

# THE BOND DISSOCIATION ENERGIES OF GROUP IIA DIATOMIC OXIDES

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## I. INTRODUCTION

Unlike the low-temperature, solid-phase regime, the only group IIA oxides so far characterized in the gaseous phase have been the normal diatomic oxides and the suboxides Be<sub>2</sub>O (86), Sr<sub>2</sub>O (25), and Ba<sub>2</sub>O (1, 46, 66). Polymers of the normal oxides (BeO)<sub>n</sub> (19, 86) up to the hexamer and (BaO)<sub>2</sub> (1, 46, 66, 70) have also been reported. It would appear, at least for barium, that higher oxides are unimportant in the gaseous phase (66).

Interest in the oxides has centered generally on the long-time controversy over the bond dissociation energy values for the normal diatomic oxides. Previous reviews of Drummond and Barrow (26, 27), Brewer (12), Gaydon (31), Brewer and Searcy (15), and Medvedev (63), although outdated, illustrate well the disagreement arising through the large discrepancies which appear between reported spectroscopic, thermochemical cycle, and direct experimental values. Since research has been very active in this area in recent years and several reasons for the discrepancies have been resolved, a critical reevaluation and reworking of all the available data have been carried out. The updating process, which now makes the data strictly comparable, includes the use of the most reliable thermodynamic data available at present, the standardizing of emission studies to a common set of *f* values, corrections for dihydroxide formation in flame studies, and the use of improved collision cross-section data for mass spectrometric work. As a result of this reanalysis, it has been possible to recommend values for the bond strength of the oxides and

also values for their previously uncertain heats of sublimation.

## II. SPECTROSCOPIC DATA

A Birge-Sponer extrapolation of the vibrational level separations of the lowest observed electronic state of a molecule is not always reliable (31). This is apparent for the alkaline earth oxides, reported dissociation energy values (kcal mole<sup>-1</sup>) being BeO, 111 (55); MgO, 39; CaO, 37; SrO, 35; BaO, 127 (31). Strictly, the extrapolation is only suitable for nonpolar molecules, whereas these oxides are known to have a high degree of ionic bonding (11, 50, 94). Also, since the X<sup>1</sup>Σ electronic states considered do not correlate with ground-state atoms, M(<sup>1</sup>S) and O(<sup>3</sup>P), assumptions concerning the dissociation products of this state have to be made and the possibility that this is not in fact the ground state of the molecule has to be borne in mind. The low values for MgO, CaO, and SrO tend to support this last statement and confirm the findings of Brewer and Porter (14) and Bulewicz and Sugden (18) that the X<sup>1</sup>Σ state of MgO lies about 50 kcal above an unidentified ground state, which is most probably a triplet. In view of this review's recommended value for the heat of sublimation of MgO, this value of 50 kcal may be too high, but a value a 20–30 kcal at least would still appear to be the case. Similar findings have been reported by Lagerqvist and Huldt (45, 56) and Hollander, Kalf, and Alkemade (41, 49) for the X<sup>1</sup>Σ states of CaO and SrO which appear to lie about 20 kcal above the ground state. The values of BeO and BaO being at least of the

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right order lend support to the existence of a low-lying or ground-state  $X^1\Sigma$ , yet some recent data (41, 49) for  $X^1\Sigma$  BaO place this 14 kcal above the ground state also.

