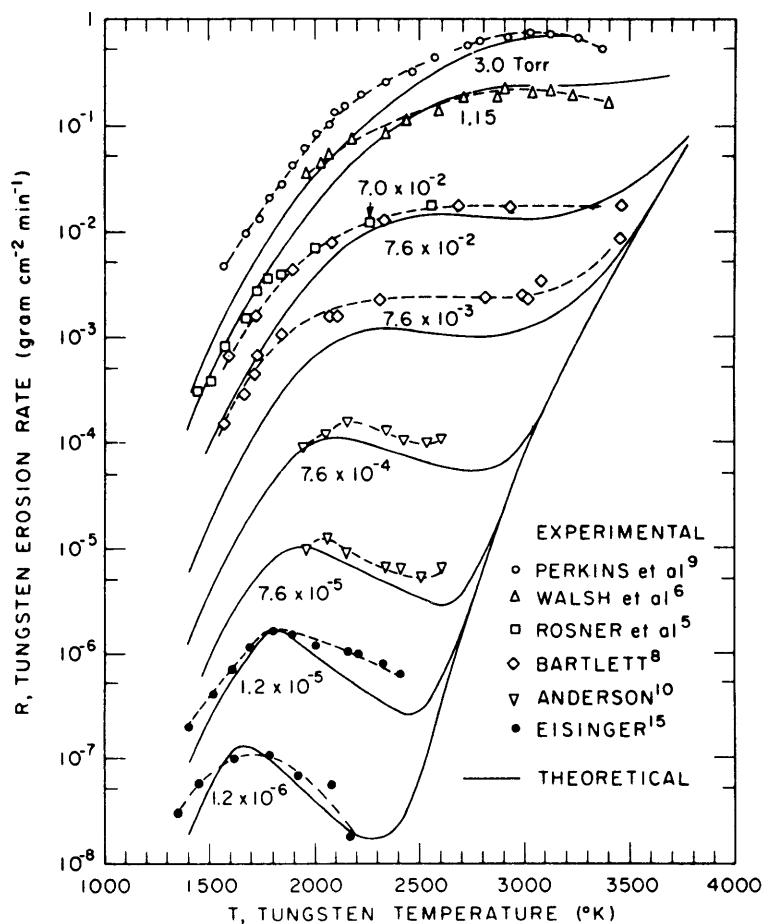


Fig. VII-5. Comparison of experimentally determined erosion rates with those values predicted by the quasi-equilibrium model with  $\zeta'_{O_2} = 360p'_{O_2}{}^{-.36} \exp(-23,000/T)$ .

maximum the erosion is proportional to the oxygen pressure raised to a power slightly greater than one. In fact, the empirical correlation by Perkins et al. gives the maximum oxidation rate as being proportional to  $p'_{O_2}{}^{1.08}$ .

That reasonable agreement between model predictions and experimental results extends to the relatively high pressures is quite surprising when one considers the greatly increased probability of gas-phase collisions between the equilibrated evaporation products and the cold incident oxygen molecules. At a pressure of 3.0 Torr the mean-free path of the oxygen is reduced to approximately  $10^{-3}$  cm. Kofstad<sup>22</sup> provides, as a rough guide, the rule that back reflection of escaping molecules will not be significant at pressures below  $\sim 0.1$ -1 Torr; however, the upper pressure limit of applicability of the quasi-equilibrium model may be somewhat larger than this, depending on experimental conditions.<sup>23</sup>



## 4. Concluding Remarks

The quasi-equilibrium model has been used to predict quite accurately (in general, within a factor of 2.5) tungsten erosion rates over a range sufficiently broad that the maximum rate exceeds the minimum rate by more than seven orders of magnitude.

The experimental data with which the calculated results are compared (see Fig.VII-5) were arbitrarily selected on the basis of providing a comparison at fairly evenly spaced pressure intervals over the range of pressures considered, and of including as many different investigators as possible. No data were selected or rejected on the basis of good or bad fit with calculated results.

The model is applicable to O-W systems in which the surface temperature is sufficiently high ( $T \gtrsim 1400^\circ\text{K}$ ) that the oxides formed are volatile, and the oxygen pressures sufficiently low<sup>2,3</sup> ( $p'_{\text{O}_2} \lesssim 1.0$  Torr) that the reaction rate is determined by surface processes, rather than by gas-phase reactions or transport effects.

Our calculations strongly suggest that  $\zeta'_{\text{O}_2}$  is the controlling factor in the erosion rate, particularly at low temperatures and/or high pressures. This conclusion is substantiated by experiments<sup>2</sup> showing that higher erosion rates result from the attack of tungsten by atomic oxygen than by molecular oxygen. These experiments also indicate that at relatively low temperatures  $\zeta'_\text{O}$  is significantly greater than  $\zeta'_{\text{O}_2}$ .

We have also shown that the relative maximum in the erosion rate is caused by the increased thermodynamic preference for the equilibrated oxygen to evaporate from the surface as atomic oxygen rather than combined with tungsten in the form of an oxide. In addition to its extreme simplicity, the principal advantage over previous correlations lies in the fact that no "fitting" or "adjusting" of parameters is necessary over the entire range of pressure and temperature. Data from an independent investigation concerning the rate at which atomic oxygen is emitted from the tungsten surface were utilized to obtain an expression for the apparent equilibration probability. Thus the model that was used contained essentially no "adjustable parameters," in the sense that the values of all parameters were fixed before comparison of calculated erosion rates with experimental data.

