DISSOCIATION ENERGIES OF GASEOUS METAL DIOXIDES

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I. INTRODUCTION

In recent years there have been a number of accurate transpiration measurements which have yielded enthalpies and entropies of formation of gaseous MO_2 molecules at high temperatures. In addition, the mass-spectrometer work of Inghram, Chupka, Berkowitz, Porter, and their associates has contributed a large amount of additional data on the thermodynamic properties of gaseous oxides, and, further, has clarified the relative stabilities of various gaseous molecules at high temperatures. This has made it possible to treat properly the vapor-pressure data obtained by other methods. In spite of the considerable number of experiments that have been carried out recently the inherent difficulties of measurements at high temperatures have seriously limited the accuracy of the enthalpies of formation obtained by use of the second law of thermodynamics. Serious temperature-dependent errors, which are difficult to avoid, in many of the measurements have made it necessary to estimate entropies or free-energy functions for the gaseous molecules so that the third law of thermodynamics might be applied. No spectroscopic data are available for molecules of any gaseous metal dioxide. There are no data that yield internuclear distances, vibrational frequencies, configuration, or degree of electronic excitation of these molecules. Thus, there is considerable uncertainty in the estimation of entropies or free-energy functions for gaseous MO_2 molecules. The chances of obtaining the experimental data needed to calculate accurate free-energy functions for these molecules appear very remote, certainly for the next ten years or more. Different workers have used different procedures to estimate these quantities. It is difficult to compare the resulting enthalpies of formation, as they have not been calculated from free-energy functions that are consistent with one another.

II. THE FREE-ENERGY FUNCTIONS

This paper presents free-energy functions of gaseous metal dioxides estimated by a consistent procedure that allows enthalpy data for various molecules to be compared with one another. The following rules for calculating the free-energy functions tabulated in table 1 were designed (*a*) to yield functions as accurate as available information permits, (*b*) to be as simple and straightforward as possible, and (*c*) to be reasonably consistent with previous estimates in the literature.

The rotational contribution is calculated assuming linear molecules and the internuclear distances observed for the gaseous monoxides. Walsh (41) has concluded that triatomic molecules with eighteen valence electrons would be bent with an angle of about 117°, and that triatomic molecules with seventeen valence electrons would be bent to about 143°. However, it is assumed that this would not be true with some of the electrons in *d* orbitals. It should be noted, however, that the assumption of a linear configuration is possibly one of the largest sources of error in the free-energy functions. A central angle of about 110° would raise the tabulated functions by 3–4 cal./degree mole. The approximation of equal M–O distances in metal monoxides and dioxides implies the same bond order in both classes of oxides. This is probably not strictly true, but the difference in bond order between the two oxides would introduce fairly small changes in the r_e values. Also, the accuracy of the internuclear distances in the monoxides is not high enough to warrant any corrections. The internuclear distances used in the calculations were obtained from Sutton's compilation (39) except for molybdenum(II) oxide and hafnium(II) oxide, internuclear distances for which were estimated by interpolation to be 1.73 and 1.74 A., respectively. The uranium–oxygen distance was taken to be 1.96 A.

