NASA TECHNICAL NOTE

NASA TN D-5653

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NASA TN D-5653

MASS SPECTROMETRIC DETERMINATION OF THE DISSOCIATION ENERGIES OF TITANIUM DICARBIDE AND TITANIUM TETRACARBIDE

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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION • WASHINGTON, D. C. • MARCH 1970

1. Report No. NASA TN D-5653	2. Government Accession No.	3. Recipient's Catalog No.
4. Title and Subtitle MASS SPECTROMETRIC DETERMINATION OF THE DISSOCIATION ENERGIES OF TITANIUM DICARBIDE AND TITANIUM TETRACARBIDE		5. Report Date March 1970
		6. Performing Organization Code
7. Author(s) Carl A. Stearns and Fred J. Kohl		8. Performing Organization Report No. E-5458
9. Performing Organization Name and Address Lewis Research Center National Aeronautics and Space Administration Cleveland, Ohio 44135		10. Work Unit No. 129-03
		11. Contract or Grant No.
		13. Type of Report and Period Covered Technical Note
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, D.C. 20546		
		14. Sponsoring Agency Code

15. Supplementary Notes

16. Abstract

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$$TiC_2(g) = Ti(g) + 2C(g) \qquad D^o_{0,\,atom} = 1162 \pm 19 \text{ kJ mole}^{-1}$$

$$TiC_4(g) = Ti(g) + 4C(g) \qquad D^o_{0,\,atom} = 2403 \pm 20 \text{ kJ mole}^{-1}$$

Comparisons of second- and third-law results are discussed in terms of the ground-state degeneracies selected to make the third-law calculations for the dicarbide and tetracarbide molecules.

17. Key Words (Suggested by Author(s)) High-temperature mass spectrometry Knudsen effusion Dissociation energies Vaporization of titanium carbide Titanium dicarbide Titanium tetracarbide	18. Distribution Statement Unclassified - unlimited		
19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No. of Pages 20	22. Price* $3.00

MASS SPECTROMETRIC DETERMINATION OF THE DISSOCIATION
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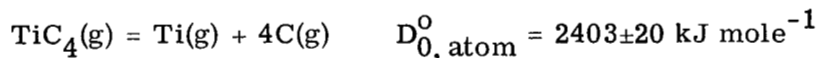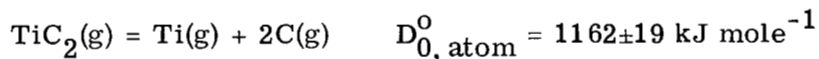# TITANIUM TETRACARBIDE

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SUMMARY

The Knudsen effusion method was used in conjunction with a double-focusing mass spectrometer to study the vaporization of the titanium-carbon system over the temperature range from 2518 to 2790 K. Titanium dicarbide (TiC_2) and titanium tetracarbide (TiC_4) molecules were identified in the gas phase. Heats of the various equilibrium reactions involved were determined by both the second- and third-law methods.

Third-law enthalpies were combined with published thermodynamic data to calculate the atomization energy of TiC_2 and TiC_4:

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Comparisons of second- and third-law results are discussed in terms of the ground-state degeneracies selected to make the third-law calculations for the dicarbide and tetracarbide molecules.

INTRODUCTION

Although Drowart et al. (ref. 1) have recently reported an atomization energy $D^o_{0,\,atom}$ of 1201 ± 21 kilojoules per mole for titanium dicarbide (TiC_2), several other mass-spectrometric vaporization studies of the titanium-carbon system have failed to reveal any titanium carbide molecular species in the gas phase. Chupka et al. (ref. 2) investigated the Ti-C system to temperatures as high as 2500 K and concluded that the

^{60}TiC$^+$ peak intensity was smaller than any of the peaks attributed to carbon species C$^+$, C$_2{}^+$, and C$_3{}^+$. Neither the dicarbide nor the tetracarbide species of Ti was reported in this study. Starostina et al. (ref. 3) likewise did not detect any Ti$_x$C$_y$ gas-phase molecules. On the other hand, Bolgar et al. (ref. 4) concluded from Langmuir experiments over the temperature range from about 1300 to 2300 K that there is a molecular species which decomposes just after leaving the surface. However, Storms (ref. 5) recommends that the conclusion of Bolgar et al. be viewed with doubt because their values for the evaporation rate are so high. The uncertainties regarding the vaporization of the Ti-C system prompted us to investigate this system at higher temperatures than previously employed.

Dicarbide and tetracarbide molecular species have been reported for a number of metal-carbon systems (refs. 6 to 11); this fact led us to speculate that the dicarbide and tetracarbide species of titanium might be stable molecules. The purpose of our study was therefore two-fold: (1) to determine if TiC$_2$ and TiC$_4$ were stable enough to be detected in the vapor phase at high temperatures, and (2) to determine the thermodynamic properties of TiC$_2$(g) and TiC$_4$(g).

PROCEDURE AND EXPERIMENTAL RESULTS

The high-temperature Knudsen cell and mass-spectrometer system has been described in detail previously (refs. 11 and 12). For the present investigation, the tungsten Knudsen cell was fitted with a graphite liner made from Ultra Carbon UFS graphite rod. The cell was heated by electron bombardment, and temperatures were measured with a calibrated Micro-Optical disappearing-filament optical pyrometer. The pyrometer was sighted through a flat glass window into three blackbody holes located near the top, middle, and bottom of the cell. Any vertical gradients in the cell were minimized by adjustment of the upper or lower filament power. For the experiment, the pyrometer indicated the same temperature at each blackbody hole. Experimentally determined window corrections were applied to all temperature readings.

Sample Preparation and Analysis

The sample was prepared by loading the graphite Knudsen cell liner with a homogeneous mixture of 0.0624 gram of titanium powder and 0.0251 gram of Ultra Carbon UFS-4 powdered graphite. This mixture gave an atomic ratio of C to Ti of 1.60 to 1. The 100-mesh Ti powder was obtained from Chas. Hardy, Inc. and was nominally 99.9 percent pure. Spectrographic analysis of the Ti indicated that aluminum, calcium,

chromium, copper, iron, magnesium, nickel, silicon, and tin were trace impurities. The graphite powder showed aluminum, silicon, magnesium, and iron as trace impurities.

