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The Chemical Effects of the Martian Environment on Power System Component Materials: A Theoretical Approach

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THE CHEMICAL EFFECTS OF THE MARTIAN ENVIRONMENT

ON POWER SYSTEM COMPONENT MATERIALS: A THEORETICAL APPROACH

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SUMMARY

In the foreseeable future, an expedition may be undertaken to explore the planet Mars. Some of the power source options being considered for such a mission are photovoltaics, regenerative fuel cells and nuclear reactors. In addition to electrical power requirements, environmental conditions en route to Mars, in the planetary orbit and on the Martian surface must be simulated and studied in order to anticipate and solve potential problems.

Space power systems components such as photovoltaic arrays, radiators, and solar concentrators may be vulnerable to degradation in the Martian environment. Natural characteristics of Mars which may pose a threat to surface power systems include high velocity winds, dust, ultraviolet radiation, large daily variations in temperature, reaction to components of the soil, atmosphere and atmospheric condensates as well as synergistic combinations. Most of the current knowledge of the characteristics of the Martian atmosphere and soil composition was obtained from the Viking 1 and 2 missions in 1976.

This paper presents a theoretical study used to assess the effects of the Martian atmospheric conditions on the power systems components. A computer program written at NASA Lewis Research Center in 1961 to 1962 for combustion research that uses a free-energy minimization technique was used to calculate chemical equilibrium for assigned thermodynamic states of temperature and pressure. The power system component materials selected for this study include: silicon dioxide, silicon, carbon, copper, and titanium. Combinations of environments and materials considered in this study include: (1) Mars atmosphere with power surface material, (2) Mars atmosphere and dust component with power surface material, (3) Mars atmosphere and hydrogen peroxide or superoxide with power system material. The chemical equilibrium calculations were performed at a composition ratio (oxidant to reactant) of 100. The temperature for the silicon dioxide material and silicon, which simulate photovoltaic cells, were 300 K and 400 K; for carbon, copper and titanium, which simulate radiator surfaces, 300, 500, and 1000 K. All of the systems were evaluated at pressures of 700, 800, and 900 Pa, which simulate the Martian atmosphere.

INTRODUCTION

In the past few years there has been a growing interest by the United States in space exploration. An exploratory expedition to the planet Mars is among the first steps for this task. Such a step will require careful planning and preparation to insure a successful mission. The discussion of electrical power systems for such a mission considers a range of power requirements and power source options (ref. 1). Some of the power systems considered are: photovoltaics, regenerative fuel cells, solar thermal, nuclear reactor and isotope power systems. Electrical power requirements are driven by crew size, electric propulsion demands, scientific and operational requirements and others. In addition, all environmental conditions in the route to Mars, in the planet orbit, and on the Martian surface should be simulated and studied in order to anticipate and solve, if possible, any problems.

Space power system components such as photovoltaics arrays, radiators, solar concentrators and superconductor power components may be vulnerable to degradation in the Martian environment. Natural characteristics of Mars which may pose a threat to surface power systems include: winds, dust, ultraviolet radiation, temperature, soil, atmospheric condensates.

The atmospheric composition on Mars was determined by measurements with mass spectrometers on the Vikings (ref. 2). Table I indicates the composition of gases present; the major component is CO_2. The average amount of atmospheric water vapor precipitation is approximately 100 μm (ref. 3). The atmospheric pressure varies from 7 to 9 mbar depending on season, weather and altitude.

The surface temperatures range from 130 to 300 K (ref. 4) and swings in daily temperature of 20 to 50 K are not uncommon (ref. 5). The winds were measured by the Viking lander 2 had velocities of 20 m/s or less greater than 99 percent of the time (ref. 6), but during dust storms winds greatly in excess of 25 m/s can be expected (ref. 7).

The composition of the soil was measured by X-ray fluorescence spectrometry at the Viking 1 landing site (ref. 8). Although direct mineralogical identification was not possible by the Landers, computerized search of analog mineral mixtures found a mixture of weathered ferro-silicate minerals, with smectite clays nontronite and montmorillonite to be similar to the major components. The results of the Viking biological experiments suggest that the Martian top regolith also contains highly oxidizing compounds which are probably generated by the high UV light flux present at the surface (refs. 9 and 10).

