



HIGH TEMPERATURE OXIDATION OF TUNGSTEN AND MOLYBDENUM

N. M. Ghoniem

**The University of California at Los Angeles (UCLA)
Los Angeles, CA. 90095-1597, USA**

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PRESENTATION OUTLINE

- (1) IMPACT OF OXIDATION ON DESIGN WITH REFRACTORY ALLOYS.**
- (2) MODELING OF HIGH-TEMPERATURE OXIDATION.**
 - 2.1. Thermodynamics of Reactions*
 - 2.2. Non-equilibrium Analysis*
- (3) RESULTS FOR TUNGSTEN.**
- (4) RESULTS FOR MOLYBDENUM.**
- (5) CONCLUSIONS.**



DESIGN IMPACT

@ At Normal temperatures and pressures, the chemical reaction of a gas with the solid generally results in condensed products.

@ At high temperatures and low pressures, the formation of volatile products is thermodynamically favored over the growth of the condensed phase.

@ The upper temperature limit for design with refractory metals with a helium coolant will be influenced by the formation of volatile oxides.

@ The present investigation is concerned with W/He and Mo/He designs.



MODELING HIGH-TEMPERATURE OXIDATION

APPROACH:

@ Quasi-equilibrium Treatment of Heterogeneous Reactions for the systems: O-W and O-Mo.

@ Rate Limiting Step is the Trapping (adsorption) of Oxygen atoms until equilibrium.

@ Assume that the helium pressure is P_{sys} , and its temperature T^* . The oxygen partial pressure is given by:

$$P_{O_2} = \text{appm} \times 10^{-6} P_{\text{sys}}$$

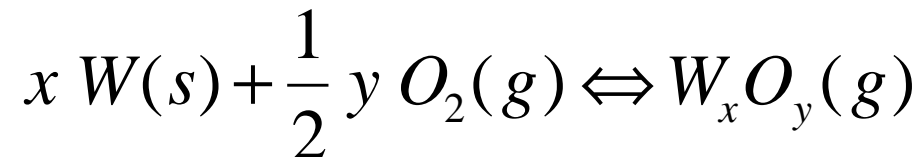


THERMODYNAMICS OF CHEMICAL REACTIONS

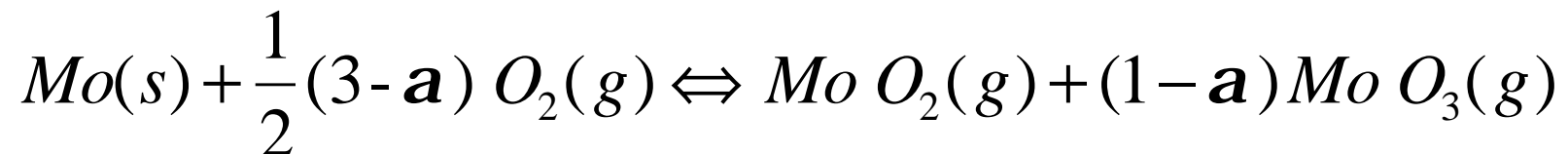
@ The rate at which oxygen molecules collide with unit area of the wall surface is given by:

$$Z_{O_2} = P_{O_2} \sqrt{2pM_{O_2}RT}$$

@ For Tungsten, the following thermodynamic reactions take place:



@ For Molybdenum, similar reactions occur. In addition, for T~1500-2500 K:





FORMATION ENTHALPIES & ENTROPIES OF OXIDES

Tungsten		Molybdenum		
Species	DHf _{298.15} (kcal/g.mole)	Species	DHf _{298.15} (kcal/g.mole)	DSf _{298.15} (cal/g.mole.K)
O(g)	59.559	O(g)	61.3	16
W O(g)	101.6	Mo O(g)	95	25.5
WO ₂ (g)	18.3	MoO ₂ (g)	11.0	9.0
W O ₃ (g)	-70.0	Mo O ₃ (g)	-80	-15.5
W ₂ O ₆ (g)	-278.2	Mo ₂ O ₆ (g)	-270	-72
W ₃ O ₈ (g)	-408.7	Mo ₃ O ₈ (g)	-400	-118
W ₃ O ₉ (g)	-483.6	Mo ₃ O ₉ (g)	-463	-132
W ₄ O ₁₂ (g)	-670.2	Mo ₄ O ₁₂ (g)	-640	-190



QUASI-EQUILIBRIUM TREATMENT OF BATTY & STICKNEY*

@ Collisions of O_2 with the surface can lead to either: (1) adsorption and equilibration, or (2) reflection.