However, the lack of spectroscopic data for these gaseous oxides is more far reaching than simply being insufficient for Birge-Sponer extrapolations. Since all other evaluations of  $D(\text{MO})$ , the dissociation energy, concern equilibria involving alkaline earth oxides, the main process of data reduction is *via* the thermodynamic data for gaseous MO. To be accurate, such data require a knowledge of the ground state of the molecule and also of low-lying electronic states. A recent thermodynamic data tabulation for the refractory oxides (75) follows the recommendations of Brewer and Trajmar (16) and assumes a  $^3\Sigma$  ground state for gaseous MgO, CaO, and SrO, estimating the fundamental parameters for MgO from the work of Brewer and Porter (14). Since the tabulation of data is not too sensitive to the fundamental parameters, the absolute values of the thermodynamic data center on the statistical weights of the electronic states. Statistical weights of  $^1\Sigma$ ,  $^3\Sigma$ , and  $^3\Pi$  electronic states are 1, 3, and 6, respectively, and contribute 0,  $R \ln 3$ , and  $R \ln 6$  to the entropy and free-energy function (fef) of the gaseous state. Consequently, systematic errors in resultant dissociation energies arising from the use of an incorrect statistical weight can be 0,  $RT \ln 3$ ,  $RT \ln 6$ , or the difference  $RT \ln 6/3$ . For BeO a low-lying triplet state seems reasonable (16) although a recent theoretical calculation (92) concludes only a  $^1\Sigma$  state to be important. In this review, Schick's tabulations (75) for BeO, MgO, CaO, and SrO have been used and converted wherever necessary by the appropriate statistical weight factor to allow for the dominance of a different ground or low-lying electronic state. BaO has posed a problem for several years now. The assumption of a  $^3\Pi$  ground or low-lying electronic state seems reasonable for such a heavy eight-electron molecule but was doubtful considering the interpretation of molecular-beam, electric-resonance experiments (17, 95) and the absence of rotational perturbations in the  $X^1\Sigma$  state (54, 58). The recent experiments of Newbury (66) are, however, highly significant. In his determination of the heat of sublimation of BaO, a discrepancy between second-law ( $\Sigma$  plot method) and third-law treatments of the data (60) could only be resolved by allowing BaO(g) an electronic statistical weight of 10 rather than 1 ( $^1\Sigma$ ). Since Schick (75) gives no tabulated data for BaO, the thermodynamic data for BaO(g) have been calculated using the program listed in the JANAF Thermochemical Tables (47). Molecular parameters were taken from Lagerqvist, Lind, and Barrow (58) assuming a  $^1\Sigma$  ground state. Values of  $(-fef)$  were found to agree to within better than 0.5% with those tabulated by Kelley and King (51, 52). In use,  $R \ln 3$  and  $R \ln 6$  were added to these values to allow for the predominance of a low-lying or ground state  $^3\Sigma$  or

$^3\Pi$ , respectively. Data for BaO(c) were taken from Kelley and King (51, 52).

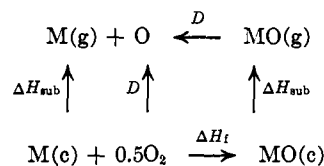
Third-law calculations based on the relationship (60)

$$\Delta H^\circ_{298} = -RT \ln K_p + T\Delta[-(F^\circ_T - H^\circ_{298})/T]$$

have been carried out in this work considering the following electronic states as being dominant: BeO  $^1\Sigma$ ,  $^3\Sigma^*$ ,  $^3\Pi$ ; MgO, CaO, SrO  $^3\Sigma^*$ ,  $^3\Pi$ ; BaO  $^3\Sigma$ ,  $^3\Pi^*$ . Asterisked states are those favored by the author as being closest to the true state of affairs.

### III. THERMOCHEMICAL CYCLE VALUES

Bond dissociation energy values for the alkaline earth oxides can be had by considering the cycle



whereby

$$D(\text{MO}) = -\Delta H_{\text{sub}}(\text{MO}) - \Delta H_f(\text{MO(c)}) + 0.5D(\text{O}_2) + \Delta H_{\text{sub}}(\text{M})$$

Of the required thermochemical values,  $\Delta H_{\text{sub}}^\circ(\text{MO})$ , the heat of sublimation of the oxide has always been the least certain.