The Martian atmosphere always contains suspended dust particles which result from local and/or global dust storms that occur each year. The information obtained from the Mariner 9 and the Viking missions suggest that the dust is a mixture of many materials such as granite, basalt, basaltic glass, obsidian, quartz, andesite or montmorillonite, and the average particle size into the atmosphere is about 2 μm (ref. 11). Aerosols made of soil material and water ice are also known to be present in the Martian atmosphere. Such particles are injected in the atmosphere during dust storms. Three types of aerosol particles can be present: a water ice ground fog, a higher level ice cloud (polar hood), and suspended soil particles (ref. 12). A ground fog is composed of water ice particles having an average radius of about 2 μm, and the depth of the fog is 0.4 km. A polar hood is an ice condensation cloud of CO_2, H_2O or a mixture of both. Suspended soil particles constitute the dominant source of nondiurnal variation in atmospheric opacity. The rate of removal of dust particles from the Martian atmosphere is probably controlled by a combination of three processes: gravitational sedimentation of dust grains, eddy mixing and growth by H_2O and CO_2 ice condensation followed by gravitational sedimentation.

A significant amount of solar ultraviolet flux penetrates the surface of Mars, which affects the chemical balance of the atmosphere (ref. 6). Below 2000 Å, no solar radiation reaches the surface due to absorption by CO_2. The high flux of ultraviolet radiation continually regenerates free radicals in the atmosphere and on the surface of soil and dust particles. Any surface exposed to either the atmosphere or the soil could be subject to attack by reactive species, permanently degrading their performance.

This paper presents a theoretical study to predict the chemical effects of the Mars environment on power system components. The conditions selected in this study are presented in Table I for candidate high temperature radiator materials and photovoltaic cell material. The candidate radiator materials are carbon (C), copper (Cu), and titanium (Ti). Representative of the photovoltaic material was silicon dioxide (SiO_2) and silicon (Si). A free-energy minimization technique is used to calculate chemical equilibrium for assigned thermodynamic states of temperature and pressure. The results obtained presents which reactions are thermodynamically favorable for an assigned temperature and pressure. Thermodynamics allows the determination of the changes that can be expected, but does not allow calculation of the rates of chemical or physical process (how fast it would occur).

METHOD

Thermodynamics is the branch of science that embodies the principles of energy transformation in macroscopic systems and allows calculations of chemical equilibrium (corresponding to an infinite reaction time). Chemical equilibrium calculations can be made through the use of equilibrium constants for simple problems or applying the concept of minimization of free energy when the equilibrium composition is

determined by a number of simultaneous reactions. The computations required for simultaneous reactions can be complex and tedious, and several computer programs have been developed to perform such calculations. The computer program selected for our study was developed at NASA Lewis Research Center in 1961 to 1962 for combustion research (ref. 13). This program employs a free-energy minimization technique to calculate chemical equilibrium for assigned thermodynamic states of temperature and pressure.

The total Gibbs free energy function for the system is given by:

$$G = \Sigma(n_i G_i) \tag{1}$$

and this is the equation to be minimized with respect to the n_i (number of moles of species i) at constant T (temperature) and P (pressure).

The general criterion for equilibrium is expressed as:

$$(dG)_{T, P} = 0 \tag{2}$$

meaning that at the equilibrium state differential variation can occur in the system at constant temperature and pressure without changes in G. Combining the fundamental property relation which is a combination of the first and second laws of thermodynamics (3), and the differential Gibbs free energy equation (4), the Gibbs-Duhem equation (5) is obtained.

$$d(nU) = T\ d(nS) - P\ d(nV) + \Sigma(\mu_i\ dn_i) \tag{3}$$

$$d(nG) = d(nU) + P\ d(nV) + (nV)\ dP - T\ d(nS) - (nS)\ dT \tag{4}$$

$$d(nG) = -(nS)\ dT + (nV)\ dP + \Sigma(\mu_i\ dn_i) \tag{5}$$

where U is the internal energy, T temperature, S entropy, P pressure, V volume, and μ is the chemical potential.

Since the system is at constant temperature and pressure, equation 5 provides the criterion of chemical-reaction equilibrium as:

$$d(nG) = \Sigma(\mu_i\ dn_i) \tag{6}$$

Using the definition of fugacity (7),

$$\mu_i = G^\circ_i + RT\ \ln f_i/f_i^\circ \tag{7}$$

where the subscript denotes a property value for a standard state, R is the gas constant and f is the fugacity. The ratio of fugacities in equation (7) is called the activity coefficient, $a_i = f_i/f_i^\circ$. This activity coefficient is defined according to the conditions and standard states of the system. Substitute equation (7) into equation (6), the equilibrium constant K is defined as:

$$G^\circ = -RT\ \ln K \tag{8}$$

which can be applied to solve simple chemical equilibrium problems.