The Ti-C mixture was heated in situ in the Knudsen cell chamber of the mass spectrometer. The temperature was raised over a period of several hours to 2350 K while the chamber pressure was maintained below 1×10^{-5} torr. The sample was held at 2350 K for 40 minutes, and then the temperature was lowered to 2075 K. The sample was held at this temperature for 18 hours, and the pressure remained below 3×10^{-6} torr. The ratio of sample area to orifice area was greater than 100 to 1.

After the ion intensity measurements were made, the TiC-C residue was removed from the Knudsen cell for X-ray diffraction analysis. The TiC lattice parameter a_o was found to be 432.5±0.2 picometers. According to Storms (ref. 5), this lattice parameter could represent an atom ratio composition of combined carbon to titanium of approximately 0.7 to 1.0. Lattice parameter alone is not a good measure of composition because small amounts of oxygen cause significant increases in a_o. With the graphite liner present in the experiment there was an excess of carbon, and hence we assume unit activity for C(s). When the temperature range of the experiment and the above facts are considered, the phase diagram for Ti-C (ref. 5) leads us to estimate that the composition of the sample was between 0.9 and 1.0 atom ratio for C to Ti.

Vapor Species Identification and Measurements

All ion intensity measurements were made by using ionizing electrons of 20-electron-volt energy with an anode current of 150 microamperes. The resolution of the mass spectrometer was 1800, based on the 10 percent valley definition. This resolution was sufficient to separate organic background peaks from metal ion peaks at the same nominal mass-to-charge ratio m/e.

Pressure calibration of the Knudsen cell - mass-spectrometer system was obtained by the integral gold calibration technique (ref. 13). Multiplier gains for low-intensity species were measured by ion counting techniques.

The Ti^+, TiC_2^+, and TiC_4^+ ion peaks were identified by their mass-to-charge ratio and isotopic abundance distribution. For the low-intensity TiC_4^+ species, zirconium (Zr^+) and molybdenum (Mo^+) isotopes (impurities in the tungsten cell) fall at the same nominal m/e (i.e., 96) as the major TiC_4^+ isotope. The resolution of the spectrometer was sufficient to separate the TiC_4^+ from these metal ion peaks. The resolution was not capable of separating one metal from the other. Figure 1 shows a typical portion of an actual spectrum where TiC_4^+ was measured.

No positive identification of TiC^+ could be made because of the presence of rela-
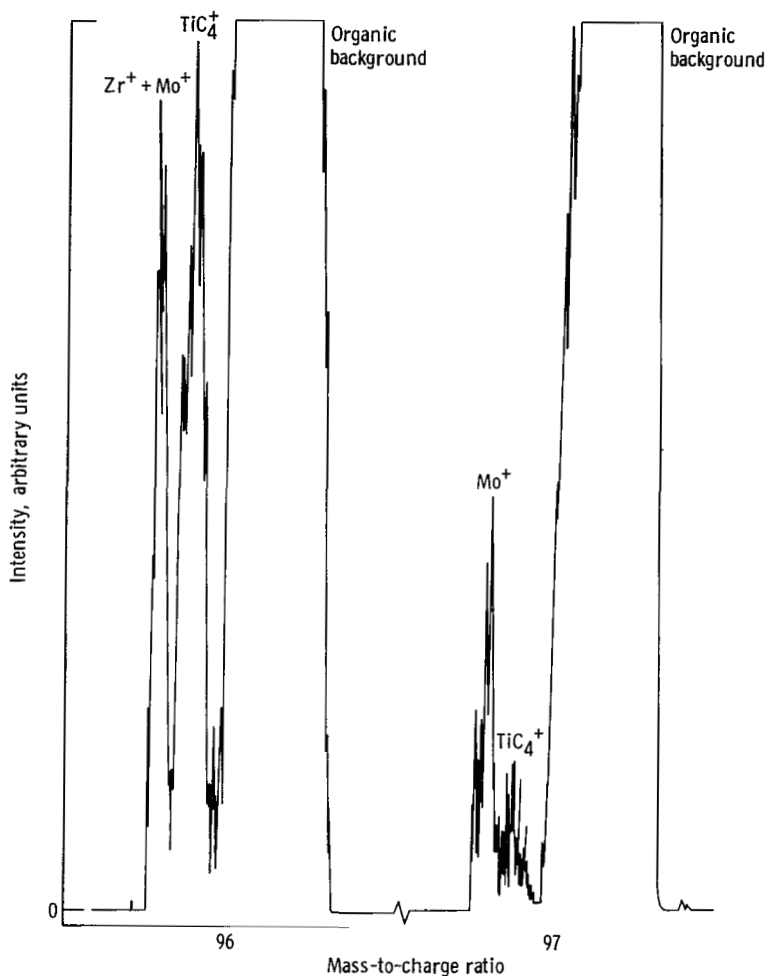
Figure 1. - Typical spectrum in region of mass-to-charge ratios 96 and 97, showing separation of TiC_4^+, Zr^+, Mo^+, and organic background.

tively large nickel (Ni^+) and cobalt (Co^+) peaks. The Co^+ peak has a single isotope at $m/e = 59$ and Ni^+ has peaks at $m/e = 58$, 60, and 61. The TiC^+ isotopic distribution puts peaks at $m/e = 58$, 59, 60, 61, and 62, with 60 being the major peak. The resolution of the spectrometer was not sufficient to separate TiC^+ from Ni^+ or Co^+.

Shutter profile measurements were used to establish positively which molecules were originating from the Knudsen cell. Measured ion currents for each species originating from the Knudsen cell correspond to the difference in output signal measured with the shutter in the open and closed positions, respectively. The "shutter effect" for all Ti-containing species was 100 percent.

