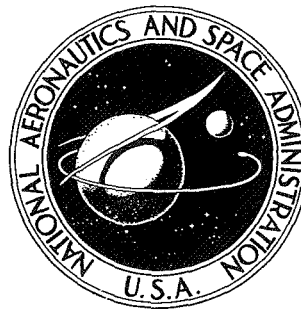


NASA TECHNICAL NOTE



NASA TN D-5719

NASA TN D-5719

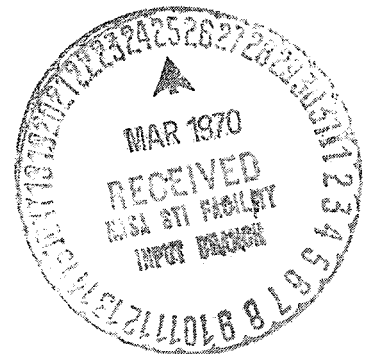
CASE FILE COPY

MASS SPECTROMETRIC DETERMINATION
OF THE DISSOCIATION ENERGY
OF VANADIUM AND CHROMIUM DICARBIDE
AND VANADIUM TETRACARBIDE

by Fred J. Kohl and Carl A. Stearns

Lewis Research Center

Cleveland, Ohio



1. Report No. NASA TN D-5719	2. Government Accession No.	3. Recipient's Catalog No.	
4. Title and Subtitle MASS SPECTROMETRIC DETERMINATION OF THE DISSOCIATION ENERGY OF VANADIUM AND CHROMIUM DICARBIDE AND VANADIUM TETRACARBIDE		5. Report Date March 1970	6. Performing Organization Code
		8. Performing Organization Report No. E-5469	
7. Author(s) Fred J. Kohl and Carl A. Stearns		10. Work Unit No. 129-03	11. Contract or Grant No.
9. Performing Organization Name and Address Lewis Research Center National Aeronautics and Space Administration Cleveland, Ohio 44135		13. Type of Report and Period Covered Technical Note	
		14. Sponsoring Agency Code	
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, D. C. 20546		15. Supplementary Notes	
16. Abstract The Knudsen effusion method was used in conjunction with a double-focusing mass spectrometer to study the vaporization of the vanadium-carbon and chromium-carbon systems over the temperature ranges 2417 to 2603 and 2083 to 2176 K, respectively. The molecular species VC ₂ , VC ₄ , and CrC ₂ were identified, and experimentally determined third-law enthalpies were combined with published thermodynamic data to yield the following dissociation energies: $\text{VC}_2(\text{g}) = \text{V}(\text{g}) + \text{C}_2(\text{g}) \quad D_0^{\circ}(\text{V-C}_2) = 570 \pm 20 \text{ kJ/mole}$ $\text{VC}_4(\text{g}) = \text{V}(\text{g}) + 2\text{C}_2(\text{g}) \quad D_0^{\circ}(\text{C}_2\text{-V-C}_2) = 1193 \pm 22 \text{ kJ/mole}$ $\text{CrC}_2(\text{g}) = \text{Cr}(\text{g}) + \text{C}_2(\text{g}) \quad D_0^{\circ}(\text{Cr-C}_2) = 445 \pm 18 \text{ kJ/mole}$ Atomization energies were also calculated. Results are discussed in terms of the metal oxide - metal dicarbide bond strength analogy.			
17. Key Words (Suggested by Author(s)) Vanadium and chromium carbides; High-temperature mass spectrometry; Knudsen effusion; Dissociation energies; Vaporization of chromium carbide; Vaporization of vanadium carbide; Vanadium dicarbide; Vanadium tetracarbide; Chromium dicarbide		18. Distribution Statement Unclassified - unlimited	
19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No. of Pages 15	22. Price * \$3.00

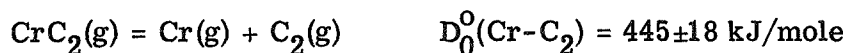
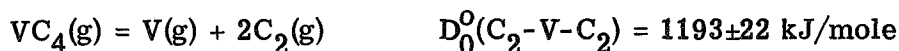
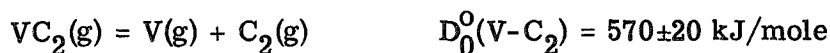
MASS SPECTROMETRIC DETERMINATION OF THE DISSOCIATION ENERGY OF VANADIUM AND CHROMIUM DICARBIDE AND VANADIUM TETRACARBIDE

by Fred J. Kohl and Carl A. Stearns

Lewis Research Center

SUMMARY

The Knudsen effusion method was used in conjunction with a double-focusing mass spectrometer to study the vaporization of the vanadium-carbon and chromium-carbon systems over the temperature ranges 2417 to 2603 and 2083 to 2176 K, respectively. The molecular species VC_2 , VC_4 , and CrC_2 were identified, and experimentally determined third-law enthalpies were combined with published thermodynamic data to yield the following dissociation energies:



Atomization energies were also calculated. Results are discussed in terms of the metal oxide - metal dicarbide bond strength analogy.

