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VAPORIZATION OF THE GROUP IVB METAL CARBIDES

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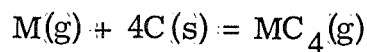
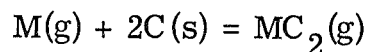
VAPORIZATION OF THE GROUP IVB METAL CARBIDES

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SUMMARY

The high temperature vaporization of the metal-carbon systems Ti-C, Zr-C, Hf-C and Th-C was studied by the Knudsen effusion-mass spectrometric method. For each system the metal dicarbide and tetracarbide molecular species were identified in the gas phase. Ion intensities of the carbides and metals were measured as a function of temperature. Second- and third-law methods were used to determine enthalpies for the reactions



Experimentally determined reaction enthalpies were combined with published thermodynamic data to obtain the following dissociation energies in kcal mole⁻¹; $D_0^{\circ}(\text{Ti-C}_2) = 136 \pm 6$, $D_0^{\circ}(\text{Zr-C}_2) = 137 \pm 6$, $D_0^{\circ}(\text{Hf-C}_2) = 160 \pm 7$, $D_0^{\circ}(\text{Th-C}_2) = 169 \pm 6$; $D_0^{\circ}(\text{C}_2\text{-Ti-C}_2) = 291 \pm 6$; $D_0^{\circ}(\text{C}_2\text{-Zr-C}_2) = 308 \pm 7$, $D_0^{\circ}(\text{C}_2\text{-Hf-C}_2) = 322 \pm 7$ and $D_0^{\circ}(\text{C}_2\text{-Th-C}_2) = 335 \pm 6$. Thermodynamic functions used in the calculations are discussed in terms of assumed molecular structures and electronic contributions to the partition functions. The trends shown by the dissociation energies of the carbides of Group IVB are compared to neighboring groups and discussed in relation to the corresponding oxides and chemical bonding.

INTRODUCTION

Previous vaporization studies of some transition metal¹⁻⁹ and rare-earth-carbon¹⁰⁻¹⁴ systems have established that the dicarbide and tetracarbide molecular species exist as stable molecules in the gas phase. The work reported here is an extension of such studies to the Group IVB metals

(Ti, Zr, Hf, and Th). The mass spectrometric-Knudsen effusion method was used to study the vaporization of the respective metal carbides. The primary objective of this research has been to obtain experimental thermochemical data which can be used to elucidate certain basic thermodynamic properties of simple gaseous molecules. These studies also establish the nature of high temperature chemical reactions and provide vapor pressure data which are of engineering value.

EXPERIMENTAL

For the experimental program an original design Knudsen cell inlet system¹⁵ has been coupled to a commercial double focusing mass spectrometer. The physical arrangement is such that the neutral molecular beam emanating from the Knudsen cell is coaxial with the ion beam produced by electron impact. The Knudsen cell, ion source, and mass analyzer are each contained in separate vacuum chambers which are interconnected but differentially pumped. The mass analyzer is of the Mattauch-Herzog type and is operated at a resolution of approximately 2000 based on the 10 percent valley definition.

Ion intensities are measured with an electron multiplier and vibrating reed electrometer plus ion counter.^{16,17} The seventeen stage Allen type multiplier is operated at up to 256 volts per stage and the maximum gain is approximately 10^7 . To facilitate simultaneous ion counting and current measurements, the ion counter is coupled to the last multiplier dynode and the electrometer is connected to the anode. The ion counting system consists of an amplifier-discriminator and digital counter. This system is transformer coupled to the dynode. The ion counter is used primarily to measure multiplier gain for each ion species being investigated. The sensitivity and dynamic range of the apparatus provide the ability to measure partial pressures from 10^{-3} to 10^{-10} atmospheres.

The mass spectrometer design requires a somewhat unconventional Knudsen cell with the effusion orifice in the side wall rather than in the top. A schematic representation of the Knudsen cell assembly is shown in figure 1. The carbide sample is contained in a graphite liner inside

the cell. Both tungsten and tantalum cells have been used in this study. A hole in the liner is made sufficiently large so that the effusion orifice is defined by a knife edge opening in the cell wall. The cell is heated by radiation and electron bombardment from two independently powered tungsten ribbon filaments circumscribing the cell at locations near its top and bottom. Tantalum heat shields completely surround the cell. The cell and shield assembly can be remotely moved in two orthogonal directions relative to the shutter slit and ion source entrance slit.

