Spacecraft Interactions as Influenced by Thermochemical Considerations

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Spacecraft in low Earth orbit undergo harsh environmental interactions that sometimes resemble the phenomenon observed in high-temperature vaporization and oxidation. For example, it has been reported that an osmium surface is removed, and surfaces of aluminum, silver, copper, iridium, niobium, nickel, and tungsten, are oxidized, even though the surface temperature when the measurements are made is ~250°K. Similar results are observed for the case of nonmetallic samples, e.g., graphite and synthetic organic materials, which are removed quickly. The purpose of this paper is to examine the data from the space experiments in light of thermochemical data and to consider possible implications or insight that may be gained for planning future experiments.

Nomenclature

ΔF = free energy of reaction, kcal/mole
$\Delta S(i)$ = entropy of species i, cal deg^{-1} mole^{-1}
$\Delta S_r(i)$ = entropy of reaction for reaction i, cal deg^{-1} mole^{-1}
$\Delta H_f(i)$ = heat or enthalpy of formation of species i, kcal/mole
$\Delta H_v(i)$ = heat or enthalpy of vaporization of species i, kcal/mole
$\Delta H_r(i)$ = heat of reaction for reaction i, kcal/mole
R = gas constant = 1.987 cal
T = temperature, °K
K_{eq} = equilibrium constant, which is defined as the product of the partial pressures (or activities of the products divided by the product of the partial pressures or activities of the reactants)
s = solid phase
c = condensed phase
g = gas phase
E_{cm} = energy of collision in the center of mass frame of reference
E_{Lab} = energy of collision in the laboratory frame of reference
m_t = mass of target, amu
m_p = mass of projectile, amu

Introduction

THE environment of spacecraft in low Earth orbit (200–400 km altitude) is rather harsh because of two important factors: 1) the ambient atmosphere is very corrosive (~70% is atomic oxygen),[1] and 2) the collisions between the ambient species and spacecraft surfaces are rather violent because of the orbital velocity (~7.7 km·s^{-1}). Table 1 summarizes the composition of the atmosphere at altitudes of 250, 300, 350, and 400 km. The orbital velocity of 7.7 km·s^{-1} means that any surface directly in the velocity vector will be bombarded by O having an energy of ~4.9 eV and N_2 having an energy of ~8.6 eV (these are mean energies; because of the Maxwellian distribution in the velocities, the energies can be somewhat higher). In this paper we will not consider surface catalyzed reactions leading to optical emissions, such as the Shuttle glow. Such reactions are basically low-temperature phenomenon, and interested readers are referred to a number of reviews in Refs. 2–5.

Experiments

Intentional and unintentional materials experiments on the Space Shuttle have indicated that this interaction between the surfaces and the ambient atmosphere leads to effects that resemble those of high-temperature vaporization and oxidation. For example, Peters et al.[6] reported the results of a study in which thin films of Ag, C, Os, and Au were exposed to that environment on Shuttle flight STS-4 at 310 km altitude. They observed that Ag gained weight, C and Os disappeared, and Au was unaffected. On another flight, STS-8, which flew at an altitude of 225 km, Peters et al.[7] reported that Al, Nb, Ni, and W had gained mass, presumably due to the formation of their respective oxides. In addition to the experiments on metals, samples of carbon were eroded quite efficiently[7]; diamond was the least affected of the carbon samples, and graphite was the most affected. The studies on carbon showed the presence of striated valleys in the eroded samples, an observation that is referred to as carpeting. In all of these experiments, the products formed when materials are lost were not identified; on the other hand, mass gain was identified after the flights as being due to the formation of oxide coatings. It should be stressed that the bulk temperature when these experiments were conducted was quite low, between 225 and 300°K, depending on the solar zenith angle.

Experiments on the effect of orbital environment on carbon-containing materials indicate that such materials are even more unstable than the metals discussed previously. The most reactive material is polyethylene and the least reactive material is Teflon.[8] As in the case of the metals, there is no information as to the nature of the products that are formed in these reactions. Undoubtedly, CO and CO_2 are formed.

The observations may be shown schematically in Fig. 1. Table 2 shows a summary of the observations as reported in a recent review,[9] as well as a listing of the thermal conductivity of the elements as reported in a review.[10]

Discussion

In this analysis, we will follow the tree shown in Fig. 1 and begin by discussing the observations on 1) metals (including Si) and 2) nonmetals (carbonaceous materials).