INTRODUCTION

Only a few vaporization studies of the vanadium-carbon (V-C) and chromium-carbon (Cr-C) systems have been reported in the literature (refs. 1 to 5). Two of these studies suggest or present evidence for the existence of gaseous metal-carbon molecular species. Drowart et al. (ref. 1) gave no details of their study but did report an atomization energy of 1167 ± 21 kilojoules per mole for VC_2 . Doan (ref. 2) used spark-source mass spectrometry to study the Cr-C system and reported peaks that correspond to the CrC^+ and CrC_2^+ molecular ions. His ratios of metal carbide to metal for these two species were

1×10^{-5} and 3×10^{-4} , respectively. The other investigators (refs. 3 to 5) reported vapor pressures of the metal atoms over various metal-carbon condensed phases.

Recent identifications of gaseous dicarbide and tetracarbide molecules of high stability in equilibrium over condensed phases of various rare-earth-carbon systems (refs. 6 to 11) and transition metal-carbon systems (refs. 12 and 13) prompted the present investigation of the V-C and Cr-C systems. Knudsen effusion molecular-beam mass spectrometric methods appeared to be ideally suited to these studies. The objectives were to use this method to identify metal-carbide molecules and to measure their dissociation energy. The study was limited in both cases to compositions of condensed phase metal carbide in equilibrium with excess carbon at each temperature.

PROCEDURE

The Knudsen cell mass spectrometer system and experimental method used in this study were the same as described previously (refs. 6, 12, and 14). The tungsten Knudsen cell had a 0.076-centimeter-diameter zero-length (knife edge) orifice. The cell was fitted with a graphite liner made from Ultra Carbon UFS^a graphite rod. A 0.25-centimeter-diameter hole in the wall of the liner was alined to the effusion orifice.

For the study of the V-C system, a homogeneous mixture of graphite (Ultra Carbon UFS-4) and vanadium, in the atomic ratio of 2.1 to 1.0, was loaded into a new cell liner. The vanadium was 99 percent pure as obtained from Cerac Inc. The mixture was heated in the Knudsen cell to 2330 K. Eight hours were required to reach this temperature with the pressure maintained at less than 1×10^{-5} torr. The cell was kept at temperature for an additional 16 hours before measurements were started. At the conclusion of the experiment, X-ray diffraction analysis showed the residue to be a mixture of graphite and cubic vanadium carbide with a lattice parameter of 416.5 ± 0.2 picometers. According to Storms (ref. 4), this lattice parameter corresponds to a composition of approximately VC_{0.88}, which is close to the upper phase limit for the VC phase.

For each of the two experiments (I and II) on the Cr-C system, the cell liners were loaded with a homogeneous mixture of Cr₃C₂ and graphite (Ultra Carbon UFS-4) in the weight ratio of 10 to 1. The Cr₃C₂, of unspecified purity, was purchased from Astro Metals Inc. Spectrographic analysis for metallic impurities revealed moderate amounts of aluminum plus trace amounts of boron, copper, iron, vanadium, nickel, silicon, and

^aCertain commercial products are identified by name in this report to specify the experiment completely. In no case does such identification imply a recommendation or endorsement by NASA, nor does it imply that the products are the best available for the purpose.

titanium. Each Cr_3C_2 -C mixture was heated in a Knudsen cell to 1400 K over a period of 24 hours prior to the start of the ion intensity measurements. For the last 10 hours of the preheating period, the pressure was maintained at less than 2×10^{-6} torr. X-ray diffraction analysis of the sample residue from experiment II showed that the solid phase was a mixture of graphite, Cr_3C_2 , and a small amount of Cr_7C_3 .

The ion species were identified by their mass-to-charge ratio (m/e) and isotopic abundances. A movable slit between the ion source and the Knudsen cell was used as a shutter. The shutter could be used to block the molecular beam, to allow optimum passage of the beam, or to scan the beam to study its profile. The shutter was used to establish which species were originating from the Knudsen cell. The shutter effect is the difference in measured ion intensity with the shutter in the open and closed positions. All intensity measurements were made with ionizing electron energies of 20 eV and an anode current of 150 microamperes. Appearance potentials were measured by recording ion intensity against electron energy (ionization efficiency curve) and applying the linear extrapolation method.

RESULTS AND CALCULATIONS

The only pertinent ion species detected were V^+ , VC_2^+ , VC_4^+ , Cr^+ , and CrC_2^+ . A careful search at the maximum temperature of each experiment failed to reveal any monocarbides or higher carbides other than those just noted.

In the vanadium experiment, ion intensities were measured at 13 temperatures in the range from 2417 to 2603 K. Below 2417 K, the intensity of the carbide species was too low to measure, and above 2603 K, the intensity of V^+ became high enough to indicate that the pressures were approaching the point where the conditions of effusive flow no longer applied. The shutter effect for V^+ , VC_2^+ , and VC_4^+ was 100 percent.