At the highest temperature (2790 K) of this study, a thorough search was made for additional ion species of higher molecular weight containing Ti and C. No such species were detected, and we believe that if any were present their partial pressure was below

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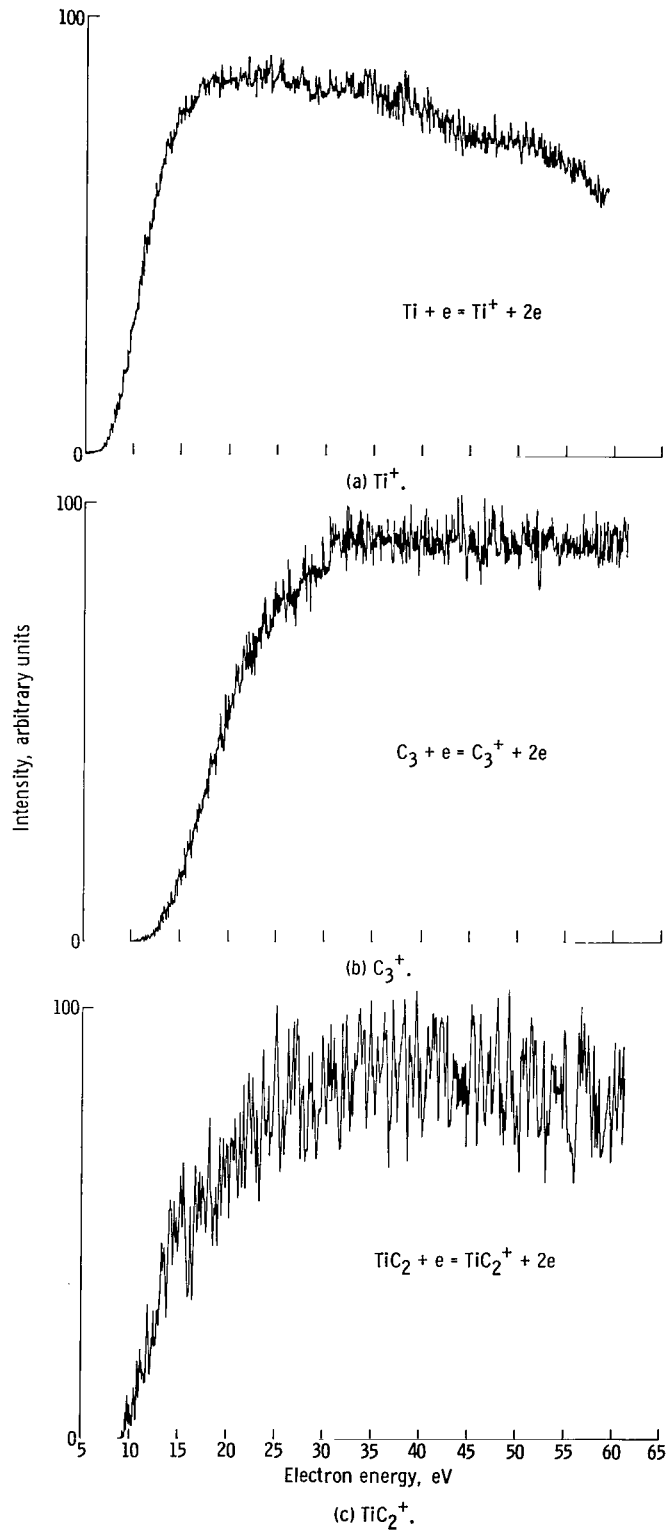$$Ti + e = Ti^+ + 2e$$

(a) Ti^+.

$$C_3 + e = C_3^+ + 2e$$

(b) C_3^+.

$$TiC_2 + e = TiC_2^+ + 2e$$

(c) TiC_2^+.

Intensity, arbitrary units

Electron energy, eV

Figure 2. – Ionization efficiency curves for Ti^+, C_3^+, and TiC_2^+.

5×10^{-5} newtons per square meter, which is the lower detection limit of our system when the resolution is set at 1800.

Ion intensities of Ti^+, TiC_2^+, and TiC_4^+ were measured at various temperatures in the range from 2518 to 2790 K. Data points were taken for both increasing and decreasing sequences of temperature. Ion intensities at any particular temperature were found to remain constant for a period of at least 20 hours.

Appearance Potentials

Ionization efficiency curves were recorded for Ti^+, C_3^+, and TiC_2^+; these are presented in figure 2. For TiC_4^+, the intensity was so low that a good recording of the ion-
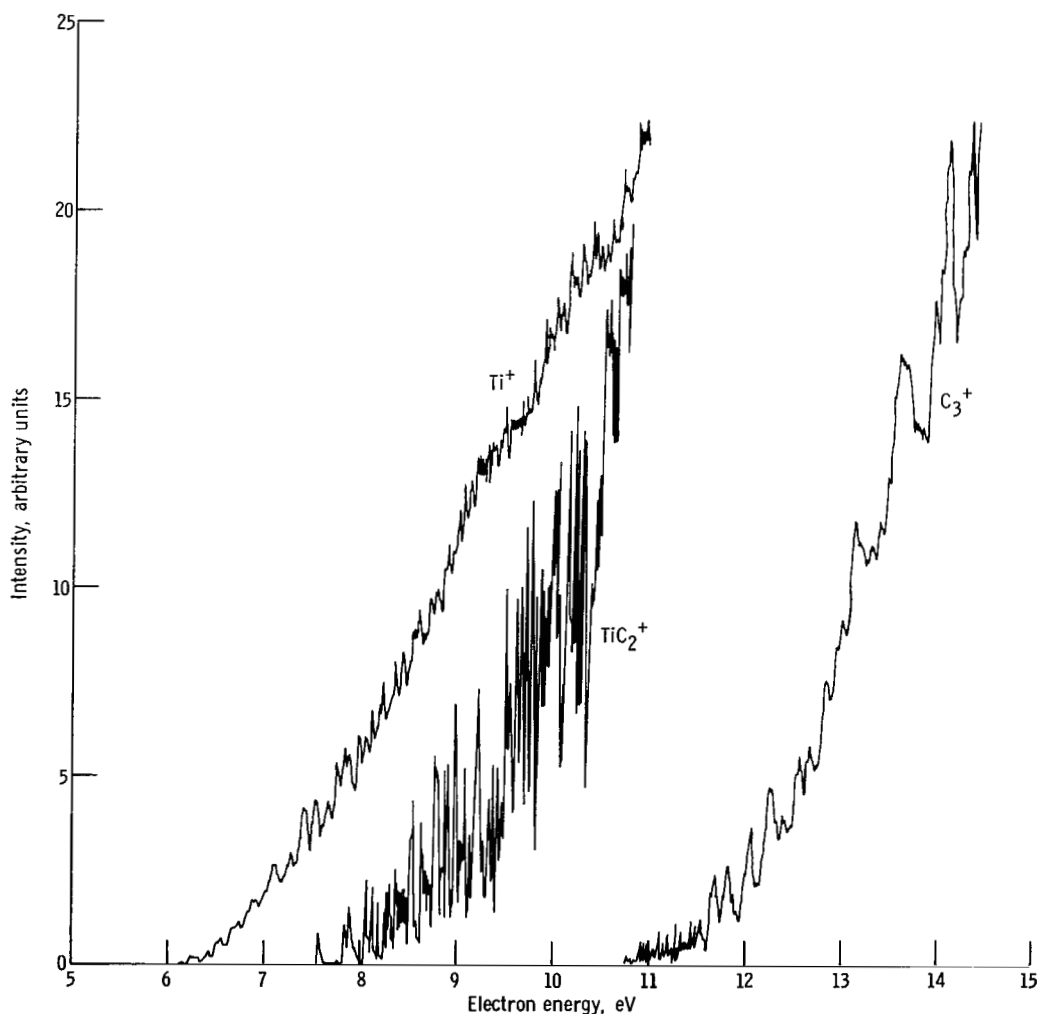

