ELECTRON QUENCHANT LITERATURE

W. G. Browne, et al

General Electric Company

Prepared for:

Space and Missile Systems Organization

September 1971

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General Electric Company
Environmental Sciences Laboratory
Re-Entry and Environmental Systems Division

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13. ABSTRACT

Data on the high temperature behavior of molecules which have been previously identified as effective electron quenchants has been collected. Attention has been directed to the physical, chemical, thermodynamic and kinetic data on the oxides/acids of rhenium, molybdenum, tungsten and boron. The electron affinities of these acids, ~100 kcal/gmol, are the highest values of any gaseous species in the literature. An important mode of electron capture involves the process of dissociative-attachment. The existence of two negative ions in H/O/metal systems appears to be common.

The vapor pressure of HBO_2, n.b.p. 1390°K, is too low to volatilize sufficient boric acid into a reentry boundary layer at high altitudes. It is suggested that more volatile boron-containing materials, such as cyclic B-N-H compounds, can be incorporated as an integral part of the structure of a low temperature ablator by a process of co-polymerization.

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5. Rhenium compounds						
6. Molybdenum compounds						
7. Tungsten compounds						
8. Boron compounds						

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FOREWORD

This report summarizes the work performed on the Strategic Re-Entry Technology (STREET-G) Study, Task 4.10 conducted from January 1971 to September 1971 and is prepared under Contract No. F04701-70-C-0179. The prime contractor is the General Electric Company, Re-Entry and Environmental Systems Division, Philadelphia, Pennsylvania. This work was monitored by RSSE, Space and Missile Systems Organization, Los Angeles, California.

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I. INTRODUCTION

The objective of this work was to characterize the behavior of molecules which have been identified as effective wake electron quenchants. A wake quench candidate is deemed to be effective if it efficiently attaches free electrons to produce negative ions when the candidate is added in small quantities to a high temperature plasma containing heat shield ablation products. The interest in wake electron quenchants stems from their use in applications related to the obfuscation of reentry observables.

In order to attach rapidly free electrons in a reentry ablation environment a quench should possess all of the following attributes:

1. Large electron affinity,
2. Good thermal stability,
3. Resistance to chemical attack by H, O and OH,
4. Large electron attachment cross-section,
5. Be compatible with heat shield material with regard thermal, mechanical, ablative and V & H characteristics.

Experimental electron suppression studies in atmospheric H_2/air and H_2/N_2O flames in the Meker burner-microwave cavity apparatus by Dr. R. Carabetta have identified the oxides/acids of rhenium, molybdenum, tungsten, boron, chromium, vanadium, titanium and iron as effectively lowering the free electron concentration by the processes of either electron attachment and/or compound formation.

II. LITERATURE REVIEW

Chemical abstracts has been searched from 1965 to 1971 for physical, chemical, thermodynamic and kinetic data on the oxides/acids/ions/fragments containing Re, Mo, W, B, Cr, V, Ti and Fe. The list of electron affinities for the various quenchants compiled from the chemical literature is cited in Table I. Several features are noteworthy. First, the electron affinities of the acids, $\sim$ 100 kcal (4.3 ev), are the highest values of any gaseous species in the literature. Second, the existence of two negative ions in an elemental system appears to be common. Electron affinities for H_2MoO_4 and H_2WO_4 reported by Dr. W. Miller, Aerochem, are dependent upon an assumed bond dissociation energy for $H\text{-}HMoO_4$ and $H\text{-}HWO_4$ of 110 kcal/gmol. The identification of the negative ions in the chromium and vanadium systems is tentative at this time. The bond strengths of the acids and alkali salts of quenchants are listed in Table II.

The equilibrium constants Keq, where

$$A + e^- \rightleftharpoons B^- + C \qquad (1)$$

$$Keq = \frac{[B^-][C]}{[A][e^-]} \qquad (2)$$

and [ ] represents the concentration of the individual species, for electron attachment and alkali salt formation are listed in Table III. Dissociative attachment and charge transfer are the modes for electron capture. The mechanism for rhenium oxide quenching is thought to be as follows:

$$Re_2O_7 + H_2O \longrightarrow 2HReO_4 \qquad (3)$$

$$HReO_4 + e^- \longrightarrow H + ReO_4^- \qquad (4)$$

It has been suggested by Zavitsanos[1] that dissociative attachment to Re_2O_7 occurs at low electron energies,

$$Re_2O_7 + e^- \longrightarrow ReO_3 + ReO_4^- \qquad (5)$$

At 2800°K and one atmosphere pressure in a fuel lean (R = 0.635) H_2/N_2O flame the electron suppression effectiveness (by either electron attachment and/or compound formation) for the candidates on a per atom basis was reported by Dr. Carabetta to be in the progression Re > Mo > W > B. On a mass basis, the greatest electron reduction occurred with boron compounds. Particular attention has been focused on compounds of Re, Mo, W and B in reviewing the chemical literature.