The calculation of erosion rates by using the quasi-equilibrium approach need not be limited to the oxygen-tungsten system, and will be applied to other systems of interest as free-energy data become available.

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Footnotes and References

1. D. E. Rosner and H. D. Allendorf, *J. Electrochem. Soc.* 114, 305 (1967); G. A. Etemad, *AIAA J.* 4, 1543 (1966); B. W. Marshall, *AIAA J.* 4, 1899 (1966).
2. The erosion-rate data of Rosner and Allendorf<sup>1</sup> shown in Figs. VII-1 and VII-5 were obtained by exposing a tungsten filament to a mixture of an inert carrier gas and oxygen at a total pressure of  $\sim 1$  Torr and measuring the change in the filament radius. The pressure reported in Figs. VII-1 and VII-5 is the partial pressure of  $O_2$ .
3. P. N. Walsh, J. M. Quets, and R. A. Graff, *J. Chem. Phys.* 46, 1144 (1967). Their erosion-rate data shown in Fig. VII-5 were obtained by impinging oxygen onto a flat tungsten surface and measuring the recession rate. The pressure reported is the equivalent stagnation pressure at the surface.
4. R. A. Perkins, W. L. Price, and D. D. Crooks, Air Force Materials Laboratory Technical Documentary Report MLTDR-64-162 (1965).
5. R. W. Bartlett, *Trans. AIME* 230, 1097 (1964). His erosion-rate data shown in Figs. VII-1 and VII-5 were obtained by exposing heated tungsten rods to oxygen and measuring the diameter recession rates.
6. R. A. Perkins, W. L. Price, and D. D. Crooks, Lockheed Missiles and Space Company Technical Report 6-90-62-98 (1962). Their erosion-rate data shown in Figs. VII-1 and VII-5 were obtained by impinging oxygen radially onto a tungsten rod and measuring the recession rate. The pressure reported is an equivalent stagnation pressure at the surface.
7. H. U. Anderson, University of California Radiation Laboratory Report UCRL 10135 (1962). His erosion-rate data shown in Figs. VII-1 and VII-5 were obtained by exposing a hot tungsten filament to oxygen in a reaction vessel and determining the weight loss by measuring the change in the electrical resistance of the filament.
8. J. Becker, E. Becker, and R. Brandes, *J. Appl. Phys.* 32, 411 (1961).
9. R. A. Perkins and D. D. Crooks, *J. Metals* 13, 490 (1961).
10. P. Blackburn, K. Andrew, E. Gulbransen, and F. Brassart, Wright Air Development Center, WADC TR-59-575-II, June 1961.
11. J. N. Ong, Jr., *J. Electrochem. Soc.* 109, 284 (1962).
12. J. Eisinger, *J. Chem. Phys.* 30, 412 (1959). His erosion-rate data shown in Figs. VII-1 and VII-5 were converted from chemical pumping efficiency data obtained indirectly as follows: A tungsten ribbon was heated to various temperatures in low-pressure oxygen, and the resulting decrease in the steady-state chamber pressure was used to calculate the rate at which oxygen molecules impinging on the filament surface were "pumped" by reacting to form volatile oxides that condense on the chamber walls. Under the assumption that  $WO_3$  is the dominant product, the rate at which tungsten is eroded may then be calculated.
13. I. Langmuir, *J. Am. Chem. Soc.* 35, 105 (1913).
14. P. O. Schissel and O. C. Trulson, *J. Chem. Phys.* 43, 737 (1965).
15. J. C. Batty and R. E. Stickney, "Thermodynamics and Kinetics of Heterogeneous Reactions," Technical Report 473, Research Laboratory of Electronics, M. I. T., Cambridge, Mass., June 2, 1969; see Appendix B.
16. For a discussion of mass spectrometry see R. T. Grimley, in J. L. Margrave (ed.), The Characterization of High Temperature Vapors (John Wiley and Sons, Inc., New York, 1967), pp. 195-243.
17. J. C. Batty and R. E. Stickney, op. cit.; see Part II.

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18. J. C. Batty, Ph.D. Thesis, Department of Mechanical Engineering, Massachusetts Institute of Technology, June 1969.
19. D. R. Stull (ed.), JANAF Tables of Thermochemical Data (Dow Chemical Company, Midland, Michigan, 1965, and Second Addendum, 1967).
20. The equilibrium constants used in these calculations are the JANAF values<sup>19</sup> modified by adjusting  $\Delta H_{298.15}^{\circ}$  within the tabulated limits of probable error; also J. C. Batty and R. E. Stickney, op. cit., see Table 2.
21. We assume the oxygen coverage on the surface is sufficiently low that it has a negligible effect on the sublimation rate  $R_W$ .
22. P. Kofstad, High Temperature Oxidation of Metals (John Wiley and Sons, Inc., New York, 1966), pp. 255-260.
23. Oxygen depletion effects were minimized in the high-pressure experiments by impinging the oxygen directly onto the surface in the form of a jet. Under these conditions, the use of effective stagnation pressures may extend the range of applicability to considerably higher values of pressure. Although not shown in Fig. VII-5, the comparison of model results with data provided by Walsh et al.<sup>3</sup> for an effective stagnation pressure of 11.5 Torr results in as good agreement as that found at lower pressures.