Before we consider the experiments, however, it will be worthwhile to define the terms and units that will be used in

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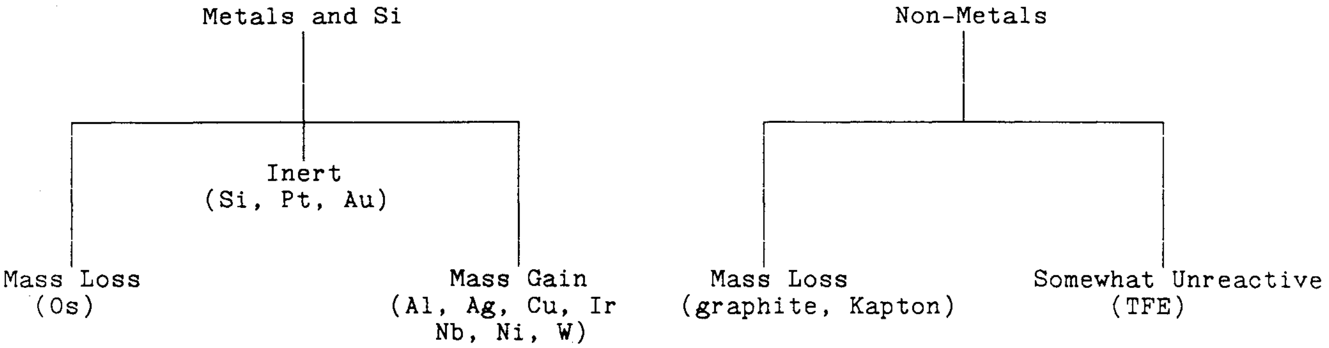

Fig. 1 Schematic representation of materials experiments.

Table 1 Composition of the low-Earth-orbit atmosphere[a]

	Altitude, km			
Species	250	300	350	400
O	1.9(9)[b]	7.5(8)	3.1(8)	1.3(8)
N_2	4.3(8)	8.6(7)	1.9(7)	4.2(6)
O_2	2.7(7)	4.4(6)	7.6(5)	1.4(5)

[a]Reference 1. [b]Read $a(b)$ as $a \times 10^b$. Units are molecules·cm^{-3}.

this paper. Under equilibrium conditions, the equilibrium constant of a given reaction, k_{eg}, is given by

$$\Delta F = -RT\ell n k_{eq} = \Delta H - T\Delta S \qquad (1)$$

where T is in absolute degrees, ΔH is the heat of reaction, and ΔS is the entropy. In this work we will use, as units, kilocalories per mole for ΔH. In the discussion ΔH will be calculated first for $T = 298°K$, since that is the temperature for which there are accurate thermochemical data. For spacecraft in low Earth orbit, the interaction between the O atoms and the surfaces occurs at orbital velocity, i.e., for O atoms having a velocity of ~7.7 km/s (≡113 kcal/mole). Therefore, under these circumstances we will simply add the kinetic energy of O atoms to the heat term; i.e., we will add 102 kcal/mole per O atom to the reaction. This means that the heat term, ΔH, will be much larger than the entropy term; consequently, the entropy term will not be considered in the treatment. The concept of equilibrium is somewhat hazy under the condition of low Earth orbit, since the kinetic energy of O (~7.7 km/s) corresponds to a temperature of ~60,000°K, and the actual temperature of the surface is ~250°K. For this reason, only the heats of reaction will be calculated (i.e., k_{eq} will not be considered). The appropriateness of the treatment can be seen by considering the reaction

$$W(s) + 2O(g) \rightarrow WO_2(s) \qquad (2)$$

a reaction that will be considered in more detail later. The JANAF Tables[11] give -141.0 ± 0.2 kcal/mole and $+59.6 \pm 0.02$ kcal/mole for $\Delta H_f[WO_2, c, 298]$ and $\Delta H_f[0, g, 298]$, respectively. The ΔS at 298°K is given as 12.1, 7.8, and 38.5 cal deg^{-1} mole^{-1} for $WO_2(s)$, $W(s)$, and $O(g)$, respectively. If we substitute the heat and entropy of reaction (-260 kcal/mole and -72.7 cal deg^{-1} mole^{-1}, respectively) derived from these values into Eq. (1), we obtain an equilibrium constant of $>10^{+100}$. Had we not included the entropy term, k_{eq} would have been slightly larger. Adding the kinetic energy of O to its ΔH_f leads to a still larger equilibrium constant. The implication of this discussion is that the entropy term is unimportant by comparison with heat of reaction and with orbital velocity. Changing the temperature from 298 to 200°K has a negligible effect, since $\{-\Delta H/RT\}$ is quite large; a change of 30% in T means that k_{eq} will increase by a factor of $\sim \ell n(300/200)$.