TABLE 1

Free-energy functions for gaseous dioxides

Oxide	$-\frac{F^\circ - H^\circ_{298}}{T}$ in calories/degree mole						$H^\circ_{298} - H^\circ_0$
	298.15°	1000°	1500°	2000°	2500°	3000°K.	
							kcal./mole
SiO_2 (calcd.)	54.5	60.6	64.6	67.8	70.4	72.7	2.52
TiO_2 (calcd.)	56.6	63.0	67.1	70.4	73.1	75.4	2.67
VO_2 (calcd.)	60.0	66.8	71.1	74.6	77.4	79.7	2.79
CrO_2 (calcd.)	61.3	68.6	73.1	76.6	79.5	81.9	2.92
MnO_2 (estd.)	62.2	69.6	74.2	77.9	80.8	83.4	
ZrO_2 (calcd.)	58.6	65.0	69.2	72.5	75.3	77.6	2.73
NbO_2 (calcd.)	61.3	67.9	72.3	75.9	78.7	81.2	2.73
MoO_2 (calcd.)	62.4	69.3	73.9	77.6	80.6	83.1	2.81
TcO_2 (estd.)	62.8	69.7	74.3	78.0	80.9	83.5	
RuO_2 (estd.)	62.4	69.3	73.9	77.6	80.5	83.1	
RhO_2 (exptl.)	62.8	69.7	74.3	78.0	80.9	83.5	
PdO_2 (estd.)	62.5	69.4	74.0	77.7	80.6	83.2	
HfO_2 (calcd.)	60.5	67.0	71.2	74.5	77.3	79.6	2.77
TaO_2 (calcd.)	63.4	70.0	74.3	77.7	80.6	83.0	2.77
WO_2 (calcd.)	64.4	71.1	75.4	78.8	81.8	84.2	2.85
ReO_2 (estd.)	64.3	71.0	75.3	78.7	81.7	84.1	
OsO_2 (estd.)	63.1	69.7	74.0	77.4	80.3	82.7	
IrO_2 (estd.)	62.2	68.8	73.1	76.5	79.4	81.8	
PtO_2 (exptl.)	61.8	68.4	72.7	76.1	79.0	81.4	
ThO_2 (exptl.)	63.4	70.4	74.9	78.5	81.6	84.2	
PaO_2 (estd.)	64.2	71.3	75.9	79.6	82.7	85.3	
UO_2 (calcd.)	65.2	72.5	77.2	81.0	84.2	86.9	2.84

(16), a value which is consistent with the value of 1.92 given by Sutton for the uranyl ion.

The vibrational frequencies used to calculate the vibrational contribution to the free-energy function were also obtained from the values observed for the monoxides, where they are known. It has been assumed that the stretching-force constant, k_1, of the dioxide is equal to the stretching-force constant of the corresponding monoxide. The bending-force constant, k_δ/l^2, was evaluated assuming the ratio $k_\delta/l^2 : k_1$ to be 0.0336 for all molecules. This value was obtained from the ratio observed for carbon dioxide. Thus, all three fundamental frequencies were evaluated using the valence-force model. The bending frequencies are small and doubly degenerate and thus make a considerable contribution to the free-energy function. Therefore the uncertainty in their estimation causes a relatively large uncertainty in the free-energy functions. An uncertainty of ±200 cm.$^{-1}$ in the MO frequency, corresponding to an uncertainty of ±80 cm.$^{-1}$ in the MO_2 bending frequency evaluated by this method, causes an uncertainty of ±2 cal./degree mole in the calculated free-energy function. The vibrational frequencies of the monoxides were taken from Rosen's tables (34) when the molecule of interest was listed there. A value for uranium(II) oxide of 920 cm.$^{-1}$ was derived from the frequencies observed by Conn and Wu (14) for uranyl ion, assuming the same stretching-force constant. The following values were estimated: NbO, 942; MoO, 840; HfO, 895; TaO, 902; and WO, 803 cm.$^{-1}$ These last values are only rough estimates and are not to be interpreted as the best values possible from presently available information.

The electronic contribution is the most difficult to compute. Gaseous MO_2 oxides of metals of Group IV have been assumed to have a $^1\Sigma$ ground state with no excited electronic states close to the ground state. For the other MO_2 gaseous oxides one would expect appreciable electronic contributions to the partition function due to both the multiplicity of the ground state and the presence of low-lying excited electronic states. The procedure followed to calculate the electronic contribution to the partition function is, when possible, to calculate the electronic partition function for the M^{4+} ion or, lacking that, to calculate the electronic partition function for an isoelectronic ion. The validity of this procedure is difficult to justify experimentally for the MO_2 gases because of the lack of data accurate enough to yield a reliable experimental entropy or free-energy function. The only comparisons that can be cited are for molybdenum(IV) oxide, where the free-energy function calculated by the method described agrees with the free-energy function calculated from experimental data within the error of the measurements, and for uranium(IV) oxide, for which the experimental and calculated free-energy functions differ by 3.2 cal./degree mole. The calculated and experimental values are tabulated in table 2 along with other such comparisons where experimental data are available but where the electronic contribution is not a factor. The