The temperature range for the two chromium experiments was from 2083 to 2176 K. In the first chromium experiment, ion intensities were measured at 11 temperatures, and in the second experiment, intensities were measured at seven temperatures. The high and low limits of the temperature range studied were dictated by the same factors that prevailed in the vanadium experiment. The shutter effect for Cr^+ was 100 percent, but for CrC_2^+ the shutter effect was between 80 and 100 percent. Ion intensity values were derived by making measurements with the shutter open and closed and taking differences. It was not possible to identify the nonshutterable background peak at $m/e = 76$ that interfered with the CrC_2^+ peak, and the resolution of the mass spectrometer was not high enough to separate it from the CrC_2^+ .

The measured ion currents I_i are related to partial pressures P_i at temperature T by the equation

$$P_i = \frac{kI_i T E_i}{\sigma_i \gamma_i n_i} \quad (1)$$

where k is the sensitivity constant for the apparatus, E_i is the experimentally determined factor to correct ion intensities measured at the working voltage to the maximum of the ionization efficiency curve (ratio of intensity at maximum to intensity at measurement electron energy), σ_i is the relative maximum electron impact ionization cross section, γ_i is the relative multiplier gain, and n_i is the fractional isotopic abundance of the species i .

For a reaction of the form



the equilibrium constant K_P is given as

$$K_P = \frac{P_{MC_x}}{(P_M)(a_C)^x} \quad (3)$$

where a_C is the activity of the solid graphite phase. Reactions of this type are termed pressure independent since K_P is directly proportional to the ratio of the pressures of the gaseous products and reactants. Therefore, for such reactions,

$$K_P = \frac{I_1 E_1 \sigma_2 \gamma_2 n_2}{I_2 E_2 \sigma_1 \gamma_1 n_1} \quad (4)$$

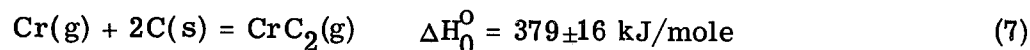
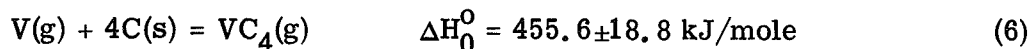
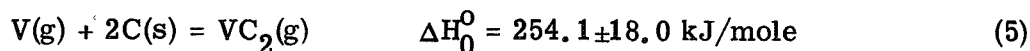
where 1 and 2 refer to the products and reactants, respectively, and the activity of graphite is taken as 1.

Ionization efficiency curves could only be obtained for V^+ and VC_2^+ because the other ion intensities were too low to obtain meaningful results. The measured appearance potential for VC_2^+ was 8.6 ± 0.5 eV, with the 6.74-eV value for V^+ (ref. 15) used as the internal standard. The factor E_i was required to correct ion intensities obtained with a working ionizing energy of 20 eV to the maximum of the ionization efficiency curve. The factor E_i was measured directly for V^+ and VC_2^+ , but for VC_4^+ , $E_{VC_4^+} = E_{VC_2^+}$ was assumed. For chromium, $E_{CrC_2^+} = E_{VC_2^+}$ was assumed.

Relative maximum ionization cross sections σ_i for atoms were taken from Mann (ref. 16), and the cross sections for VC_2 , VC_4 , and CrC_2 were calculated by summing the respective metal atom cross section with the cross section of the appropriate number

of carbon atoms. All carbide ion intensities were too low to measure the absolute gain of the electron multiplier, and, therefore, the relative gains γ_i for the various species were taken to be the same as those measured in a previous work (ref. 12) on the titanium-carbon system.

Three pressure-independent reactions were considered. These reactions and the corresponding calculated third-law heats are



The value for chromium was obtained by combining the results of experiments I and II. Unit activity for C(s) was assumed because the graphite liner always assured an excess of carbon. Values of the various parameters just discussed are listed in table I. Equilibrium constants for reactions 5 to 7 are listed in tables II to IV for each measurement temperature.

TABLE I. - RELATIVE MULTIPLIER GAINS, CROSS SECTIONS, ION INTENSITY FACTORS, AND APPEARANCE POTENTIALS FOR VANADIUM- AND CHROMIUM-CONTAINING IONS

Ion	Relative multiplier gain, γ_i	Relative maximum electron impact ionization cross section, α_i	Ion intensity correction factor, E_i	Appearance potential, A. P., eV
V ⁺	1.0	5.58	1.00	^a 6.74
VC ₂ ⁺	^b 1.4	9.04	1.36	8.6 ± 0.5
VC ₄ ⁺	^c 1.4	12.50	^d 1.36	-----
Cr ⁺	1.0	5.45	1.00	-----
CrC ₂ ⁺	^b 1.4	8.91	^e 1.36	-----

^aRef. 15 (standard).

