OXIDATION OF TUNGSTEN AND MOLYBDENUM: THE EFFECTS OF BOUNDARY LAYER TRANSPORT

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PRESENTATION OUTLINE

(1) QUASI-EQUILIBRIUM OXIDATION OF W AND Mo.

(2) **BOUNDARY LAYER TRANSPORT MODEL.**

(3) **TEMPERATURE LIMITS FOR W.**

(4) **TEMPERATURE LIMITS FOR Mo.**

QUASI-EQUILIBRIUM TREATMENT OF HETEROGENEOUS REACTIONS

@ **SURFACE IMPINGEMENT RATE OF OXYGEN:**

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

@ **FOR OXYGEN MOLECULES AT A TEMPERATURE T*, THE EQUILIBRATED OXYGEN FLUX IS:**

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

@ **W AND Mo ARE DESCRIBED BY:**

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

W AND Mo 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_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 - KINETIC LIMITATION

@ SOLVE FOR :

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

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

$$P_{O_2'} = P_{O_2} + P_O + \sum_{1}^{N} P_i$$

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

$$Z_{M_xO_y} = P_i \sqrt{2p\, M_{M_xO_y} RT}$$

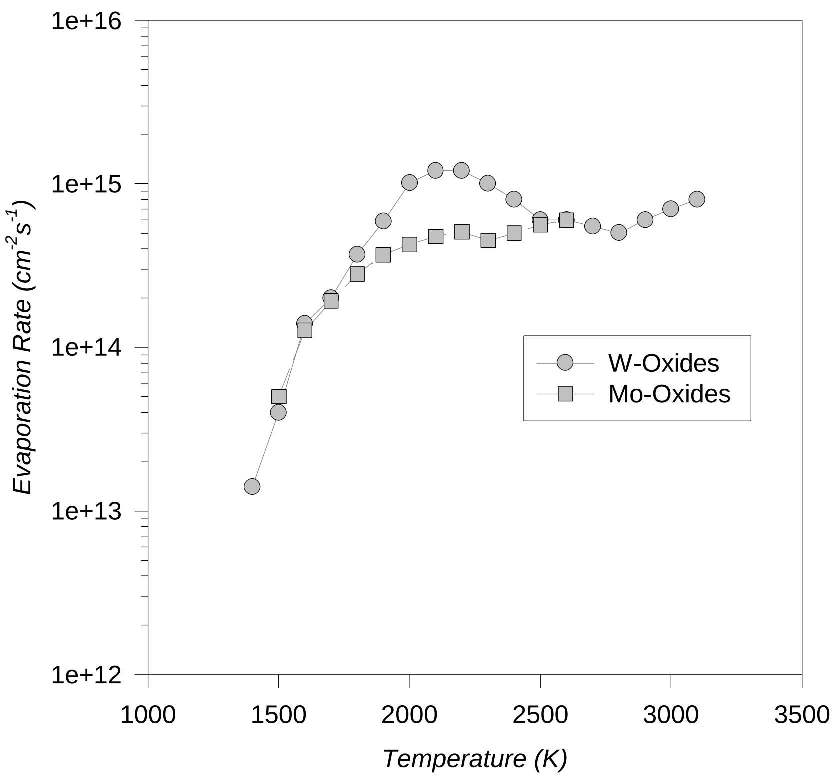
For W $\quad z_{O_2} = \exp[10.3498 - \dfrac{2.7607 \times 10^4}{T}]$ **, T (^{o}K)**

For Mo $\quad z_{O_2} = 3.2 \times 10^4 \times 10^{-1.186\times 10^4 / T}$ **, T(^{o}K)**