TABLE 2

Comparison of experimental and calculated free-energy functions

Oxide	T	$-\frac{F^\circ - H^\circ_{298}}{T}$	
		Experimental	Calculated
	°K.	*cal./degree mole*	*cal./degree mole*
SiO_2	1800	65.3	66.5
	1900	65.7	67.1
TiO_2	1880	67.9	69.6
ZrO_2	2400	75.0	74.7
MoO_2	1600	76.9	74.6
UO_2	1800	76.3	79.5

principal justification for the recipe used to calculate the electronic contribution is that it has been found to be a satisfactory procedure for the MX_2 halides of the transition metals, where more experimental data are available to check the calculated free-energy functions (8). The only other justification for the procedure is that it is straightforward in those instances where spectroscopic data for the ions are available and that no other procedure has been proposed which yields reasonable values for the electronic contribution to the partition function.

The electronic levels for the dioxides of vanadium, niobium, chromium, and molybdenum were taken from the levels listed by Moore (30) for the corresponding M^{4+} ion. The U^{4+} levels were approximated by the Th^{2+} levels listed by Charles (11). The electronic contributions to the free-energy functions of tantalum(IV) oxide and tungsten(IV) oxide were estimated by extrapolation of the values calculated for the other two members of the group.

Unfortunately, even this procedure cannot be used for the oxides of the platinum metals, or the manganese to rhenium group, since no data exist for isoelectronic ions of sufficiently close nuclear charge to be of value. Fortunately, there are sufficient data available to allow calculation of experimental free-energy functions for the oxides of rhodium, platinum, and thorium by use of the second law of thermodynamics. The free-energy functions for these three oxides at the temperatures tabulated in table 1 were obtained from experimental values at a single temperature by assuming the same variation of free-energy function with temperature as shown by the calculated free-energy functions. The calculated free-energy functions were joined smoothly to the experimental values for platinum(IV) and rhodium(IV) oxides to yield interpolated values for the oxides of the intermediate elements.

The free-energy functions for rhodium(IV), platinum(IV), and thorium(IV) oxides and the other experimental ones tabulated in table 2 were obtained in the following way. The enthalpies of reaction derived from a second-law treatment were converted to ΔH°_{298} values, using $H^\circ_T - H^\circ_{298}$ for the gas calculated from the molecular constants used to evaluate the calculated free-energy functions or estimated by comparison with similar molecules. The $H^\circ_T - H^\circ_{298}$ values for the solid and other thermodynamic quantities for the solid were taken from the sources cited below in the section describing the calculations and data for each molecule. This ΔH°_{298} value was combined with the ΔF°_T value derived from the observed high-temperature equilibrium constant to yield an experimental value of $-(\Delta F^\circ - \Delta H^\circ_{298})/T$ at a temperature in the range of study. This value of $-(\Delta F^\circ - \Delta H^\circ_{298})/T$ was added to the value of $-(F^\circ - H^\circ_{298})/T$ for the solid if the reaction studied was $MO_2(s) = MO_2(g)$, or combined with the free-energy functions of the other species in the actual reaction occurring, to yield $-(F^\circ - H^\circ_{298})/T$ for the gaseous metal dioxide at one temperature. It is difficult to assign an absolute uncertainty to the free-energy functions collected in table 1, but the odds that they are in error by more than 5 cal./degree mole are probably less than one in twenty.

III. DISSOCIATION ENERGIES

These free-energy functions have been used to evaluate all available data for gaseous MO_2 oxides and to obtain enthalpies of dissociation into gaseous atoms at 298.15°K. for these molecules. The values of ΔH°_{298} evaluated for the reaction $MO_2(g) = M(g) + 2O(g)$ are presented in table 3 and are based on third-law calculations. Thus use of the ΔH values of table 3 together with the free-energy functions of table 1 will reproduce the experimental equilibrium constants. The ΔH°_{298} values in table 3 are about 2 kcal./mole larger than the corresponding ΔH°_0 or D°_0 values. Numbers in parentheses are estimated from the other values in the table. Whenever possible the calculations were carried out starting with the original data, and all auxiliary thermodynamic quantities were consistent with the free-energy functions in table 1. Unless other references are cited below, all thermodynamic data necessary for the calculations were obtained from Lewis, Randall, Pitzer, and Brewer (27). In addition to the values in table 3, the following heats of dissociation are known: NaO_2, 160 ± 10 (4); SeO_2, 203 ± 5 (7); TeO_2, 217 ± 7 kcal./mole (7).