Cell temperatures are measured by sighting a calibrated optical pyrometer into the three blackbody holes. The depth to diameter ratio of each hole is at least 9 to 1. By appropriate adjustment of the power to each heating filament, the temperature read at each blackbody hole can be made identical within the precision of the pyrometer.

PROCEDURE, RESULTS, AND DISCUSSION

The carbides of Ti, Zr, Hf, and Th were prepared separately in the Knudsen cell chamber by heating mixtures of each metal powder with excess graphite powder. This was done in the same Knudsen cell and graphite liner as was used in the subsequent experiments. At temperatures above 2000 K the metal and graphite reacted to form the carbon-saturated metal carbide phase. In general, the carbide phase is substoichiometric and varies slightly in composition with temperature.¹⁸

The mass spectrum of each metal carbide was examined in detail to high values of mass-to-charge ratio. In addition to the metal and various carbon polymers, the dicarbide, MC_2^+ , and tetracarbide, MC_4^+ , ions were positively identified for each system. Shutter measurements were used to establish which ion species had neutral precursors originating from the Knudsen cell. For all carbide species the shutter effect was 100 percent. When possible, appearance potentials were measured to identify parent molecular species. Measured values of the appearance potentials are listed in table I.

Ion intensities were measured as a function of temperature. Measured intensities were corrected for cross section, multiplier gain, isotopic abundance, and ionization efficiency. In table II the intensity ratios of M/MC_x

are listed for the systems studied together with the ratios for systems in neighboring groups. Within Group IVB it is apparent that the abundance of the carbide species increases as the metal weight increases. This same trend can be noted in the neighboring groups of elements. This table clearly shows that for the heavier elements the carbide species become significant vaporization products. Plots of intensity of each species versus temperature indicate that as the temperature is increased the carbide species become more important.

Second- and third-law heats of reaction were calculated from measured ion intensities. The pressure independent reactions considered here are listed in table III together with the temperature range over which measurements were made and the respective heats of reaction. The low temperature of each range is the temperature below which reliable measurements of the intensity could not be made for the least abundant species. The upper temperature of each range was set by experimental conditions involving the Knudsen cell. Both the tungsten and tantalum cells carbided during the duration of the various experiments. With tungsten cells which had carbided, melting of the cell became a problem above 2875 K. Tantalum cells proved more useful and the upper limit of 3100 K was caused by failure of tungsten cell supports.

Second-law heats were obtained from the least squares slopes of log equilibrium constant ($\log K_p$) versus reciprocal temperature ($1/T$). In those cases where no second-law heats are listed in table III, insufficient data was available at this time to obtain reliable values. Third-law heats were calculated from measured ion intensities and free-energy functions derived for the respective molecular species. The free-energy functions were calculated on the basis of estimated molecular parameters and assumed molecular structures.

Because the derived value of the free-energy functions have a significant influence on the value of the third-law heat, it is essential that the bases for deriving the thermodynamic functions be enumerated. Tables IV and V list the estimated parameters used. In the absence of experimentally established structures, we initially assumed a linear asymmetric

structure for the dicarbides. For reasons to be presented later this structure was deemed acceptable for TiC_2 , HfC_2 , and ThC_2 , but not necessarily appropriate for ZrC_2 . Therefore, for ZrC_2 both symmetric and bent structures were also considered. For reason to be presented later, a bent asymmetric structure with an apex angle of 120 degree was finally used for $\text{ZrC}_2(\text{g})$. The bent structure added $4.1 \text{ cal deg}^{-1} \text{ mole}^{-1}$ to the free energy functions at 3000 K compared to the linear asymmetric structure.

For all the tetracarbide molecular species a linear symmetric structure of the type C -C-M-C-C was assumed.

The interatomic distances used in calculating free-energy functions were estimated on the basis of values reported for the corresponding oxides.¹⁹ Vibrational frequencies were calculated by use of the valance force approximation formulation^{20,21} and estimated force constants derived from oxides and the C_2 molecule. The bending force constant was estimated by considering those determined for other triatomic molecules.