The set of equations that need to be solved are derived here for convenience. The problem is solved by finding a set of equations of n_i which minimizes nG at constant T and P subject to the restraints of the material balances.

The material balance equations are developed as follows. Let B_j be the total number of atoms of the j element present in the system, a_{ij} be the number of atoms of the j element present in each chemical species i. Then for each element j,

$$\Sigma(n_i a_{ij}) = B_j \qquad (9)$$

it can also be written as,

$$\Sigma(n_i a_{ij}) - B_j = 0 \qquad (10)$$

multiplying the above equation by a constant λ (Lagrange's multiplier), and performing a summation over all j:

$$\Sigma\{\lambda_j[\Sigma(n_i a_{ij}) - B_j]\} = 0 \qquad (11)$$

This equation added to equation (1) and partially differentiated with respect to n_i, which when set to zero (equilibrium criterion) leads to:

$$\Delta G_{fi}^{\,\circ} + RT \ln a_i + \Sigma(\lambda_j a_{ij}) = 0 \qquad (12)$$

where $\Delta G_{fi}^{\,\circ}$ is the standard Gibbs function of formation of compound i from its constituent elements at temperature T. The material balance equations, equation (12), and the summation of the mole fraction equal to 1.0 must be solved simultaneously in order to obtain the equilibrium compositions at a specified temperature and pressure.

Details of calculations and numerical methods used are discussed elsewhere (ref. 13). It is important to note that the standard state is taken as the pure ideal gas at 1 atm for each constituent in the gas phase.

The conditions selected in this study are presented in Table I for candidate high temperature radiator materials and photovoltaic cell material. The candidate radiator materials are carbon (C), copper (Cu) and titanium (Ti). Representing the photovoltaic cell materials were silicon dioxide (SiO_2) and silicon (Si). The temperatures selected are based on operational conditions expected for the materials. Space nuclear and solar dynamic power systems requires high temperature radiators for overall system efficiency. The SP-100 may be required to operate at temperatures as low as 500 K and as high as 950 K (ref. 14). Photovoltaic cells are expected to operate close to ambient temperature, for that reason silicon dioxide conditions were set for 200 to 400 K range. The pressures selected are based on the Martian atmospheric pressure which ranges from 700 to 900 Pa.

The reactive species introduced in this model include iron oxide (Fe_2O_3), hydrogen peroxide (H_2O_2) and a sodium superoxide (Na_2O_2) which are expected to be present at the surface of Mars. The amount (moles) assumed for these species are not expected to be the same as the ones that might be found on Mars, neverless the effects of these species are investigated and presented. The oxidant to fuel ratio (weight ratio), O/F, is needed as an input for the computer program. Several ratios were investigated as shown in Table I, the results presented in this paper are for O/F equal to 100.0. The above ratio presents a more likely scenario where carbon dioxide (CO_2) is the major component and the other components are in considerably lower amounts, Table II presents some of the systems investigated.

RESULTS AND DISCUSSION

The degradation obtained for the different systems selected are shown in figure 1. The results showed no differences in degradation for cases run at 700, 800 or 900 Pa. It was found that at high temperature (>500 K) the reaction between carbon and carbon dioxide is thermodynamically favorable.

Degradation of graphite, formerly carbon, would increase with temperature up to the point where all the graphite was consumed as shown in figure 2. The addition of other components such as H_2O_2, and Fe_2O_3 show the same trends, degradation and finally consumption of all the graphite. The results suggest that by adding Fe_2O_3, the graphite degradation is greater than for the other two cases involving CO_2 and CO_2/H_2O_2. Carbon/carbon composites are attractive materials for use in applications requiring strength, light weight and toughness at high temperatures. However, carbon in any form will react with oxygen, burning away rapidly at temperatures as low as 500 °C (ref. 15).

