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PART XXII

VAPORIZATION OF COMPOUNDS AND ALLOYS AT HIGH TEMPERATURES

PART XXII. MASS SPECTROMETRIC DETERMINATION OF
THE DISSOCIATION ENERGY OF THE MOLECULES
MgO, CaO, SrO and Sr₂O

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(Prepared under Contract No. AF 61(052)-225 by the
Universite Libre de Bruxelles, Brussels, Belgium;
John Drowart, G. Exsteen and G. Verhaegen)

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FOREWORD

This report was prepared by the University of Brussels, Belgium, under USAF Contract No. AF61(052)-225. The contract was initiated under Project No. 7350, "Refractory Inorganic Non-Metallic Materials," Task No. 735001, "Non-graphitic." The work was administered under the direction of the Air Force Materials Laboratory, Deputy Commander/Research and Engineering, Aeronautical Systems Division, Wright-Patterson Air Force Base, Ohio. Mr. F. W. Vahldiek was the project engineer.

ABSTRACT

→ The dissociation energy of the molecules MgO, CaO, SrO was determined. $D_0^{\circ}(\text{MgO})=85\pm5$; $D_0^{\circ}(\text{CaO})=92\pm5$; $D_0^{\circ}(\text{SrO})=102\pm5$ kcal/mole. The ground state was considered to be $^1\Sigma$. This choice is discussed. A review and discussion of the literature values for $D_0^{\circ}(\text{MgO}, \text{CaO}, \text{SrO})$ is made. The molecule Sr_2O was identified and its atomization energy determined: $\Delta H_{\text{at}}^{\circ}(\text{Sr}_2\text{O})=193\pm6$ kcal/mole.

This technical documentary report has been reviewed and is approved.



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TABLE OF CONTENTS

	PAGE
INTRODUCTION	1
EXPERIMENTAL PROCEDURE AND DATA	2
EXPERIMENTAL DATA	3
FREE ENERGY FUNCTIONS	7
ERROR LIMITS	8
RESULTS	13
DISCUSSION	14
REFERENCES	26

TABLES

TABLE	PAGE
1. Relative Ionization Cross-Sections (), Multiplier Yields (), and Measured Appearance Potentials (AP) of Species of Interest in this Study	6
2. Relative Intensities and Enthalpies (kcal/mole) for Reactions Involving MgO	9
3. Relative Ion Intensities and Enthalpy Changes (kcal/mole) for Reactions Involving CaO	10
4. Relative Intensities and Enthalpy Changes (kcal/mole) for Reactions Involving SrO	11
5. Relative Intensities and Enthalpy Changes (kcal/mole) for Reactions Involving Sr ₂ O	12
6. Dissociation Energies of MgO, CaO and SrO (kcal/mole)	13
7. Atomization Energy of Sr ₂ O (kcal/mole)	14
8. Comparison of Data for the Dissociation Energy of MgO	15
9. Comparison of Data for the Dissociation Energy of CaO	16
10. Comparison of Data for the Dissociation Energy of SrO	17
11. Comparison of the Dissociation Energies and Force Constants of the ¹ States	22
12. Comparison of the Dissociation Energies by the Ionic Model	24

INTRODUCTION

Numerous measurements and discussions⁽¹⁻⁷⁾ of the dissociation energy of the gaseous monoxides of magnesium⁽⁹⁻¹⁶⁾, calcium^(9,10,13,17-21) and strontium^(9,12,13,17,18, 21-26) have already been made. The stability of these molecules has been calculated on the basis of an electrostatic model⁽⁸⁾ and investigated experimentally by several thermochemical methods: interpretation of total vapour pressure measurements for the condensed oxides^(11,15-17,22), flame spectrophotometry^(9,10,13,14,19,26) and mass spectrometric measurements of partial pressures and of their variation with temperature^(12,18,20,21,23-25).

The results obtained by the different techniques and in different investigations are in disagreement (see tables 8-10), as pointed out in the reviews⁽³⁻⁷⁾. In one of these⁽⁶⁾ the discrepancy between the thermochemical results based on photometric measurements in flames and those based on mass spectrometry was attributed to fragmentation of these molecules under electron impact, a view already refuted⁽²⁷⁾.

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Difficulties are in addition associated with the calculation of the thermodynamic functions and thus of dissociation energies based thereon. These difficulties result from the fact that for the three molecules the lowest known electronic state, 1_2 (28-36) cannot correlate with the normal states of the atoms.

The present paper reports a determination of the dissociation energy of these oxides and of the molecule Sr_2O made by mass spectrometric measurements of relative partial pressures, and a comparison of the data with those given in the literature.

EXPERIMENTAL PROCEDURE AND DATA

The oxides MgO , CaO and SrO were contained in molybdenum and tungsten Knudsen cells, which had effusion areas of $5 \cdot 10^{-3} \text{ cm}^2$. The crucibles were heated by electron bombardment and protected against radiation losses by four concentric tantalum shields. Their temperature was measured by sighting with a Leeds and Northrup disappearing filament optical pyrometer into a threaded hole drilled in the bottom of the crucible. The pyrometer was calibrated both against the melting point of gold and against a standard lamp⁽³⁷⁾.

A collimated beam issuing from the crucible was ionized by low energy electrons (4-25 eV). The measurement of the intensity distribution made with a movable slit intersecting the molecular beam enabled one to verify that the gaseous species originated indeed from within the Knudsen cell.

The ions formed were mass-analyzed in a 60° -sector single-focussing mass spectrometer, equipped with a secondary electron multiplier. This spectrometer, the auxiliary equipment and set-up were previously described⁽³⁸⁻⁴⁰⁾, as well as the experimental procedure and treatment of data⁽⁴¹⁾.

The magnesium and calcium oxides were Merck products used as such. The strontium oxide was prepared from the hydroxide $\text{Sr}(\text{OH})_2 \cdot \text{H}_2\text{O}$ (Hopkins and Williams) heated in a platinum boat at 90°C during 12 hours and at 900°C for one hour under a stream of dry nitrogen.

EXPERIMENTAL DATA

As expected, the oxides of Mg, Ca and Sr, (M) were reduced by the Mo and W, (Me) crucibles. In addition, in the temperature range investigated, molybdates and tungstates (MMeO_3), and molybdates and tungstates (MMeO_4) were formed in the gas and in condensed phase. The condensed ternary oxides and their thermochemical properties are known⁽⁴²⁻⁴⁴⁾ and their formation in the SrO-W system had already been observed⁽⁴⁵⁾ under conditions similar to those prevailing in the present experiments. The gaseous ternary oxides will be discussed in a subsequent paper.