Rhenium Compounds

The pertinent species in the H/Re/O system appear to include the following molecules: $HReO_4$, ReO_4^-, Re_2O_7, ReO_4, ReO_2, ReO_3, and ReO. The vapor pressures of $HReO_4$, Re_2O_7, ReO_3, and ReO_2 are shown in Figure 1.[2-4] The normal boiling point of Re_2O_7 is ~635°K. Skinner[5] has recently studied the major vapor species present in the Re-O system using Knudsen cell-mass spectrometry. The sublimation of $Re_2O_{7(s)}$ yields Re_2O_7 according to the vapor pressure relation $\log P_{Re_2O_7} = -(7.437 \pm 0.081)\frac{1000}{T} + (12.350 \pm 0.209)$ over the temperature range 327-463°K where the pressure is in atmospheres. Mass spectrometry of the vapors from the Re-ZnO reaction revealed evidence of ReO_3 and Re_2O_6. Measurements as a function of temperature yielded values for the enthalpies of formation at 298°K of ReO_3 and Re_2O_6 of -67.0 ± 3.5 and -209 ± 20 kcal/gmole, respectively. Similar MgO-Re measurements permitted upper limits to the dissociation energies of ReO and ReO_2 to be established. At 1980°K the following values pertain: ReO_2 $\Delta H_f^\circ > -5.5 \pm 5.0$ kcal/gmol and Re O $\Delta H_f^\circ > 51.8 \pm 5.0$ kcal/gmol. For ReC, the upper dissociation limit is 155 kcal/gmole, which is higher than the average bond energy of ReO_3, 144 kcal/bond.

Brewer and Rosenblatt[6] estimated the free energy function from 298-3000°K for ReO_2. They evaluated the electronic partition function, where possible, by calculating the electronic partition function for the Re^{4+} ion or, lacking this, to calculate the electronic partition function for an isoelectronic ion. The free energy function of ReO as a function of temperature has also been estimated by Brewer and Rosenblatt[7]. The electron partition function of the gaseous diatomic oxide was taken to be the same as the electronic partition function of the isoelectronic ion W^+ as calculated from electronic levels listed by Moore[8].

King, et al[9]. reported the heats of formation at 298°K for $ReO_{2(s)}$, $ReO_{3(s)}$ and $Re_2O_{7(s)}$ as -107.3 ± 0.8, -140.8 ± 0.9 and -301.9 ± 1.8 kcal/gmole respectively. Kazenas, et al[10], measured mass spectrometrically the vapor phases above $ReO_{3(s)}$ at 620°K and $ReO_{2(s)}$ at 1030°K. They identified the species Re_2O_7, ReO_3 and $HReO_4$ (ostensibly formed from water vapor). Foster[11] has measured the free energy of formation of $ReO_{2(s)}$ from 950°-1100°K. The entropy of ReO_4^- has been calculated by Krestov[12] over a wide range of temperature. Yatsimirskii's rule is invoked, "the entropy of gaseous species with the same steric configuration and the same number of electrons but differing from one another by their charge is approximately the same (to within 0.5 e.v.)". Consequently, the entropy of ReO_4^- should be similar to OsO_4. Raman spectra and force constants for OsO_4 have been reported recently[13]. McDowell and Goldblatt[14] have computed thermal function for OsO_4 from 273-600°K. Semenov and Skolkova[15] in a mass spectrometric study of the Re-O system at 1300-1800°K report ΔH_f° (1500°K) of ReO = -3 ± 0.7 kcal/mole. In the

reaction of ReO_3 and Re_2O_7 with steam at 370-700°K $HReO_4$ molecules were observed in the gas phase.

Infra-red and Raman spectra for Na $ReO_{4(s)}$[16,18] $HReO_4$[17] (crystalline), Re_2O_7[18] have been measured. For $HReO_4$ crystalline

(A) 999 & 990 cm^{-1}

(A) 996 & 955 cm^{-1}

(E) 905 & 901 cm^{-1}

$HOReO_3$ has C_{3v} symmetry. In Re_2O_7 the arrangement appears to be $O_3Re\text{-}O\text{-}ReO_3$ with the Re-O-Re stretch frequencies being 870 & 690 cm^{-1}. All alkali perrhenates have broadbands at 900 cm^{-1} due probably to monomers and dimers. Drowart, et al[19] have reported a thermochemical study of the vaporization of sodium perrhenate using a mass spectrometer. The vapor contains comparable amounts of monomer and dimer molecules.