Table 2 Summary of materials experiments in space[a]

Material	Thickness, nm	Effect	Thermal conductivity[b]
Al film	3.4	Oxidation	2.36
Ir film	32.3	Oxidation	1.48
Ni film	54.2	Oxidation	0.941
Nb film	16.8	Oxidation	0.533
Ag bulk	Bulk	Oxidation	4.29
Cu bulk	Bulk	Oxidation	4.03
W film	4.8	Oxidation	1.77
Os bulk	Bulk	Loss	0.90
Au film	35.5	None	3.19
Pt film	10	None	0.717
Si bulk	Bulk	None	1.68
Be			2.18
Ti			0.224

[a]The data about W film were taken from Ref. 5 and all the other data were taken from a summary by Ref. 8.
[b]Reference 10. Units are W·cm^{-1}·K^{-1} at $T = 273°K$.

It should be kept in mind that, for a given reaction, even if it is very exothermic, the heat of reaction may not necessarily lead to vaporization, since the heat capacity and thermal conductivity of the sample will determine how this energy is absorbed. In this vein, materials that are good thermal conductors, e.g., Al, Ag, and Cu, would not be expected to evaporate due to the quick conduction of the heats of reaction. On the other hand, materials that are poor thermal conductors would be expected to evaporate if the heat of reaction is sufficient to cause sublimation or decomposition.

The conversion of kinetic energy of a projectile (E_{Lab}) into usable energy in the collision of the projectile with a target (E_{CM}, the center-of-mass energy), depends on the relative masses of the collision partners:

$$E_{CM} = [(m_t)/(m_p + m_t)]E_{Lab}$$

where m_p is the mass of projectile (O) and m_t the mass of the target (surface). For the case under discussion, the collision of O atoms with a surface, the mass of the target is so much greater than that of the projectile that the $E_{CM} \sim E_{Lab}$.

Metals and Silicon

We will discuss briefly the probable cause for loss or gain of mass in view of existing thermochemical data. The metals that are not affected by the low-Earth-orbit environment are inert in the thermochemical sense; this means that they will not be affected by the atomic energy, even though they may still participate in catalytic reactions.

Metals that Lose Mass

Os is the only metal that shows a definite mass loss; is is also the only metal that has a stable gaseous oxide at high temperatures.

Osmium. Of the metals that have been exposed to low-Earth-orbit environment, Os is the only one that has a stable gaseous oxide, OsO_4, at room temperature. Correlations of thermochemical data[11] lead to $\Delta H_f[\mathrm{OsO}, g, 298] = +105 \pm 20$ kcal/mole. This means that at 298°K

$$\mathrm{Os}(c) + \mathrm{O}(g) \rightarrow \mathrm{OsO}(g) \qquad (3)$$

is endothermic by 46 kcal/mole. If all of the orbital energy is available for reaction, then reaction (3) can become exothermic by 67 kcal/mole in the low-Earth-orbit environment.

Metals that Gain Mass

Even though these metals may have gaseous monoxides that are stable at high temperatures, their solid oxides are extremely stable.