EXPERIMENTAL DATA FOR W and Mo AT FIXED Z

@ **TOTAL EVAPORATION RATE =** $\sum_{i=1}^{n} x.Z_{M_xO_y}$

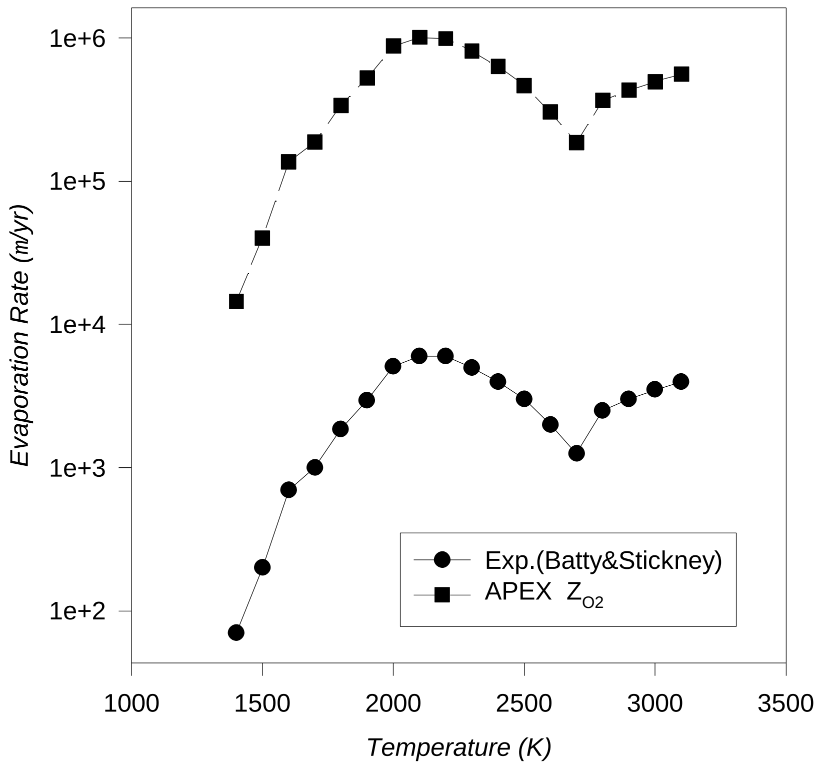
Experimental Data of W and Mo Oxidation
Z_{O2}' = 1.2×10^{17} $cm^{-2}s^{-1}$



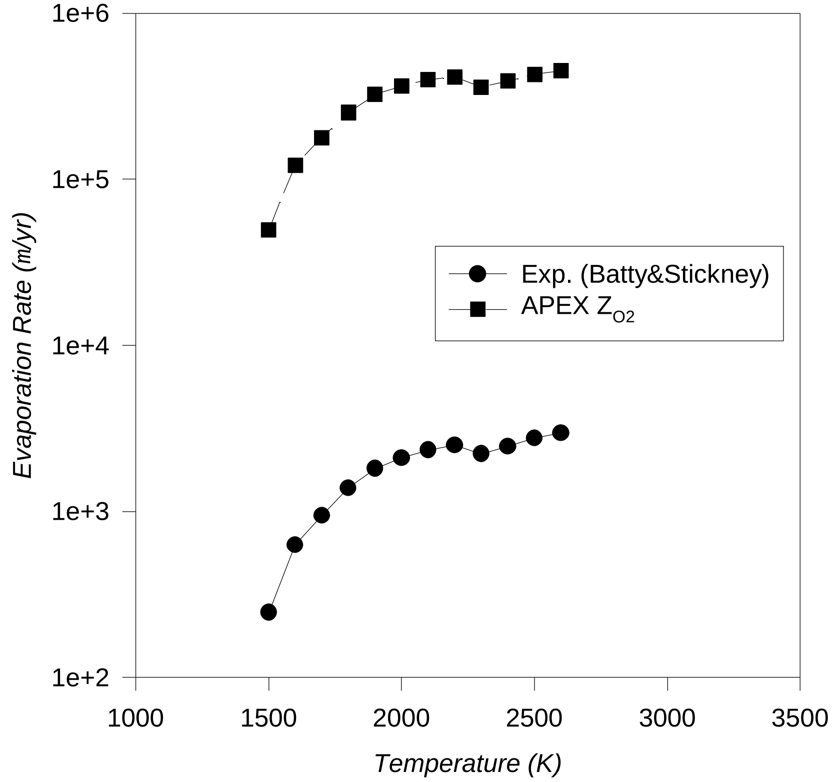
TOTAL EVAPORATION RATES OF W and Mo AT 1ppm O_2