An interesting organo-metallic compound containing rhenium has been synthesized by Sinitsyn, et al[20] by extraction of $HReO_4$ with tri-n-octylamine. Tri-n-octylammonium perrhenate is a colorless, viscous product insoluble in water but quite soluble in benzene, alcohol and acetone. It decomposed exothermically, beginning at 310°C; first eliminating 3 octyl radicals, second, splitting off ammonia. This compound may have value for passive quench applications where a water insoluble, but organic soluble, rhenium compound is desired. Conceivably, it could be incorporated as an integral part of the heat shield by the process of copolymerization with a low temperature ablator.

Molybdenum Compounds

Considerable thermochemical data[21] is available on molybdenum oxides/acids. The saturated vapor of solid MoO_3, consists of Mo_3O_9, Mo_4O_{12} and Mo_5O_{15} molecules. The partial pressures have been determined in the temperature range 800°-1000°K

by Kazenas and Tsvetkov[22]. These data are shown in Table IV. The formative equilibrium for molybdic acid is as follows:

$$MoO_3(c) + H_2O \rightleftarrows H_2MoO_4 \qquad (6)$$

The vapor pressure of H_2MoO_4 is shown as a function of temperature in Figure 2. The original work on the bond strength of MoO, MoO_2, MoO_3 and the oxidation characteristics of Mo were reported by Drowart, et al[23] and Berkowitz-Mattuck, et al[24]. Porter[25] has measured the vapor phase in equilibrium with Na_2MoO_4 by the mass spectrometry - Knudsen effusion technique in the temperature range 1200-1800°K.

Tungsten Compounds

The JANAF tables[21] have a rather complete thermochemical description of the species W, WO, WO_2, WO_3, $(WO_3)_2$, $(WO_3)_3$, W_3O_8, $(WO_3)_4$ and H_2WO_4. The vapor pressures of WO_3, $(WO_3)_n$ where n is 2-4, and H_2WO_4 are shown in Figure 3. We have performed vapor composition calculations at 10^{-2} and 10^{-4} atmospheres for the WO_3 system. These computations at various temperatures are presented in Table V. The prevalence of the dimer, trimer and tetramer at high temperatures is characteristic of the W-O and Mo-O systems as noted previously[26,27]. Porter[25] has examined the thermochemical behavior of Na_2WO_4 at 1200-1800°K.

Boron Compounds

Under the impetus of the high energy fuels program in the 1950's the neutral thermochemistry of species in the B-H-O system has been investigated thoroughly. The JANAF tables[21] contain a complete thermochemical description of the following gaseous boron-containing species: B, BO, B_2O, BO_2, B_2O_3, HBO_2, H_3BO_3. Finch and Gardner[28] have recently reviewed the status of the thermochemistry of boron compounds.

Measurements in flame system by Jensen[29,30] reveal that the two significant negative ions in H-B-O mixture are BO_2^- and BO^-. Ostensibly, the important negative ion reactions include the following:

$$B_2O_3 + H_2O \rightleftharpoons 2HBO_2 \quad (7)$$

$$HBO_2 + e^- \rightleftharpoons H + BO_2^- \quad (8)$$

$$HBO_2 + e^- \rightleftharpoons OH + BO^- \quad (9)$$

$$BO_2^- + H \rightleftharpoons OH + BO^- \quad (10)$$

$$BO_2^- + O \rightleftharpoons O_2 + BO^-. \quad (11)$$

Thermodynamic properties have been generated for BO^- using $\Delta H_{f_o}^o$ = -58 kcal/gmole, D(B-O) = 215 kcal/gmol; $^1\Sigma_g^+$ ground state; Be = 1.85 cm^{-1}; α_e = 0.017 cm^{-1}; ω_e = 2000 cm^{-1}; $\omega_e x_e$ = 13.

Equilibrium composition computations have been performed for a boron quenchant in the presence of ablation products. The conditions examined and the conclusions drawn are shown in Table VI. In examining the probable reactions involving the important boron-containing species HBO_2, BO_2, BO and B we posit the mechanism cited in Table VII.

Figure 4 depicts the vapor pressure of HBO_2 and B_2O_3 as a function of temperature. It is noteworthy that the vapor pressure of HBO_2, normal boiling point of 1390°K, is too low to vaporize sufficient boric acid into the boundary layer at high altitudes. A survey of more volatile boron-containing compounds reveals that cyclic B-N-H compounds appear to be attractive, see Table VIII.

Conceivably, an organically substituted borazine can be incorporated as an integral part of the structure of a low-temperature ablator, such as epoxy, by a process of copolymerization starting with a halogenated borazine.

Seshadri et al[31] have examined spectroscopically the structure of sodium metaborate. The propensity to form $NaBO_2$ in sodium-contaminated systems is quite pronounced since $D(Na-BO_2)$ is 114 kcal/gmol.