Listed below are the original data treated, the reaction assumed to be occurring, and the sources of the auxiliary thermodynamic quantities used for each molecule in table 3. The dissociation energies of carbon dioxide, nitrogen(IV) oxide, ozone, sulfur dioxide, and chlorine(IV) oxide were evaluated directly from the heats of formation tabulated by Lewis, Randall, Pitzer, and Brewer (27).

A. Oxides of Group IV metals

SiO_2: The partial pressures of SiO_2 in equilibrium with cristobalite reported by Porter, Chupka, and

TABLE 3

ΔH°_{298} *for* $MO_2(g) = M(g) + 2O(g)$ *in kcal./mole*

CO_2 384.0 ± 0.5	NO_2 224.0 ± 0.1	O_3 145 ± 1	FO_2 (<100)			
SiO_2 300 ± 10	PO_2 (270) ± 25	SO_2 256.5 ± 1	ClO_2 123.3 ± 2			
TiO_2 315 ± 5	VO_2 298 ± 10	CrO_2 (230) ± 15	MnO_2 (220) ± 25			
ZrO_2 347 ± 5	NbO_2 (320) ± 25	MoO_2 282 ± 5	TcO_2 (255) ± 15	RuO_2 (230) ± 15	RhO_2 206 ± 5	PdO_2 <156
HfO_2 (360) ± 20	TaO_2 351 ± 15	WO_2 307 ± 10	ReO_2 (280) ± 15	OsO_2 (255) ± 20	IrO_2 (235) ± 15	PtO_2 213 ± 5
ThO_2 370 ± 15	PaO_2 (360) ± 20	UO_2 354 ± 15				

Inghram (33) are based on gold as a standard of vapor pressure. Their pressures were corrected to agree with a pressure of gold at 1750°K. of 4.3×10^{-6} atm. (21). A value of ΔH°_{298} (vap.) = 135 kcal./mole is obtained from a second-law treatment of their results, using the value of $H^\circ_T - H^\circ_{298}$ (g) calculated from the same molecular constants used to calculate the free-energy functions and using Kelley's (24) values of $H^\circ_T - H^\circ_{298}$ (cristobalite). The third-law treatment yields ΔH°_{298} (vap.) = 137 kcal./mole.

TiO_2: Vapor pressures over rutile and the high-temperature enthalpy of vaporization from a second-law treatment have been reported by Berkowitz, Chupka, and Inghram (6). Treatment of their data, using Kelley's (24) $H^\circ_T - H^\circ_{298}$ (rutile), yields a second-law value of ΔH°_{298} (vap.) = 139.6 kcal./mole and a third-law value of 143.0.

ZrO_2: Chupka, Berkowitz, and Inghram (13) measured the vapor pressure and the high-temperature heat of vaporization of $ZrO_2(g)$ over $ZrO_2(s)$. Their second-law heat yields ΔH°_{298} (vap.) = 179.6 using Kelley's (24) $H^\circ_T - H^\circ_{298}$ (s). The free-energy functions for $ZrO_2(s)$ tabulated by Lewis, Randall, Pitzer, and Brewer (27) were extended to a value of −33.3 cal./degree mole at 2500°K. using C_p = 17.80 cal./degree mole. Third-law treatment of the absolute pressures yields ΔH°_{298} (vap.) = 179.8 kcal./mole.