All of the species deduced to be present in the gas phase were identified from their mass, isotopic distribution, approximate appearance potential and ionization efficiency curve. The former were obtained by the linear extrapolation method. The energy scale was corrected against the spectroscopic values for the ionization potentials of Mg, Ca and Sr⁽⁴⁶⁾. The different values measured in this study are given in Table 1 and compared with literature data whenever possible. In the case of the MgO^+ ion, complications resulted from the presence of small amounts of Ca impurities. The Mg and Ca natural isotopes and their abundances are Mg^{24} , 78.6, Mg^{25} , 10.1 and Mg^{26} , 11.3, and Ca^{40} , 96.92, Ca^{42} , 0.64, Ca^{43} , 0.13, Ca^{44} , 2.13, Ca^{46} , 0.003 and Ca^{48} , 0.179%⁽⁴⁷⁾. The most abundant MgO^+ and Ca^+ peaks thus superpose at mass 40, while the Mg^{25}O^+ intensities at mass 41 at which no interference occurs, were too low for appearance potential measurements. Similar difficulties resulted from the presence of S and Fe impurities in the other

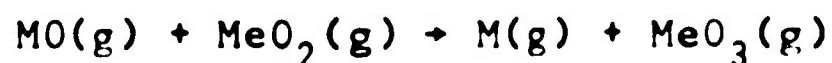
oxide samples. These impurities initially interfered with the O_2 and CaO measurements respectively. The measured intensities of these molecules were therefore carefully controlled by appearance potential measurements and were retained only after exhaustion of the impurities.

The ionization efficiency curves showed the $MMeO_3$ and $MMeO_4$ molecules to fragment in part under electron impact above 13-15 eV and to lead to the formation of MO^+ ions. In this respect the molecular ions $MMeO_3^+$ and $MMeO_4^+$ are analogous to the $In_2MoO_4^+$ ion which also fragments to a large extent⁽⁴⁸⁾. The measurements referred to below were therefore in general made with low energy electrons to avoid contribution of fragment MO^+ ions to the intensity of the ions formed from the MO molecules, object of this investigation. For MgO, the measurements were carried out with 20 eV electrons after ascertaining that the relative pressures of ternary oxides ($MgMoO_{3,4}$) were well below those of MgO so that they could not contribute appreciably through fragmentation to the $Mg^{25}O^+$ intensity.

Because of the complex composition of the gas phase, no absolute pressure calibrations based on quantitative vaporizations of the samples were carried out. Neither were pressures calculated from the known thermodynamic properties of the condensed oxides^(7,49) because of the formation of molybdates or tungstates. Rather were the dissociation energies derived from iso-molecular reactions of the type:



and



Even for these all-gas phase reactions complications were caused by the reactions in the condensed phase, which made the relative pressures (ionic intensities) vary with time at constant temperature. Therefore the relative intensities of reaction partners

given below (Tables 2a-5c) measured essentially simultaneously are valid only for the particular reaction indicated. Other reactions should not be calculated with these relative intensities since they do not pertain to constant solid phase composition.

The equilibrium constant K of the above reactions were calculated from the relative intensities (I_i^+) using the relation

$$K = \prod_i P_i^{v_i} = \prod_i (I_i^+ (n-1) AP_i / \sigma_i \gamma_i (E_i - AP_i))^{v_i}$$

(v_i = stoichiometric coefficient with appropriate sign)

The relation is based on the assumption that the relative ionization cross section σ_i varies linearly with the energy ($E_i - AP_i$) above the threshold for ionization AP_i up to a maximum value at $E_i = nAP_i$ with n constant for the different species and approximately equal to 3. The relative cross sections at the maximum were based on those calculated by Otvos and Stevenson⁽⁵⁰⁾. The relative secondary electron multiplier yield γ_i were taken from the calibration curve of the multiplier taking, where necessary, molecular effects into account⁽⁵¹⁾. The σ and γ values used in the evaluation of the data are summarized in Table 1. The relative measured intensities I_i^+ are given in Table 2a to 5c, the energy E_i of the ionizing electrons being given between brackets when $E_i < 3AP_i$.

TABLE 1.

Relative Ionization Cross-Sections (σ), Multiplier Yields (γ), and Measured Appearance Potentials (AP) of Species of Interest in this Study.

Species	σ	γ^a	AP(eV)	AP _{lit} (eV)
Mg	15.9	0.98	-	7.6 ⁽⁴⁶⁾
Ca	42.1	0.92	-	6.1 ⁽⁴⁶⁾
Sr	64.3	0.69	-	5.7 ⁽⁴⁶⁾
O	3.3	1.02	14.0	13.6 ⁽⁴⁶⁾
O ₂	5.3	1.10	11.9	12.2 ⁽⁵²⁾
MoO ₂	59	0.63	9.2	9.4 ⁽⁵³⁾
MoO ₃	62	0.60	11.8	12.0 ⁽⁵³⁾
WO ₂	70	0.39	9.8	9.9 ⁽⁵³⁾
WO ₃	73	0.41	11.9	11.7 ⁽⁵³⁾
MgO	19	1.04	-	-
CaO	45	0.95	6.5	-
SrO	67	0.69	6.1	-
Sr ₂ O	129	0.45	4.8	-

^a Multiplier yields (γ) are normalized relative to ²⁰Ne: $\gamma_{M=20} = 1.00$

FREE ENERGY FUNCTIONS.

The values of the free energy functions ($G_T^0 - H_0^0/T$) used to compute reaction enthalpies (ΔH_0^0) from the equilibrium constants using the relation $\Delta H_0^0 = -RT \ln K - T\Delta(G_T^0 - H_0^0/T)$ were taken from the following tabulations: gaseous Mg, Ca, Sr, O and O₂, Stull and Sinke⁽⁵⁴⁾; gaseous MoO₂, MoO₃, WO₂ and WO₃, De Maria, Burns, Drowart and Inghram⁽⁵³⁾. For consistency, the enthalpies of formation of MoO₂, MoO₃, WO₂ and WO₃ given by the latter authors were also used.