Zavitsanos' has reported an attachment cross section for HBO_2 (reaction 8) of 3×10^{-17} cm^2. Combining the cross section with the mean thermal speed of the electron yields a rate coefficient $k_8 = 3.7 \times 10^{14}$ cm^3/gmol sec at 1373°K.

TABLE I

ELECTRON AFFINITIES

Ion Formed	Electron Affinity kcal/gmol	Technique	Reference
BO_2^-	94 98	ESP, microwave mass spect.	2 3
BO^-	58	mass spect.	3
$HMoO_4^-$	(98)	mass spect., ESP	4
MoO_3^-	60	mass spect., ESP	4
HWO_4^-	(96)	mass spect., ESP	1
WO_3^-	73	mass spect., ESP	1
$HCrO_3^-$	?	mass spect., ESP	1
CrO_2^-	?	mass spect., ESP	1
$H_2VO_4^-$	?	mass spect., ESP	1
HVO_3^-	?	mass spect., ESP	1

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5. JANAF Thermochemical Tables.

TABLE II

BOND STRENGTHS

Bond	Dissociation Energy (0°K) kcal/gmol	Reference
$Na-BO_2$	114	5
$H-BO_2$	117	5
$K-BO_2$	114	2
$K-HMoO_4$	121	4
$H-HMoO_4$	110	4

TABLE III

EQUILIBRIUM CONSTANTS

Reaction	K(eq)
$HBO_2 + e^- = H + BO_2^-$	1500 exp (-10,000/T)
$H_2MoO_4 + e^- = H + HMoO_4^-$	24 exp (500/T)
$H_2WO_4 + e^- = H + HWO_4^-$	25 exp (1300/T)
$K + HBO_2 = H + KBO_2$	37 exp (-2500/T)
$K + H_2MoO_4 = H + KHMoO_4$	3.5 exp (3500/T)
$K + H_2WO_4 = H + KHWO_4$	4.0 exp (2900/T)

	$K_{(2000^\circ K)}$
$H_2CrO_3 + e^- = HCrO_3^- + H$	2.0
$H_3VO_4 + e^- = H_2VO_4^- + H$	1.8
$H + H_2VO_4^- = HVO_3^- + H_2O$	50
$H + HCrO_3^- = CrO_2^- + H_2O$	10
$H + HWO_4^- = WO_3^- + H_2O$	15
$H + HMoO_4^- = MoO_3^- + H_2O$	150

TABLE IV

VAPOR PRESSURE OF $MoO_{3(s)}$

$800^{\circ} < T < 1000^{\circ}K$

$$\text{LOG P } (Mo_3O_9) = \frac{14900}{T} - 14.39 \text{ MM HG}$$

$$\text{LOG P } (Mo_4O_{12}) = \frac{17300}{T} - 16.88 \text{ MM HG}$$

$$\text{LOG P } (Mo_5O_{15}) = \frac{20240}{T} - 19.47 \text{ MM HG}$$

SATURATED VAPOR COMPOSITION, %

T, °K	Mo_3O_9	Mo_4O_{12}	Mo_5O_{15}
800	75.5	23.2	1.3
850	65.5	30.0	4.5
900	54.5	37.6	7.9
950	45.7	42.5	11.8
1000	36.0	44.5	19.5

TABLE V

VAPOR COMPOSITION OF WO_3 SYSTEM

Press = 1.0×10^{-2} ATM.

	MOL FRACTIONS						
T^oK	WO	WO_2	WO_3	W_2O_6	W_3O_9	W_4O_{12}	O_2
1200	0	0	1.65-10	2.292-4	2.393-1	7.604-1	1.068-6
2000	2.68-10	1.527-6	4.992-4	5.137-1	4.350-1	3.349-2	5.749-3
3000	6.184-3	1.273-1	1.186-1	6.611-1	3.081-3	7.255-6	7.446-2

Press = 1.0×10^{-4} ATM.

T^oK	WO	WO_2	WO_3	W_2O_6	W_3O_9	W_4O_{12}	O_2
1200	0	1.76-15	4.56-9	1.787-3	5.264-1	4.718-1	8.322-6
2000	1.977-7	1.487-4	6.407-3	8.669-1	9.651-2	9.767-4	9.749-3
3000	1.055-1	4.619-1	9.154-2	3.937-3	1.416-7	2.573-12	3.369-1

TABLE VI

EQUILIBRIUM COMPOSITION COMPUTATIONS FOR BORON QUENCHANT + ABLATION PRODUCTS

C_2H_2 + O_2 + 1% HBO_2 + TRACE CESIUM

$0.5 < R < 2.4$ $\qquad 2000^{\circ} < T < 4000^{\circ}K$

$0.025 < p < 0.1$ ATM

INCLUDED HBO_2, BO_2, BO, B_2O_3, B_2O_2, HBO, B, BO_2^-, BO^-, B^+, HBO^+

GENERATED DATA FOR BO^-: $^1\Sigma$ STATE ; $D(B\text{-}O^-)$ = 215 $\frac{KCAL}{GMOL}$