^b $\gamma_{\text{V}^+}/\gamma_{\text{VC}_2^+}$ and $\gamma_{\text{Cr}^+}/\gamma_{\text{CrC}_2^+}$ were taken to be same as that measured for $\gamma_{\text{Ti}^+}/\gamma_{\text{TiC}_2^+}$ (ref. 12).

^c $\gamma_{\text{VC}_2^+}/\gamma_{\text{VC}_4^+}$ was taken to be same as that measured for $\gamma_{\text{TiC}_2^+}/\gamma_{\text{TiC}_4^+}$ (ref. 12).

^dAssume that $E_{\text{VC}_4^+} = E_{\text{VC}_2^+}$ (measured).

^eAssume that $E_{\text{CrC}_2^+} = E_{\text{VC}_2^+}$ (measured).

TABLE II. - THIRD-LAW ENTHALPIES FOR REACTION $V(g) + 2C(s) = VC_2(g)$

Temperature, T, K	Equilibrium constant, K_P	Log of equilibrium constant, $\log_{10} K_P$	Change of Gibbs free energy function, $-\Delta \left[\frac{G_T^O - H_0^O}{T} \right],$ J/(deg)(mole)	Third-law enthalpy, $\Delta H_0^O,$ kJ/mole
2503	1.21×10^{-3}	-2.917	45.97	254.8
2568	1.80	-2.745	45.72	252.4
2539	1.37	-2.863	45.83	255.5
2547	1.69	-2.785	45.80	252.5
2580	1.95	-2.710	45.68	251.7
2549	1.59	-2.799	45.79	253.3
2503	1.33	-2.876	45.97	252.9
2488	1.22	-2.914	46.02	253.3
2470	1.18	-2.928	46.09	252.3
2452	8.41×10^{-4}	-3.075	46.15	257.5
2417	7.28×10^{-4}	-3.138	46.27	257.0
2557	1.50×10^{-3}	-2.824	45.76	255.2
2603	1.84×10^{-3}	-2.735	45.59	255.0
Average				^a 254.1 ± 1.9

^aError quoted is standard deviation of points. See text for overall estimated uncertainty.

TABLE III. - THIRD-LAW ENTHALPIES FOR REACTION $V(g) + 4C(s) = VC_4(g)$

Temperature, T, K	Equilibrium constant, K_P	Log of equilibrium constant, $\log_{10} K_P$	Change of Gibbs free energy function, $-\Delta \left[\frac{G_T^O - H_0^O}{T} \right],$ J/(deg)(mole)	Third-law enthalpy, $\Delta H_0^O,$ kJ/mole
2503	3.16×10^{-6}	-5.500	73.93	448.6
2568	3.18	-5.498	73.72	459.6
2539	3.45	-5.462	73.82	452.9
2547	3.00	-5.523	73.79	457.2
2580	4.61	-5.336	73.68	453.7
2549	3.12	-5.506	73.78	456.8
2503	2.48	-5.606	73.93	453.7
2557	3.32	-5.479	73.76	456.8
2603	3.97	-5.401	73.61	460.8
Average				^a 455.6 ± 3.7

^aError quoted is standard deviation of points. See text for overall estimated uncertainty.

TABLE IV. - THIRD-LAW ENTHALPIES FOR REACTION $\text{Cr(g)} + 2\text{C(s)} = \text{CrC}_2\text{(g)}$

Temperature, T, K	Equilibrium constant, K_P	Log of equilibrium constant, $\log_{10} K_P$	Change of Gibbs free energy function, $-\Delta \left[\frac{G_T^0 - H_0^0}{T} \right],$ J/(deg)(mole)	Third-law enthalpy, $\Delta H_0^0,$ kJ/mole
Experiment I				
2083	$4.1_8 \times 10^{-7}$	-6.379	62.32	384
2119	7.6_1	-6.119	62.24	380
2133	9.2_8	-6.032	62.21	379
2111	6.8_9	-6.162	62.26	381
2116	7.6_3	-6.117	62.25	380
2154	$1.0_2 \times 10^{-6}$	-5.991	62.17	381
2125	$1.0_5 \times 10^{-6}$	-5.979	62.23	376
2124	$6.5_5 \times 10^{-7}$	-6.184	62.23	384
2146	$1.0_1 \times 10^{-6}$	-5.996	62.18	380
2166	$1.2_3 \times 10^{-6}$	-5.910	62.14	380
2100	$1.0_4 \times 10^{-6}$	-5.983	62.28	371
Experiment II				
2101	$9.2_7 \times 10^{-7}$	-6.033	62.28	374
2132	$1.4_1 \times 10^{-6}$	-5.851	62.21	371
2154	$9.2_0 \times 10^{-7}$	-6.036	62.17	383
2188	$1.7_9 \times 10^{-6}$	-5.747	62.10	377
2121	$8.2_5 \times 10^{-7}$	-6.084	62.24	379
2147	$1.3_4 \times 10^{-6}$	-5.873	62.18	375
2176	$1.2_5 \times 10^{-6}$	-5.903	62.11	381
Average				^a 379±4

^aError quoted is standard deviation of points. See text for overall estimated uncertainty.