@ TOTAL EVAPORATION RATE = $\sum_{i=1}^{n} x.Z_{M_xO_y}$

Total Evaporation Rate of Tungsten
Based on APEX O_2 Impingment Rates (1 ppm)

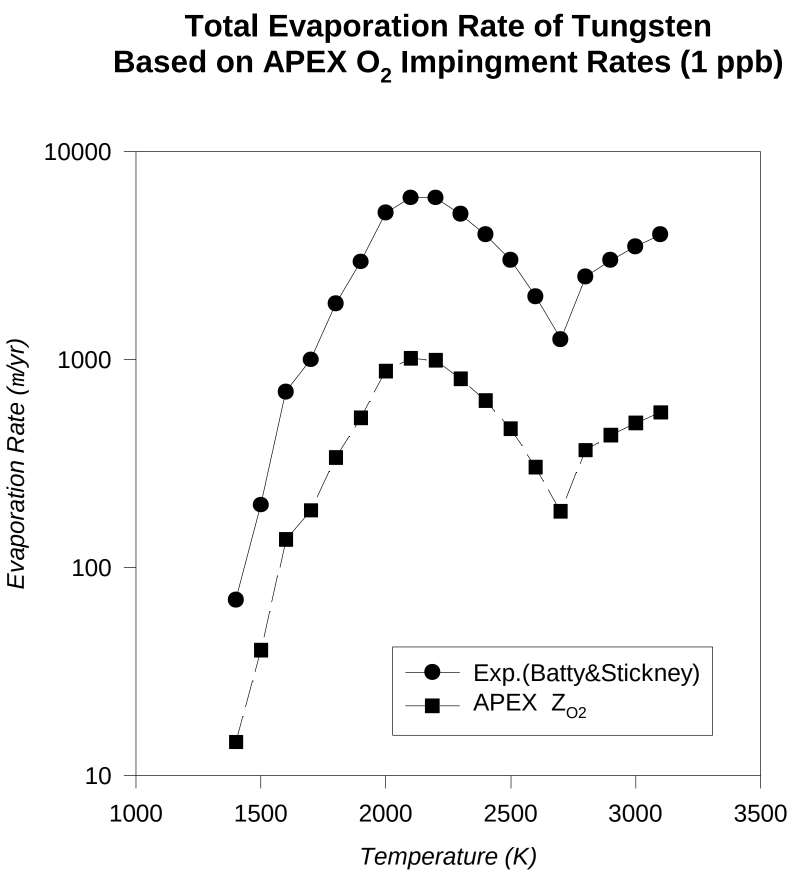


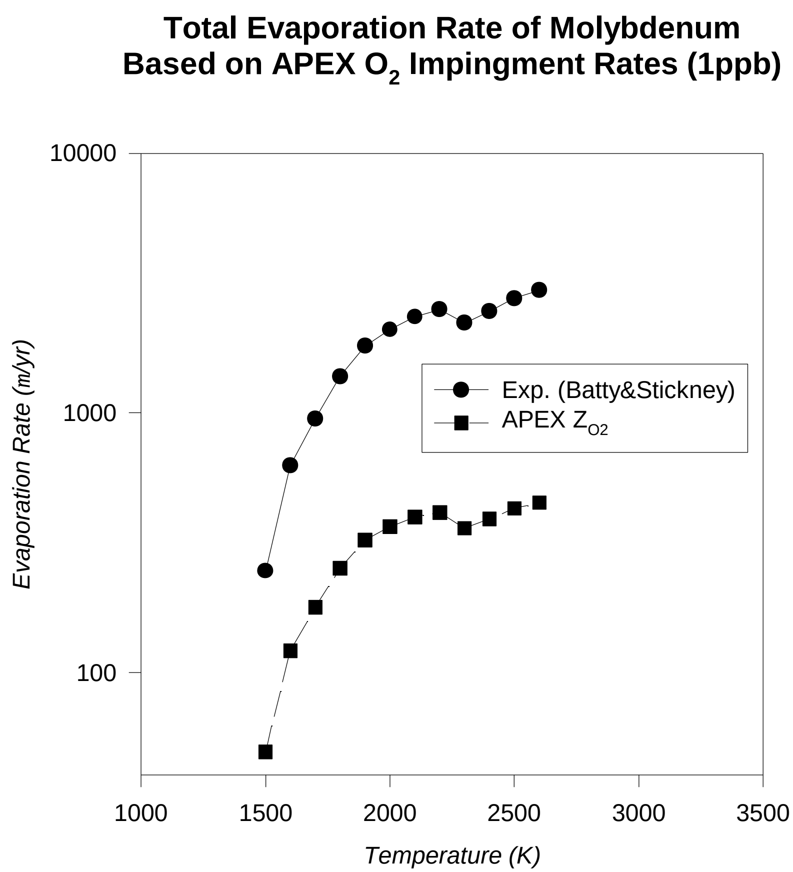
Total Evaporation Rate of Molybdenum
Based on APEX O_2 Impingment Rates (1ppm)



TOTAL EVAPORATION RATES OF W and Mo AT 1ppb O_2

@ **TOTAL EVAPORATION RATE =** $$\sum_{i=1}^{n} x.Z_{M_xO_y}$$