Figure 3. – Appearance potential curves for Ti^+, TiC_2^+, and C_3^+.

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TABLE I. - RELATIVE ION INTENSITIES (20-eV

ELECTRONS) AT 2703 K AND APPEARANCE

POTENTIALS FOR C_3 AND TITANIUM-

CONTAINING SPECIES

Ion	Parent	Relative intensity	Appearance potential, eV
$^{36}C_3^+$	C_3	0.28	$12.1 \pm 0.3\ (12.6)^a$
$^{48}Ti^+$	Ti	1.00	$^a6.82$ (standard)
$^{72}TiC_2^+$	TiC_2	1.2×10^{-2}	8.7 ± 0.5
$^{96}TiC_4^+$	TiC_4	1.9×10^{-4}	9.0 ± 1.0

[a]Ref. 14.

ization efficiency curve could not be obtained. Appearance potentials were measured for Ti^+, C_3^+, and TiC_2^+ by recording the initial portion of the curve on an expanded scale and applying the linear extrapolation method. Typical expanded scale curves are shown in figure 3. The literature value of the ionization potential for Ti, 6.82 electron volts (ref. 14), was used as an internal standard for calibration of the electron energy scale.

Appearance potentials and relative intensities for pertinent ions at 2703 K are listed in table I. The value of 9.0 ± 1.0 electron volts for the appearance potential of TiC_4^+ was estimated from experimental observations and is in accord with the trend observed for other tetracarbides in that the appearance potential for the tetracarbide is higher than that of the metal and metal dicarbide (refs. 6, 7, 9, and 11). The low values of the appearance potentials for Ti^+, TiC_2^+, and TiC_4^+ indicate that they are parent ions formed directly by electron impact of Ti, TiC_2, and TiC_4 molecules, respectively. The measured appearance potential of 12.1 ± 0.3 electron volts for C_3^+ is in reasonable agreement with that previously reported for the parent C_3 (ref. 14).

CALCULATIONS

Pressures

Measured ion currents I_i for individual species i were converted to corresponding partial pressures P_i at temperature T by the relation

$$P_i = \frac{k I_i T E_i}{\sigma_i \gamma_i n_i} \tag{1}$$

where k is the constant determined by the integral gold calibration, σ_i is the relative maximum ionization cross section, γ_i is the relative multiplier gain, n_i is the fractional isotopic abundance of the species i, and E_i is an experimentally determined factor

TABLE II. - MULTIPLIER GAIN, CROSS SECTION, AND ION

INTENSITY CORRECTION FACTOR, FOR VARIOUS IONS

Ion	Multiplier gain, γ_i	Cross section, σ_i	Intensity correction factor, E_i
Ti^+	1.21×10^7	5.97	1.00
TiC_2^+	1.70×10^7	9.43	1.16
TiC_4^+	1.71×10^7	12.89	[a]1.16
Au^+	8.27×10^6	6.46	1.42

[a]Assume $E_{TiC_4^+} = E_{TiC_2^+}$.

TABLE III. - PARTIAL PRESSURES OF GASEOUS

SPECIES OVER TiC_x - C SYSTEM

Temperature, T, K	Partial pressure, N/m^2		
	P_{Ti}	P_{TiC_2}	P_{TiC_4}
2585	1.18	5.30×10^{-3}	---------
2631	1.68	8.52×10^{-3}	---------
2644	2.57	1.38×10^{-2}	1.13×10^{-4}
2703	4.35	2.80×10^{-2}	3.27×10^{-4}
2774	7.08	6.20×10^{-2}	8.53×10^{-4}
2741	5.29	3.95×10^{-2}	4.50×10^{-4}
2690	3.30	1.99×10^{-2}	1.84×10^{-4}
2657	2.55	1.35×10^{-2}	1.45×10^{-4}
2618	1.54	6.53×10^{-3}	5.63×10^{-5}
2558	9.61×10^{-1}	3.55×10^{-3}	---------
2518	5.73×10^{-1}	1.51×10^{-3}	---------
2551	8.42×10^{-1}	2.74×10^{-3}	---------
2608	1.49	6.58×10^{-3}	---------
2669	2.75	1.42×10^{-2}	1.28×10^{-4}
2725	4.29	3.02×10^{-2}	3.35×10^{-4}
2757	5.41	3.97×10^{-2}	4.80×10^{-4}
2790	7.56	6.95×10^{-2}	1.05×10^{-3}