#### A. HEATS OF SUBLIMATION OF GROUP IIA DIATOMIC OXIDES

When mass spectrometric investigations showed that BeO (19, 86), MgO (72), CaO (70), and SrO (1, 6, 70, 72) vaporized predominantly to their elements rather than molecules under neutral conditions, it became clear that earlier values of  $\Delta H_{\text{sub}}^\circ(\text{MO})$  based on vapor-pressure measurements (14, 20, 28, 64) were, in fact, lower limit values and consequently had been overestimating  $D(\text{MO})$ . Through the extensive dissociation of BeO, MgO, CaO, and SrO on vaporization, only determinations deriving the partial pressure of the oxide component of the vapor and certain transpiration experiments carried out under dry oxidizing conditions can be relied upon for values of  $\Delta H_{\text{sub}}^\circ(\text{MO})$ . The results of a complete reworking, with the exception of the recent publication of Newbury (66), of all the relevant references are shown in Table I.

Although mass spectrometric determinations yield most of the reliable data in Table I, the limitations of the method must be realized. Uncertainties center on the calibration of the instrument to yield absolute concentrations or partial pressures, and result from uncertainties in the ionization cross-section values and detector sensitivities for the various detected species. Generally an error of the order of a factor of 3 seems reasonable for such measurements (46). This corre-

TABLE I  
HEATS OF SUBLIMATION OF MO AT 298°K

	Third law			Second law	Ref
	<sup>1</sup> Σ	<sup>2</sup> Σ	<sup>3</sup> Π		
BeO	177.6	182.2	185.1		19
	178.1	183.3	186.5		86
	177.6	182.4	185.3 ± 5		... <sup>a</sup>
MgO	>146.3	>149.0			72
		162.4	165.3		3
		149.0	151.6		2
		155.7	158.4 ± 7		... <sup>a</sup>
CaO			146.7 ± 15		4 <sup>b</sup>
SrO	161.2	164.1 ± 5			13, 72 <sup>b</sup>
			110.4	110.9	66
BaO		108.1	110.4		46
		108.1	110.4		8
		105.3	107.2		37
		105.4	107.2		20
		104.9	106.7		79
			110.5 ± 3		... <sup>a</sup>

<sup>a</sup> Recommended values. <sup>b</sup> Questionable values; see discussion.

sponds to an error of about 2.2 kcal mole<sup>-1</sup> at 1000°K and 4.4 kcal mole<sup>-1</sup> at 2000°K in values of  $\Delta H_{\text{sub}}^{\circ 298}$ (MO). In quoting the probable errors in Table I this has been borne in mind. The mass spectrometric data of ref 19, 46, 72, and 86 have been recalculated using relative ionization cross-sections estimated by Otvos and Stevenson (68).

The two mass spectrometric studies of BeO (19, 86) are basically identical, and the mean of all the experimental data is considered a reliable value. With BeO, the extent of dissociation in the vapor phase is such that the use of full vapor-pressure data, *e.g.*, Erway and Seifert (28), leads to values of  $\Delta H_{\text{sub}}^{\circ 298}$ (BeO) about 19 kcal mole<sup>-1</sup> too low. For MgO, the mass spectrometric work of Porter, Chupka, and Inghram (72) and the effusion studies of Altman (3) support a predominance of dissociation to elements, contrary to the previous findings of Brewer and Porter (14). This is further borne out, since the full vapor-pressure data of Brewer and Porter (14) leads to a value of 129.2 (<sup>3</sup>Σ) or 132.1 (<sup>3</sup>Π). However, owing to interference from Ca impurity, the mass spectrometric results (72) can only give a lower limit to  $\Delta H_{\text{sub}}^{\circ}$ (MgO), and reliance must be placed on two transpiration studies (2, 3). Unfortunately, these are at odds with one another, and until further work is published the mean of the two estimates has been taken.