Third-law heats were calculated according to the relation

$$\Delta H_0^0 = -2.303 RT \log_{10} K_P - T \Delta \left(\frac{G_T^0 - H_0^0}{T} \right) \quad (8)$$

where R is the gas constant and $\Delta \left[\frac{G_T^0 - H_0^0}{T} \right]$ is the change of the Gibbs free energy function for the reaction under consideration. The values of $\Delta \left[\frac{G_T^0 - H_0^0}{T} \right]$ and ΔH_0^0 are presented in tables II to IV.

The values of the free energy functions used for V(g) and Cr(g) were taken from Hultgren et al. (ref. 17), and those used for C(s) were taken from the JANAF tables (ref. 18). The heat contents and free energy functions for $\text{VC}_2\text{(g)}$ and $\text{CrC}_2\text{(g)}$ were calculated on the basis of estimated molecular parameters for an assumed linear asym-

TABLE V. - ESTIMATED MOLECULAR PARAMETERS FOR
 VC_2 , VC_4 , AND CrC_2

	Molecule		
	VC_2	VC_4	CrC_2
Internuclear separation, pm			
V-C	*162	162	----
Cr-C	----	---	*168
C-C	**131	131	131
Moment of inertia, g-cm ²	15.74×10^{-39}	44.71×10^{-39}	16.59×10^{-39}
Force constants, N/m			
k_{V-C}^\dagger	7.36×10^2	7.36×10^2	-----
k_{Cr-C}^\dagger	-----	-----	5.82×10^2
k_{C-C}^{**}	9.25×10^2	9.25×10^2	9.25×10^2
$k_\delta, N \cdot m/rad^\ddagger$	6.70×10^{-19}	-----	6.70×10^{-19}
$f_{13,22}^\S$	-----	1.30×10^2	-----
Frequencies (degeneracy), cm ⁻¹			
ω_1	780(1)	812(1)	709(1)
ω_2	494(2)	1883(1)	488(2)
ω_3	1814(1)	1013(1)	1767(1)
ω_4	-----	1841(1)	-----
ω_5	-----	136(2)	-----
ω_6	-----	570(2)	-----
ω_7	-----	468(2)	-----
Ground-state statistical weight	₄	₄	# ₅

* Calculated by use of modified Badger's rule (ref. 25).

** From C_2 (ref. 26).

† Force constants for V-C and Cr-C were assumed to be same as those of corresponding oxides (ref. 26).

‡ See ref. 27.

§ See ref. 19.

|| Ground state of $^4\Sigma$ was assumed for VC_2 by analogy to VO (ref. 28).

The same electronic contribution was assumed for VC_4 .

Ground state of $^5\Sigma$ was assumed for CrC_2 by analogy with apparent ground state for CrO (private communication with K. D. Carlson of Case Western Reserve University).

metric M-C-C molecule. For VC₄(g), a linear symmetric C-C-V-C-C structure was assumed, and the method of Engler and Kohlrausch (ref. 19) was used to estimate fundamental vibration frequencies. All thermodynamic functions were calculated with a computer program (ref. 20) using the rigid rotator - harmonic oscillator approximation. Pertinent molecular parameters are listed in table V, and heat contents and free energy functions are given in tables VI and VII. The estimated total errors associated with the third-law heats ΔH_0^0 were obtained by combining the standard deviations from the mean of all data points listed in tables II to IV with estimated uncertainties in the values of the

TABLE VI. - HEAT CONTENTS AND FREE ENERGY
FUNCTIONS FOR VC₂(g) AND VC₄(g)

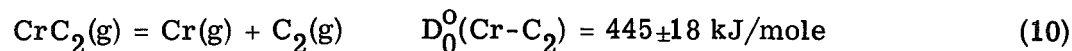
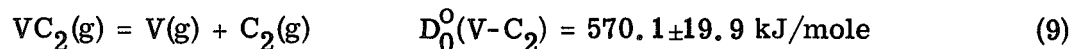
Temperature, T, K	Heat content, $H_T^0 - H_0^0$, kJ/mole	Free energy function, $-(G_T^0 - H_0^0)/T$, J/(deg)(mole)
VC ₂ (g)		
298.15	10.10	213.83
2000	106.37	297.14
2100	112.46	299.75
2200	118.57	302.25
2300	124.69	304.65
2400	130.81	306.96
2500	136.95	309.19
2600	143.09	311.35
2700	149.24	313.43
2800	155.40	315.44
2900	161.56	317.39
3000	167.72	319.29
VC ₄ (g)		
298.15	14.72	233.74
2000	184.09	369.51
2100	195.00	374.02
2200	205.94	378.36
2300	216.90	382.53
2400	227.88	386.56
2500	238.88	390.45
2600	249.90	394.21
2700	260.94	397.84
2800	271.98	401.37
2900	283.04	404.78
3000	294.11	408.10