$$\log_{10} P_{Ti} = -\frac{28950\,(\pm740)}{T} + 11.279\,(\pm0.278)$$

$$\log_{10} P_{TiC_2} = -\frac{41620\,(\pm1040)}{T} + 13.773\,(\pm0.390)$$

$$\log_{10} P_{TiC_4} = -\frac{50380\,(\pm2590)}{T} + 15.047\,(\pm0.956)$$

Pressure, N/m^2

10^1

10^0

10^{-1}

10^{-2}

10^{-3}

10^{-4}

10^{-5}

3.5 3.6 3.7 3.8 3.9 4.0×10^{-4}

Reciprocal temperature, T^{-1}, K^{-1}

2800 2700 2600 2500
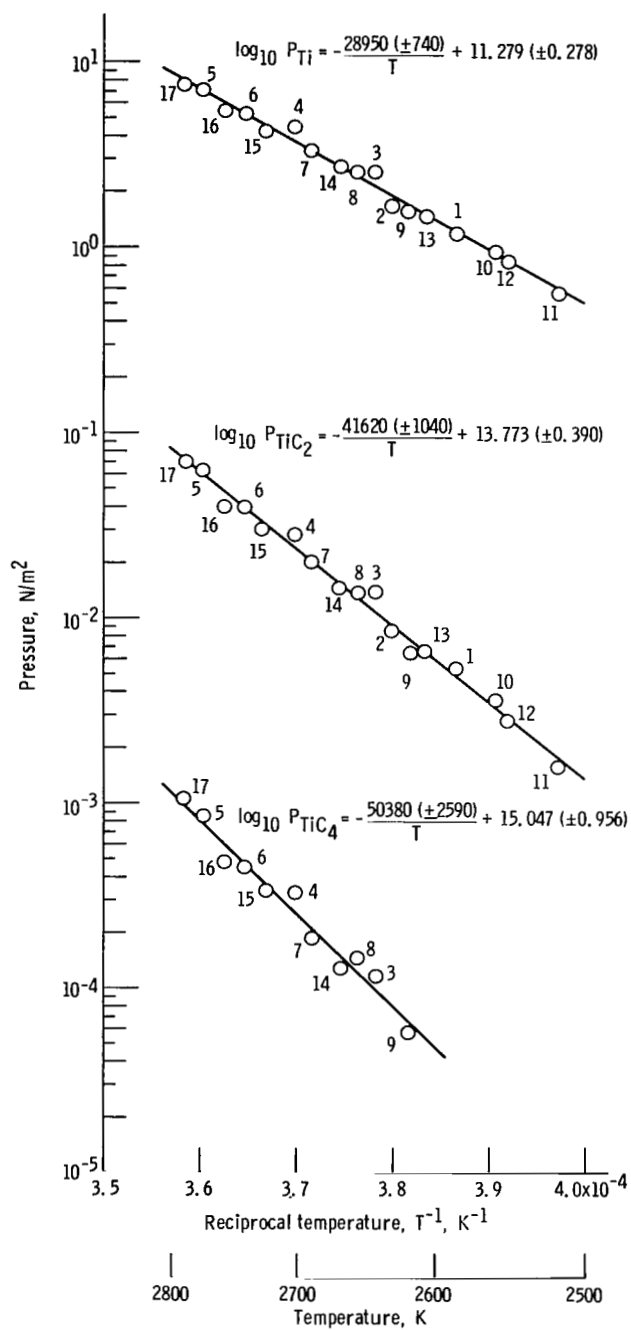
Temperature, K

Figure 4. – Partial pressures of Ti, TiC_2, and TiC_4 over TiC_x – C(s) as function of reciprocal temperature. (The points are numbered in chronological order.)

to correct ion intensities measured with electrons of 20-electron-volt energy to the maximum of the ionization efficiency curve (i. e., ratio of ion intensity at maximum of ionization efficiency curve to intensity at electron energy value used in measurements). The factor E_i was actually measured for Ti^+ and TiC_2^+, but for TiC_4^+ it was assumed to be the same as for TiC_2^+ because an experimental measurement was not feasible. Table II lists the values of σ_i, γ_i, and E_i used in our calculations. Ionization cross sections for atoms were taken from Mann (ref. 15), and the cross sections for TiC_2^+ and TiC_4^+ were derived by summing the atomic cross sections for Ti and two or four carbon atoms, respectively. Calculated partial pressures are listed in table III and plotted against reciprocal temperature in figure 4.

Heats of Reactions

Many equilibrium reactions may be considered in a thermodynamic analysis of the vaporization for the Ti-C system. We shall only consider the seven reactions listed in table IV. Reactions (1) to (4) are pressure independent because the equilibrium constant K_p depends only on the ratio of corrected intensities and not on the pressure relating

TABLE IV. - ENTHALPIES FOR REACTIONS IN TITANIUM-CARBON SYSTEM

Reaction	Second-law enthalpy, kJ mole^{-1}		Third-law enthalpy, ΔH_0^o, kJ mole^{-1}
	ΔH_T^o [a]	ΔH_0^o [b]	
(1) Ti(g) + 2C(s) = TiC$_2$(g)	242.7±10.5 (T = 2658)	264.0±16.3	256.7±19.2 [b] (217.6±20.9) [c]
(2) TiC$_2$(g) + 2C(s) = TiC$_4$(g)	190.8±27.2 (T = 2705)	186.6±31.4	178.0±19.7 [b]
(3) Ti(g) + 4C(s) = TiC$_4$(g)	443.9±31.8 (T = 2705)	462.3±48.5	434.8±19.7 [b]
(4) Ti(g) + TiC$_4$(g) = 2TiC$_2$(g)	62.8±29.7 (T = 2705)	89.5±30.1	78.7±19.7 [b]
(5) TiC$_x$(s) = Ti(g) + XC(s)	554.4±14.2 (±32.2) [b] (T = 2658)		
(6) TiC$_x$(s) + (2-X)C(s) = TiC$_2$(g)	796.6±19.7 (±46.0) [b] (T = 2658)		
(7) TiC$_x$(s) + (4-X)C(s) = TiC$_4$(g)	964.4±49.4 (±93.7) [b] (T = 2705)		

[a]Errors quoted are standard deviations of the slopes.
[b]Overall estimated uncertainty. See text.
[c]Calculated from $D_{0,\,atom}^o$ (TiC$_2$) given in ref. 1.