No absolute mass spectrometric determination of CaO partial pressures has been reported, and consequently only a second-law treatment (Clausius-Clapeyron) of the mass spectrometric data of Babeliowsky, Boerboom, and Kistemaker (4) is available. The other available mass spectrometric data (70), obtained by studying the evaporation from an oxide-coated filament, give 178 kcal mole<sup>-1</sup> and appear unreliable. The total vapor-pressure data of Claassen and Veenemans (20) appear con-

sistent with the results of ref 4, giving a lower limit to  $\Delta H_{\text{sub}}^{\circ 298}$ (CaO) of 142.2 (<sup>3</sup>Σ) or 144.5 (<sup>3</sup>Π). However, as will become evident later, the mass spectrometric value (4) also appears unreliable, being of the order of 19 kcal too low. Since their value resulted from a temperature-dependent plot over a limited temperature range, this is not too surprising.

The pressure data of Porter, Chupka, and Inghram (72), as recalculated by Brewer and Drowart (13), lead to a direct value for  $\Delta H_{\text{sub}}^{\circ 298}$ (SrO). However, as will be seen later, comparison with indirect values establishes its inaccuracy. Because of the extensive dissociation in the vapor phase, full vapor-pressure data of Claassen and Veenemans (20) and Moore, Allison, and Struthers (64) necessarily lead to low values of 131.1 (<sup>3</sup>Σ) or 133.3 (<sup>3</sup>Π) and 128.3 (<sup>3</sup>Σ) or 129.9 (<sup>3</sup>Π), respectively. As with CaO, the mass spectrometric data of Pelchowitch (70) (second-law Clausius-Clapeyron treatment) give a value too high, 169 kcal mole<sup>-1</sup>. It is to be remembered, however, that such experiments dealing with the rate of evaporation from coated oxide filaments can lead to values greater than  $\Delta H_{\text{sub}}$  since the data actually yield the energy of activation of sublimation which may not be equal to  $\Delta H_{\text{sub}}$ .

To a first approximation, BaO vaporization is normal, and consequently all available vapor-pressure data can be considered. The most reliable value for  $\Delta H_{\text{sub}}^{\circ 298}$ (BaO) appears to be that from the recent, extensive and careful study of Newbury (66). In this case, mass spectrometric and vacuum thermobalance experiments were carried out in parallel, the latter data also being used to calibrate the mass spectrometer. The excellent agreement between this, a mass spectrometric study by Inghram, Chupka, and Porter (46), and Knudsen cell-effusion experiments of Blewett, Liebhafsky, and Hennesly (8) and the reasonable agreement with some other published data (20, 37, 79) soundly establishes  $\Delta H_{\text{sub}}^{\circ}$ (BaO). Other available data, Pelchowitch (70) 100–121, Nikonov and Otmakhova (67) 102 (<sup>3</sup>Σ), 103.8 (<sup>3</sup>Π), and Aldrich (1) 94 kcal mole<sup>-1</sup>, appear unreliable.

#### B. HEATS OF FORMATION OF THE SOLID GROUP IIA DIATOMIC OXIDES

With the exceptions of SrO and BaO, the heats of formation (kcal mole<sup>-1</sup>) of the solid oxides,  $\Delta H_f^{\circ 298}$ (MO(c)) are reasonably well established: BeO, -143.1 ± 0.5 (23); MgO, -143.8 ± 0.5 (42, 80); CaO, -151.8 ± 0.5 (43); SrO, -142.5 ± 2 (29, 61); BaO, -135.5 ± 3.5 (29, 61). However, until further determinations are made for SrO and BaO to resolve the disagreement between the data of ref 29 and 61, mean values have been taken.

#### C. HEATS OF SUBLIMATION OF GROUP IIA METALS

In order to ascertain the most reliable values for  $\Delta H_{\text{sub}}^{\circ 298}$ (M), a recalculation of all the vapor-pressure