ThO_2: Vapor-pressure data for thorium(IV) oxide are given by Shapiro (36) and by Ackerman, Thorn, and Gilles (2). Inghram, Chupka, and Berkowitz (23) have shown that owing to the reduction of thorium(IV) oxide by tantalum both ThO(g) and $ThO_2(g)$ are present in the vapor over $ThO_2(s)$ in a tantalum crucible. The vapor-pressure measurements quoted above (2, 36) were carried out on tungsten filaments and in tungsten cells. In treating these measurements it is assumed that the rate of reduction of thorium(IV) oxide by tungsten is slow enough for the vapor to be predominantly $ThO_2(g)$. High-temperature heat contents and entropies for $ThO_2(s)$ were taken from Kelley (24) and were extended above 2000°K. by assuming a constant heat capacity of 22 cal./degree mole. These heat contents and entropies were used along with S°_{298} (s) = 15.6 cal./degree mole (32) to generate free-energy functions for the solid. Values of $-(F^\circ - H^\circ_{298})/T$ of 34.9 cal./degree mole at 2150°K. and 39.3 cal./degree mole at 2800°K. were obtained. Shapiro's high-temperature enthalpy of vaporization from a second-law treatment yields ΔH°_{298} (vap.) = 179.7 kcal./mole, using a value of $H^\circ_{2150} - H^\circ_{298}$ (g) = 26.4 kcal./mole extrapolated from the heat contents calculated for the gaseous dioxides of titanium, zirconium, and hafnium. This heat of vaporization in conjunction with Shapiro's measured pressures yields an experimental value of $(F^\circ - H^\circ_{298})/T$ for $ThO_2(g)$ at 2150°K. of −79.1 cal./degree mole. Using the same ΔH°_{298} (vap.) and the absolute pressure measured by Ackerman, Thorn, and Gilles, one obtains a gaseous free-energy function equal to −84.8 cal./degree mole at 2800°K., which is equivalent to −81.4 cal./degree mole at 2150°K. The value of −79.5 cal./degree mole at 2150°K. was picked to derive the free-energy functions of $ThO_2(g)$ listed in table 1. A heat of formation of $ThO_2(s)$ at 298.15°K. of −293.2 kcal./mole (20) and a heat of sublimation for Th(s) of 137.3 kcal./mole (15) were used to obtain the heat of dissociation into gaseous atoms shown in table 3 from the above heat of vaporization.

B. Oxides of Group V metals

VO_2: Berkowitz, Chupka, and Inghram (5) report an equilibrium constant for the reaction $V(g) + VO_2(g) = 2VO(g)$. Values of $-(F^\circ - H^\circ_{298})/T$ for VO(g) of 65.0 cal./degree mole at 1500°K. and 67.3 cal./degree mole at 2000°K. were obtained by converting the monoxide functions calculated by Brewer and Chandrasekharaiah (9) (these free-energy functions were calculated in essentially the same way as the functions for the gaseous dioxides presented in the present paper) to a base of 298.15°K. Berkowitz, Chupka, and Inghram (5) also report the vapor pressure of VO(g) over VO(s).

The free-energy functions for VO(s) were calculated from Kelley's (24) high-temperature heat contents and entropies, and S°_{298} (s) = 9.31 cal./degree mole (40) to be −19.6 cal./degree mole at 1500°K. and −23.0 cal./degree mole at 2000°K. The third-law ΔH°_{298} value is computed to be 0.8 kcal./mole for the reaction $V(g) + VO_2(g) = 2VO(g)$ and 133.9 kcal./mole for the reaction $VO(s) = VO(g)$. These values were combined with a heat of formation of VO(s) of −100 kcal./mole (29) to derive the dissociation energy of vanadium(IV) oxide.

TaO_2: The vapor pressures of tantalum(IV) oxide over a mixture of tantalum and tantalum(V) oxide reported by Inghram, Chupka, and Berkowitz (22) were treated by the third-law method to yield a ΔH°_{298} of 150.3 kcal./mole for the reaction

$$\tfrac{1}{5}Ta(s \text{ or } l) \quad + \quad \tfrac{2}{5}Ta_2O_5(s) \quad = \quad TaO_2(g)$$

For this calculation the free-energy functions for $Ta_2O_5(s)$ of Lewis, Randall, Pitzer, and Brewer (27) were extrapolated above 2000°K., assuming C_p = 50 cal./degree mole, to a value of −79.0 cal./degree mole at 2200°K. Free-energy functions for Ta(s) were taken from Stull and Sinke (38).