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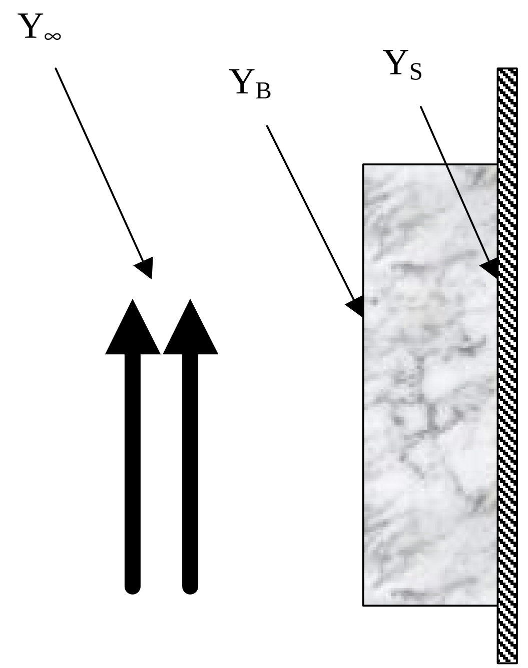
BOUNDARY LAYER TRANSPORT MODEL

@@ SURFACE KINETIC RATE

$$\frac{dX_K}{dt} = A_1\, k_K \left(Y_S - Y_B \right) = \frac{1}{R_K} \left(Y_S - Y_B \right)$$

@@ BOUNDARY DIFFUSION RATE

$$\frac{dX_D}{dt} = A_2\, k_m \left(\frac{Y_B - Y_\infty}{P_t} \right) = \frac{1}{R_B} \left(Y_B - Y_\infty \right)$$



@@ SOLVE FOR $\frac{dX_D}{dt} = \frac{dX_K}{dt}$ TO OBTAIN Y_B.