Aluminum. $Al_2O_3(c)$ is extremely stable, with a heat of formulation of $\Delta H_f[\mathrm{Al_2O_3}, c, 298] = -400.5 \pm 0.3$ kcal/mole.[11] This means that at 298°K the reaction

$$2\,\mathrm{Al}(c) + 3\,\mathrm{O}(g) \rightarrow \mathrm{Al_2O_3}(c) \qquad (4)$$

is exothermic by 578 kcal/mole. At orbital energies it is even more exothermic. The fact that Al exposed to the low-Earth-orbit environment does not lose mass suggests that

$$\mathrm{Al}(c) + \mathrm{O}(g) \rightarrow \mathrm{AlO}(g) \qquad (5)$$

does not occur, even though it is simpler than reaction (4) and even though it is exothermic in the low Earth environment by 43 kcal/mole at 298°K $\{\Delta H_f[\mathrm{AlO}, g, 298] = 16 \pm 2$ kcal/mole$\}$.[12] This observation of Al also illustrates the difficulty of relating the high impact velocity of O to a thermodynamic temperature, since the vaporization of $Al_2O_3(c)$ is known to yield other gaseous oxides.[13]

Silver. The gain of mas by silver films when exposed to the environment of low Earth orbit is undoubtedly due to the formation of $Ag_2O(c)$, since $\Delta H_f[\mathrm{Ag_2,O}, c, 298] = -7.4$ kcal/mole, which means that

$$2\,\mathrm{Ag}(c) + \mathrm{O}(g) \rightarrow \mathrm{Ag_2O}(c) \qquad (6)$$

is exothermic at room temperature by 67 kcal/mole. At orbital velocity, the reaction is even more exothermic. Again, the fact that mass is not lost means that

$$\mathrm{Ag}(c) + \mathrm{O}(g) \rightarrow \mathrm{AgO}(g) \qquad (7)$$

does not occur, even though in the low-Earth-orbit environment it would be exothermic by 97 ± 5 kcal/mole, since $\Delta H_f[\mathrm{AgO}, g, 298] = 75 \pm 5$ kcal/mole.[12] It may be that the high thermal conductivity of Ag is sufficient to dissipate the heat of reaction before it can be distributed to the reactants. Incidentally, it is worth noting that reaction (7) is the basis of an attempt to measure the height profile of atomic oxygen in the upper atmosphere[14]; in this experiment, however, the velocity of atomic oxygen is essentially thermal. The reaction alters the conductivity of a thin film of Ag by an amount that is proportional to the integrated flux of atomic oxygen.

Copper. $\Delta H_f[\mathrm{Cu_2O}, c, 298] = -40.3$ kcal/mole,[15] leading to the conclusion that

$$2\,\mathrm{Cu}(c) + \mathrm{O}(g) \rightarrow \mathrm{Cu_2O}(c) \qquad (8)$$

is exothermic by 99 kcal/mole. It is even more so if orbital energy of O is taken into account. $\Delta H_f[\mathrm{CuO}, g, 298]$ is 76 ± 5 kcal/mole,[12] which again means that

$$\mathrm{Cu}(c) + \mathrm{O}(g) \rightarrow \mathrm{CuO}(g) \qquad (9)$$

can, but does not, take place in the low Earth environment. Part of the reason may be due to the efficient conduction of the heat of reaction by the bulk.

Iridium. Iridium has a stable gaseous monoxide at high temperatures, but not at room temperature. Ir has a stable, condensed oxide, $IrO_2(c)$, whose heat of formation, $\Delta H_f[\mathrm{IrO_2}, c, 298]$, is reported to be -65.6 kcal/mole. This means that

$$\mathrm{Ir}(c) + 2\,\mathrm{O}(g) \rightarrow \mathrm{IrO_2}(c) \qquad (10)$$

is exothermic by 183.6 kcal/mole. Since Ir is a fairly good thermal conductor, it is apparent that all of this heat is transferred to the substrate. It will be useful in future experiments to measure the gaseous composition above a surface of Ir exposed to a low-Earth-orbit environment. The stable gaseous oxide of Ir is IrO(*g*). Recent analysis[12] leads to $\Delta H_f[\mathrm{IrO}, g, 298] = +121 \pm 10$ kcal/mole, which means that the reaction leading to the formation of gaseous IrO,

$$\mathrm{Ir}(c) + \mathrm{O}(g) \rightarrow \mathrm{IrO}(g) \qquad (11)$$

is endothermic by 62 kcal/mole at 298°K.