The interaction of CO_2 with copper is shown in figure 3. Reactions between copper and CO_2 were found not to be thermodynamically favorable. If some amount of hydrogen peroxide was added to the system, some changes were obtained. Some of the copper reacts to form copper oxide (CuO). Oxidizing substances may accelerate the degradation of one class of materials and retard the degradation of others. In the latter case, the behavior of the material usually represents a balance between the power of the oxidizing compounds to preserve a protective film and their tendency to accelerate the degradation when the elements responsible for the protective-film are able to destroy the film (ref. 16). The oxide film that forms on copper and copper-base alloys is not a protective film, for example in industrial oxidizing media, such as flue gas with sulfur content, copper is not recommended as a fabrication material (ref. 16).

Results obtained for Ti/CO_2 (fig. 4), shows the transformation of Ti to titanium dioxide (TiO_2). Thermodynamically it is expected that the oxide scale on titanium to consists of a sequence of layers of the different oxides of titanium (TiO, Ti_2O_3, Ti_3O_5 and TiO_2) (ref. 17), this suggests the formation of a protective film on the titanium surface. Titanium is an excellent corrosion resistant material for oxidizing atmospheres. The presence of a thin, tough oxide surface film provides excellent resistance to oxidation and other reducing environments (refs. 17 and 18). Additional oxidizing agents, such as H_2O_2 and Fe_2O_3, are expected to increase the oxidation of titanium (fig. 5).

The results obtained for the radiator surfaces show thermodynamically favorable reactions at the operational temperatures. Some of which could be critical to the performance of the system. These reactions may be significant contributors to system mechanical degradation depending upon the radiator surface material used to obtain high thermal emittance. However, metal oxides generally have enhanced emittance compared to their parent metals.

For the use of metals in dry oxygen atmospheres at low temperatures, the instability may be of no practical consequence for many metals because rates of reactions are low. However, reaction rates increase rapidly with an increase in temperature, and in applications of metals at elevated temperatures the question of corrosion resistance becomes very important (ref. 17). The total chemical reaction for the reaction of a metal M and oxygen gas O_2 to form the oxide M_aO_b may be written as,

$$aM + (b/2)O_2 = M_aO_b \qquad (13)$$

from this equation the oxidation of metals may appear as a simple chemical reaction. The reality is that the reaction path and the oxidation behavior may depend on several factors, and the reaction mechanism could be complex.

The silicon dioxide material was investigated with all of the aforementioned environmental conditions, in addition to Na_2O_2. None of the systems shows any degradation of SiO_2. However, when silicon (Si) was analyzed, figure 6, it was found that silicon was thermodynamically favorable for a reaction with a CO_2 atmosphere. The silicon changes to silicon oxide (SiO) at 200 K, as temperature is increased the SiO is transformed to SiO_2 (300 K) and no further changes were found to occurs up to 400 K. The SiO_2 formed was suspect to be a thin, noncrystalline film, which is known to be a very protective film from the oxidation of silicon. The addition of other oxidizing components, such as hydrogen peroxide and sodium superoxide, shows the same trend which is the oxidation of silicon.

CONCLUSION

The effects of the Martian environment on candidate radiator and photovoltaic array materials have been thermodynamically investigated. Although thermodynamics does not give any information about kinetics (how fast a reaction will occur), it predicts (at infinite time of reaction) what changes could occur. The results obtained in this study show thermodynamically that radiator surfaces would be degraded. Some of the materials such as copper and titanium will develop oxide films, which could be protective. Unfortunately, if a protective film is formed it is unknown how the thermal cycling, environmental conditions such as UV light, superoxides and other dust components will affect the integrity of the protective layer. An increase of the thermal emittance would be expected as consequence of the oxidation of the surfaces. Based on thermodynamics, carbon/carbon composites would have to be protected in order to survive the Mars environment.

The silicon dioxide material does not showed any signs of degradation on CO_2 enviroment, which suggests that SiO_2 will be compatible with the Mars environment. However, silicon (Si) does thermodynamically react with the Martian atmosphere. Oxidation of silicon could be critical to the photovoltaic arrays on Mars.

The results obtained in this study suggest the need for further investigations on the effect of Martian environment on power system component materials. Experimental work is required to determine the kinetics of these Martian reactions and the influence that thermal cycling, UV light and any other environmental conditions might have on them.