@@ FINAL EVAPORATION RATE: $$\frac{dX}{dt} = \frac{Y_S - Y_\infty}{R_K + R_B} = f \times \frac{dX_K^*}{dt}$$

@@ WHERE (f) IS A BOUNDARY LAYER FACTOR, AND $\frac{dX_K^*}{dt}$ IS THE KINETIC RATE WITHOUT THE BOUNDARY LAYER.

@@ THE BOUNDARY LAYER "RESISTANCE" IS GIVEN BY:

$$R_B \cong \frac{P_t}{r_g V St_m f_b}, \quad \text{where the Stanton \#}$$

$$St_m = 0.0296 \ \mathrm{Re}^{-0.2} \ Sc_i^{-0.4}, \quad \text{and the Schmidt \#}$$

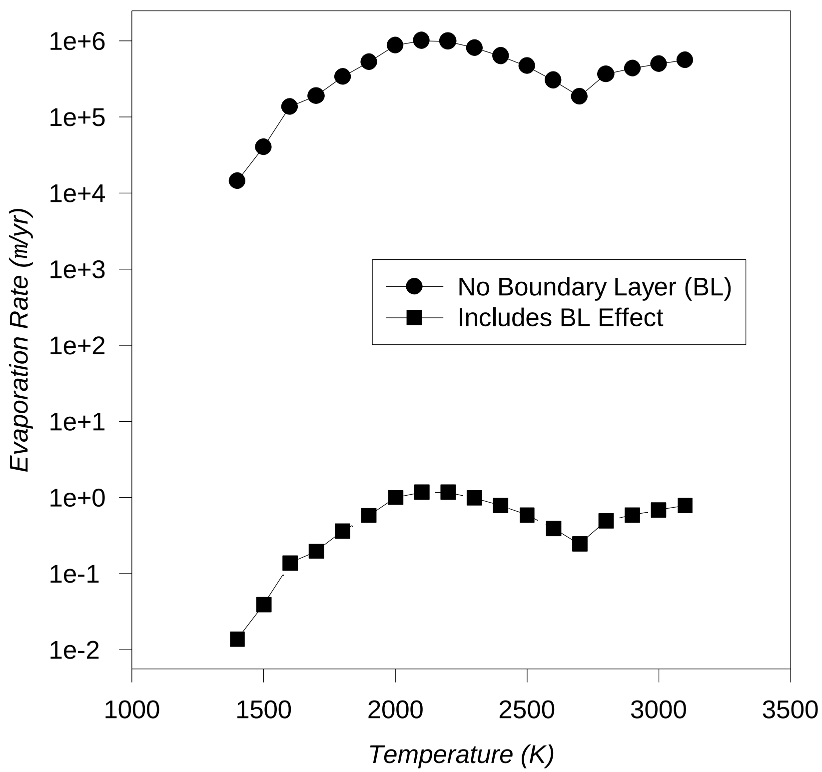
$$Sc_i = 0.145 \ M_i^{0.556} \quad \text{and } f_b \approx 1 \ \text{ is a "blowing" factor}$$

@@ AND THE KINETIC "RESISTANCE" IS GIVEN BY:

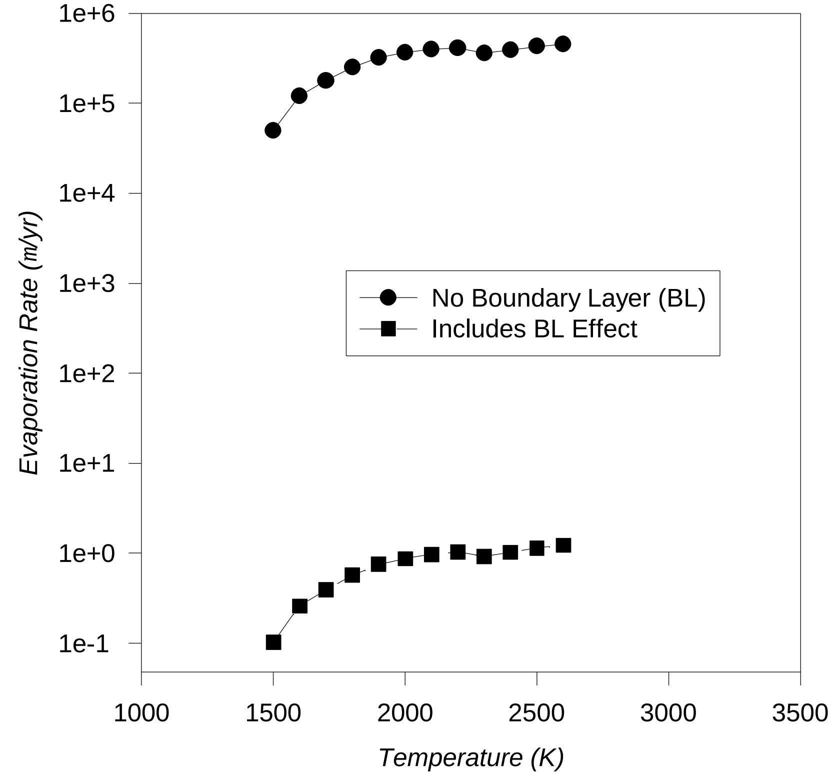
$$R_{Ki} = \sqrt{\frac{2pRT_S}{M_i}}$$

EFFECT OF BOUNDARY LAYER RESISTANCES ON EVAPORATION RATES (1ppm O_2)

Total Evaporation Rate of Tungsten
Based on APEX O_2 Impingment Rates (1 ppm)

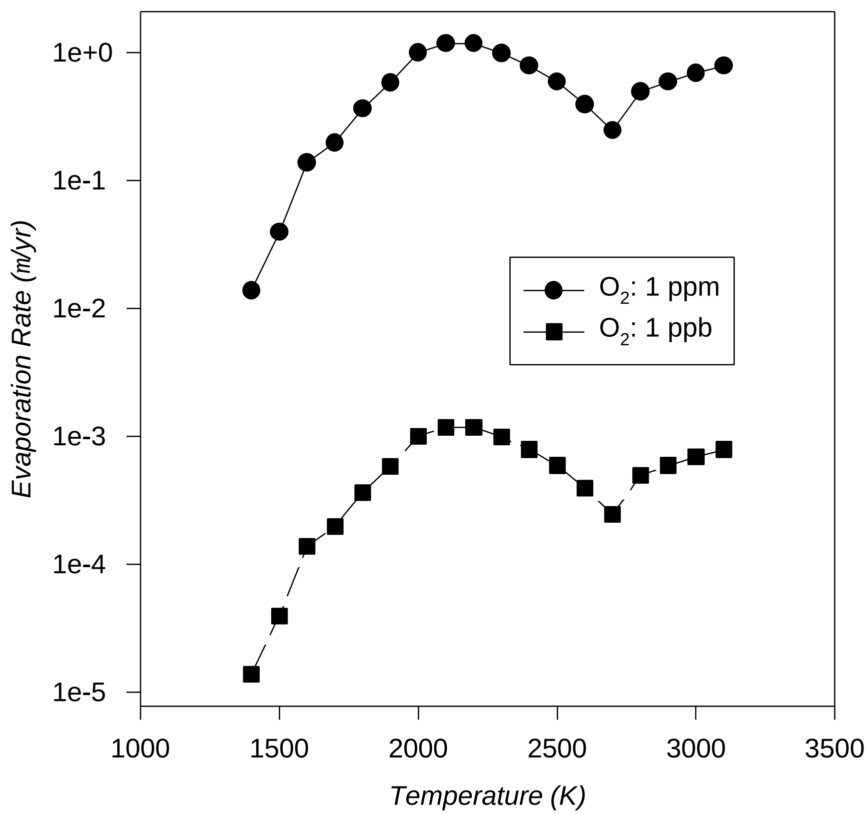


Total Evaporation Rate of Moly
Based on APEX O_2 Impingment Rates (1 ppm)