Niobrium. $\Delta H_f[\mathrm{NbO}, c, 298] = -97$ kcal/mole,[15] leading to a heat of reaction of -156 kcal/mole for

$$\mathrm{Nb}(c) + \mathrm{O}(g) \rightarrow \mathrm{NbO}(c) \qquad (12)$$

at 298°K. Since the orbital velocity leads to O atoms having 102 kcal/mole of kinetic energy, the reaction in low-Earth-orbit becomes exothermic by 269 kcal/mole. As in the case of Ni, the reaction that might lead to mass loss,

$$\mathrm{Nb}(c) + \mathrm{O}(g) \rightarrow \mathrm{NbO}(g) \qquad (13)$$

does not seem to take place, even though at orbital velocities it would be exothermic by 122 kcal/mole, since $\Delta H_f[\mathrm{NbO}, g, 298] = +51$ kcal/mole.[15]

Nickel. $\Delta H_f[\mathrm{NiO}, c, 298] = -57.3$ kcal/mole,[15] leading to a heat of reaction of ~ -117 kcal/mole for

$$\mathrm{Ni}(c) + \mathrm{O}(g) \rightarrow \mathrm{NiO}(c) \qquad (14)$$

at 298°K. If the kinetic energy of O is taken into account, reaction (14) would be exothermic by 230 kcal/mole. In contrast, that could lead to mass loss,

$$\mathrm{Ni}(c) + \mathrm{O}(g) \rightarrow \mathrm{NiO}(g) \qquad (15)$$

is exothermic by 97 kcal/mole at orbital altitudes, since $\Delta H_f[\mathrm{NiO}, g, 298] = +75$ kcal/mole.[15]

Tungsten. Tungsten has a number of oxides stable at high temperatures, WO(*g*), $WO_2(g)$, $WO_2(s)$, and $WO_3(g)$; however, the gaseous oxides are not stable at room temperature. Consequently, the processes by which these oxides can be formed,

$$\mathrm{W}(s) + 2\,\mathrm{O}(g) \rightarrow \mathrm{WO_2}(s) \qquad (2)$$

$$\mathrm{W}(s) + \mathrm{O}(g) \rightarrow \mathrm{WO}(g) \qquad (16)$$

$$\mathrm{W}(s) + 2\,\mathrm{O}(g) \rightarrow \mathrm{WO_2}(g) \qquad (17)$$

$$\mathrm{W}(s) + 3\,\mathrm{O}(g) \rightarrow \mathrm{WO_3}(g) \qquad (18)$$

are not observed at room temperature. Recent analyses of thermochemical data give $\Delta H_f[\mathrm{WO}, g, 298] = +102 \pm 10$ kcal/mole,[12] $\Delta H_f[\mathrm{WO_2}, g, 298] = +18.3 \pm 2$ kcal/mole,[11] $\Delta H_f[\mathrm{WO_2}, s, 298] = -140.9 \pm 0.2$ kcal/mole,[11] and $\Delta H_f[\mathrm{WO_3}, g, 298] = -70 \pm 7$ kcal/mole.[11] From these heats of formation and from $\Delta H_f[\mathrm{O}, g, 298] = +59.6 \pm 0.02$ kcal/mole, we derive at 298°K ΔH_r [Eq. (16)] $= +42 \pm 10$

kcal/mole, ΔH_r [Eq. (17)] = -101 ± 2 kcal/mole, ΔH_r [Eq. (2)] = -260 ± 1 kcal/mole, and ΔH_r [Eq. (18)] = -248.8 ± 7 kcal/mole. At orbital velocity, the heats of reaction become ΔH_r [Eq. (16)] = -71 kcal/mole, ΔH_r [Eq. (17)] = -214 ± 2 kcal/mole, ΔH_r [Eq. (18)] = -475 ± 1 kcal/mole, and ΔH_r [Eq. (18)] = -566 ± 7 kcal/mole; in other words, they all become exothermic. The fact that mass gain is observed suggests that $WO_2(s)$ is formed. Since mass gain is observed, we have to conclude that the combination of thermal capacity of the substrate, the thermal conductivity of the smaple, and internal excitation are enough to stabilize the solid oxide phase so that it will not be vaporized via

$$WO_2(s) \rightarrow WO(g) + O(g) \qquad (19)$$

which is endothermic by 301 kcal/mole at 298°K. It would be interesting in this connection to look for thermal emission from a tungsten surface exposed to low-Earth-orbit environment.