USED E.A.(BO_2) = 94 KCAL/GMOLE

E.A.(BO) = 57.5 KCAL/GMOLE

CONCLUSIONS

1. HBO_2, BO_2, BO AND B ARE THE IMPORTANT BORON-CONTAINING SPECIES.
2. BO_2^- IS THE ONLY IMPORTANT NEGATIVE ION.

TABLE VII

REACTION SCHEME FOR H/B/O SYSTEM

$HBO_2 + H \longrightarrow H_2 + BO_2$

$HBO_2 + O \longrightarrow OH + BO_2$

$HBO_2 + OH \longrightarrow H_2O + BO_2$

$HBO_2 + M \longrightarrow H + BO_2 + M$

$HBO_2 + M \longrightarrow OH + BO + M$

$BO_2 + H \longrightarrow OH + BO$

$BO_2 + M \longrightarrow O + BO + M$

$BO + H \longrightarrow OH + B$

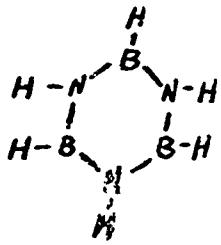
$BO + M \longrightarrow O + B + M$

TABLE VIII

VOLATILE BORON-CONTAINING CARRIERS

1. The vapor pressure of HBO_2, b.p. 1390°K, is too low to volatilize sufficient boric acid into the boundary layer at high altitudes.

2. A survey of known boron compounds reveals that cyclic B-N-H-X compounds have boiling points, ~50°-150°C.



m.p. -58°C

b.p. 55°C

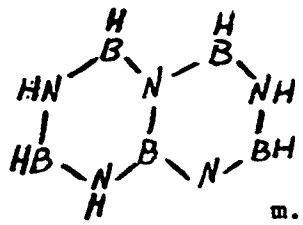
BORAZINE

(BORAZOLE)

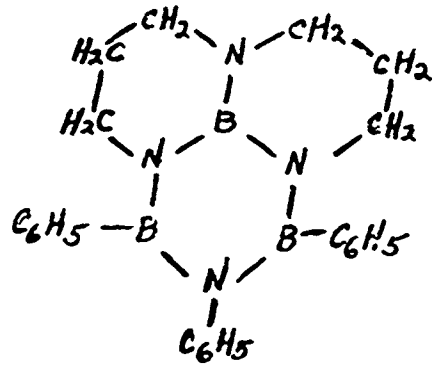
3. $B_3H_6N_3$ is thermally stable at 500°C. $B_3H_6N_3$ reacts with O_2.

Heat of Combustion	Kcal/G
B_2H_6	19.2
B_5H_9	17.5
$B_{10}H_{14}$	16.7
$B_3H_6N_3$	6.88

4. Cyclic B-N-H-X compounds polymerize to yield polycyclic molecules whose melting points are 100°-200°C higher than the monomer.