C. Oxides of Group VI metals

CrO_2: Wang, Dreger, Dadape, and Margrave (42) have measured the vapor pressure of solid chromium(III) oxide in a vacuum, in an inert gas, and in oxygen. Although their data indicate the predominant vapor species to be $Cr_2O_3(g)$ (or a polymer thereof), they report a small enhancement of vaporization by oxygen. This allows one to set an upper limit on the pressure of chromium(IV) oxide equal to the measured pressure of chromium(III) oxide, by assuming an equilibrium

$$\tfrac{1}{2}Cr_2O_3(s) \quad + \quad \tfrac{1}{4}O_2(g) \quad = \quad CrO_2(g)$$

Using the free-energy functions in table 1, one calculates an upper limit of 230 kcal./mole to the dissociation energy.

MoO_2: Burns, DeMaria, Drowart, and Grimley (10) measured the vapor pressure and high-temperature heat of sublimation of $MoO_2(g)$ in equilibrium with $MoO_2(s)$. The entropy of $MoO_2(s)$ has been determined to be 11.06 cal./degree mole at 298.15°K. (25). High-temperature heat contents and entropies have been measured by King, Weller, and Christensen (26), who report $H^\circ_{1600} - H^\circ_{298}$ = 24.75 kcal./mole and $S^\circ_{1600} - S^\circ_{298}$ = 29.89 cal./degree mole. The heat of formation of $MoO_2(s)$ was taken to be −140.8 kcal./mole (28). An enthalpy of sublimation at 298.15°K. of 139.2 kcal./mole is obtained from the second-law treatment, while use of the free-energy functions for $MoO_2(g)$ yields 135.4 kcal./mole.

WO_2: Chupka, Berkowitz, and Giese (12) report data for the reaction $W(s) + 2BeO(s) = WO_2(g) + 2Be(g)$. DeMaria, Burns, Drowart, and Inghram (16, 17) measured the partial pressures of tungsten(IV) oxide and aluminum in equilibrium with tungsten and aluminum oxide permitting evaluation of the equilibrium constant for the reaction

$$W(s) \quad + \quad \tfrac{2}{3}Al_2O_3(s) \quad = \quad WO_2(g) \quad + \quad \tfrac{4}{3}Al(g)$$

The free-energy functions for W(s), Al(g), and Be(g) were taken from Stull and Sinke (38), those for BeO(s) were obtained from the National Bureau of Standards (31), and those for $Al_2O_3(s)$ came from Sinke (37). Third-law treatment of these data yields ΔH_{298} = 12.4 kcal./mole for the reaction $W(s) + O_2(g) = WO_2(g)$ from the aluminum reaction and ΔH°_{298} = 9.3 kcal./mole from the beryllium equilibrium. A value of 12 kcal./mole was taken to obtain the dissociation energy of 307 kcal./mole.

UO_2: The pressure and heat of sublimation of UO_2(vap.) over $UO_2(s)$ have been measured by Ackerman, Gilles, and Thorn (1). A mass-spectrometer examination of the vapors over mixtures of uranium metal and aluminum(III) oxide has also been reported (16). Using Kelley's (24) $H^\circ_T - H^\circ_{298}$ values for $UO_2(s)$, the second-law data yield ΔH°_{298} (vap.) = 143.1 kcal./mole. A third-law treatment of the results of Ackerman, Gilles, and Thorn gives 148.9 kcal./mole for this quantity, while the mass-spectrometer results yield ΔH°_{298} (vap.) = 157 kcal./mole, assuming the reaction taking place to be $UO_2(s) = UO_2(g)$ and assuming column 6 in table 4 of DeMaria, Burns, Drowart, and Inghram's paper to be P_{UO_2} and not P_{UO} as labeled. A ΔH°_{298} (vap.) value of 149 kcal./mole was used to obtain the dissociation energy of 354 kcal./mole. The heat of sublimation of uranium metal was taken to be 125 kcal./mole (27).

D. Oxides of the platinum metals

RuO_2: Alcock and Hooper (3) have measured the rate of sublimation of ruthenium metal in a stream of oxygen. Their results show the main species vaporizing to be Ru_xO. Their measured Ru_xO pressure sets an upper limit to the pressure of ruthenium(IV) oxide in the equilibrium $Ru(s) + O_2(g) = RuO_2(g)$. Using the estimated free-energy functions and a heat of sublimation of ruthenium of 144 kcal./mole (38), an upper limit of 235 kcal./mole is set upon the dissociation energy of $RuO_2(g)$.