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TABLE I- Selected Conditions for Photovoltaic and Radiator Candidate Materials

SYSTEM	TEMPERATURE (K)	PRESSURE (N/m²)	OXIDANT/FUEL WEIGHT RATIO
PHOTOVOLTAIC MATERIAL/ENVIRONMENT			
SIO_2/CO_2	200, 300, 400	700, 800, 900	1, 10, 20, 100
$SIO_2/CO_2/Na_2O_2$	SAME	SAME	SAME
$SIO_2/CO_2/Fe_2O_3$	SAME	SAME	SAME
$SIO_2/CO_2/H_2O_2$	SAME	..SAME	SAME
$SI/CO_{2...}$	SAME	SAME	SAME
$SI/CO_2/Na_2O_2$	SAME	SAME	SAME
$SI/CO_2/Fe_2O_3$	SAME	SAME	SAME
$SI/CO_2/H_2O_2$	SAME	SAME	SAME
$SI/CO_2/Na_2O_2/Fe_2O_3/H_2O_2$	SAME	SAME	SAME
RADIATOR/ENVIRONMENT			
C (carbon)/CO_2	300, 600, 800, 1000	SAME	SAME
$C/CO_2/H_2O_2$	SAME	SAME	SAME
$C/CO_2Fe_2O_3$	SAME	SAME	SAME
Cu/CO_2	SAME	SAME	SAME
$Cu/CO_2/H_2O_2$	SAME	SAME	SAME
TI/CO_2	300, 500, 1000	SAME	SAME
$TI/CO_2/Fe_2O_3$	SAME	SAME	SAME
$TI/CO_2/H_2O_2$	SAME	SAME	SAME
$TI/CO_2/Fe_2O_3/H_2O_2$	SAME	SAME	SAME

TABLE II- Initial Number of Moles for Systems at
Oxidant to Fuel Weight Ratio of 100.

System	Moles
SiO_2	100.0
CO_2	13,656.0
SiO_2	100.0
CO_2	13,631.0
Na_2O_2	13.63
Si	100.0
CO_2	6,382.0
Si	100.0
CO_2	6350.5
H_2O_2	3.30
Fe_2O_3	6.33
Na_2O_2	3.24
C	100.0
CO_2	2727.0
Cu	100.0
CO_2	14,432.0
Ti	100.0
CO_2	10,886.0
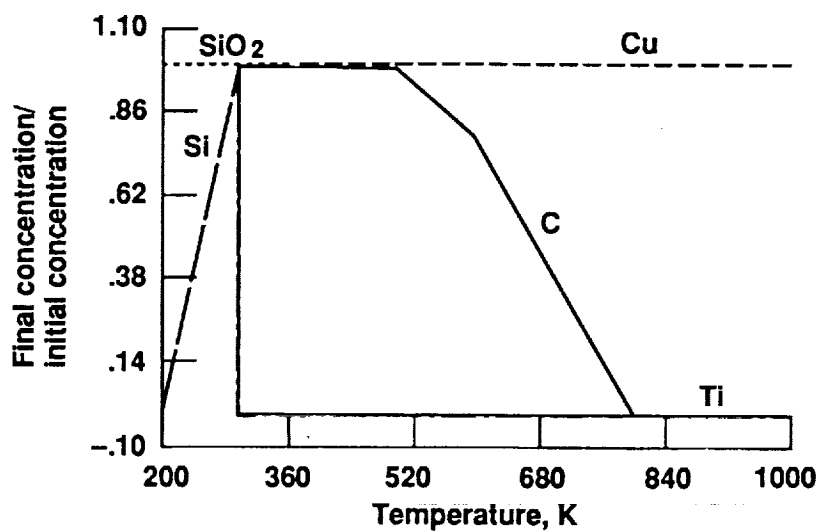
Figure 1.—Degradation of carbon, titanium,
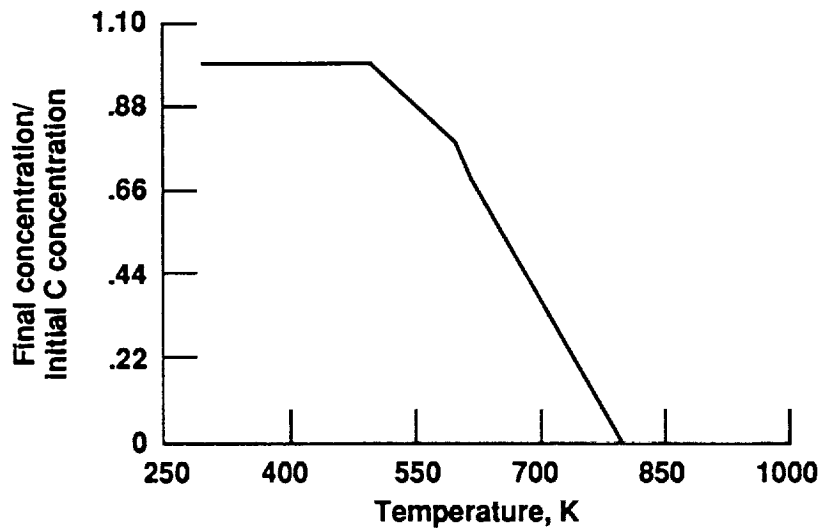copper, silicon, and silicon dioxide.