TABLE II  
 HEATS OF SUBLIMATION OF ALKALINE EARTH METALS AT 298°K

Be		Ca	
Holden, Speiser, Johnston (40)	77.84 ± 0.95	Pilling (71)	42.19 ± 0.70
Gulbransen, Andrew (34)	78.16 ± 0.50	Hartmann, Schneider (36)	42.28 ± 0.20
	78.0 ± 0.5 <sup>a</sup>	Douglas (24)	42.30 ± 0.40
		Tomlin (87)	42.21 ± 0.21
		Priselkov, Nesmeyanov (73)	42.21 ± 0.20
		Muradov (65)	42.42 ± 0.03
		Bohdansky, Schins (10)	42.26 ± 0.11
			42.27 ± 0.1 <sup>a</sup>
Mg		Sr	
Hartmann, Schneider (36)	35.65 ± 0.26	Hartmann, Schneider (36)	39.48 ± 0.12
Leitgebel (59)	35.18	Priselkov, Nesmeyanov (73)	38.64 ± 0.39
Baur, Brunner (5)	35.35 ± 0.40	Boerboom, Reyn, Kistemaker (9)	39.04 ± 0.23
Coleman, Egerton (21)	35.30 ± 0.05	Bohdansky, Schins (10)	39.32 ± 0.28
Schneider, Esch (76)	35.35		39.1 ± 0.4 <sup>a</sup>
Schneider, Stoll (77)	35.25 ± 0.14		
Vetter, Kubaschewski (93)	35.18 ± 0.11		
Smith (81), Smythe (82)	35.13 ± 0.50		
Scheil, Wolf (74)	35.50 ± 0.04		
Mashovets, Puchkov (62)	35.42 ± 0.03		
Gilbreath (32)	35.34 ± 0.06		
	35.3 ± 0.15 <sup>a</sup>		
		Ba	
		Hartmann, Schneider (36)	41.71 ± 0.42
		Bohdansky, Schins (10)	44.63 ± 0.12
			43.0 ± 2.0 <sup>a</sup>

<sup>a</sup> Recommended values.

 TABLE III  
 THERMOCHEMICAL CYCLE VALUES FOR THE BOND DISSOCIATION ENERGIES OF ALKALINE EARTH OXIDES<sup>a</sup>

	BeO			MgO		CaO	SrO		BaO
$-\Delta H_{\text{sub}}^{\circ 298}(\text{MO})$	-177.6 ( <sup>1</sup> Σ)	-182.4 ( <sup>2</sup> Σ)	-185.3 ± 5 ( <sup>3</sup> Π)	-155.7 ( <sup>1</sup> Σ)	-158.4 ± 7 ( <sup>3</sup> Π)	-146.7 ± 15 ?	-161.2 ( <sup>2</sup> Σ)	-164.1 ? ( <sup>3</sup> Π)	-110.5 ± 3
$-\Delta H_f^{\circ 298}(\text{MO}(c))$		+143.1	± 0.5	+143.8 ± 0.5		+151.8 ± 0.5	+142.5 ± 2		+135.5 ± 3.5
$+0.5D^{\circ 298}(\text{O}_2)$		+59.5		+59.5		+59.5	+59.5		+59.5
$+\Delta H_{\text{sub}}^{\circ 298}(\text{M})$		+78.0	± 0.5	+35.3 ± 0.15		+42.3 ± 0.1	+39.1 ± 0.4		+43.0 ± 2.0
$D^{\circ 298}(\text{MO})$	103.0 ( <sup>1</sup> Σ)	98.2 ( <sup>2</sup> Σ)	95.3 ( <sup>3</sup> Π)	82.9 ( <sup>1</sup> Σ)	80.2 ( <sup>3</sup> Π)	106.9 ?	79.9 ( <sup>2</sup> Σ)	77.0 ( <sup>3</sup> Π)	127.5 ± 7
$D^{\circ 0}(\text{MO})$	102.0	97.2	94.3	81.9	79.2	105.9	79.0	76.1	126.6

<sup>a</sup> Values in kcal mole<sup>-1</sup>. ? denotes questionable values (see discussion in sections V.B and C).

data has been necessary. These have been treated by the third-law method (60) using free-energy functions of the gaseous and condensed phases as tabulated by Schick (75) for Be, Mg, Ca, and Sr. Data for Ba were taken from the tables of Stull and Sinke (84). Wherever possible, the original datum points were used and an average taken; otherwise the mean value was obtained by graphical summation over the temperature range investigated.