For the three molecules MgO, CaO and SrO as well as for BeO⁽²⁸⁾ and BaO⁽²⁸⁾, the lowest known electronic state is a ¹Σ state in which until now no perturbations were observed. As often pointed out, this state cannot correlate with the atoms in their normal states, the expected state being a ³Σ or ³Π state. In a recent paper, the latter states were calculated, by analogy with C₂ to lie close to the ¹Σ state for both BeO and MgO⁽⁵⁵⁾. For BaO, the X¹Σ state was shown to be the ground state^(56,57) whereas for BeO the observation of its absorption spectrum⁽⁵⁸⁾ shows the X¹Σ also to be the ground state (or close to it). Molecular beam work by the electric resonance method for SrO likewise suggests the X¹Σ to be the ground or a low lying state⁽⁵⁹⁾. For BaO^(60,61), SrO⁽⁶²⁾ and CaO⁽³²⁾ perturbations in the excited A¹Σ led to the identification of six, six and four states or substates respectively. For BaO, the most likely interpretation adopted^(60,61) was to consider the perturbing states as components of both ³Σ and ³Π states, which one is inclined to correlate with the atoms in their ground state. If the same is done for SrO, and CaO, the ³Σ and ³Π states lie at about 11550 (or less), and 10870 cm⁻¹ above the X¹Σ state (see fig.1). In the absence of further experimental data, the free energy function was therefore based on the molecular constants of the X¹Σ states.

For MgO, the small contribution of the $^1\Pi$ level at 3503 cm^{-1} (28) to the electronic partition function was taken into account. The numerical values are given in ref. 7 and 63.

The free energy function of Sr_2O was evaluated here assuming this molecule to have a linear symmetric structure as predicted by Walsh's rules⁽⁵⁴⁾. The force constants and bond lengths of the two Sr-O bonds were taken the same as in SrO ($d_{\text{Sr-O}} = 1.92\text{ \AA}$ and $k = 3.32 \cdot 10^5\text{ dynes/cm}$). The bending force constant: $k_\delta/d^2 = 1.17 \cdot 10^4\text{ dynes/cm}$, was estimated by analogy with other linear symmetric molecules⁽⁵⁵⁾. A valence force model⁽⁶⁵⁾ calculation using these parameters yields $\omega_1 = 256$, $\omega_2 = 233$ (doubly degenerate) and $\omega_3 = 888\text{ cm}^{-1}$. A statistical weight of 3 was considered. The values for the free energy function computed with these parameters are: $-(G_T^0 - H_0^0/T) = 81.1$ and $83.0\text{ cal/mole deg.}$ at 2000 and 2300°K respectively.

ERROR LIMITS

The error limits cited in tables 2a to 5c are statistical 95% probabilities: $2\sigma = 2\sqrt{\frac{\epsilon^2}{n-1}}$ where σ is the standard deviation and ϵ the difference between each of the n experimental values and the mean.

The uncertainties given with the values of $D_0^0(\text{MgO})$, $D_0^0(\text{CaO})$ and $D_0^0(\text{SrO})$ (Table 6) further take into account estimated possible systematic errors. These include an uncertainty of 1% in the temperature, 60% in the $\sigma\gamma$ products and 60% in the dependence of the cross section with the excess energy above the threshold for ionization.

For Sr_2O , apart from larger experimental errors, additional uncertainties arise from the need to estimate completely its structural and molecular properties.

TABLES 2a and b.

Relative Intensities and Enthalpy (kcal/mole)
for Reactions Involving MgO.

TABLE 2a. $\text{MgO(g)} + \text{O(g)} \rightarrow \text{Mg(g)} + \text{O}_2\text{(g)}$

T°K	$I^+ \text{Mg}$	$I^+ \text{O}_2$	$I^+ \text{O}$	$I^+ \text{MgO}$	ΔH°_0
2225	1.0	5.8×10^{-5}	2.4×10^{-4}	1.3×10^{-3}	-31.5
2026	1.0	1.1×10^{-4}	9.5×10^{-4}	4.1×10^{-4}	-30.3
2114	1.0	1.3×10^{-4}	7.9×10^{-4}	4.7×10^{-4}	-32.7
2110	1.0	1.5×10^{-4}	8.7×10^{-4}	7.6×10^{-4}	-30.9
2152	1.0	1.0×10^{-4}	5.1×10^{-4}	6.7×10^{-4}	-32.6
2137	1.0	1.4×10^{-4}	7.6×10^{-4}	6.9×10^{-4}	-32.1
2127	1.0	1.3×10^{-4}	9.5×10^{-4}	3.2×10^{-4}	-33.5
2274	1.0	7.9×10^{-5}	4.7×10^{-4}	7.8×10^{-4}	-32.9
				Average	-32.1 ± 2.1

TABLE 2b. $\text{MgO(g)} + \text{WO}_2\text{(g)} \rightarrow \text{Mg(g)} + \text{WO}_3\text{(g)}$

T°K	$I^+ \text{Mg}$	$I^+ \text{WO}_3$	$I^+ \text{WO}_2$	$I^+ \text{MgO}$	ΔH°_0
2109	1.0	1.2×10^{-1}	8.7×10^{-2}	1.9×10^{-3}	-59.9
2225	1.0	5.3×10^{-2}	5.8×10^{-2}	1.3×10^{-3}	-63.3
2181	1.0	2.2×10^{-2}	3.0×10^{-2}	8.2×10^{-4}	-63.0
2222	1.0	4.5×10^{-2}	4.5×10^{-2}	1.5×10^{-3}	-62.6
2106	1.0	8.3×10^{-3}	1.0×10^{-2}	7.2×10^{-4}	-61.7
2152	1.0	6.3×10^{-3}	8.7×10^{-3}	6.7×10^{-4}	-63.1
				Average	-62.3 ± 2.6

TABLES 3a, b and c.