In addition to the paucity of experimental data on molecular geometry, the electronic contribution to the partition function is uncertain for the molecules being studied. Therefore we considered three alternate methods of estimating the electronic contribution. The first and simplest alternative is to assume a $^1\Sigma^+$ ground state which results in a zero electronic contribution. This assumption is based on the postulate²² that the bonding of the C_2^{-2} group is similar to O^{-2} and the fact that $^1\Sigma^+$ is the ground state for ZrO , HfO , and ThO .¹⁹

The second possibility is to consider electronic contributions from the ground state and low lying excited states (below $12\,000 \text{ cm}^{-1}$). The observed and estimated electronic energy levels for TiO and ZrO have been discussed by Brewer and Green.²³ The ground state for TiO is a $^3\Delta$ and the low lying excited states are $^1\Delta$, $^1\Sigma^+$, $^3\Pi$, and $^1\Pi$. For ZrO the excited states are $^3\Delta$, $^1\Delta$, $^3\Pi$, and $^1\Pi$. Using these electronic levels for TiC_2 and ZrC_2 the electronic contribution for the free-energy functions at 3000 K are 4.1 and $3.2 \text{ cal deg}^{-1} \text{ mole}^{-1}$, respectively. Excited states for HfO and ThO are not known so that similar consideration could not be applied to HfC_2 and ThC_2 .

The final alternative is to assume that the energy levels of the molecule can be approximated by those of the M^{+2} ions. This method, as used by Brewer and Rosenblatt for metal oxides²⁴, is based on an ionic model of the type $M^{+2}C_2^{-2}$ and assumes that the C_2^{-2} ion neither makes an electronic contribution to the partition function nor perturbs the energy levels of M^{+2} . The energy levels which we used for M^{+2} were taken from the summary of Brewer and Rosenblatt.²⁴ At 3000 K the contributions to the free energy functions are 5.8, 5.4, 4.8, and 6.2 cal deg⁻¹mole⁻¹ for TiC_2 , ZrC_2 , HfC_2 , and ThC_2 respectively.

Our final selections of structures and electronic contributions used in deriving free-energy functions were made by comparing second- and third-law heats of reaction. Referring again to table III, the third-law heat for the reaction involving TiC_2 was calculated with free-energy functions derived for a linear asymmetric structure with an electronic contribution of the TiO states. This particular combination was found to yield the best second- and third-law agreement.

For the reaction involving ZrC_2 it was found necessary to use the asymmetric structure bent 120° plus the electronic contribution for the Zr^{+2} states. This combination resulted in the best agreement between the two calculated heats for the reaction.

Free-energy functions for ThC_2 were derived using the linear asymmetric structure and $^1\Sigma^+$ ground state. As shown by the reaction in table III this combination resulted in excellent agreement between the two calculated heats for the reaction. Because no second-law data was available for the HfC_2 reaction we calculated the third-law heat with free-energy functions derived on bases similar to those used for ThC_2 .

For the tetracarbide molecules less definitive structural information is available than for the dicarbides. Therefore, as mentioned earlier, we assumed linear symmetric structures for these molecules in all cases. Electronic contributions identical to the respective dicarbides were used for each tetracarbide. In the one case where second-law data was available, that is, TiC_4 , this combination yielded good agreement between the two heats for the reaction.

The third-law heats of reaction for the dicarbides and tetracarbides shown in table III each follow the trend of decreasing as the weight of the metal is increased.

The dissociation energies listed in table VI were calculated by combining the third-law heats of reaction with the heat of formation of $C_2(g)$, $^{25} \Delta H_{0,f}^{\circ} = 198.2 \pm 0.9 \text{ kcal mole}^{-1}$. In the cases where second-law heats were available the third-law values were used because they had smaller estimated errors.

Comparing the bond dissociation energies for the carbides with those for the corresponding oxides²⁶ provides some interesting insights. In each case it is to be noted that the strength of the M-O bond is greater than that of the corresponding M-C₂ bond. Likewise, the dioxide dissociation energy is greater than that of the corresponding metal tetracarbide. Similar comparisons for other metal-carbon and metal-oxygen systems have shown that the metal-carbon bonds are some 10 to 30 kcal weaker than the corresponding metal-oxygen bond. From table VI it is apparent that this tendency holds for all of the molecules of Group IVB metals except Zr. The differences in bond strengths for the Zr carbides is somewhat greater at 40 kcal mole⁻¹.

Thermodynamic circumstances dictate that the metal carbide molecules of the Group IVB elements are important components of the high temperature vapors of these materials. The lack of experimentally determined geometric and electronic structural parameters for these molecules make this family an ideal one on which to perform sophisticated theoretical and experimental investigations.