m. p. 27-30°C



m. p. 259-260°C

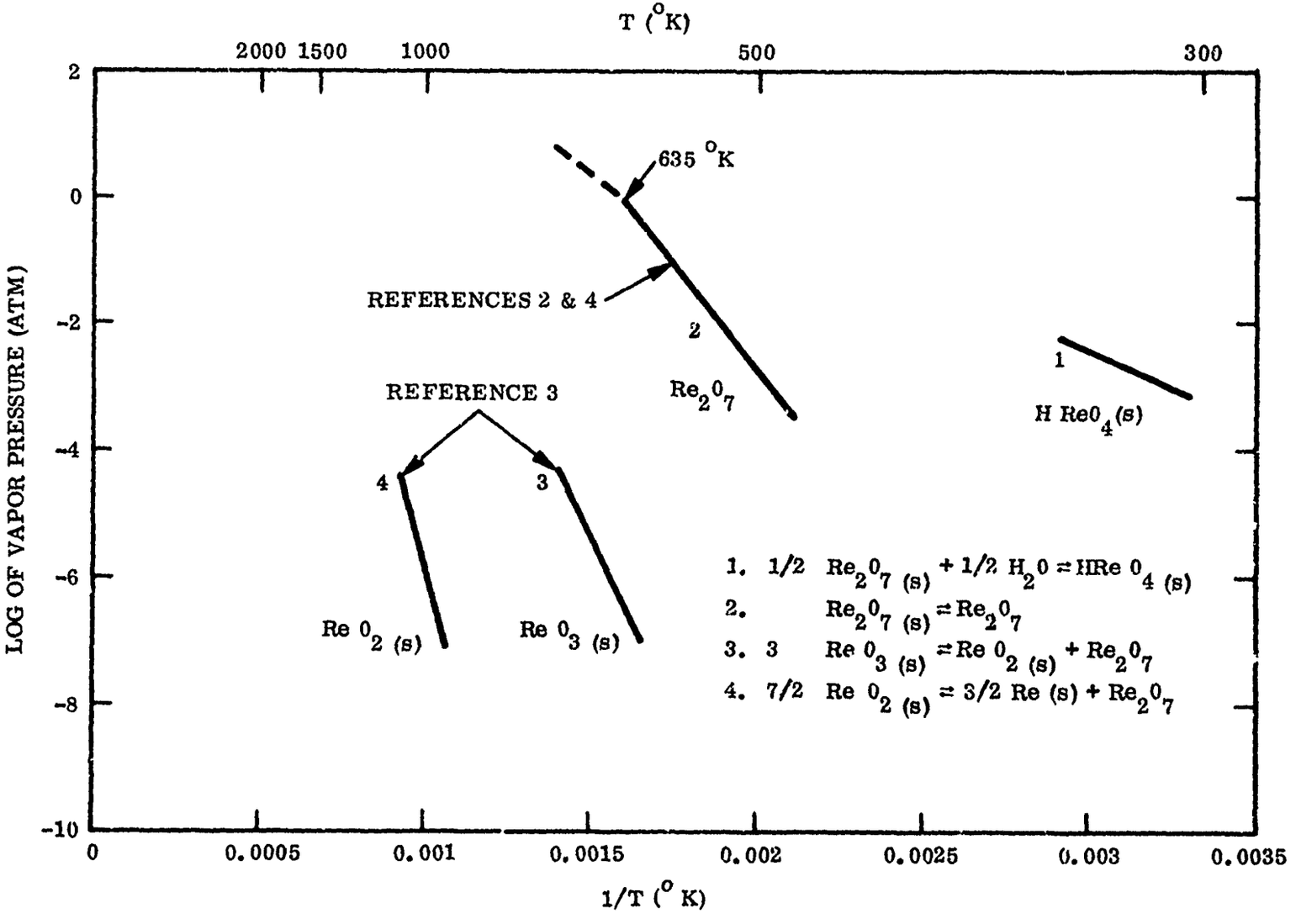


Figure 1. Vapor Pressure of Rhenium Compounds

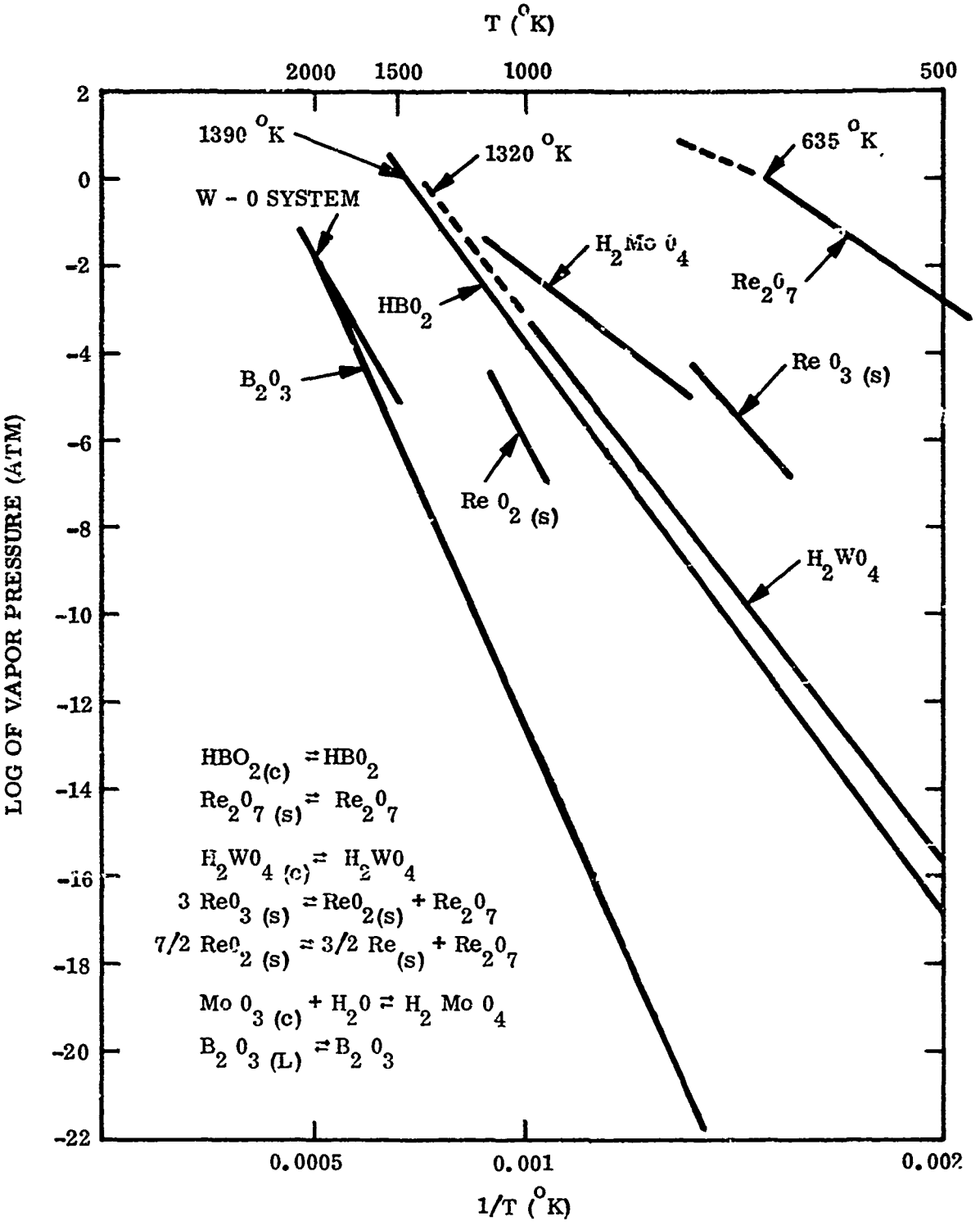