Relative Ion Intensities and Enthalpy Changes (kcal/mole)
for Reactions Involving CaO

TABLE 3a. $\text{CaO(g)} + \text{O(g)} \rightarrow \text{Ca(g)} + \text{O}_2\text{(g)}$

T°K	I^+Ca	I^+O_2	I^+O	I^+CaO	ΔH_0°
2410	1.0	2.0×10^{-3}	3.5×10^{-3}	1.6×10^{-2}	-29.2
2233	1.0	8.7×10^{-5}	4.3×10^{-4}	2.5×10^{-3}	-30.7
2168	1.0	1.9×10^{-3}	3.2×10^{-3}	8.7×10^{-3}	-24.8
2231	1.0	1.7×10^{-3}	2.7×10^{-3}	1.7×10^{-2}	-26.8
				Average	-27.9 ± 5.0

TABLE 3b. $\text{CaO(g)} + \text{MoO}_2\text{(g)} \rightarrow \text{Ca(g)} + \text{MoO}_3\text{(g)}$

T°K	I^+Ca	I^+MoO_3	I^+MoO_2	I^+CaO	ΔH_0°
2393	$1.0(8.1)^a$	5.7×10^{-3}	2.3×10^{-2}	$2.7 \times 10^{-3}(10.1)$	-55.1
2410	$1.0(8.1)$	6.8×10^{-3}	2.9×10^{-2}	$2.7 \times 10^{-3}(10.1)$	-55.7
2405	$1.0(8.1)$	6.0×10^{-3}	3.3×10^{-2}	$2.7 \times 10^{-3}(10.1)$	-57.7
				Average	-56.2 ± 2.7

^a energy of ionizing electrons (see text)

TABLE 3c. $\text{CaO(g)} + \text{WO}_2\text{(g)} \rightarrow \text{Ca(g)} + \text{WO}_3\text{(g)}$

T°K	I^+Ca	I^+WO_3	I^+WO_2	I^+CaO	ΔH_0°
2334	$1.0(10.2)$	2.2×10^{-4}	1.7×10^{-3}	$1.4 \times 10^{-3}(10.2)$	-54.4
2328	$1.0(9.5)$	2.8×10^{-2}	4.4×10^{-2}	$6.0 \times 10^{-3}(9.5)$	-51.9
				Average	-53.2 ± 3.5

TABLES 4a, b and c.
Relative Intensities and Enthalpy Changes (kcal/mole)
for Reactions Involving SrO.

TABLE 4a. $\text{SrO(g)} + \text{O(g)} \rightarrow \text{Sr(g)} + \text{O}_2\text{(g)}$

T°K	$\text{I}^+ \text{Sr}$	$\text{I}^+ \text{O}_2$	$\text{I}^+ \text{O}$	$\text{I}^+ \text{SrO}$	ΔH_0°
2233	1.0(13.5)	1.6×10^{-4} (18.5)	2.5×10^{-3} (18.5)	9.0×10^{-3} (11.5)	-15.8
2156	1.0(13.3)	1.6×10^{-4} (21.3)	2.7×10^{-3} (18.3)	9.4×10^{-3} (11.3)	-13.4
2265	1.0(13.5)	2.7×10^{-4} (18.5)	3.6×10^{-3} (18.5)	1.2×10^{-2} (11.5)	-15.5
2321	1.0(12.0)	6.9×10^{-4} (19.0)	5.0×10^{-3} (19.0)	1.3×10^{-2} (12.0)	-17.4
				Average	-15.5 ± 3.3

TABLE 4b. $\text{SrO(g)} + \text{WO}_2\text{(g)} \rightarrow \text{Sr(g)} + \text{WO}_3\text{(g)}$

T°K	$\text{I}^+ \text{Sr}$	$\text{I}^+ \text{WO}_3$	$\text{I}^+ \text{WO}_2$	$\text{I}^+ \text{SrO}$	ΔH_0°
2326	1.0(11.9)	2.7×10^{-2} (17.9)	8.7×10^{-2} (17.9)	2.5×10^{-2} (11.9)	-45.2

TABLE 4c. $\text{SrO(g)} + \text{MoO}_2\text{(g)} \rightarrow \text{Sr(g)} + \text{MoO}_3\text{(g)}$

T°K	$\text{I}^+ \text{Sr}$	$\text{I}^+ \text{MoO}_3$	$\text{I}^+ \text{MoO}_2$	$\text{I}^+ \text{SrO}$	ΔH_0°
2044	1.0	2.8×10^{-4}	1.1×10^{-3}	5.9×10^{-3}	-45.6
1987	1.0	2.7×10^{-4}	8.0×10^{-4}	4.5×10^{-3}	-46.5
1992	1.0	2.7×10^{-4}	7.3×10^{-4}	4.1×10^{-3}	-47.6
2060	1.0(10.0)	2.4×10^{-4}	9.5×10^{-4}	2.0×10^{-3} (10.0)	-49.8
2070	1.0(12.8)	1.7×10^{-4}	7.1×10^{-4}	2.8×10^{-3} (12.8)	-48.3
2086	1.0(12.8)	2.1×10^{-3}	1.1×10^{-3}	2.1×10^{-3} (12.8)	-49.0
2173	1.0(9.3)	2.6×10^{-2} (17.3)	9.7×10^{-2} (17.3)	2.4×10^{-2} (13.3)	-48.0
2233	1.0(13.3)	1.2×10^{-2} (16.3)	3.7×10^{-2} (16.3)	2.1×10^{-2} (13.3)	-46.3
				Average	-47.6 ± 2.7

TABLES 5a, b and c.

Relative Intensities and Enthalpy Changes (kcal/mole) for Reactions Involving Sr_2O .

TABLE 5a. $\text{Sr}_2\text{O}(\text{g}) + \text{O}(\text{g}) \rightarrow 2\text{SrO}(\text{g})$

$T^\circ\text{K}$	$I^+\text{SrO}$	$I^+\text{O}$	$I^+\text{Sr}_2\text{O}$	ΔH°_0
2060	1.0	2.2×10^{-2}	1.6×10^{-1}	-8.1
2086	1.0(12.8)	1.9×10^{-2} (16.8)	8.2×10^{-2}	-6.4
2228	1.0(11.3)	2.8×10^{-1} (18.3)	2.4×10^{-2}	-9.6
			Average	-8.0 ± 3.2

TABLE 5b. $\text{Sr}_2\text{O}(\text{g}) + 2\text{O}(\text{g}) + \text{Mo}(\text{s}) \rightarrow 2\text{Sr}(\text{g}) + \text{MoO}_3(\text{g})$