@ Define the equilibration probability as:

$$z_i = \Gamma_i / Z_i$$

@ For oxygen molecules at a temperature T^* , different from the wall temperature T , the equilibrated oxygen flux is:

$$\Gamma_{O_2'} = z_{O_2'} Z_{O_2'}$$

J.C. Batty and R.E. Stickney, *Journ. Chem. Physics*, Volume 51, No. 10, (1969) p 4475



QUASI-EQUILIBRIUM TREATMENT OF BATTY & STICKNEY* (Cont.)

@ Let $i \equiv W_x O_y(g)$, and the Gibbs Energy as: $\Delta G_i(T) = \Delta H_i(T) - T\Delta S_i(T)$

@ Now, we have the following system:

$$K_i = \frac{P_i}{(P_{O_2})^{y/2}} = \exp(-\Delta G_i(T) / RT) \quad i = 1, 2, \dots, N$$

$$P_O = \sqrt{P_{O_2}} \exp(-\Delta G_O / RT)$$

$$P_{O_2'} = P_{O_2} + P_O + \sum_1^N P_i$$

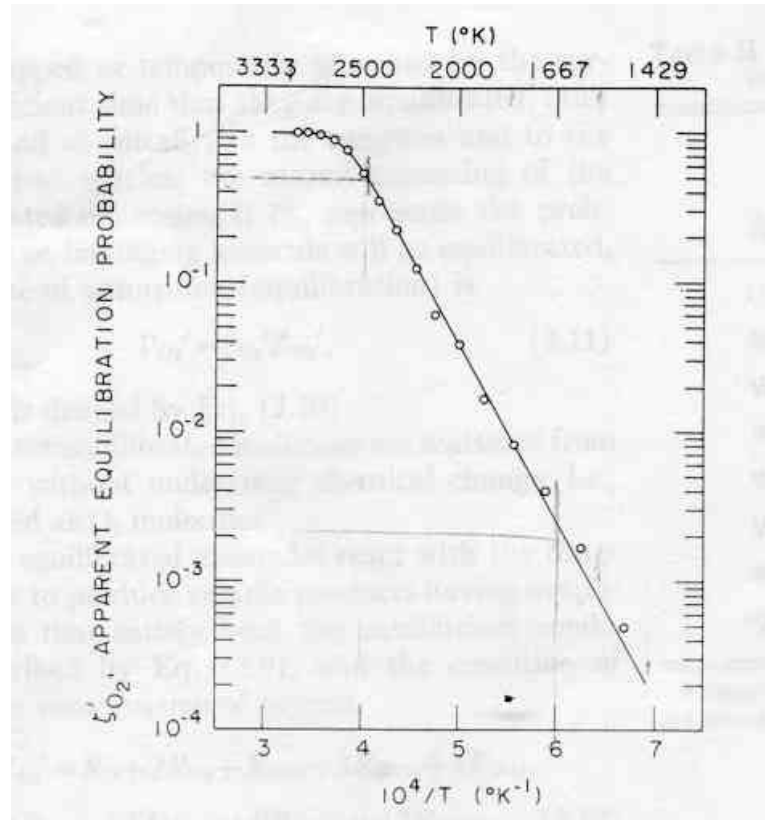
@ $P_{O_2'}$ is obtained from $G_{O_2'}$. Requires equilibration probability