constant k. Appropriate corrected intensity ratios for reactions (1) to (3) are plotted against reciprocal temperature in figure 5. Second-law heats, ΔH_T^O, for these reactions were obtained from the least-squares slopes of the lines in figure 5. For the pressure-dependent reactions, (5) to (7), the second-law heats were obtained from the least-squares slopes of the $\log_{10} P_i$ (which is equal to $\log_{10} K_p$) versus $1/T$ plots presented in figure 4. The uncertainties listed for ΔH_T^O in table IV are only the standard deviations of the data points. The heats corrected to zero K were calculated by use of $H_T^O - H_0^O$
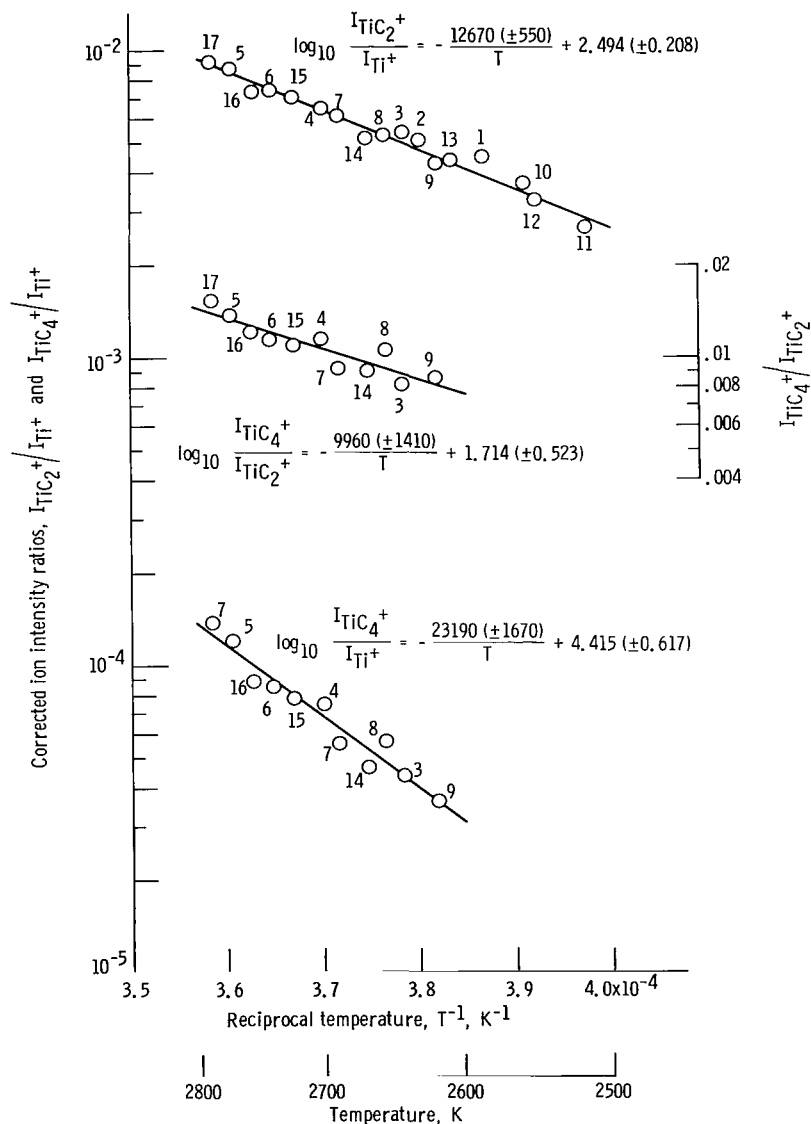

Figure 5. – Ion intensity ratios $I_{TiC_2}{}^+ / I_{Ti}{}^+$, $I_{TiC_4}{}^+ / I_{TiC_2}{}^+$, and $I_{TiC_4}{}^+ / I_{Ti}{}^+$.

values for the respective constituents. The overall estimated errors for the second-law heats, ΔH_0^O, were obtained by combining the standard deviations with the uncertainty resulting from an estimated maximum temperature error of ± 10 K.

Third-law heats, ΔH_0^O, were calculated from the relation

$$\Delta H_0^O = -2.303 \, RT \log_{10} K_p - T \, \Delta\left(\frac{G_T^O - H_0^O}{T}\right) \tag{2}$$

where R is the gas constant and $\Delta\left[(G_T^O - H_0^O)/T\right]$ is the change of the Gibbs free-energy function for the reaction. Values of the free-energy functions used in our calculations are discussed in a later section. Calculated third-law heats for reactions (1) and (3) are listed in tables V and VI together with other pertinent parameters for each data point. The estimated errors associated with the third-law ΔH_0^O values summarized in
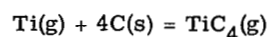
TABLE V. - THIRD-LAW ENTHALPIES FOR REACTION
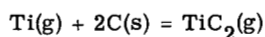
$Ti(g) + 2C(s) = TiC_2(g)$

Temperature, T, K	$\log_{10} K_p$	Change of Gibbs free-energy function, $-\Delta\left[(G_T^O - H_0^O)/T\right]$, J deg^{-1} mole^{-1}	Third-law enthalpy, ΔH_0^O, kJ mole^{-1}
2585	-2.348	53.32	254.0
2631	-2.295	53.17	255.5
2644	-2.270	53.13	255.4
2703	-2.191	52.95	256.5
2774	-2.058	52.72	255.5
2741	-2.127	52.83	256.4
2690	-2.220	52.99	256.9
2657	-2.276	53.09	256.8
2618	-2.373	53.21	258.2
2558	-2.433	53.40	255.7
2518	-2.579	53.52	259.1
2551	-2.488	53.42	257.8
2608	-2.355	53.25	256.5
2669	-2.287	53.06	258.5
2725	-2.153	52.88	256.4
2757	-2.134	52.78	258.1
2790	-2.037	52.67	255.8
			Average 256.7±1.3[a]

[a]The error quoted is the standard deviation of the points. See text for overall estimated uncertainty.

TABLE VI. - THIRD-LAW ENTHALPIES FOR REACTION

$$Ti(g) + 4C(s) = TiC_4(g)$$

Temperature, T, K	$\log_{10} K_p$	Change of Gibbs free-energy function, $-\Delta[(G_T^O - H_0^O)/T]$, J deg^{-1} mole^{-1}	Third-law enthalpy, ΔH_0^O, kJ mole^{-1}
2644	-4.357	81.27	435.4
2703	-4.124	81.12	432.7
2774	-3.919	80.93	432.6
2741	-4.070	81.02	435.6
2690	-4.254	81.16	437.4
2657	-4.245	81.24	431.8
2618	-4.437	81.34	435.3
2669	-4.332	81.21	438.1
2725	-4.107	81.06	435.1
2757	-4.052	80.98	437.1
2790	-3.857	80.89	<u>432.0</u>
			Average 434.8±2.2[a]

[a] The error quoted is the standard deviation of the points. See text for overall estimated uncertainty.

table IV were obtained by combining the standard deviations from the mean of all respective data points with the following estimated uncertainties for the other parameters: K_p, ±50 percent; T, ±10 K; and $\Delta[(G_T^O - H_0^O)/T]$, ±6.3 joules per degree per mole.