Inert Materials

Three materials, Au, Pt, and Si, showed no effect from exposure to low-Earth-orbit environment. Au and Pt are easily understood since they do not have stable oxides in either the gas phase or in the condensed phase at room temperature or at high temperatures. Si does have a stable oxide, SiO_2 (silica), which was not formed even though its formation is favored thermochemically. This seeming inertness is probably due to the formation of a stable layer of $SiO(c)$ (actually $Si\text{-}SiO_2$, which is a stable condensed phase).

Carbonaceous Materials

The situation in this case is somewhat complicated by the lack of thermochemical information regarding many of the materials that have been tested. However, for C (in the form of graphite) we can make estimates of heats of reaction for

$$C(c, \text{graphite}) + 2\,O(g) \rightarrow CO_2(g) \qquad (20)$$

using $\Delta H_f[CO_2, g, 298] = -94.1$ kcal/mole[15] and ΔH_f[C, graphite, 298] = 0 kcal/mole,[15] we derive ΔH_r[Eq. (20)] ~ -153, exclusive of the kinetic energy of O atoms. It is likely that the other composites that have been tested will have similar thermodynamic properties; i.e., they will be eroded rather quickly. Recently reported work has extended these studies to Kapton and other insulators that are found to be affected rather quickly upon exposure to atomic oxygen in low Earth orbit.[16]

Applications

In view of the treatment mentioned earlier, we consider below two materials that have not been flown in low-Earth-orbit erosion experiments: Ti and Be. Both are candidates for use in space because of special properties.

Titanium

Even though no experiments have been conducted on Ti, it is likely to be a candidate for space structures because of its high strength and low density. Titanium is a relatively poor thermal conductor; thus we might expect that any heat generated in the reaction of the Ti with atomic oxygen will go into the sample rather than being conducted into the bulk. We consider in this analysis three possible reactions:

$$Ti(s) + O(g) \rightarrow Ti_2O_3(s) \qquad (21)$$
$$Ti(s) + O(g) \rightarrow TiO(s) \qquad (22)$$
$$Ti(s) + O(g) \rightarrow TiO(g) \qquad (23)$$

Using $\Delta H_f[Ti_2O_3, s, 298] = -363\pm2$ kcal/mole, $\Delta H_f[TiO, s, 298] = -129.7\pm1$ kcal/mole, and $\Delta H_f[TiO, g, 298] = +13\pm2$ kcal/mole,[11] we derive ΔH_r [Eq. (21)] = -540 ± 5 kcal/mole, ΔH_r [Eq. (22)] = -188 ± 3 kcal/mole, and ΔH_r [Eq. (23)] = -46 ± 3 kcal/mole, all at 298°K. The heat of vaporization of $TiO(s)$, ΔH_v[TiO, s, 298], is given by the difference in the

Table 3 Summary of temperatures of formation used in this paper

Species	ΔH_f(298°K, thermal), kcal/mole	S(298°K), cal deg^{-1} mole^{-1}
$Ag(c)$	0	10.2[a]
$AgO(g)$	$+75\pm5$[b]	
$Ag_2O(c)$	-7.4[a]	29.0
$Al(c)$	0	6.76
$AlO(g)$	$+16\pm2$[c]	52.19
$Al_2O_3(c)$	-400.5 ± 0.3[c]	12.18
$BeO(c)$	-145.4 ± 0.9[c]	3.29
$BeO(g)$	$+32.6$[c]	47.23
C(graphite)	0	1.37
C(diamond)	$+0.5$[a]	0.56
$CO(g)$	-27.2[a]	31.69
$CO_2(g)$	-94.1 ± 0.01[c]	51.10
$Cu(c)$	0	7.93
$CuO(g)$	$+73.2\pm10$[c]	56.1
$Cu_2O(c)$	-40.8 ± 0.5[c]	22.1
$Ir(c)$	0	8.5[a]
$IrO(g)$	$+121\pm10$[b]	
$IrO_2(c)$	-274.1[a]	
$Nb(c)$	0	8.71
$NbO(c)$	-100.3 ± 3[c]	[11 ± 2][c]
$NbO(g)$	$+47.5\pm5$[c]	57.12
$Ni(c)$	0	7.14[c]
$NiO(c)$	-57.3[a]	9.01
$NiO(g)$	$+75$[a]	
$O(g)$	$+59.55\pm0.02$[c]	38.49
$Os(c)$	0	7.8[a]
$OsO(g)$	$+105\pm20$[b]	
$Si(c)$	0	4.49
$SiO(g)$	-24.0 ± 2[c]	50.56
$SiO_2(c)$	-217.7[a]	10.0
$Ti(c)$	0	7.35
$TiO(c)$	-129.7 ± 3[c]	8.31
$TiO(g)$	$+13\pm2$[c]	55.80
$Ti_2O_3(s)$	-363 ± 2[c]	18.46
$W(c)$	0	7.81
$WO(g)$	$+102\pm10$[c]	[59.3][c]
$WO_2(c)$	-140.9 ± 0.2[c]	12.08
$WO_2(g)$	$+18.3\pm7$[c]	[68.3][c]
$WO_3(c)$	-201.4 ± 0.2[c]	18.14
$WO_3(g)$	-70 ± 7[c]	[68.5][c]