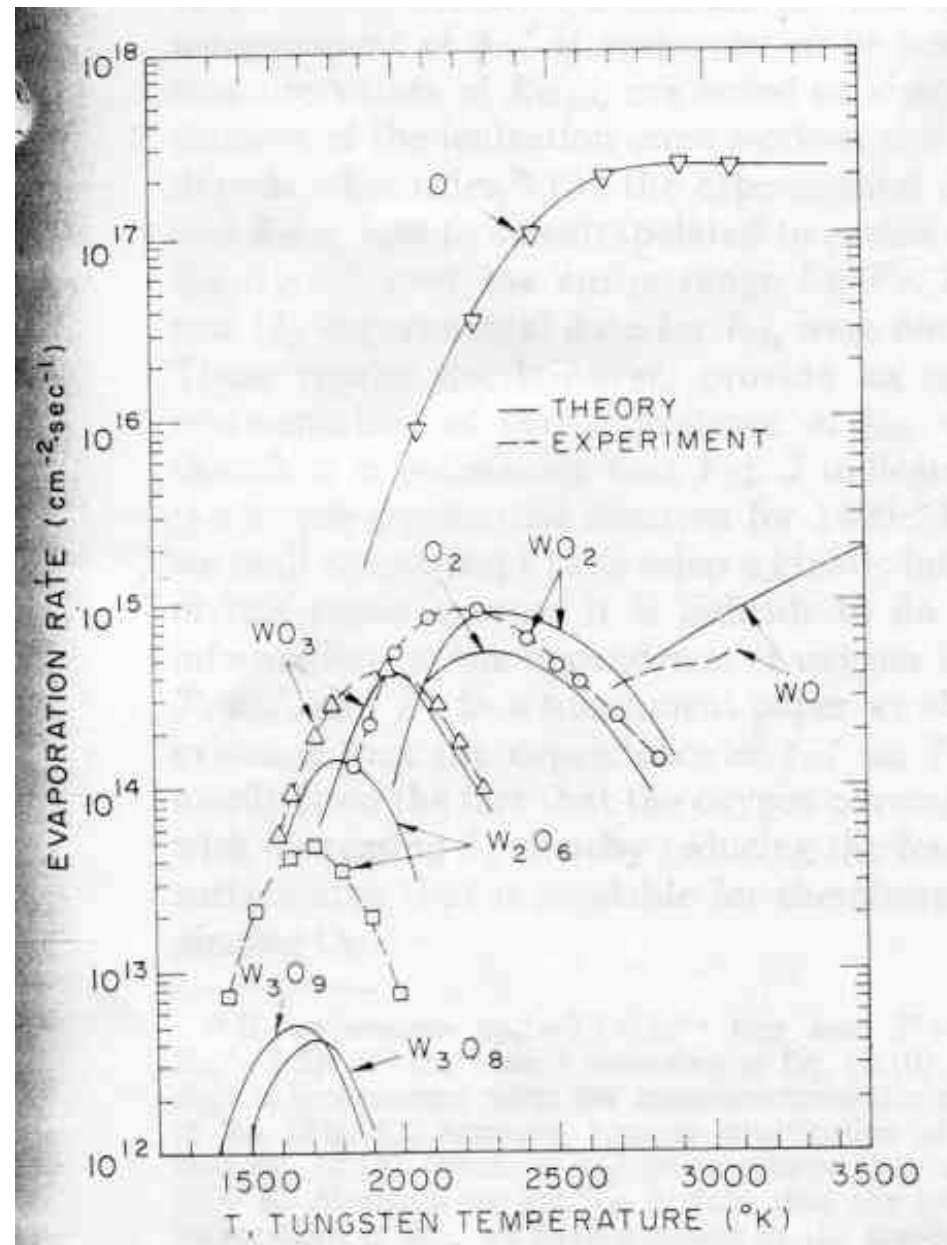


EQUILIBRATION PROBABILITY IS DETERMINED EXPERIMENTALLY

For W

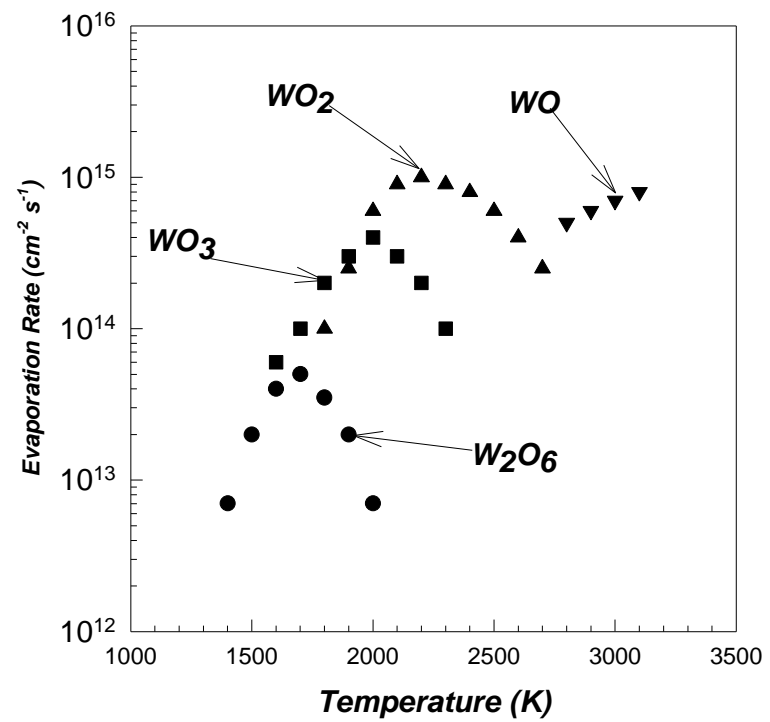
$$z_{O_2} = \exp\left[10.3498 - \frac{2.7607 \times 10^4}{T}\right], \quad T (^{\circ}\text{K})$$