TABLE VII. - HEAT CONTENTS AND FREE
ENERGY FUNCTIONS FOR CrC₂(g)

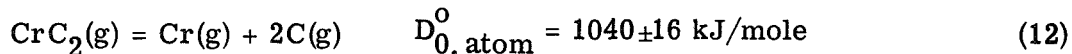
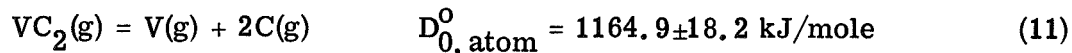
Temperature, T, K	Heat content, H _T ^o - H ₀ ^o , kJ/mole	Free energy function, -(G _T ^o - H ₀ ^o)/T, J/(deg)(mole)
298.15	10.19	216.43
1800	94.78	294.89
1900	100.86	297.75
2000	106.95	300.49
2100	113.05	303.10
2200	119.17	305.62
2300	125.29	308.03
2400	131.43	310.36
2500	137.57	312.60

following: K_P, ±50 percent; T, ±10 K; and $\Delta \left[(G_T^o - H_0^o)/T \right]$, ±6.3 joules per degree per mole. The estimated error for the values of the relative cross sections accounts for a large part of the overall estimated error in K_P. The estimated error for $\Delta \left[(G_T^o - H_0^o)/T \right]$ does not include a possible difference in ground-state statistical weight for the metal-dicarbide molecules.

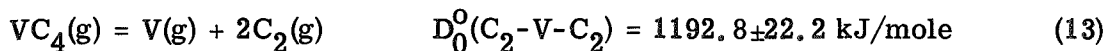
The heat of formation of C₂(g), $\Delta H_{0,f}^o = 824.2 \pm 8.4$ kilojoules per mole (ref. 18), was combined with the third-law heats of reactions (eqs. (5) and (7), respectively), to give the following dissociation energies:



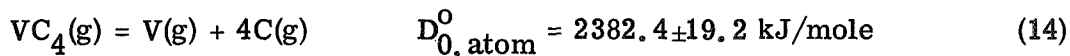
The atomization energies $D_{0,atom}^o$ of V-C-C and Cr-C-C were obtained by combining, respectively, the heats of reactions (5) and (7) with the heat of formation of C(g), which is 709.5 ± 1.9 kilojoules per mole (ref. 18):



The heat of formation of C₂(g) was combined with the third-law heat of reaction (eq. (6)) to give the dissociation energy of C₂-V-C₂



The atomization energy of $VC_4(g)$ was calculated by combining the heat of reaction (eq. (6)) with the heat of formation of $C(g)$:



DISCUSSION

Second-law treatments of the experimental data were not attempted because of the relatively short temperature ranges covered in each experiment. However, the absence of any severe trend with temperature in the third-law heats serves to indicate that no large systematic temperature error existed.

The value obtained for the atomization energy of $VC_2(g)$, 1165 ± 18 kilojoules per mole, is in excellent agreement with that reported by Drowart et al. (ref. 1), 1167 ± 21 kilojoules per mole. The results obtained for the Cr-C system, however, differ in two respects from findings reported by Doan (ref. 2). First, no monocarbide was detected, and, second, the ratio of CrC_2^+ to Cr^+ is smaller by a factor of 10^{-2} to 10^{-3} than that reported by Doan. These differences in results are not particularly disturbing because Doan's results were obtained by sparking, a process which is not well understood. The mechanism of vaporization and ion production by sparking is complex. The energy dissipated by the spark vaporizes, ionizes, and physically removes material from the electrodes. The neutral and ionic species formed do not necessarily represent an equilibrium vaporization process. On the other hand, the present results are derived from the Knudsen method, which samples an equilibrium process.

The comparisons of M-C₂ and M-O bond strengths that have previously been made for rare-earth-, Group IIIA-, Group IVA- (refs. 6 to 11, 21, and 22), and transition metal-carbon systems (ref. 12) can now be extended to include the dicarbides of vanadium and chromium. The comparison of M-C₂ and M-O bond strengths is made because it has been postulated that the bonding of the C₂⁼ group is similar (isoelectronic) to that of the O⁼ ion (refs. 21 and 22). The V-C₂ bond energy (570 ± 20 kJ) follows the apparent trend that the oxide bond energy, $D_0^{\circ}(V-O) = 617 \pm 11$ kilojoules (ref. 23), is somewhat higher than the bond energy of the corresponding dicarbide. However, the difference between $D_0^{\circ}(V-C_2)$ and $D_0^{\circ}(V-O)$ is not as large as that of some of the other metal oxides and dicarbides, notably titanium (ref. 12), and some of the rare earths (refs. 6 and 21). The case of chromium seems to be an exception because the dicarbide bond energy (445 ± 18 kJ) is slightly higher than that of the oxide, $D_0^{\circ}(Cr-O) = 423 \pm 29$ kilojoules (ref. 23). However, the overlapping uncertainties make the situation nebulous enough that no positive conclu-

sion can be made.