REFERENCES

1. C. A. Stearns and F. J. Kohl, High Temp. Sci. 2, 274 (1970).
2. F. J. Kohl and C. A. Stearns, J. Phys. Chem. 74, 2714 (1970).
3. F. J. Kohl and C. A. Stearns, J. Chem. Phys. 52, 6310 (1970).
4. F. J. Kohl and C. A. Stearns, J. Chem. Phys. 54, 1414 (1971).
5. C. A. Stearns and F. J. Kohl, J. Chem. Phys. 54, (1971), in press.
6. J. Drowart, A. Pattoret and S. Smoes, Proc. Brit. Cer. Soc. 8, 67 (1967).

7. T. S. Starostina, L. N. Sidorov, P. A. Akishin, and N. M. Karasev, *Izv. Akad. Nauk SSSR, Neorg. Mater.* 3, 647 (1967).
8. E. Storms, B. Calkin, and A. Yencha, *High Temp. Sci.* 1, 430 (1969).
9. E. K. Storms, Thermodynamics (IAEA, Vienna, 1966), Vol. 1, p. 309.
10. D. D. Jackson, G. W. Barton, O. H. Krikorian, and R. S. Newburg, *J. Phys. Chem.* 68, 1516 (1964).
11. G. Balducci, A. Capalbi, G. DeMaria, and M. Guido, *J. Chem. Phys.* 51, 2876 (1969) and references cited therein.
12. G. Balducci, A. Capalbi, G. DeMaria, and M. Guido, *J. Chem. Phys.* 50, 1969 (1969) and references cited therein.
13. E. E. Filby and L. L. Ames, *High Temp. Sci.* 3, 41 (1971).
14. E. E. Filby and L. L. Ames, *J. Phys. Chem.* 75, 848 (1971).
15. C. A. Stearns and F. J. Kohl, NASA TN D-5027 (1969).
16. F. J. Kohl and C. A. Stearns, NASA TN D-5646 (1970).
17. F. J. Kohl and C. A. Stearns, NASA TN D-7039 (1971).
18. E. K. Storms, The Refractory Carbides (Academic Press, New York, 1967).
19. C. J. Cheetham and R. F. Barrow, in Advances in High Temperature Chemistry, L. Eyring, ed. (Academic Press, New York, 1967), Vol. 1.
20. G. Herzberg, Infrared and Raman Spectra of Polyatomic Molecules, Vol. 2 of Molecular Spectra and Molecular Structure (Van Nostrand, Princeton, 1945), p. 173-174.
21. W. Engler and K. W. F. Kohlrusch, *Z. Physik Chem. (Leipzig)* B34, 214 (1936).
22. W. A. Chupka, J. Berkowitz, C. F. Giese, and M. G. Inghram, *J. Phys. Chem.* 62, 611 (1958).
23. L. Brewer and D. W. Green, *High Temp. Sci.* 1, 26 (1969).
24. L. Brewer and G. M. Rosenblatt, in Advances in High Temperature Chemistry, L. Eyring, ed. (Academic Press, New York, 1969), Vol. II.
25. JANAF Thermochemical Tables (Dow Chemical Co., Midland, Mich., Dec. 31, 1969).
26. J. Drowart and P. Goldfinger, *Angew. Chem. Int. Ed.* 6, 581 (1967).

TABLE I. APPEARANCE POTENTIALS

ION	Ti	Zr	Hf	Th
M ⁺	^a 6.82	^a 6.84	^a 7	^a 6.95
MC ₂ ⁺	8.7±0.5	7.5±0.5	--	6.5±0.3
MC ₄ ⁺	9.0±1.0	-----	--	10.0±1.0

^aKISER, R. W., INTRODUCTION TO MASS SPECTROMETRY & ITS APPLICATIONS, PRENTICE-HALL, 1965.

TABLE II. ABUNDANCE RATIOS OF CARBIDE VAPORIZATION SPECIES

GROUP IIIB	GROUP IVB	GROUP VB	GROUP VIIB
Sc/ScC ₂ = 6x10 ² Sc/ScC ₄ = 2x10 ⁵ (2300 ^o K)	Ti/TiC ₂ = 4x10 ² Ti/TiC ₄ = 6x10 ⁴ (2500 ^o K)	V/VC ₂ = 8x10 ² V/VC ₄ = 3x10 ⁵ (2500 ^o K)	Cr/CrC ₂ = 1x10 ⁶ (2100 ^o K)
Y/YC ₂ = 8 Y/YC ₄ = 8x10 ² (2500 ^o K)	Zr/ZrC ₂ = 4 Zr/ZrC ₄ = 1x10 ² (2800 ^o K)	^a Nb/NbC ₂ = 40 (2500 ^o K)	Mo
La/LaC ₂ = 2 La/LaC ₃ = 8x10 ² La/LaC ₄ = 70 (2500 ^o K)	Hf/HfC ₂ = 3 Hf/HfC ₄ = 30 (3000 ^o K)	Ta/TaC ₂ ≈ 2x10 ² (3000 ^o K)	W
	Th/ThC ₂ = 7x10 ⁻¹ Th/ThC ₃ ≥ 50 Th/ThC ₄ = 5 (2700 ^o K)		^b U/UC ₂ = 4 U/UC ₄ = 3x10 ² (2450 ^o K)

