HIGH TEMPERATURE OXIDATION

OF TUNGSTEN AND MOLYBDENUM

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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:**

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

THERMODYNAMICS OF CHEMICAL REACTIONS

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

$$Z_{O_2} = P_{O_2}\sqrt{2p\,M_{O_2}RT}$$

@ For Tungsten, the following thermodynamic reactions take place:

$$x\,W(s)+\frac{1}{2}y\,O_2(g)\Leftrightarrow W_xO_y(g)$$

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

$$Mo(s)+\frac{1}{2}(3-a)\,O_2(g)\Leftrightarrow Mo\,O_2(g)+(1-a)\,Mo\,O_3(g)$$

FORMATION ENTHALPIES & ENTROPIES OF OXIDES

Tungsten		Molybdenum		
Species	**$\Delta Hf_{298.15}$ (kcal/g.mole)**	**Species**	**$\Delta Hf_{298.15}$ (kcal/g.mole)**	**$\Delta Sf_{298.15}$ (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_3O_8 (g)	**-408.7**	**Mo_3O_8 (g)**	-400	-118
W_3O_9 (g)	**-483.6**	**Mo_3O_9 (g)**	-463	-132
W_4O_{12} (g)	**-670.2**	**Mo_4O_{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:

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

$$\text{P}_\text{O} = \sqrt{P_{O_2}}\exp(-\Delta G_O/RT)$$

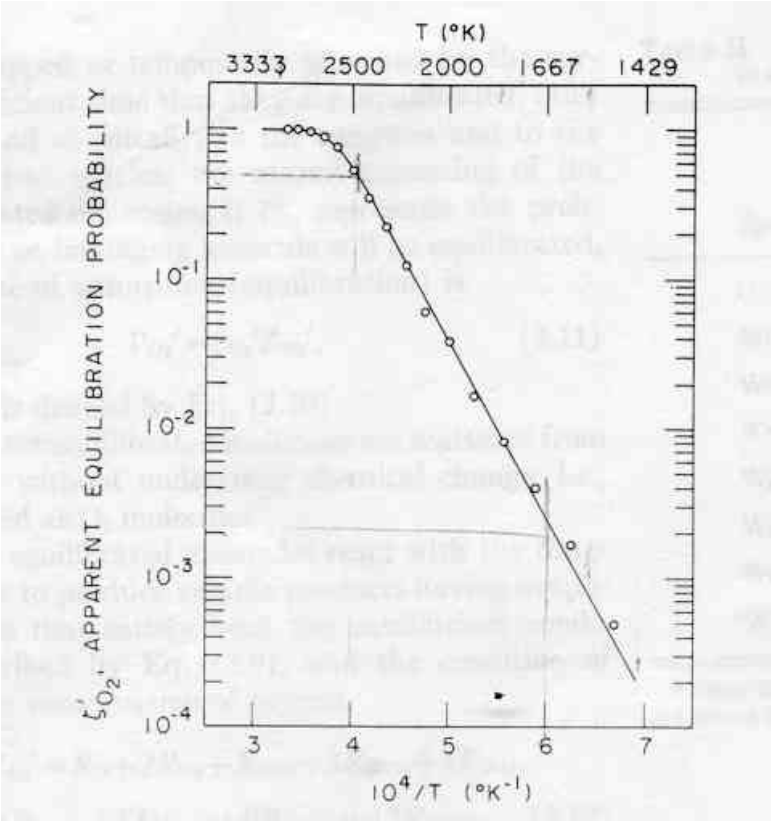
$$P_{O_2'} = P_{O_2} + P_O + \sum_1^N P_i$$