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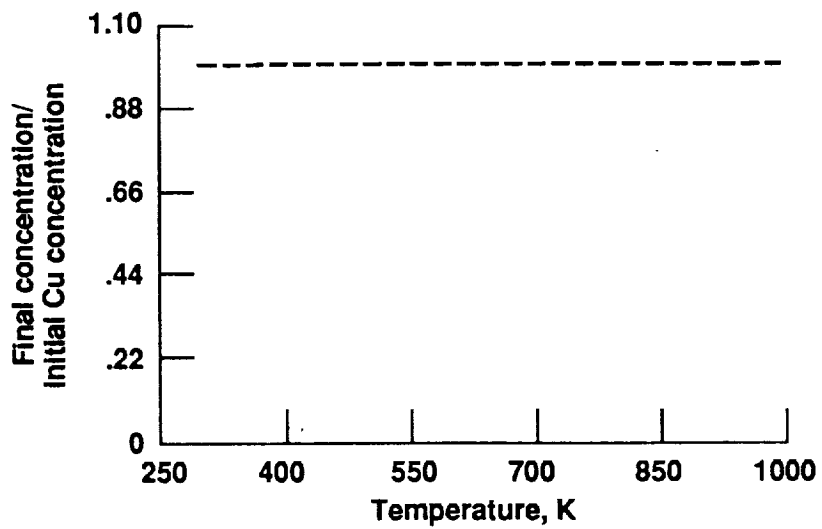**Figure 2.—Degradation of carbon in a CO_2 atmosphere.**

Figure 3.—Degradation of copper in a CO_2 atmosphere.
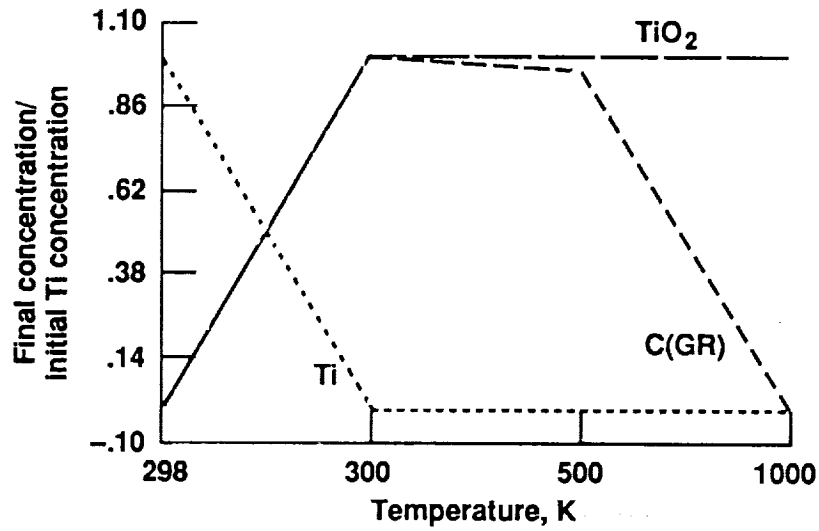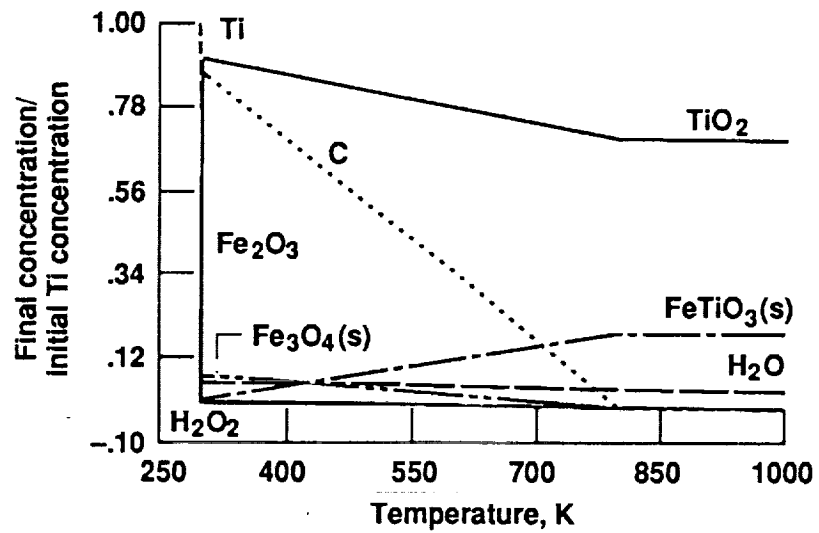
9