^aE. STORMS, B. CALKIN, & A. YENCHA, HIGH TEMP SCI 1, 430 (1969).

^bE. STORMS, "THERMODYNAMICS," VOL I, (VIENNA IAEA, 1966) p 309.

TABLE III. HEATS OF REACTION IN KCAL MOLE⁻¹

REACTION	TEMP RANGE, °K	SECOND LAW, ΔH ₀ ^o	THIRD LAW, ^a ΔH ₀ ^o
Ti(g) + 2C(s) = TiC ₂ (g) Ti(g) + 4C(s) = TiC ₄ (g)	2518-2790	62.4±6.8 109.8±20.1	62.7±5.8 105.3±6.0
Zr(g) + 2C(s) = ZrC ₂ (g) Zr(g) + 4C(s) = ZrC ₄ (g)	2670-3003	64.3±8.9 -----	60.9±6.4 88.2±7.1
Hf(g) + 2C(s) = HfC ₂ (g) Hf(g) + 4C(s) = HfC ₄ (g)	2952-3066	----- -----	38.5±7.0 74.8±6.6
Th(g) + 2C(s) = ThC ₂ (g) Th(g) + 4C(s) = ThC ₄ (g)	2686-2906	29.0±8.7 -----	29.7±6.1 61.0±6.2

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^aESTIMATED UNCERTAINTIES DO NOT INCLUDE UNCERTAINTIES DUE TO ESTIMATED GEOMETRY AND ELECTRONIC CONTRIBUTION.

TABLE IV. BASES FOR THERMODYNAMIC FUNCTIONS

MOLECULE	SYMMETRY	r_{M-C} Å	POSSIBLE ELECTRONIC CONTRIBUTIONS
TiC ₂	C _{∞v}	1.63	1 _Σ ⁺ TiO STATES (³ Δ GROUND STATE) Ti ⁺² STATES
ZrC ₂	C _{∞v} C _s , 120°	1.75	1 _Σ ⁺ ZrO STATES (1 _Σ ⁺ GROUND STATE) Zr ⁺² STATES
HfC ₂	C _{∞v}	1.77	1 _Σ ⁺ Hf ⁺² STATES
ThC ₂	C _{∞v}	1.90	1 _Σ ⁺ Th ⁺² STATES
MC ₄	D _{∞h}	----	SAME AS MC ₂