It is interesting to note that the bond energies for C_2-V-C_2 , $D_0^0 = 1193 \pm 22$ kilojoules, and $O-V-O$, $D_0^0 = 1213 \pm 42$ kilojoules (ref. 23), are comparable. This is in contrast to the case of titanium, where the $O-Ti-O$ species, $D_0^0 = 1311 \pm 21$ kilojoules (ref. 24), is markedly more stable than C_2-Ti-C_2 , $D_0^0 = 1214 \pm 23$ kilojoules (ref. 12).

The value of the atomization energy for $VC_4(g)$ obtained in this study indicates that this molecule is reasonably stable. The stabilities of VC_2 and VC_4 and the existence of stable oxides of niobium and tantalum (ref. 23) suggest that the corresponding carbides of niobium and tantalum might be stable molecules.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, January 14, 1970,
129-03.

REFERENCES

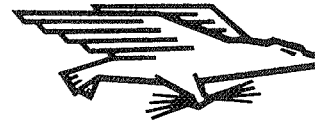
1. Drowart, J.; Pattoret, A.; and Smoes, S.: Mass Spectrometric Studies of the Vaporization of Refractory Compounds. *Proc. Brit. Cer. Soc.*, vol. 8, 1967, pp. 67-89.
2. Doan, Arthur S., Jr.: Existence of Metal Carbide Molecules in Vapor State. Presented at the 1st NBS Materials Research Symposium, Gaithersburg, Md., Oct. 3-7, 1966. NASA TM X-52216, 1966.
3. Fujishiro, S.; and Gokcen, N. A.: Thermodynamic Properties of VC at High Temperatures. *J. Electrochem. Soc.*, vol. 109, no. 9, Sept, 1962, pp. 835-838.
4. Storms, Edmund K.: *The Refractory Carbides*. Academic Press, 1967, pp. 47-60 and 102-121.
5. Fujishiro, S.; and Gokcen, N. A.: Thermodynamic Properties of Cr_3C_2 at High Temperatures. *Trans. AIME*, vol. 221, no. 2, Apr. 1961, pp. 275-279.
6. Kohl, Fred J.; and Stearns, Carl A.: Mass Spectrometric Investigation of Vaporization Thermodynamics of Yttrium Dicarbide-Carbon System and Dissociation Energy of Yttrium Dicarbide and Tetracarbide. NASA TN D-5646, 1970.
7. Balducci, G.; Capalbi, A.; DeMaria, G.; and Guido, M.: Atomization Energy of the NdC_4 Molecule. *J. Chem. Phys.*, vol. 48, no. 11, June 1, 1968, pp. 5275-5276.
8. Balducci, G.; Capalbi, A.; DeMaria, G.; and Guido, M.: Thermodynamics of Rare-Earth-Carbon Systems. I. The Cerium-Carbon System. *J. Chem. Phys.*, vol. 50, no. 5, Mar. 1, 1969, pp. 1969-1974.

9. Balducci, G.; Capalbi, A.; DeMaria, G.; and Guido, M.: Tetracarbide Molecules in the Vapor Phase Over Rare-Earth-Graphite Systems. *J. Chem. Phys.*, vol. 43, no. 6, Sept. 15, 1965, pp. 2136-2137.
10. Balducci, G.; Capalbi, A.; DeMaria, G.; and Guido, M.: Thermodynamics of Rare-Earth-Carbon Systems. II. The Holmium-Carbon and Dysprosium-Carbon Systems. *J. Chem. Phys.*, vol. 51, no. 7, Oct. 1, 1969, pp. 2871-2876.
11. Balducci, G.; DeMaria, G.; and Guido, M.: Thermodynamics of Rare-Earth-Carbon Systems. III. The Erbium-Carbon System. *J. Chem. Phys.*, vol. 51, no. 7, Oct. 1, 1969, pp. 2876-2879.
12. Stearns, Carl A.; and Kohl, Fred J.: Mass Spectrometric Determination of the Dissociation Energies of Titanium Dicarbide and Titanium Tetracarbide. NASA TN D-5653, 1970.
13. Starostina, T. S.; Sidorov, L. N.; Akishin, P. A.; and Karasev, N. M.: Mass Spectrometric Investigation of the Composition of the Vapor Above the Systems TiC-C and ZrC-C. *Izv. Akad. Nauk, SSSR, Neorganicheskie Materialy*, vol. 3, no. 4, 1967, pp. 647-648.
14. Stearns, Carl A.; and Kohl, Fred J.: The Dissociation Energy of Gaseous Titanium Mononitride. NASA TN D-5027, 1969.
15. Kiser, Robert W.: *Introduction to Mass Spectrometry and Its Applications*. Prentice-Hall, Inc., 1965, App. IV.
16. Mann, Joseph B.: Ionization Cross Sections of the Elements Calculated From Mean-Square Radii of Atomic Orbitals. *J. Chem. Phys.*, vol. 46, no. 5, Mar. 1, 1967, pp. 1646-1651.
17. Hultgren, Ralph; Orr, Raymond L.; Anderson, Philip D.; and Kelley, Kenneth K.: *Selected Values of Thermodynamic Properties of Metals and Alloys*. Univ. California, Dept. Mineral Tech., Apr. 1967.
18. Stull, D. R., ed.: *JANAF Thermochemical Tables*. Dow Chemical Co., 1961.
19. Engler, W.; and Kohlrausch, K. W. F.: The Raman Spectrum of N_3H and C_3O_2 . *Z. Physik Chem. (Leipzig)*, vol. B34, 1936, pp. 214-224.
20. McBride, Bonnie J.; and Gordon, Sanford: FORTRAN IV Program for Calculation of Thermodynamic Data. NASA TN D-4097, 1967.
21. DeMaria, G.; Balducci, G.; Capalbi, A.; and Guido, M.: High-Temperature Mass Spectrometric Study of the System Neodymium-Carbon. *Proc. Brit. Cer. Soc.*, vol. 8, 1967, pp. 127-136.