Figure 2. Vapor Pressure of Wake Quenchants

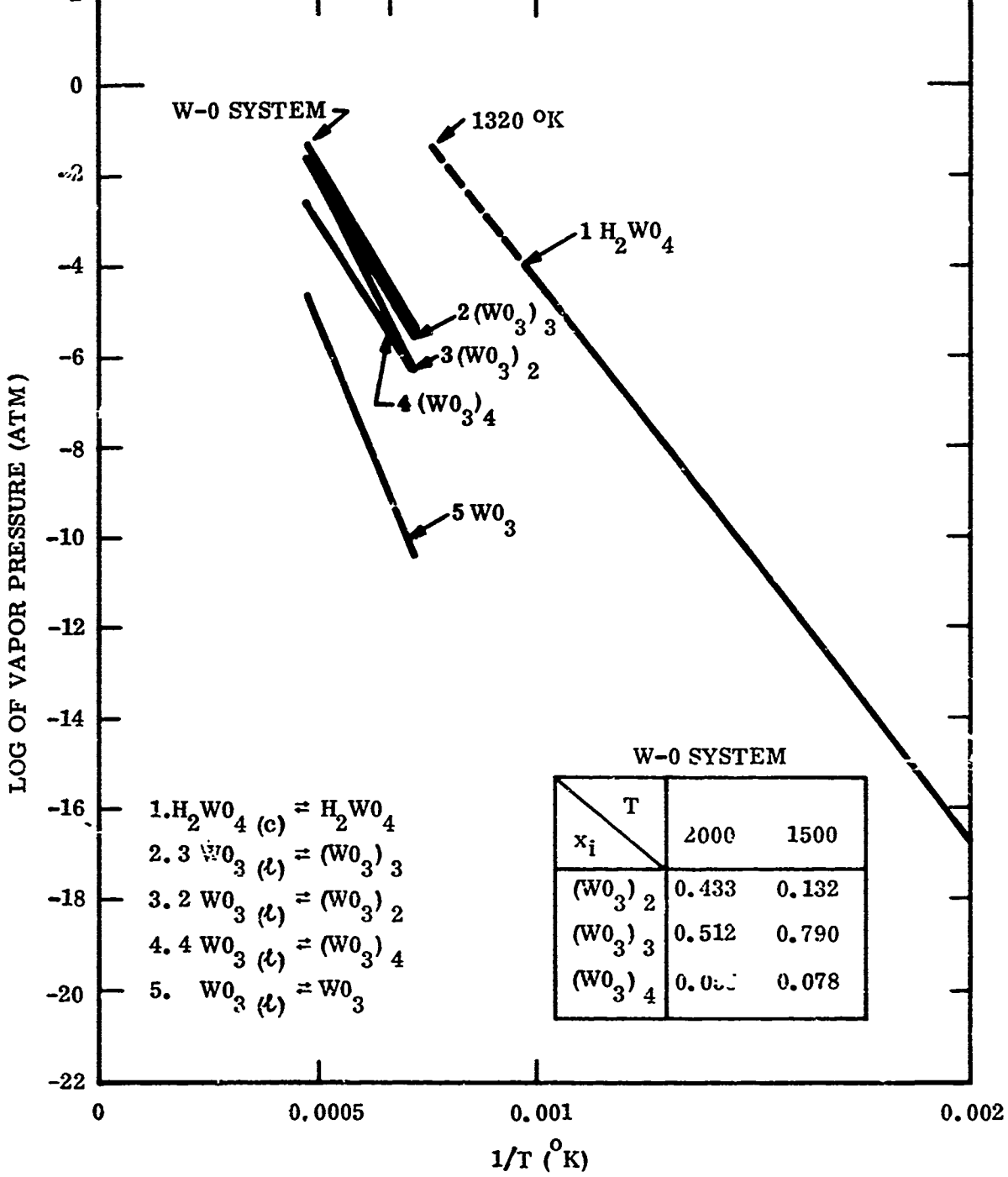


Figure 3. Vapor Pressure of Tungsten Compounds