Figure 4.—Degradation of titanium in a CO_2 atmosphere.

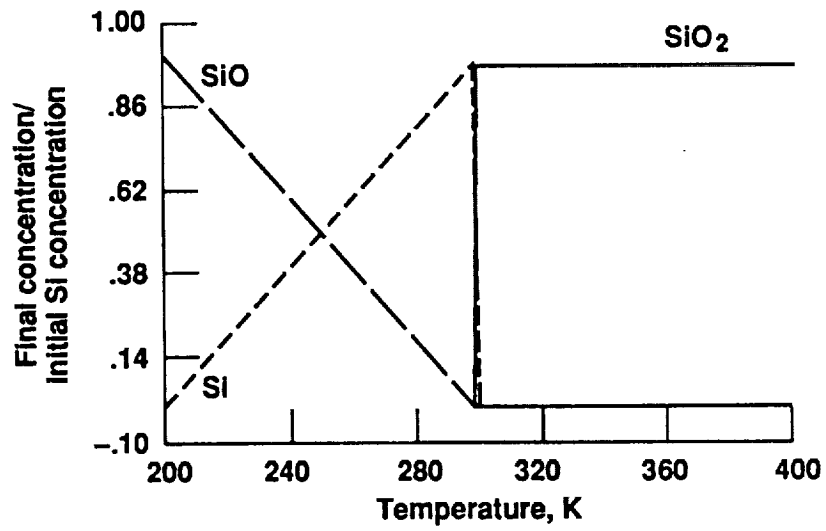Figure 5.—Degradation of titanium in an oxidizing atmosphere.

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Figure 6.—Degradation of silicon.

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16. Abstract

In the forseeable future, an expedition may be undertaken to explore the planet Mars. Some of the power source options being considered for such a mission are photovoltaics, regenerative fuel cells and nuclear reactors. In addition to electrical power requirements, environmental conditions en route to Mars, in the planetary orbit and on the Martian surface must be simulated and studied in order to anticipate and solve potential problems. Space power systems components such as photovoltaic arrays, radiators, and solar concentrators may be vulnerable to degradation in the Martian environment. Natural characteristics of Mars which may pose a threat to surface power systems include high velocity winds, dust, ultraviolet radiation, large daily variation in temperature, reaction to components of the soil, atmosphere and atmospheric condensates as well as synergistic combinations. Most of the current knowledge of the characteristics of the Martian atmosphere and soil composition was obtained from the Viking 1 and 2 missions in 1976. This paper presents a theoretical study used to assess the effects of the Martian atmospheric conditions on the power systems components. A computer program written at NASA Lewis Research Center in 1961 to 1962 for combustion research that uses a free-energy minimization technique was used to calculate chemical equilibrium for assigned thermodynamic states of temperature and pressure. The power system component materials selected for this study include: silicon dioxide, silicon, carbon, copper, and titanium. Combinations of environments and materials considered in this study include: (1) Mars atmosphere with power surface material, (2) Mars atmosphere and dust component with power surface material, (3) Mars atmosphere and hydrogen peroxide or superoxide with power system material. The chemical equilibrium calculations were performed at a composition ratio (oxidant to reactant) of 100. The temperature for the silicon dioxide material and silicon, which simulate photovoltaic cells, were 300 and 400 K; for carbon, copper and titanium, which simulate radiator surfaces, 300, 500, and 1000 K. All of the systems were evaluated at pressures of 700, 800, and 900 Pa, which simulate the Martian atmosphere.

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