The most reliable data are listed in Table II, values being quite accurately established for Be, Mg, Ca, and Sr. Further data are required for Ba. Sources of vapor-pressure data not appearing in Table II led to values which fell outside the accepted range and were considered unreliable.

By incorporating the recommended values above into the thermochemical cycle calculation, the values listed in Table III for the bond dissociation energies of the gaseous diatomic oxides are obtained. The required value for  $D^{\circ 298}(\text{O}_2)$  and the enthalpy data required to convert  $D^{\circ 298}(\text{MO})$  to  $D^{\circ 0}(\text{MO})$  have been taken from Schick (75) and Stull and Sinke (84).

#### IV. DIRECT EXPERIMENTAL VALUES

Two general techniques, flame studies and effusion-mass spectrometry, have led to direct experimental determinations of  $D(\text{MO})$ . Reported values are at variance with one another, resulting partly, as will be seen, either from the use of outdated thermodynamic or other data or through an incomplete understanding of the system under investigation.

##### A. FLAME STUDIES

In order to determine the equilibrium constant,  $K_p$ , of the relationship

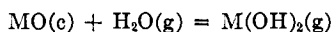


the partial pressures in the flame of the three entities are required. Since  $p_{\text{MO}}$  is too difficult to measure directly, this is generally taken to be equal to the equivalent partial pressure of the total metal atoms  $p_{(\text{M})}$ , initially added, less the partial pressures of all the metal species in the flame with the exception of MO. As is now known (78, 85), the fate of an alkaline earth metal salt entering a flame may be any one of several and results in

atomic M, ions  $M^+$  and  $MOH^+$ , or molecular MO, MOH, and  $M(OH)_2$ , so that

$$p_{MO} = p_{(M)_0} - (p_M + p_{M^+} + p_{MOH^+} + p_{MOH} + p_{M(OH)_2})$$

Of these quantities  $p_{(M)_0}$  is known, and  $p_M$  and  $p_{M^+}$  can be measured spectroscopically. Assumptions concerning  $MOH^+$ , MOH, and  $M(OH)_2$  have resulted in some of the discrepancies in reported values. Since thermodynamic data are now available for the reaction



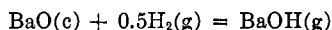
for the cases of  $M = Be$  [1560–1810°K (7)],  $Mg$  [1660–2010°K (2)], and  $Ba$  [1400–1900°K (66, 83)], approximate calculations of the importance of  $M(OH)_2(g)$  in flames can be made by coupling equilibrium data for the above reaction with that of  $MO(c) = MO(g)$  based on the heats of sublimation shown in Table I, and calculated *via* the third law using free-energy functions (75) based on  $^3\Sigma$ ,  $^3\Sigma$ , and  $^3\Pi$  ground states, respectively. Results in the form of the ratio  $p_{M(OH)_2}/p_{MO}p_{H_2O}$  atm $^{-1}$  are listed in Table IV. In spite of the possible errors

TABLE IV  
VALUES FOR  $p_{M(OH)_2}/p_{MO}p_{H_2O}$  (ATM $^{-1}$ )

Temp. °K	Be	Mg	Ba
1500	$1.3 \times 10^{13}$	$1.6 \times 10^6$	$8.4 \times 10^3$
2000	$1.4 \times 10^6$	$1.3 \times 10^3$	68
2500	$1.6 \times 10^5$	20	4

in the equilibrium data, these values are probably correct to within a factor of 10. Consequently, it is to be expected that dihydroxides will be more dominant than the diatomic oxides except at very high temperatures and in flames with very low water content. This has been verified recently for Ca, Sr, and Ba in  $H_2-O_2-N_2$  flames (85).