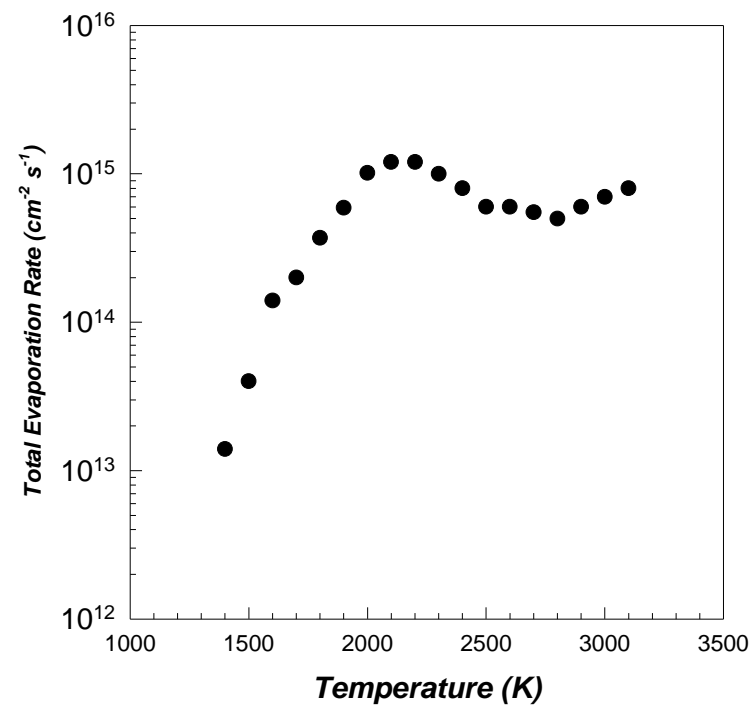


Experimental Data on W Oxidation $Z_{O_2}' = 1.2 \times 10^{17} \text{ cm}^{-2} \text{ s}^{-1}$