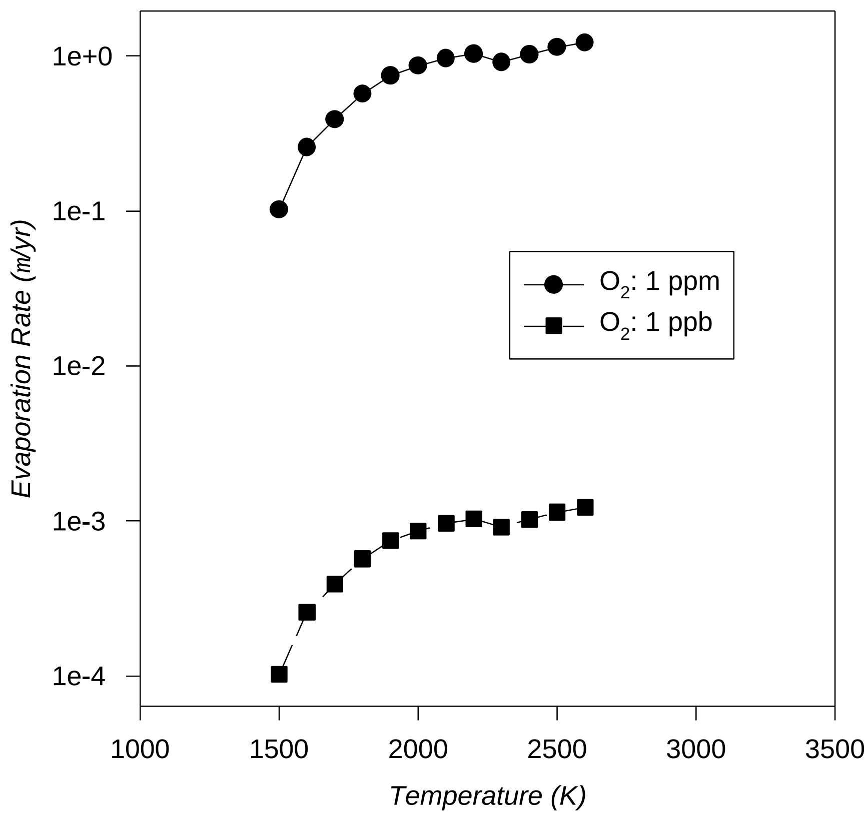


EVAPORATION RATES OF W and Mo INCLUDING BOUNDARY LAYER RESISTANCES (1ppm & 1ppb O_2)

Total Evaporation Rate of Tungsten Including the Effects of Layer Resistances at 1 ppm and 1 ppb O_2



Total Evaporation Rate of Moly Including the Effects of Layer Resistances at 1 ppm and 1 ppb O_2



CONCLUSIONS

(1) BASED ON EXPERIMENTAL DATA, THE IMPINGMENT RATE OF O_2 WAS ESTIMATED TO ESTIMATE STATIC EVAPORATION RATES.

(2) THE BOUNDARY LAYER RESISTANCE TO OXIDE PRODUCT TRANSPORT IS SIGNIFICANT AT THE HIGH HELIUM PRESSURES OF THE APEX STUDY

(3) BASED ON THE BL-EFFECT THE EVAPORATION RATE IS ~0.1 mm/yr FOR *Mo* and ~0.01 mm/yr FOR *W* at 1 ppm O_2 AT 1500^{o}C.

(4) AT 2000^{o}C THE EVAPORATION RATE IS ~1O^{-3}mm/yr FOR BOTH *Mo* and *W* at 1 ppb O_2.

(5) FOR AN OXIDATION RATE LIMIT OF 0.1 mm/yr THE OPERATING TEMPERATURE FOR *Mo* IS 1500^{o}C AND FOR *W* IT IS 1600^{o}C.