Data on  $p_{MOH^+}$  and  $p_{MOH}$  are still sparse. It is reasonable to assume that  $p_{MOH^+}$  is only comparable to  $p_{M^+}$  (78), neither being a large contributor to  $p_{(M)_0}$ . At 1900°K, Newbury's data (66) for



when coupled with that for  $BaO(c) = BaO(g)$  give

$$p_{BaOH}/p_{H_2}^{1/2}p_{BaO} = 3.6 \text{ (1900°K)}$$

showing that in hydrogen-rich flames  $p_{BaOH}$  may be of the order of  $p_{BaO}$  at this temperature. However, both are only a few percentage of the  $Ba(OH)_2$  present. This is confirmed to within a factor of 2 by the data of Stafford and Berkowitz (83). Consequently, since a 20% error in  $p_{MO}$  at 2000°K only results in a change of 0.9 kcal mole $^{-1}$  in  $D_{298}^\circ(MO)$ ,  $p_{MOH}$  and  $p_{MOH^+}$  will be ignored in the present reanalysis, as done previously.

Determinations of  $D(MO)$  have resulted from studies in a multitude of different flames, of the hydrogen, ethylene, acetylene, and carbon monoxide types. In

all the reported determinations, the basic assumption of  $p_{MO} = p_{(M)_0} - p_M$  or  $p_{(M)_0} - p_M - p_{M^+}$  was made. Obviously a reevaluation of all the flame data is necessary taking into account a correction for dihydroxide formation. Also, since the majority of methods are based on spectroscopic measurements of the alkaline earth element resonance lines ( $^1P_1 - ^1S_0$ ), a correction to a common set of  $f$  values has also been included using the following values (33): Mg, 2852 Å, 1.55; Ca, 4227 Å, 1.65; Sr, 4607 Å, 1.85; Ba, 5535 Å, 1.6.

### 1. BeO

No flame studies of  $D(BeO)$  have yet been made.

### 2. MgO

Four studies have been reported, none of which appears to be at all reliable. Bulewicz and Sugden's study (18) did not measure the ratio  $p_{MgO}/p_{Mg}$  as above but calculated it on invalid assumptions. Consequently, no reliance should be placed on their fortuitous value of 98 kcal mole $^{-1}$ . It is interesting that in the  $H_2-O_2-N_2$  flame studied,  $p_{H_2O} \sim 0.25$  atm at 2000°K, and therefore  $p_{Mg(OH)_2}/p_{MgO} \sim 325$ . A correct treatment by them should have led to  $D_{298}^\circ(MgO) \sim 23$  kcal mole $^{-1}$  too high.

Huldt and Lagerqvist (44) measured the intensity of emission of Mg (2852 Å) in an acetylene-air flame at 2410°K. Their results are probably meaningless since the magnesium salt was sprayed into the flame at  $p_{(M)_0} \sim 10^{-4}$  atm. With such a concentration, emission intensity measurements would suffer extensive self-absorption. Bulewicz and Sugden (18) reverted to absorption measurements, as they could not eliminate the self-absorption in their initial emission studies when using concentrations of magnesium very much lower than this. Besides, the 2852-Å Mg line emission was probably still chemiluminescent rather than thermal in nature at the point of measurement (69).

Veits, Gurvich, and Korobov (88, 91) measured photographically the emission of the "forbidden" Mg transition ( $^3S_1 - ^1S_0$ ) at 4571 Å. Their results, which would appear to be free from self-absorption or chemiluminescent effects (18), unfortunately were not reported in detail and so are unavailable for recalculation. A more recent study by de Galan and Winefordner (30) determined  $p_M$  by integrated absorption in a flame of low water content,  $p_{H_2O} = 0.038$  atm (2450°K). However, as their value for BaO appears high by about 10 kcal mole $^{-1}$ , the same may be true for their MgO value (Table V).