[a]Reference 15. [b]Reference 12. [c]Reference 11.

Table 4 Summary of reactions and their temperatures

Reaction	ΔH_r(298°K), kcal/mole
(2) $W(s) + 2\,O(g) \rightarrow WO_2(s)$	-260 ± 1
(3) $Os(c) + O(g) \rightarrow OsO(g)$	$+46\pm20$
(4) $2\,Al(c) + 3\,O(g) \rightarrow Al_2O_3(c)$	-578 ± 1
(5) $Al(c) + O(g) \rightarrow AlO(g)$	-43 ± 2
(6) $2\,Ag(c) + O(g) \rightarrow Ag_2O(c)$	-67
(7) $Ag(c) + O(g) \rightarrow AgO(g)$	$+15$
(8) $2\,Cu(c) + O(g) \rightarrow Cu_2O(c)$	-99
(9) $Cu(c) + O(g) \rightarrow CuO(g)$	$+16$
(10) $Ir(c) + O(g) \rightarrow IrO(g)$	$+62\pm10$
(11) $Ir(c) + O(g) \rightarrow IrO(g)$	$+62\pm10$
(12) $Nb(c) + O(g) \rightarrow NbO(c)$	-156
(13) $Nb(c) + O(g) \rightarrow NbO(g)$	-9
(14) $Ni(c) + O(g) \rightarrow NiO(c)$	-117
(15) $Ni(c) + O(g) \rightarrow NiO(g)$	$+16$
(16) $W(s) + O(g) \rightarrow WO(g)$	-42 ± 10
(17) $2\,W(s) + 2\,O(g) \rightarrow WO_2(g)$	-102 ± 2
(18) $W(s) + 3\,O(g) \rightarrow WO_3(g)$	-249 ± 7
(19) $WO_2(s) \rightarrow WO(g) + O(g)$	$+301\pm10$
(20) $C(c, \text{graphite}) + 2O(g) \rightarrow CO_2(g)$	-153
(21) $Ti(s) + O(g) \rightarrow Ti_2O_3(s)$	-540
(22) $Ti(s) + O(g) \rightarrow TiO(s)$	-188
(23) $Ti(s) + O(g) \rightarrow TiO(g)$	-46
(24) $Be(c) + O(g) \rightarrow BeO(c)$	-205

heat of formation of the solid and the gas phases of TiO and is equal to + 142.7 ± 2 kcal/mole. Oxidation of the surface via reactions (21) and (22) might lead to the formation of an insulating layer, but since the heat of vaporization of TiO(*s*) formed in reaction (22) is less than the heat of reaction at orbital velocity, it seems likely that any oxide formed will evaporate. Likewise, the formation of $Ti_2O_3(s)$ is likely to be temporary because of the large amounts of energy deposited in the interaction at orbital velocities; thermochemical measurements indicate that all of the stable solid phases of Ti-O vaporize to give TiO(*g*) and Ti(*g*).[17] The combination of the thermochemical data with the thermal conductivity information shown in Table 2 suggests that a Ti surface will be eroded on exposure to low Earth orbit.