TABLE V. ESTIMATED VIBRATIONAL FREQUENCIES (cm⁻¹)
OF MC₂ AND MC₄ MOLECULES

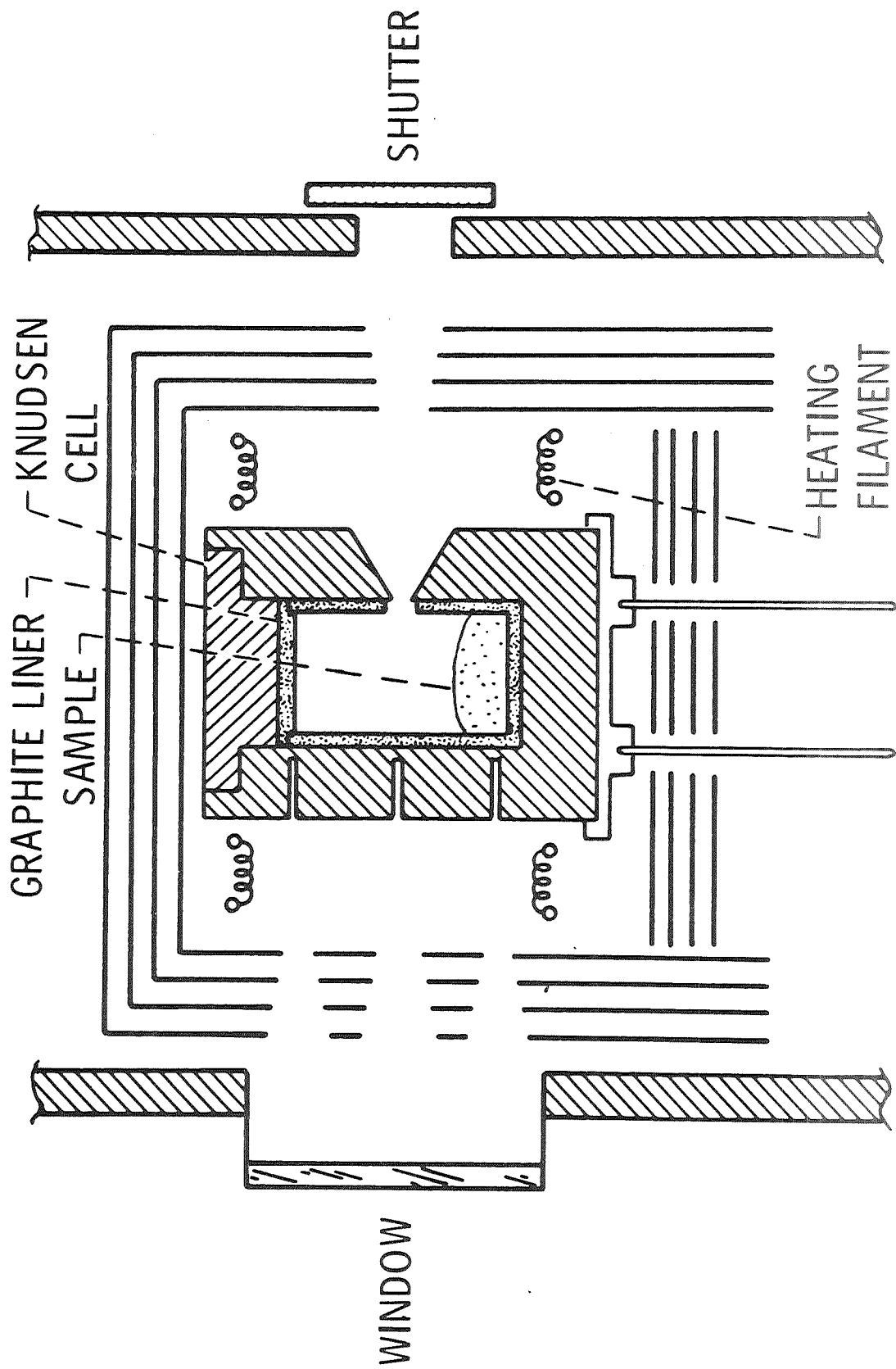
	TiC ₂	ZrC ₂		HfC ₂	ThC ₂
	C _{∞v}	C _{∞v}	C _s , 120°	C _{∞v}	C _{∞v}
ω ₁	780	713	1003	673	605
ω ₂	494 (2)	477 (2)	329	474 (2)	463 (2)
ω ₃	1810	1797	1677	1791	1751
	TiC ₄	ZrC ₄	HfC ₄	ThC ₄	
	D _{∞h}	D _{∞h}	D _{∞h}	D _{∞h}	
ω ₁	808	804	801	761	
ω ₂	1878	1874	1872	1836	
ω ₃	1020	891	812	734	
ω ₄	1836	1818	1810	1771	
ω ₅ (2)	137	118	108	101	
ω ₆ (2)	573	531	516	494	
ω ₇ (2)	468	454	453	437	

VIBRATIONAL FREQUENCIES WERE CALCULATED BY USE OF THE VALENCE FORCE FORMULATION & ESTIMATED FORCE CONSTANTS CS-58548

TABLE VI. BOND ENERGIES FOR GROUP IV B METAL OXIDES^a
AND DICARBIDES IN KCAL MOLE⁻¹

	Ti	Zr	Hf	Th
D ₀ (M-O)	158±5	181±5	183±6	198±5
D ₀ (M-C ₂)	136±6	137±6	160±7	169±6
D ₀ (O-M-O)	313±5	345±10	360±20	388±5
D ₀ (C ₂ -M-C ₂)	291±6	308±7	322±7	335±6

^aJ. DROWART & P. GOLDFINGER, ANGEW CHEM INTER ED ENGL 6, 581 (1967).



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Figure 1. - Schematic Knudsen Cell Assembly