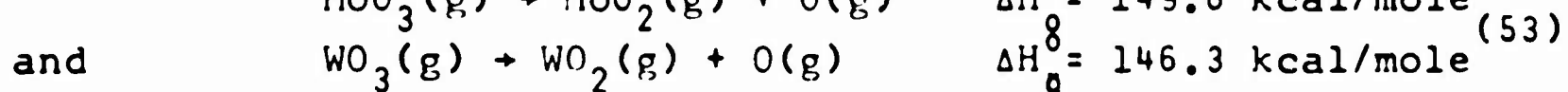
$T^\circ\text{K}$	$I^+\text{Sr}$	$I^+\text{MoO}_3$	$I^+\text{O}$	$I^+\text{Sr}_2\text{O}$	ΔH°_0
2149	1.0	1.7×10^{-2}	3.2×10^{-3}	3.7×10^{-4}	-61.0

TABLE 5c. $\text{Sr}_2\text{O}(\text{g}) + 3\text{O}(\text{g}) \rightarrow 2\text{Sr}(\text{g}) + 2\text{O}_2(\text{g})$

$T^\circ\text{K}$	$I^+\text{Sr}$	$I^+\text{O}_2$	$I^+\text{O}$	$I^+\text{Sr}_2\text{O}$	ΔH°_0
2149	1.0	3.1×10^{-4}	3.2×10^{-3}	3.7×10^{-4}	-41.3
2260	1.0	4.9×10^{-4}	3.5×10^{-3}	1.6×10^{-4}	-45.6
2179	1.0	3.3×10^{-5}	5.5×10^{-4}	2.9×10^{-4}	-46.4
				Average	-44.4 ± 5.3

RESULTS

From the reaction enthalpies given in table 2a-4c together with the dissociation energy of oxygen, $D_0^0(\text{O}_2) = 117.96 \text{ kcal/mole}^{(66)}$ and the enthalpies of the reactions



the values given in Table 6 were calculated for the dissociation energies of MgO, CaO and SrO.

TABLE 6. Dissociation Energies of MgO, CaO and SrO (kcal/mole)

Molecule	Equilibrium	$D_0^0(\text{MO})$	Average
MgO	O/O ₂	85.9	85.0 ± 5
	WO ₂ /WO ₃	84.0	
CaO	O/O ₂	90.1	92.2 ± 5
	MoO ₂ /MoO ₃	93.4	
	WO ₂ /WO ₃	93.1	
SrO	O/O ₂	102.5	101.9 ± 5
	MoO ₂ /MoO ₃	101.1	
	WO ₂ /WO ₃	102.0	

The enthalpy of atomization of Sr₂O was calculated from the equilibria given in Tables 5a-5c using $D_0^0(\text{SrO})=101.9$, $\Delta H_{\text{osub}}^0(\text{Mo})= 157.1^{(54)}$ and $\Delta H_{\text{oat}}^0(\text{MoO}_3)=411.1^{(53)}$ kcal/mole. The values are summarized in Table 7.

TABLE 7. Atomization Energy of Sr_2O (kcal/mole)

Equilibrium	$\Delta H_{\text{oat}}^{\circ}(\text{Sr}_2\text{O})$	Selected value
$\text{Sr}_2\text{O}(\text{g}) + \text{O}(\text{g}) \rightarrow 2\text{SrO}(\text{g})$	195.8	193.4 \pm 6
$\text{Sr}_2\text{O}(\text{g}) + 2\text{O}(\text{g}) + \text{Mo}(\text{s}) \rightarrow 2\text{Sr}(\text{g}) + \text{MoO}_3(\text{g})$	193.0	
$\text{Sr}_2\text{O}(\text{g}) + 3\text{O}(\text{g}) \rightarrow 2\text{Sr}(\text{g}) + 2\text{O}_2(\text{g})$	191.5	

DISCUSSION

For each of the molecules MgO , CaO and SrO the dissociation energy obtained here is compared with the literature values in Tables 8-10. All values have been recalculated with the free energy functions used here, i.e. a $^1\Sigma$ ground state has been considered throughout.

The mass spectrometric studies are considered first. In the case of MgO , only an upper limit⁽¹²⁾ is available, while for CaO and SrO a number of determinations have been made. For CaO only one determination⁽²¹⁾ is in agreement with the value found here. The value was obtained in a similar manner but using the equilibrium between gaseous S , SO , Ca and CaO . Pelchovitch⁽¹⁸⁾ encountered experimental difficulties in his measurements for CaO . Babeliowski's⁽²⁰⁾ value appears unreliable; the latter author measured the variation with temperature of the ionic intensity of mass 56 (CaO) over a temperature range of 95°C , which corresponds to only 4% of the temperature scale. In view of the well-known uncertainties of 2d law measurements over small temperature ranges, this determination is probably enticed by very large error limits. For SrO , the situation is more favourable. The low value reported by Porter, Chupka and Inghram⁽¹²⁾ can almost certainly be explained by the fact that these authors vaporized SrO from an alumina Knudsen cell leading to the formation

TABLE 8. Comparison of Data for the Dissociation Energy of MgO.

Molecule	Method	T°K	D ⁰ (MO) kcal/mole	Ref.
MgO	Mass Spectrometry (Knudsen)	2150	85±5	This work
	Mass Spectrometry (Knudsen)	1950	<95	12
	Total Vapour Pressure (Knudsen)	2000	110	11
	Transpiration (O ₂)	2140	80	15
	Transpiration (O ₂)	1900	93	16
	Flame Spectrophotometry	2400	120	9
	Flame Spectrophotometry	3000	89	13
	Flame Spectrophotometry	2000	102	14

TABLE 9.

Comparison of Data for the Dissociation Energy of CaO.

Molecule	Method	T°K	D ⁰ (MO) kcal/mole	Ref.
CaO	Mass Spectrometry (Knudsen)	2300	92.5	This work
	Mass Spectrometry (Knudsen)	2280	94	21
	Mass Spectrometry (Knudsen, 2nd law)	2210	107	20
	Mass Spectrometry (Langmuir)	1750	100	18
	Total Vapour Pressure (Langmuir)	1675	113	17
	Flame Spectrophotometry	2020	114	9, 10
	Flame Spectrophotometry	2980	117	13
	Flame Spectrophotometry	≈ 2000	≈ 127	19

TABLE 10.

Comparison of Data for the Dissociation Energy of SrO.