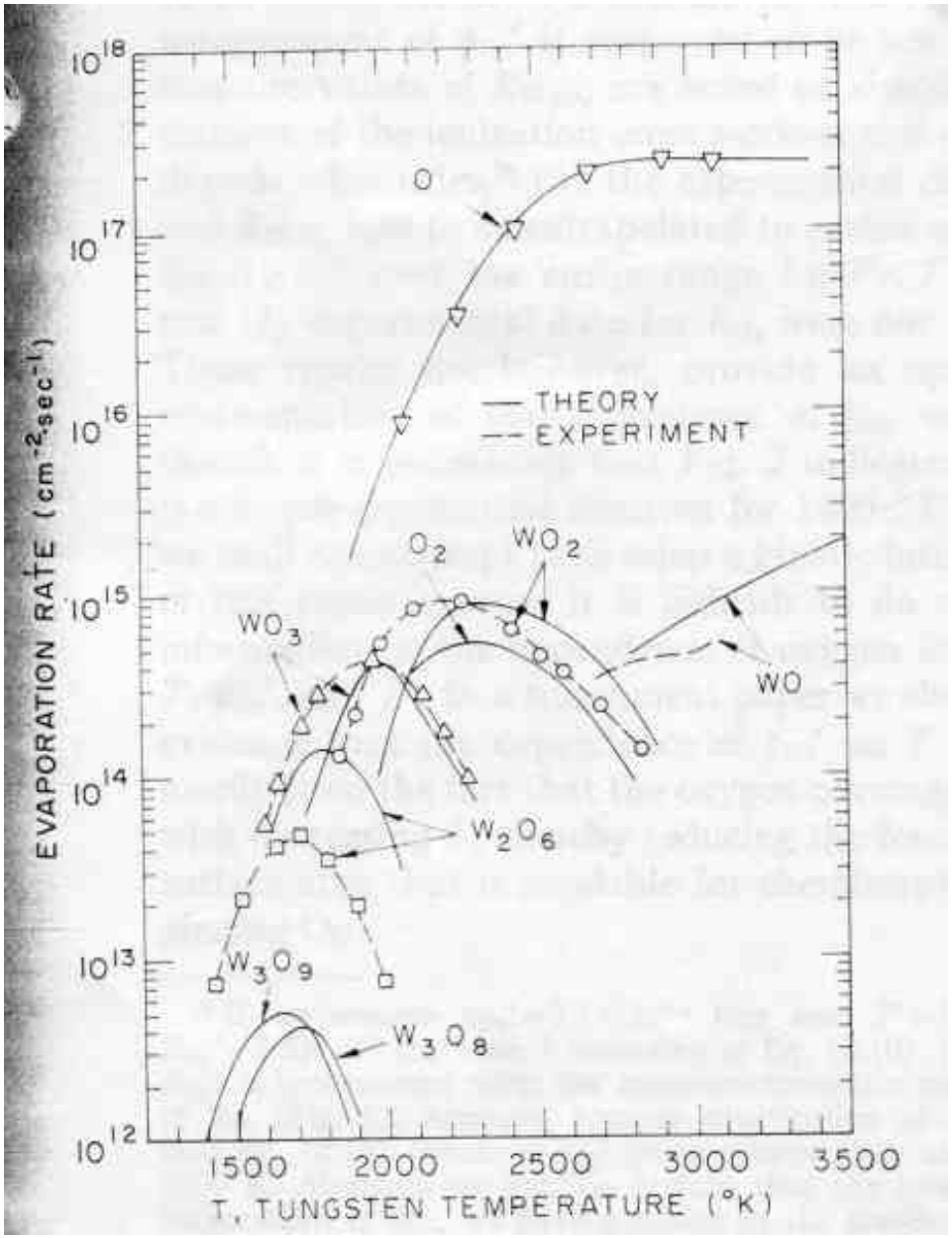
@ P_{O2}' is obtained from G_{O2}'. Requires equilibration probability