Beryllium

Be has not been flown on the Space Shuttle; however, it is a strong candidate for use in optical instrumentation in low Earth orbit because of its light weight and optical properties. Be is a relatively good thermal conductor, as the data of Table 2 shows. As in the case of Ti, we consider the following reaction:

$$\mathrm{Be}(c) + \mathrm{O}(g) \rightarrow \mathrm{BeO}(c) \qquad (24)$$

$\Delta H_f[\mathrm{Be}, c, 298] = \mathrm{O}$, whereas $\Delta H_f[\mathrm{BeO}, c, 298] = -145.4 \pm 0.9$ kcal/mole.[11] Reaction (24) is exothermic by 205 kcal/mole at 298°K. At 7.7 km/s the reaction becomes exothermic by 318 kcal/mole at 298°K. Even though the heat of vaporization of BeO(*c*) $\{\Delta H_v[\mathrm{BeO}, c, 298] = 178 \pm 3$ kcal/mole[11]$\}$ suggests that for Be mass loss should occur; however, because of its good thermal conductivity, it is likely that the interaction would lead to the buildup of an oxide coating at low Earth orbit (i.e., where O is a dominant constituent), at least for bulk samples of Be. On the other hand, at higher altitudes where [H] becomes comparable with [O], the interaction may be quite benign in that no changes will take place.

Conclusions

This paper has attempted to present a discussion of the thermochemical considerations that play a role in determining the fate of samples exposed to low-Earth-orbit environment. Tables 3 and 4 present summaries of the temperatures of formation as well as the equilibria used in this analysis. The thermochemical data were obtained from standard compilations, and the reactions used in the study are *simple* gas-solid reactions. The *simplicity* of the reactions is needed because of the rarified atmosphere in the low-Earth-orbit environment (thus arguing against multiple collisions). The discussion presented in this paper leads to three implications: 1) erosion of materials, 2) buildup of materials and change in the physical properties of materials, and 3) effects of these interactions on surfaces and sensors on low-Earth-orbit stations. These effects will be discussed briefly below.

Erosion of Materials

The erosion of materials leads to weakening of structures in space, leading to profound implication for the integrity of long-lived structures in space. For example, in some of the experiments, it was observed that Os coated with Pt still showed some erosion near the edges of the samples.[7] Leger and Visentine[18] have estimated that the Space Station may not last a full solar cycle if the designs and the materials being contemplated are not changed. In addition, mirrors and other large optical structures that need to be made of very light ultralow expansion material are liable to be modified drastically unless the designs include allowances for these contingencies.

Buildup of Materials

The buildup of materials, through the formation of oxides, leads to a change in the electrical properties of a metal. For example, the formation of NiO(*c*), $Cu_2O(c)$, and $Al_2O_3(c)$ on the respective metals can lead to electrical breakdowns and to different thermal properties; the transformation of metals into oxides will have profound effects on optical properties of surfaces that incorporate these metals in their structures, as in the case of mirrors and reflectors being contemplated for space use. The possible buildup of an oxide coating on a Ti surface means that the surface will be insulated and may eventually result in charging and arcing of the surfaces.

Effect on Optical Experiments

Mass loss from a surface exposed to the low-Earth-orbit environment means that either a gaseous product (chemical reaction) or a solid particulate (something like sputtering) has formed. Because of the high flux of O atoms ($\mathrm{flux} = [\mathrm{O}]^* v$), the column density of any gaseous products formed at the surface is likely to be equally high. Sensors and optical surfaces are affected because their surfaces become rough quickly, leading to degraded performance; in addition, if there is a gaseous cloud in front of the optical instrument, either extraneous signals may be generated by the cloud (via fluorescence) or the performance of the sensor may be degraded (via absorption of radiation by the cloud). For example, an organic surface near an infrared sensor may generate enough CO_2 via reactions (20) and (21) to raise the threshold in the 4.3-μ region. Likewise, the presence of Ti or W in that region may generate enough WO(*g*) and TiO(*g*) to distort observations in the 10- to 12-μ region, where the fundamentals seem to cluster.[19]

To obtain a more definitive analysis of the problem, a number of diverse studies are needed:

1) More quantitative space experiments.

2) Repetition of the data in Table 2 under more controlled conditions (e.g., all bulk sample or all film samples) in order to be able to separate the effect of heat capacity and thermal conductivity from the reactivity of the metal.

3) Better thermochemical data, particularly for the oxides of W, Ir, and Os.

4) Kinetic studies of the reaction of fast O atoms with surfaces.

5) Accurate surface science experiments: characterization of the surface before and after exposure to low-Earth-orbit environment.

6) Analysis of the gaseous composition above surfaces exposed to low-Earth-orbit environment.

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