22. Chupka, William A.; Berkowitz, Joseph; Giese, Clayton F.; and Inghram, Mark G.: Thermodynamic Studies of Some Gaseous Metallic Carbides. *J. Phys. Chem.*, vol. 62, no. 5, May 1958, pp. 611-614.
23. Drowart, J.; and Goldfinger, P.: Investigation of Inorganic Systems at High Temperature by Mass Spectrometry. *Angew. Chemie. Int. Ed.*, vol. 6, no. 7, July 1967, pp. 581-596.
24. Drowart, J.; Coppens, P.; and Smoes, S.: Dissociation Energy of the Molecule TiO(g) and the Thermodynamics of the System Titanium-Oxygen. *J. Chem. Phys.*, vol. 50, no. 2, Jan. 15, 1969, pp. 1046-1048.
25. Herschbach, Dudley R.; and Laurie, Victor W.: Anharmonic Potential Constants and Their Dependence upon Bond Length. *J. Chem. Phys.*, vol. 35, no. 2, Aug. 1961, pp. 458-463.
26. Herzberg, Gerhard: Spectra of Diatomic Molecules. Vol. 1 of Molecular Spectra and Molecular Structures. Second ed., D. Van Nostrand Co., Inc., 1950, app.
27. Herzberg, Gerhard: Infrared and Raman Spectra of Polyatomic Molecules. Vol. 2 of Molecular Spectra and Molecular Structure. D. Van Nostrand Co., Inc., 1945, pp. 173-174.
28. Cheetham, C. J.; and Barrow, R. F.: The Spectroscopy of Diatomic Transition Element Molecules. *Advances in High Temperature Chemistry*. Vol. 1. LeRoy Eyring, ed., Academic Press, 1967, pp. 7-41.

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON, D. C. 20546
OFFICIAL BUSINESS

FIRST CLASS MAIL



POSTAGE AND FEES PAID
NATIONAL AERONAUTICS AND
SPACE ADMINISTRATION

POSTMASTER: If Undeliverable (Section 158
Postal Manual) Do Not Return

"The aeronautical and space activities of the United States shall be conducted so as to contribute . . . to the expansion of human knowledge of phenomena in the atmosphere and space. The Administration shall provide for the widest practicable and appropriate dissemination of information concerning its activities and the results thereof."

— NATIONAL AERONAUTICS AND SPACE ACT OF 1958

NASA SCIENTIFIC AND TECHNICAL PUBLICATIONS

TECHNICAL REPORTS: Scientific and technical information considered important, complete, and a lasting contribution to existing knowledge.

TECHNICAL NOTES: Information less broad in scope but nevertheless of importance as a contribution to existing knowledge.

TECHNICAL MEMORANDUMS: Information receiving limited distribution because of preliminary data, security classification, or other reasons.

CONTRACTOR REPORTS: Scientific and technical information generated under a NASA contract or grant and considered an important contribution to existing knowledge.

TECHNICAL TRANSLATIONS: Information published in a foreign language considered to merit NASA distribution in English.

SPECIAL PUBLICATIONS: Information derived from or of value to NASA activities. Publications include conference proceedings, monographs, data compilations, handbooks, sourcebooks, and special bibliographies.

TECHNOLOGY UTILIZATION PUBLICATIONS: Information on technology used by NASA that may be of particular interest in commercial and other non-aerospace applications. Publications include Tech Briefs, Technology Utilization Reports and Notes, and Technology Surveys.

Details on the availability of these publications may be obtained from:

SCIENTIFIC AND TECHNICAL INFORMATION DIVISION
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
Washington, D.C. 20546