Molecule	Method	T°K	D°(MO) kcal/mole	Ref.
SrO	Mass Spectrometry (Knudsen)	2150	102±5	This work
	Mass Spectrometry (Knudsen)	2050	102	21
	Mass Spectrometry (Knudsen)	2100	86	12
			105	revised (see text)
	Mass Spectrometry (Langmuir)	1750	99	24
	Mass Spectrometry (Langmuir)	1675	95	18
	Total Vapour Pressure (Langmuir)	1575	114	17
	Total Vapour Pressure (Langmuir)	1600	115	22
	Flame Spectrophotometry	2300	112	9,10
	Flame Spectrophotometry	2965	115	13
	Carbon Arc Spectrophotometry	2300	100	26

of a compound $(\text{SrO})_{1-4}, \text{Al}_2\text{O}_3$ ⁽⁶⁷⁾ in the condensed phase. Such a reaction was also observed in this study when the use of an alumina liner was attempted. Adding the heat of formation of the $\text{SrO} \cdot \text{Al}_2\text{O}_3$ compound, -19 kcal/mole ⁽⁶⁷⁾ to the value obtained by the latter authors further gives $D_0^\circ(\text{SrO}) = 105 \text{ kcal/mole}$, in agreement with the other mass spectrometric results. It is less easy to explain the value $D_0^\circ(\text{SrO}) = 81 \text{ kcal/mole}$ calculable⁽⁶⁸⁾ from the data of the same authors⁽¹²⁾ using the all-gas phase reaction: $\text{SrO}(\text{g}) \rightarrow \text{Sr}(\text{g}) + 1/2\text{O}_2(\text{g})$, since this equilibrium should be independent of the solid-phase composition. The smaller differences between the Knudsen^(this work, 21) and Langmuir^(18, 23-25) mass spectrometric investigations might result from the difficulty of measuring accurately the temperature of the sample surfaces⁽²³⁻²⁵⁾.

Values of the dissociation energies of MgO , CaO and SrO have been recalculated again here from total vapour pressure measurements. The partial pressures of the diatomic oxides were obtained from the weight loss measurements of the authors^(11, 17, 22) combined with the calculated partial pressures of the metal atoms, O and O_2 . These partial pressures were calculated from the thermodynamic data for the condensed oxides, $\Delta H_{298, f}^\circ(\text{MgO}(\text{s})) = -143.84$ ⁽⁶⁹⁾, $\Delta H_{298, f}^\circ(\text{CaO}(\text{s})) = -151.79$ ⁽⁷⁰⁾, and $\Delta H_{298, f}^\circ(\text{SrO}(\text{s})) = -144.44$ ⁽⁷¹⁾ kcal/mole; values of the enthalpy of sublimation of the metals and the dissociation energy of O_2 are those listed by Stull and Sinke⁽⁵⁴⁾. Although the total vapour pressure measurements are probably quite accurate it should be emphasized that a large experimental uncertainty subsists in the values obtained for the dissociation energies of the molecules. This is due to the fact that partial pressures of the diatomic oxides are derived from differences between the measured total pressures and the calculated decomposition pressures of metal atoms, O and O_2 . This method of obtaining the dissociation energy is thus quite sensitive to minor uncertainties in the thermodynamic data for the condensed oxides (heat of formation, standard

and high temperature entropies) and for the metal (heat of sublimation), which are used to calculate the decomposition pressure. It is further very sensitive to the measured temperature, which in the Langmuir vaporization studies^(17,22) might be quite uncertain in view of the low emissivity of the oxides.

For MgO , the transpiration measurements carried out with O_2 by Altman⁽¹⁵⁾ and by Alexander, Ogden and Levy⁽¹⁶⁾ are within experimental error in agreement with the present data. From the description given by the latter authors, it may be questioned whether the correction applied for the contribution of gaseous Mg(OH)_2 was quantitative and if their value is not an upper limit.

The results obtained by flame spectrophotometry which show a large dispersion among themselves are systematically higher than the results obtained here. In this method a solution of a salt of the element studied is sprayed in known concentration into a flame, whose temperature is usually measured by the sodium line-reversal method. The intensity of a characteristic line of the element is measured and the concentration calculated therefrom through use of the f factor for that particular line. It is next assumed that the decrease in concentration of the element is solely due to the formation of the gaseous diatomic oxide. Uncertainties can thus result from temperature measurements as well as temperature gradients in the outer layers of the flame causing self-reversal of the characteristic line measured. Errors in the temperature would also cause the use of incorrect values of certain equilibria (mainly the O-O_2 equilibrium). Another source of uncertainty is in the f factors, the absolute values of which are known to be quite uncertain⁽⁷²⁾. At 3000°K an overestimation by a factor of 3 of the f value would lead to an error of $+13$ kcal/mole in the dissociation energy, since the concentrations of the metal atoms and of the oxide molecules would be respectively under and over-estimated each by a factor of 3. The experimental uncertainties

of this method have been discussed by Lagerqvist and Hult⁽⁷³⁾ who conclude that they may be of the order of 8-12 kcal/mole.

The major cause of discrepancy is probably the fact that other species than the oxides are responsible for the disappearance of the free alkaline earth metal atoms. This was pointed out by Hult and Lagerqvist⁽⁹⁾ who drew attention to the fact that the dissociation energies obtained are therefore upper limits. In the flame work studies themselves and in other spectroscopic investigations, hydroxides have been shown to be present⁽⁷⁴⁻⁸³⁾. On the basis of stabilities estimated by analogy with those of the corresponding halides, derived from spectroscopic data⁽⁴⁾, it has been thought that their concentration would not be sufficiently large to explain the discrepancy in the dissociation energy of the oxides. For CaF, thermochemical values for the dissociation energy have however been determined recently⁽⁸⁴⁾, which are about 50 kcal/mole higher than the spectroscopic values. The question of the importance of the gaseous hydroxides in flames must thus be considered as still open. A reason for believing that they may be the main cause for the discrepancies in the flame work is that in a measurement of $D(\text{SrO})$ based on the same principle but carried out in a carbon arc⁽²⁶⁾ where the nature of the "strontium carrying molecule" should be more unequivocally established, a value much closer to the mass spectrometric ones was obtained. The fact that the emission spectra of the hydroxides occur in the same region^(74,75,80,81) as those of the oxides probably also explains⁽⁷⁾ why measurements in flames⁽⁵⁶⁾ gave quite high excitation energies of the $X^1\Sigma$ states of CaO and SrO .