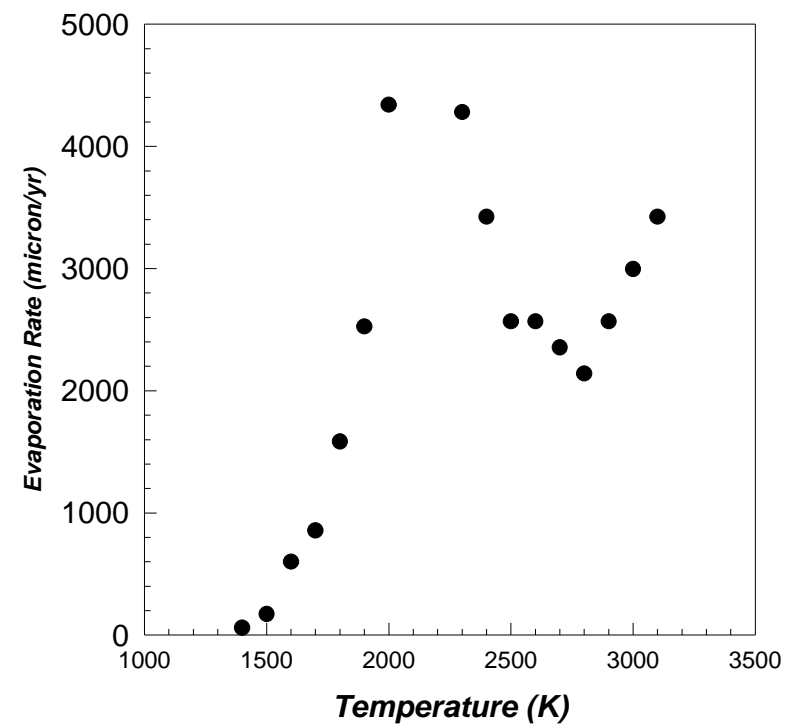


Experimental Data on W Oxidation
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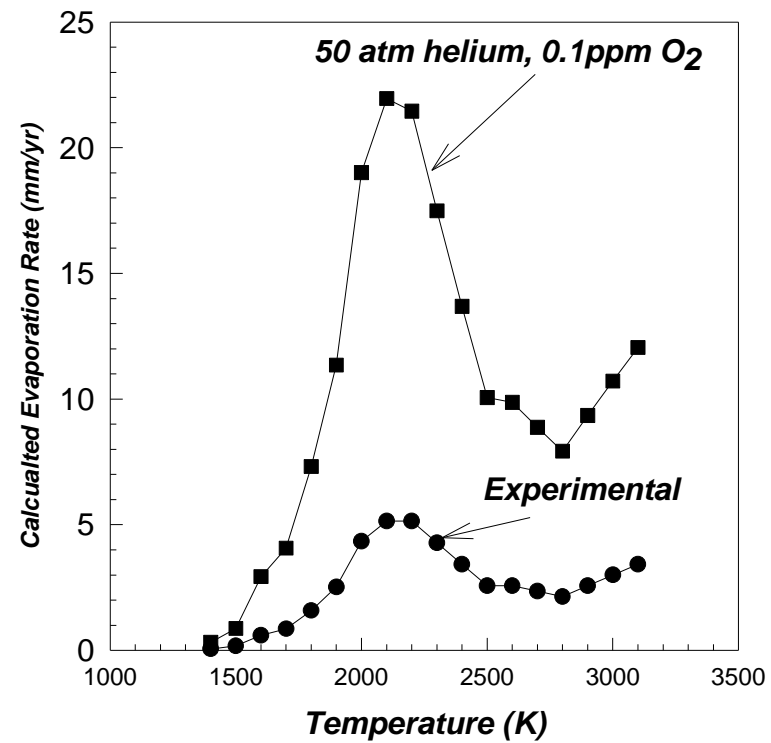


Experimental Data on W Oxidation
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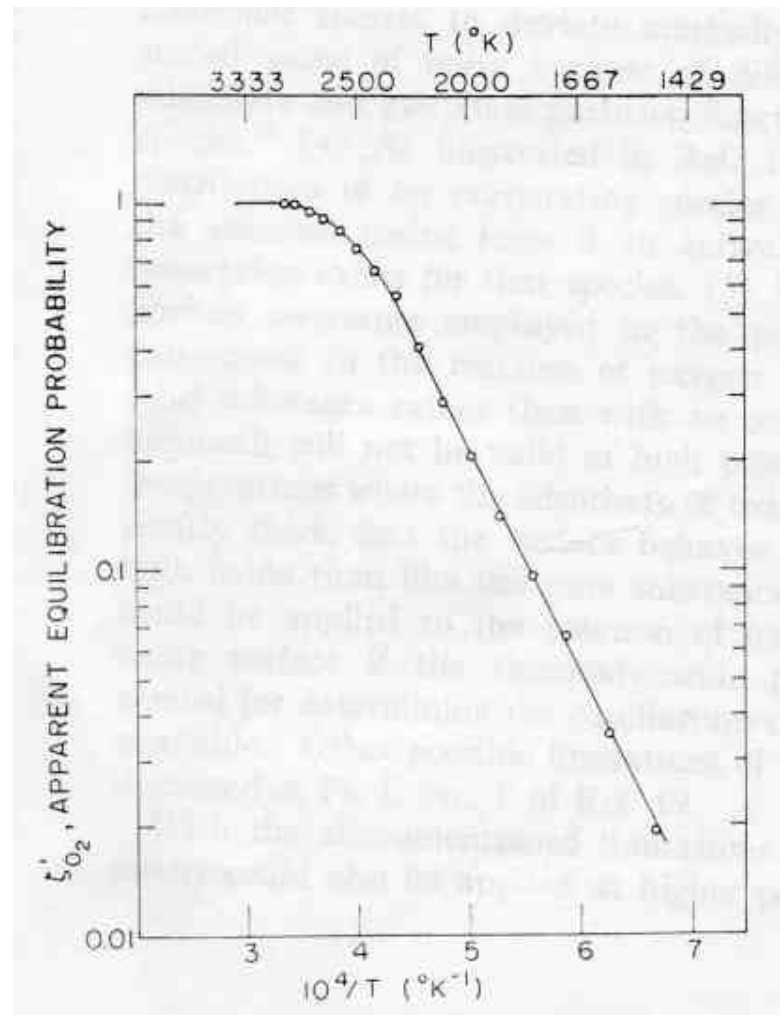