Thermodynamic Functions

Heat contents and free-energy functions for Ti(g) and C(s) were taken from JANAF tables (ref. 16). The heat contents and free-energy functions for $TiC_2(g)$ were calculated on the basis of estimated molecular parameters for an assumed linear, asymmetric Ti-C-C molecule. The Ti-C interatomic distance was calculated by the use of a modified Badger's rule (ref. 17) as 163 picometers, while the C-C interatomic distance of 131 picometers was used, the same as in C_2 (ref. 18).

The electronic ground state for TiC_2 was taken as $^3\Delta$ (statistical weight of 6), the same as TiO (ref. 19). The fundamental vibrational frequencies were calculated according to the valence force formulation given by Herzberg (ref. 20). The C-C stretching force constant was taken as 9.25×10^2 newtons per meter, the same as for C_2 (ref. 18). A value of 7.18×10^2 newtons per meter was used for the Ti-C force constant, the same as that for Ti-O (ref. 18). If a value of 0.67×10^{-18} newton meters per radian

was assumed for the bending constant k_δ, the bending force constant $k_\delta/l_1 l_2$ had a value of 0.31×10^2 newtons per meter. The calculated frequencies, in reciprocal centimeters, are $\omega_1 = 780$, $\omega_2 = 494$ (doubly degenerate), and $\omega_3 = 1810$. The moment of inertia was calculated to be 15.58×10^{-39} gram per square centimeter.

A linear symmetric C-C-Ti-C-C structure was assumed for the TiC_4 molecule. The electronic ground-state statistical weight was taken as 6. The method of Engler and Kohlrausch (ref. 21) was used to estimate the fundamental vibration frequencies. The following force constants, in newtons per meter, were used: $f_{12} = 9.25 \times 10^2$, $f_{23} = 7.18 \times 10^2$, $f_{13} = f_{22} = 1.30 \times 10^2$, $d_2 = k_\delta/l_{12} l_{23} = 0.31 \times 10^2$, and $d_3 = k_\delta/(l_{23})^2 = 0.25 \times 10^2$. When these parameters are used, the vibrational frequencies, in reciprocal centimeters, for $TiC_4(g)$ are $\omega_1 = 808$, $\omega_2 = 1878$, $\omega_3 = 1020$, $\omega_4 = 1836$, $\omega_5 = 137$, $\omega_6 = 573$, and $\omega_7 = 468$ (with ω_5 to ω_7 doubly degenerate). The moment of inertia for TiC_4 was calculated to be 45.07×10^{-39} gram per square centimeter.

The thermodynamic functions for $TiC_2(g)$ and $TiC_4(g)$ were calculated by using the rigid rotator-harmonic oscillator approximation with the aid of a computer program (ref. 22). Pertinent heat contents and free-energy functions for $TiC_2(g)$ and $TiC_4(g)$ are listed in table VII.

TABLE VII. - HEAT-CONTENTS ($H_T^o - H_0^o$) AND FREE-ENERGY

FUNCTIONS $\left[-(G_T^o - H_0^o)/T \right]$ FOR $TiC_2(g)$ AND $TiC_4(g)$

| Temperature, T, K	$TiC_2(g)$, $g_o = 6$		$TiC_4(g)$, $g_o = 6$	
	$H_T^o - H_0^o$, kJ mole^{-1}	$-(G_T^o - H_0^o)/T$, J deg^{-1} mole^{-1}	$H_T^o - H_0^o$, kJ mole^{-1}	$-(G_T^o - H_0^o)/T$, J deg^{-1} mole^{-1}
298.15	10.100	216.60	14.698	236.69
2200	118.58	305.02	205.92	381.23
2300	124.70	307.43	216.88	385.41
2400	130.83	309.74	227.86	389.43
2500	136.97	311.97	238.86	393.32
2600	143.11	314.13	249.89	397.08
2700	149.26	316.21	260.92	400.72
2800	155.41	318.22	271.96	404.24
2900	161.57	320.18	283.02	407.66
3000	167.74	322.07	294.09	410.97

Dissociation Energies

The third-law heat of reaction (1) (table IV), $\Delta H_0^O = 256.7 \pm 19.2$ kilojoules per mole, was combined with the heat of formation of $C_2(g)$, $\Delta H_{0,f}^O = 824.2 \pm 8.4$ kilojoules per mole (ref. 16) to give the dissociation energy $D_0^O(Ti\text{-}C_2)$:

$$TiC_2(g) = Ti(g) + C_2(g) \qquad D_0^O = 568 \pm 21 \text{ kJ/mole}$$
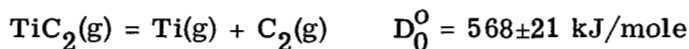
The atomization energy, $D_{0,\text{atom}}^O$, of TiC_2 was obtained by combining the third-law heat of reaction (1) with the heat of formation of $C(g)$ (ref. 16), which is 709.5 ± 1.9 kilojoules per mole, to give

$$TiC_2(g) = Ti(g) + 2C(g) \qquad D_{0,\text{atom}}^O = 1162 \pm 19 \text{ kJ/mole}$$
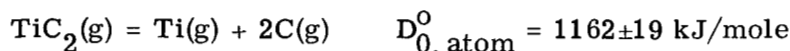
The third-law heat of reaction (3), $\Delta H_0^O = 434.8 \pm 19.7$ kilojoules per mole, was combined with the heat of formation of $C_2(g)$ to calculate the dissociation energy D_0^O $(C_2\text{-}Ti\text{-}C_2)$:

$$TiC_4(g) = Ti(g) + 2C_2(g) \qquad D_0^O = 1214 \pm 23 \text{ kJ/mole}$$
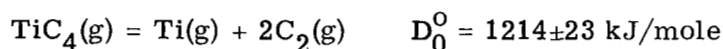
Identical values for D_0^O $(C_2\text{-}Ti\text{-}C_2)$ were obtained when either of the redundant reactions (2) or (4) was used as a starting point to derive this energy.