The presence in the flames of other molecules such as Sr_2O and Sr_2O_2 has also been suggested^(75,80,81). The present identification of the Sr_2O molecule and previously that of Ba_2O ⁽⁸⁵⁾ supports this suggestion. The data for Sr_2O show however that under the conditions prevailing in the flames its concentration would be

negligible compared to that of SrO. The same can be said for the Sr_2O_2 molecule, since in the present experiments its partial pressure was less than 10^{-3} times that of SrO. In the flames the pressures, calculated in the original publications for SrO, which are apparently much too high as discussed above are of the same order of magnitude as in the present experiments but at higher temperatures. The equilibrium $\text{Sr}_2\text{O}_2(\text{g}) \rightarrow 2\text{SrO}(\text{g})$ would thus be displaced further in favour of SrO. These conclusions are in agreement with those of Huldt and Knall⁽⁸⁶⁾, that molecules containing two Sr or Ca atoms cannot in the flames represent more than 6% of those containing only one.

In the remaining part of the discussion, which is extended to BeO and BaO the spectroscopic data and the ionic models are considered.

The spectroscopic values of the dissociation energy of the five alkaline earth oxides are based on long Birge Spomer extrapolations for the $X^1\Sigma$ states (and the $A^1\Pi$ state of MgO). These are usually correlated with the lowest excited configuration of the atoms for which the Wigner-Witmer rules allow a $^1\Sigma$ state. These atomic states are $M(^1S_0) + O(^1D_2)$ ($M=\text{Mg, Be}$), $M(^3P) + O(^3P)$ ($M=\text{Ca, Sr}$) and $\text{Ba}(^3D) + O(^3P)$. After subtracting the corresponding excitation energies from the convergence limit obtained from the Birge Spomer extrapolation, one obtains dissociation energies which are small compared with the thermochemical values, except for BaO. In spite of the excellent agreement for BaO one questions, because of the high dipole moments of $\text{BaO}^{(57)}$ and $\text{SrO}^{(59)}$ whether the Birge Spomer extrapolation does not lead for the alkaline earth oxides as for other ionic molecules⁽⁴⁾ to values which are out of the line with the true ones.

On the other hand it may be noted that the trend in the force constants for the $X^1\Sigma$ states of the five alkaline earth oxides is qualitatively similar to that in the dissociation energies, Table II. (The dissociation energy considered here is that of the

$^1\Sigma$ dissociating to the atoms in their ground states).

TABLE 11. Comparison of the Dissociation Energies and Force Constants of the $^1\Sigma$ States.

Molecule	Force constant dynes/cm $\times 10^{-5}$	r 10 $^{-8}$ cm	Dissociation Energy ^a	
			TC ^b kcal/mole	BS ^c
BeO	7.52	1.33	149	133
MgO	3.46	1.75	131	84
CaO	3.61	1.82	135	80
SrO	3.40	1.92	143	77
BaO	3.79	1.94	156	156

a Dissociation energy to the excited states of the atoms.

b Thermochemical value

c Linear Birge Sponer extrapolation.

Both trends are different from the usual monotonic decrease within a given column of the periodic table. If the assumption is made that for the molecules under consideration there is some compensation between the decrease in force constant, normally associated with the increase in atomic number or interatomic distance, and the measured increase in dissociation energy in going from MgO to the heavier members of the family, it seems that the unusual trend can be qualitatively justified.

If so, the similarity in trend for force constants and dissociation energies is not in contradiction with the $^1\Sigma$ states being the ground states of all these molecules, contrary to a suggestion in the literature⁽⁶⁰⁾. The corrolary is that the expected $^3\Sigma$ and $^3\Pi$ states formed from the atoms in their ground states have high excitation energies or dissociation energies low compared to the values measured here for the $^1\Sigma$ state. If the states observed through the perturbations in the A $^1\Sigma$ states of CaO, SrO and BaO, located at

11550, 10870 and 17477 cm^{-1} respectively, which were tentatively considered to be components of $^3\Sigma$ and $^3\Pi$ states, are indeed the $^3\Sigma$ and $^3\Pi$ states formed from the atoms in their ground states, the dissociation energies of these $^3\Sigma$ and $^3\Pi$ states are (see fig.1) $> 61 \pm 5$, 72 ± 5 and 80 ± 5 kcal/mole for CaO, SrO and BaO respectively. In BeO several perturbations have been observed^(87,88). Most of these are attributed to interactions between the known $X^1\Sigma$, $A^1\Pi$ and $B^1\Sigma$ states. Unexplained perturbations possibly due to yet unobserved states are located in the regions of 30-45⁽⁸⁷⁾ and 80-95⁽⁸⁸⁾ kcal above the $^1\Sigma$ ground state. In MgO, the only reported perturbations⁽³⁶⁾ lie above the dissociation energy obtained in this work.

One is inclined to relate the rather low values of the dissociation energy of the $^3\Sigma$, $^3\Pi$ states with the fact that the alkaline earth metals in their 1S states have closed s^2 subshells and are thus pseudo rare gases. It may for instance be mentioned in this respect that the dissociation energy of the homonuclear diatomic molecules Be_2 , Mg_2 , Ca_2 , Sr_2 and Ba_2 , as well as those of the analogous Zn_2 , Cd_2 and Hg_2 molecules are very low⁽⁸⁹⁾. The dissociation energy of the gaseous ZnO , CdO and HgO molecules, also formed from $M(^1S) + O(^3P)$ normal states have not been determined yet but seem to be rather low⁽⁴⁾. Here the excitation energy to the 3P states and the ionization potential of the metal are high compared to those of the alkaline earths, so that one can suggest that the separation between states formed from the ions and from excited states of the atoms is too large for these to interact and thereby to make the $^1\Sigma$ state sufficiently stable for it to become the ground state. This would explain why the ZnO , CdO and HgO molecules have not been observed. In reverse the upper limits of the dissociation energy of these molecules, supposed to apply to their $^3\Sigma$, $^3\Pi$ states would give some independent measure of the stability of the $^3\Sigma$, $^3\Pi$ states in the alkaline earth oxides.

The probable trend in the stability of these triplet states, $D(\text{BeO}) < D(\text{MgO}) < D(\text{CaO}) < D(\text{SrO}) < D(\text{BaO})$ could be due to increasing polarizability or decrease in the excitation energy to other atomic states from which molecular triplet states can be formed which by mutual interaction strengthen the lower one, formed from the atoms in their ground state.

These different considerations, together with the experimental data already given under "Free Energy Functions" are the reasons why the $^1\Sigma$ states are believed to be the ground states.