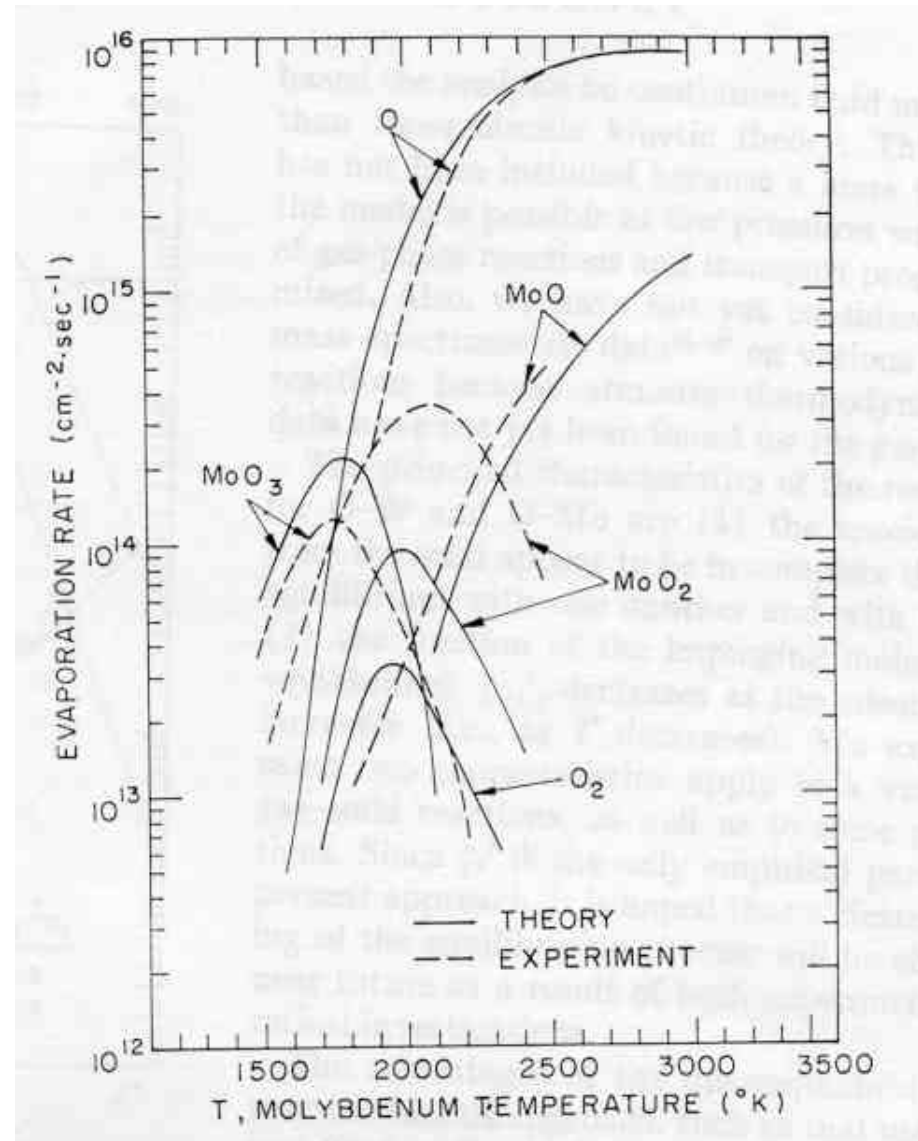
Calculated W Oxidation Rates
Experiment at $Z_{O_2}' = 1.2 \times 10^{17} \text{ cm}^{-2} \text{ s}^{-1}$





EXPERIMENTAL RESULTS FOR MOLYBDENUM







CONCLUSIONS

- (1) HIGH-TEMPERATURE OXIDATION SETS SEVERE LIMITS ON HELIUM COOLING OF REFRACTORY ALLOYS.**
- (2) FOR TUNGSTEN AND MOLYBDENUM OPERATING AT 50 ATM. HELIUM COOLANT, AT 0.1 PPM OXYGEN, THE UPPER TEMPERATURE IS ESTIMATED AT 1200- 1300 °C.**
- (3) IF HIGHER TEMPERATURES ARE BENEFICIAL TO DESIGN OBJECTIVES, THE FOLLOWING IS TO BE IMPLEMENTED:**
 - @ Reduce the oxygen impurity concentration to the ppp range.**
 - @ use oxidation-resistant coatings in the high-temperature zones.**