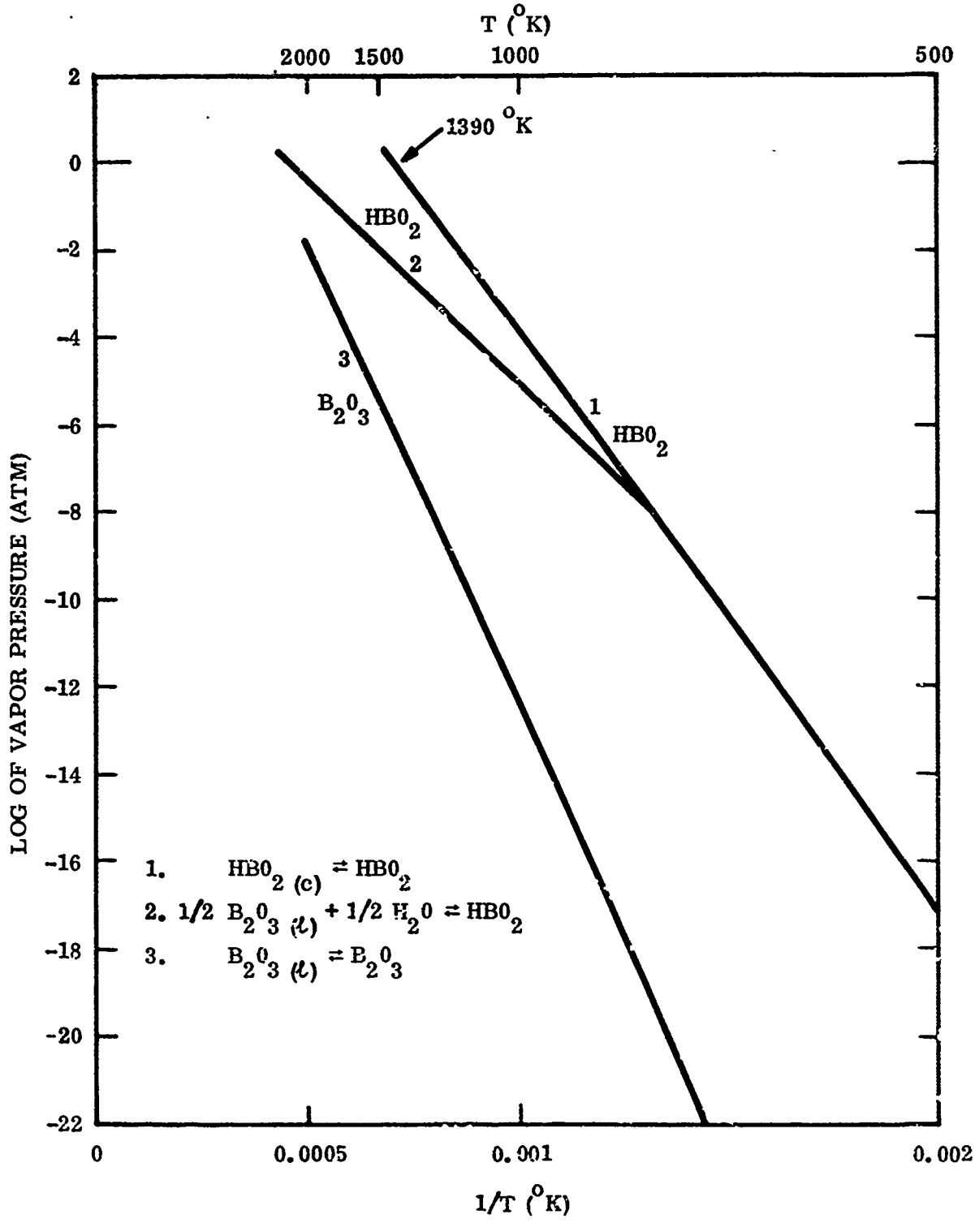


Figure 4. Vapor Pressure of Boron Compounds

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