EQUILIBRATION PROBABILITY IS DETERMINED EXPERIMENTALLY

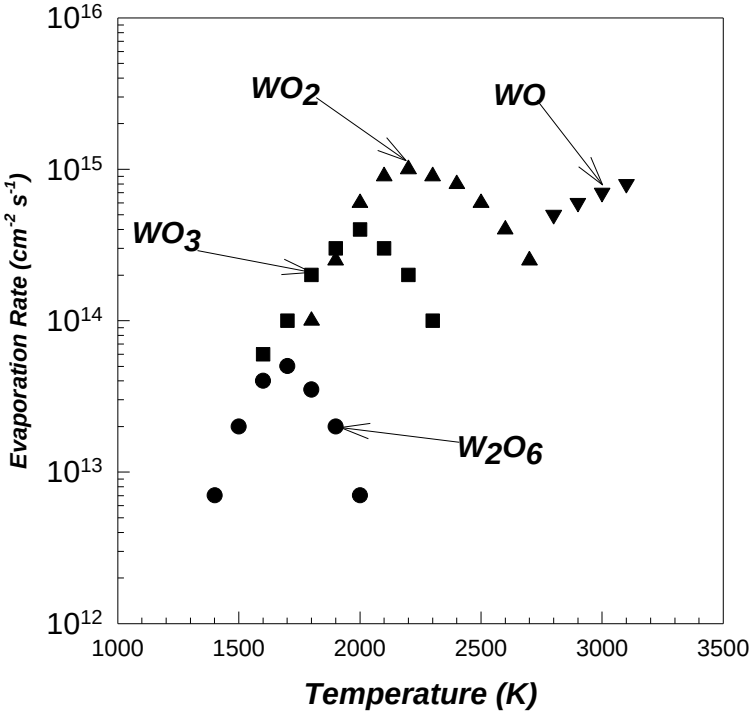
For W

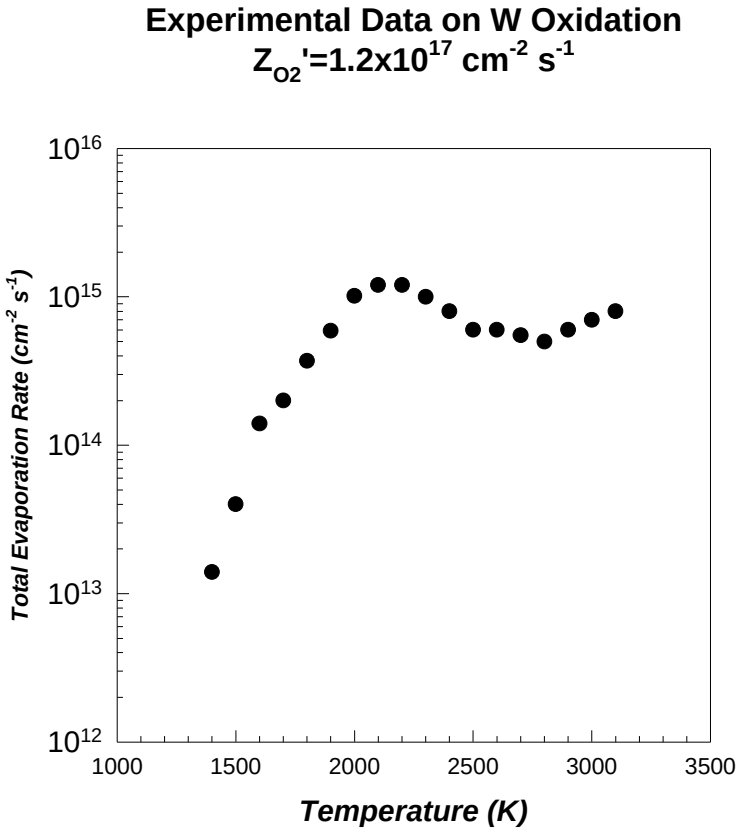
$$\zeta_{O_2} = \exp[10.3498 - \frac{2.7607 \times 10^4}{T}]$$ **, T (^{o}K)**



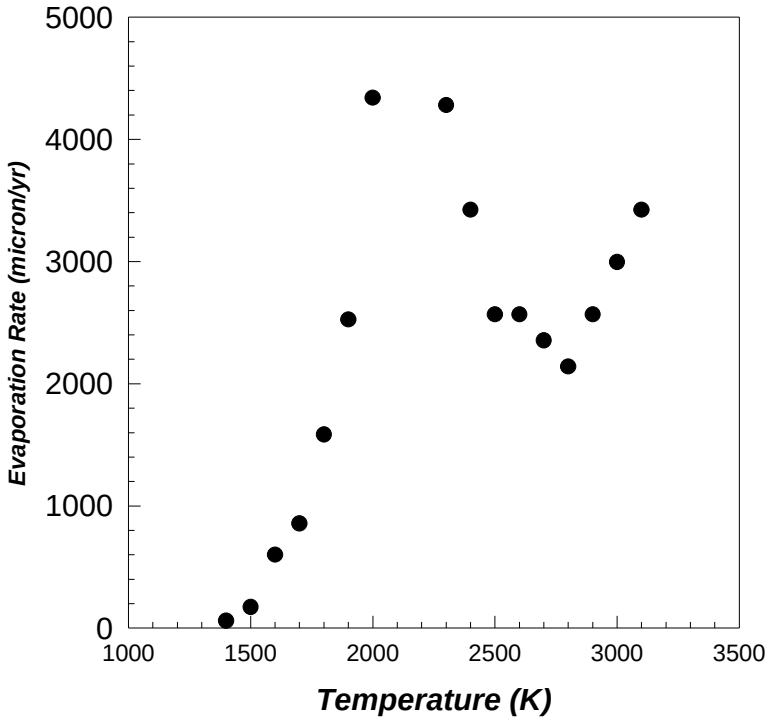

EVAPORATION RATE (cm⁻²·sec⁻¹)
10¹⁸
10¹⁷
10¹⁶
10¹⁵
10¹⁴
10¹³
10¹²
THEORY
EXPERIMENT
O
O₂
WO₂
WO₃
WO
W₂O₆
W₃O₉
W₃O₈
1500
2000
2500
3000
3500
T, TUNGSTEN TEMPERATURE (°K)