TABLE 12. Comparison of the Dissociation Energies by the Ionic Model.

Molecule	D_{298} exp.	$D_{298} \text{M}^+ \text{O}^-$ no repulsion	$D_{298} \text{M}^+ \text{O}^-$ crystal repulsion	$D_{298} \text{M}^{++} \text{O}^{=}$ no repulsion
BeO	105 ⁽⁹⁰⁾	105	63	188
MgO	87	84	57	62
CaO	94	116	93	157
SrO	104	112	92	136
BaO	131 ⁽⁸⁵⁾	121	103	161

The dissociation energies calculated from the ionic models⁽⁸⁾ $\text{M}^{++} \text{O}^{=}$ and especially $\text{M}^+ \text{O}^-$ give values in agreement with the experimental values (Table 12). The values given are those from the original publication even if they were calculated with an electron affinity of oxygen $E = 70.8$ kcal, which is presently considered too high ($E = 34.3$ kcal⁽⁹¹⁾). In the frame-work of the present discussion the interesting feature is that the trend $D(\text{BaO}) > D(\text{SrO}) > D(\text{BeO}) > D(\text{CaO}) > D(\text{MgO})$ is the same in the ionic model and in the experimental values. As noted by Brewer and Mastick⁽⁸⁾ in the discussion of their model the difference between calculated and measured values

may be due to the difficulty of estimating the repulsive components in the force fields between the ions.

As mentioned before the molecule Sr_2O has probably been observed indirectly in flames, where the intensity of some bands varies as the square of the Sr concentration⁽⁸⁰⁾. The ratio of the atomization energy of this molecule and of the dissociation energy of SrO is similar to the same ratio for Ba_2O : $D_{\text{oat}}^{\text{c}}(\text{Sr}_2\text{O})/D_{\text{o}}^{\text{c}}(\text{SrO}) = 1.90 \pm 0.15$; $D_{\text{oat}}^{\text{c}}(\text{Ba}_2\text{O})/D_{\text{o}}^{\text{c}}(\text{BaO}) = 1.72 \pm 0.20$. It is surprising that where the ionic model gives quite close agreement for the monoxides, it seems to fail completely for the suboxides for which it gives atomization energies of 21 and 15 kcal/mole for Sr_2O and Ba_2O respectively, compared to the experimental values 193 ± 6 and 223 ± 17 kcal/mole⁽⁸⁵⁾.

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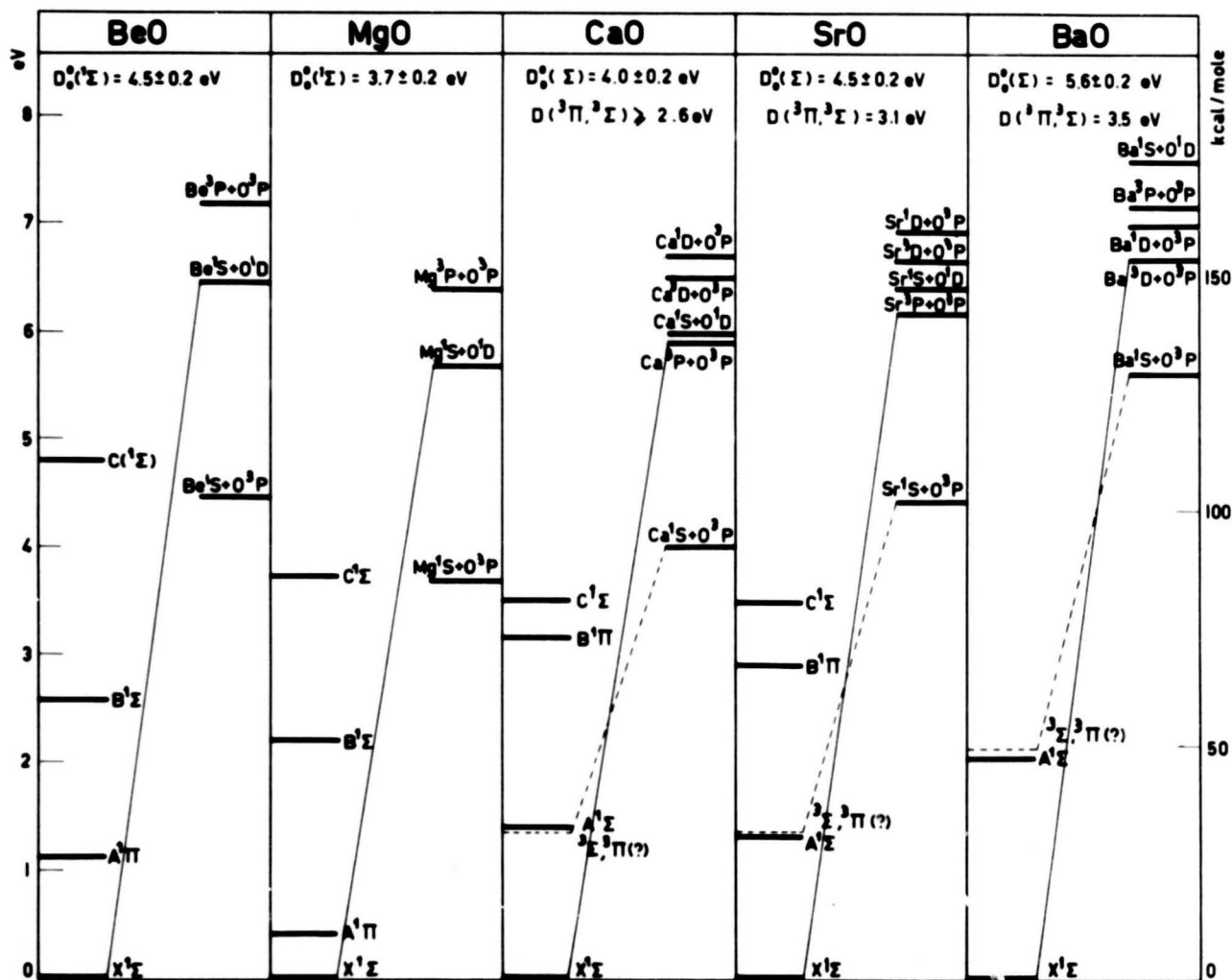


Figure 1. Term Scheme for the Alkaline-Earth Oxides.