The atomization energy, $D_{0,\text{atom}}^O$ (TiC_4), was calculated by combining the third-law heat of reaction (3) with the heat of formation of $C(g)$:

$$TiC_4(g) = Ti(g) + 4C(g) \qquad D_{0,\text{atom}}^O = 2403 \pm 20 \text{ kJ/mole}$$
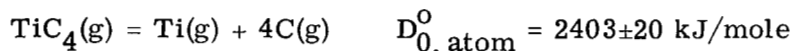
DISCUSSION

Contributions of the ground-state degeneracy of TiC_2 and TiC_4 to their respective free-energy functions have a most significant influence on the calculated values of third-law heats. Our choice of the ground state for TiC_2 was made on the basis of two comparisons. First, the second-law heat of reaction (1) of table IV was compared with third-law heats which were calculated by using free-energy functions derived from various possible ground states with statistical weights g_o of 1, 2, and 6. The use of comparisons such as this has been demonstrated by Kant and Lin (ref. 23) in their treatment of the dissociation energy of the Ti_2 molecule. The third-law heat of reaction (1) with $g_o = 1$ for TiC_2 was $\Delta H_0^O = 217.1 \pm 19.2$ kilojoules per mole; with $g_o = 2$,

ΔH_0^O = 232.4±19.2 kilojoules per mole; and with g_0 = 6, ΔH_0^O = 256.7±19.2 kilojoules per mole. The last two values agree within their uncertainties with the second-law heat of 264.0±16.3 kilojoules per mole. While the g_0 = 1 possibility is ruled out, an unequivocal choice of ground state is not possible on the basis of this comparison alone. Secondly, we compared the TiC_2 molecule with TiO because it has been postulated that the bonding of the $C_2^=$ group is similar (isoelectronic) to that of the $O^=$ ion (refs. 2 and 24). The ground state of TiO is $\cdots \pi^4\sigma\delta$, $^3\Delta$ (g_0 = 6), while $\cdots \pi^4\sigma\delta$, $^1\Delta$ (g_0 = 2) and $\cdots \pi^4\sigma^2$, $^1\Sigma$ (g_0 = 1) are low-lying excited states (ref. 19). Since the value of the third-law heat of reaction (1) calculated on the premise of g_0 = 6 agrees best with the measured second-law heat, we believe that $^3\Delta$ is a suitable ground state for TiC_2. The existence of low-lying excited states, which are quite likely with an open shell configuration, could lead to even better second-law, third-law argument.

For the case of TiC_4, the second-law heat of reaction (3) of table IV, ΔH_0^O = 462.3±48.5 kilojoules per mole, agrees within the uncertainties with the third-law heats calculated on the premise of g_0 = 1, ΔH_0^O = 394.5±19.7 kilojoules per mole; g_0 = 3, ΔH_0^O = 419.2±19.7 kilojoules per mole; and g_0 = 6, ΔH_0^O = 434.8±19.7 kilojoules per mole. Again, no unequivocal selection of a ground state can be made on the basis of this comparison alone. The probable ground state of TiO_2 is $\cdots \pi^4\sigma^2$, $^1\Sigma$ (g_0 = 1) (ref. 16), while $\cdots \pi^4\sigma\sigma$, $^3\Sigma$ (g_0 = 3), $\cdots \pi^3\sigma^2\sigma$, $^3\Pi$ (g_0 = 6), and $\cdots \pi^4\sigma\delta$, $^3\Delta$ (g_0 = 6) are possible low-lying excited states. If we were to compare TiC_4 with TiO_2, we would be inclined to select a ground state of $^1\Sigma$. In spite of this analogy, we used g_0 = 6 because the value of the third-law heat came closer to approaching the second-law value. The relatively large uncertainty in our second-law heat precludes any definite selection of the ground-state degeneracy for TiC_4.

The absence of any perceptible trend in our calculated third-law heats as a function of temperature serves to indicate that no large systematic temperature error existed in our experiment. Furthermore, the fact that the values of the measured second-law heats and calculated third-law heats for reactions (1) to (4) agreed within their uncertainties demonstrates that other systematic errors were small and that our assumptions concerning ionization cross sections and estimated thermodynamic functions were adequate. Our value of 1162±19 kilojoules per mole for the atomization energy of TiC_2 just agrees within the uncertainties with the value of 1201±21 kilojoules per mole reported by Drowart et al. (ref. 1) on the basis of an unspecified ground state for TiC_2.

The partial pressures for Ti, TiC_2, and TiC_4 that we report here are intended only to show the order of magnitude of these pressures. While the Ti pressures are of the same order of magnitude as those compiled by Storms (ref. 5) for the TiC + C system, they may not represent any improvement of his values. The listed pressures, as well as the heats, for reactions (5) to (7) pertain strictly to the TiC_x solid phase, the composition of which is not completely specified in our experiment. Storms has explicitly

pointed out that complete knowledge of both the composition of the solid phase and the oxide concentration are required if absolute values for a thermophysical property such as vapor pressure are to be determined for the titanium-carbon system.

Comparisons of experimental values of $D_0(M-O)$ and $D_0(M-C_2)$ for a number of Group IIIA, Group IVA, and rare-earth elements show that the bond energies for the $M-C_2$ are generally less than those for M-O by about 42 to 126 kilojoules (refs. 11 and 24). These comparisons of dicarbides with oxides can now be extended to at least one Group IVB metal carbide. We find that the dissociation energy of TiC_2 is 92 kilojoules less than that reported for TiO (ref. 25); for C_2-Ti-C_2, the "average" bond energy for $Ti-C_2$ is 49 kilojoules less than the "average" Ti-O bond energy of 655.7 ± 6.3 kilojoules in O-Ti-O (ref. 25). For this one Group IVB,element, Ti, the oxide-dicarbide analogy appears to hold and the developing trend encourages us to speculate further. Because the zirconium (Zr) and hafnium (Hf) oxides and dioxides are stable molecules (ref. 26), we predict from bond energy considerations that the dicarbides and tetracarbides of Zr and Hf probably do exist as stable molecules. The fact that the ZrC_2 molecule has recently been observed in relatively high concentrations in the equilibrium vapor over solid ZrC + C (ref. 3) lends credence to our speculation.

Lewis Research Center,
    National Aeronautics and Space Administration,
        Cleveland, Ohio, January 12, 1970,
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