Experimental Data on W Oxidation
$Z_{O2}'=1.2x10^{17}\ cm^{-2}\ s^{-1}$

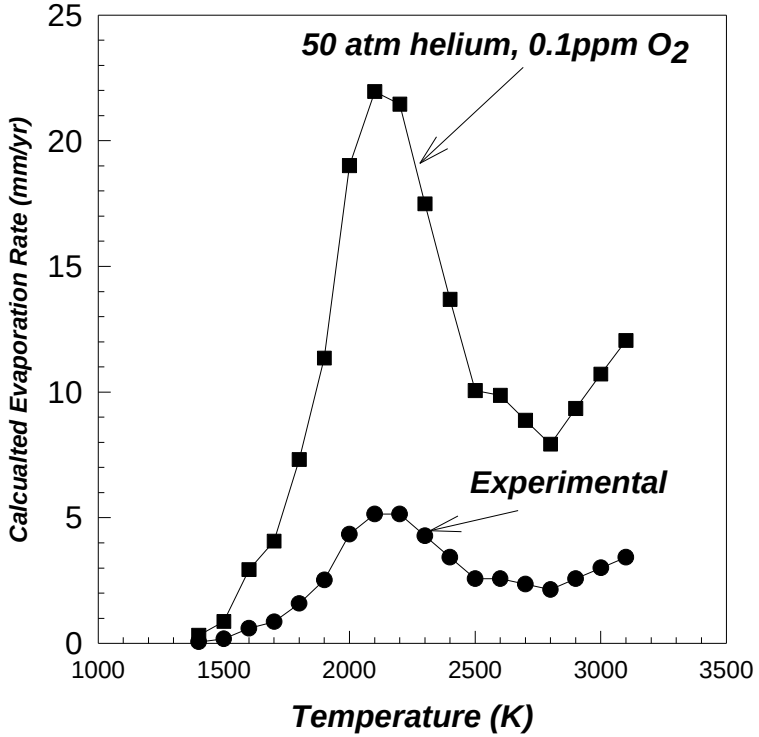



Experimental Data on W Oxidation
$Z_{O2}'=1.2x10^{17}$ cm^{-2} s^{-1}
Total Evaporation Rate (cm^{-2} s^{-1})
10^{16}
10^{15}
10^{14}
10^{13}
10^{12}
1000
1500
2000
2500
3000
3500
Temperature (K)

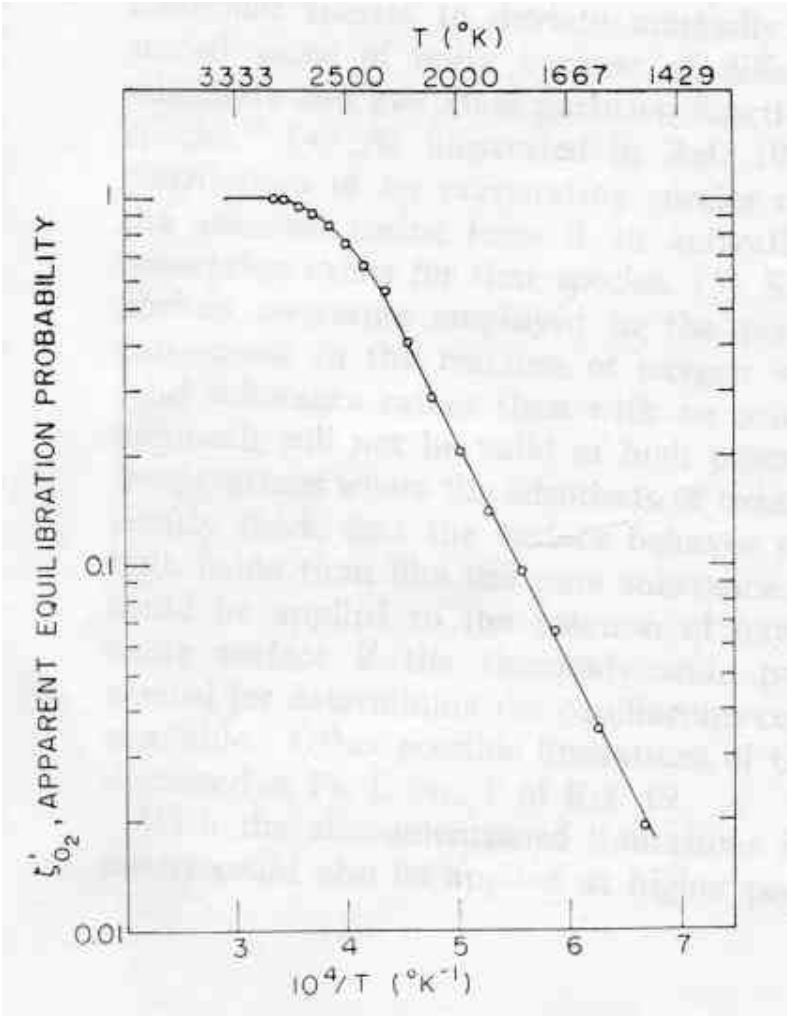
Experimental Data on W Oxidation
$Z_{O2}'=1.2x10^{17}$ cm^{-2} s^{-1}