RhO_2: Alcock and Hooper (3) report the pressure of $RhO_2(g)$ over rhodium metal in an oxygen atmosphere. Their second-law data yield ΔH°_{298} for the reaction $Rh(s) + O_2(g) = RhO_2(g)$ to be 46.9 kcal./mole when $H^\circ_{1500} - H^\circ_{298}$ for $RhO_2(g)$ is estimated to be 16.8 kcal./mole. The free-energy functions for $RhO_2(g)$ in table 1 were obtained from their measured pressures, this ΔH°_{298}, and the free-energy functions for Rh(s) and $O_2(g)$ listed by Stull and Sinke (38). The heat of sublimation of rhodium was taken to be 134 kcal./mole (19) to derive the dissociation energy of 206 kcal./mole.

IrO_2: The volatility of iridium in oxygen observed by Alcock and Hooper (3) is due to either Ir_2O_3 or IrO_3. The pressures they reported assuming IrO_3(g) were used to set an upper limit to the pressure of iridium(IV) oxide. The heat of sublimation of iridium was taken to be 150 kcal./mole (38). The dissociation energy is less than 243 kcal./mole.

PdO_2: Alcock and Hooper (3) observed only a slight increase in the volatility of palladium metal in oxygen over that in an inert atmosphere. Thus, the measured vapor pressure of palladium metal (3, 18) sets an upper limit to the dissociation energy of 156 kcal./mole, using a heat of sublimation for palladium of 91 kcal./mole (17).

PtO_2: The vapor pressure and the high-temperature heat of sublimation of platinum(IV) oxide formed by the reaction Pt(s) + O_2(g) = PtO_2(g) have been measured by Alcock and Hooper (3) and by Schäfer and Tebben (35). The free-energy functions of Pt(s) and O_2(g) were obtained from Stull and Sinke (38). The heat of sublimation of platinum metal at 298.15°K. was taken to be 135.2 kcal./mole (18) and Schäfer's estimate of $H_T^\circ - H_{298}^\circ$ for PtO_2(g) was used. Alcock and Hooper's results yield −72.3 cal./degree mole for the free-energy function of PtO_2(g) at 1500°K. and 40.5 kcal./mole as the standard enthalpy of formation of PtO_2(g) at 298.15°, while Schäfer's data give −73.1 cal./degree mole and 41.3 kcal./mole for these quantities, respectively. A value of $-(F^\circ - H_{298}^\circ)/T = 72.7$ at 1500°K. was used to derive the free-energy functions in table 1. A heat of formation of 41 kcal./mole was used to obtain the dissociation energy.

IV. DISCUSSION

The trends across the Periodic Table shown by the heats of dissociation of the gaseous MO_2 molecules are surprisingly uniform. Qualitatively, the trends are similar to those that would be predicted by an ionic model. On the basis of a simple ionic model the variation of lattice energy with cation size should be relatively small because of the very small size of a tetravalent cation with respect to the anion. Thus the interionic distance is essentially fixed by the radius of the oxide ion. Under such circumstances, the variation of ionization potential across the Periodic Table should be the major factor affecting the variation of dissociation energy. However, this picture is much too simple for quantitative predictions, as one would expect the oxide ions in these molecules to be polarized to a very large extent in view of the high fields near the small tetravalent cations.

It does not appear worthwhile at the present time to attempt to estimate quantitatively the trends to be expected either on the basis of a classical electrostatic calculation, taking into account polarization, or on the basis of the various methods of treating covalent bonding. One can, however, conclude from examination of the dissociation energies in table 3 that polarization or covalent bonding does not reverse the trends expected from the simple ionic model except for carbon dioxide and silicon dioxide. That is, the qualitative trends observed are those expected purely from the variation of ionization potentials except for the decrease in heat of dissociation in going from carbon dioxide to silicon dioxide. In that instance, one would say that extensive polarization or covalent-bond character in carbon dioxide, and perhaps in silicon dioxide, is sufficient to reverse the trend expected on the basis of a simple ionic model. It will be of interest to obtain bond distances and other molecular data for these compounds in order to obtain a more precise picture of the bonding in this type of molecule.

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