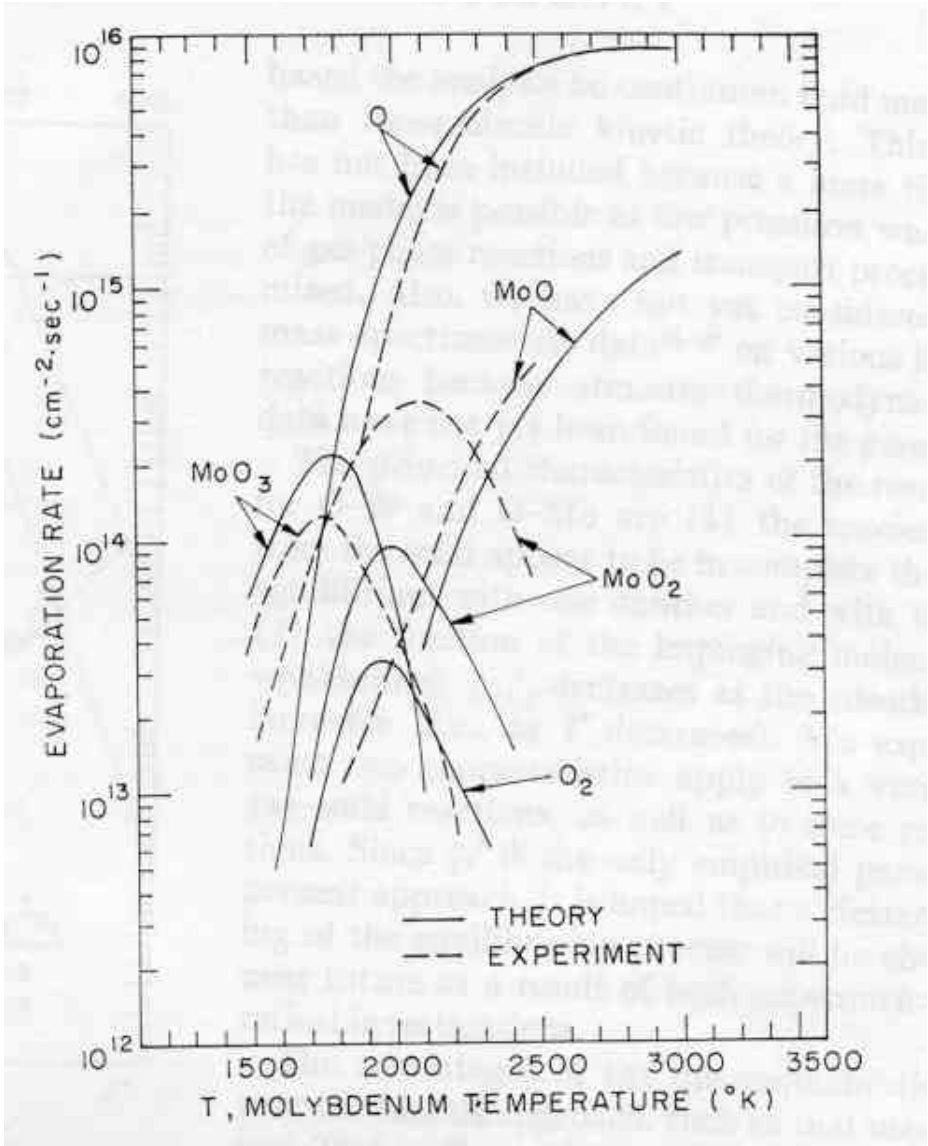


Calculated W Oxidation Rates
Experiment at $Z_{O2}'=1.2x10^{17}$ cm^{-2} s^{-1}



EXPERIMENTAL RESULTS FOR MOLYBDENUM




EVAPORATION RATE (cm⁻².sec⁻¹)
10¹⁶
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10¹²
O
MoO
MoO₃
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O₂
THEORY
EXPERIMENT
1500
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T, MOLYBDENUM TEMPERATURE (°K)

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 ^{O}C.

(3) IF HIGHER TEMPERATURES ARE BENIFICIAL 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.