### 3. CaO, SrO, BaO

Since no thermodynamic data are available for  $Ca(OH)_2(g)$  and  $Sr(OH)_2(g)$ , but their importance is established (85) in hydrogen-containing flames, reported values for  $D(MO)$  from such systems are upper

TABLE V  
DIRECT FLAME EXPERIMENTAL VALUES FOR  $D_{298}^{\circ}(\text{MO})$

MgO ( $^{\circ}\Sigma$ )	CaO ( $^{\circ}\Sigma$ )	SrO ( $^{\circ}\Sigma$ )	BaO ( $^{\circ}\Pi$ )	Comments	Ref
	<107.8	<108.9	<119.3 → 117.0	$p_{\text{H}_2\text{O}} \sim 0.07$ , 2240–2430°K	44, 57
	<114.7	<113.2		$p_{\text{H}_2\text{O}} = 0.0013$ , 2965°K	89, 90
	<117.6	<110.0		Isochore plot, 2310–3210°K	89
	<104.0	<101.3	<114.7 → 112.9	$p_{\text{H}_2\text{O}} = 0.104$ , 2480°K	38
	<112.0	<109.5	<124.0 → 122.5	$p_{\text{H}_2\text{O}} = 0.09$ , 2500°K	39
	<106.6	<105.0	<123.1 → 122.5	$p_{\text{H}_2\text{O}} = 0.088$ , 2760°K	39
			<126.1 → 126.0	$p_{\text{H}_2\text{O}} = 0.0048$ , 2965°K	35
			<133.7 → 120.9	$p_{\text{H}_2\text{O}} = 0.25$ –0.14, 1856–2037°K	35
	90.5	96.3	117.6	Dry, line-band independent $g_e$ , 2260–2460°K	49
	<98.5	<94.8	<114.8 → 113.9	$p_{\text{H}_2\text{O}} = 0.02$ , 2222, 2449°K	49
	<96.6	<97.9		$p_{\text{H}_2\text{O}} = 0.02$ , 2200, 2450°K	49
	<122.0	<118.7	<132.0 → 125.5	$p_{\text{H}_2\text{O}} = 0.355$ , 2534°K	85
<110.7 → 107.2	<118.9	<117.8	<138.5 → 137.7	$p_{\text{H}_2\text{O}} = 0.038$ , 2450°K	30

TABLE VI  
DIRECT MASS SPECTROMETRIC EXPERIMENTAL VALUES FOR  $D^{\circ}_{298}(\text{MO})$

BeO		MgO ( $^{\circ}\Sigma$ )	CaO ( $^{\circ}\Sigma$ )	SrO ( $^{\circ}\Sigma$ )	BaO ( $^{\circ}\Pi$ )	Gaseous equilibrium	Ref
( $^{\circ}\Sigma$ )	( $^{\circ}\Sigma$ )						
103.1	98.4					BeO = Be + O	19
102.6	97.7					BeO + O = Be + O <sub>2</sub>	19
102.5	97.3					BeO = Be + O	86
102.4	97.2					BeO + O = Be + O <sub>2</sub>	86
				77.1		SrO = Sr + 0.5O <sub>2</sub>	13, 72
		76.3	82.5	91.4		MO + O = M + O <sub>2</sub>	25
			89.8	97.7	124.2	M + SO = MO + S	22

limit values and cannot at present be corrected for dihydroxide formation. However, for studies in dry CO–O<sub>2</sub> flames, which take into account ionization, reliable estimates should result. For BaO, hydrogen-bearing flame values, suitably corrected, should be in substantial agreement with dry CO–O<sub>2</sub> flame values if the present understanding of the alkaline earth flame media is correct. The majority of the methods are based on emission studies of the resonance lines. One uses integrated absorption measurements of the resonance line (30) while a recent comprehensive study of the problem (49), initiated with the hope of obtaining the most reliable flame values, used both resonance line methods and line–MO band emission methods. The line–band comparison method consists of comparing the intensities of a resonance line and an MO band at two temperatures. From these data,  $D(\text{MO})$  can be obtained which is independent of the electronic statistical weight of MO. However, the method is very susceptible to even small amounts of dihydroxide formation so that for BaO, using dry and moist ( $p_{\text{H}_2\text{O}} = 0.02$  atm) flames at 2200 and 2460°K, a difference of about 9 kcal mole<sup>-1</sup> in  $D^{\circ}_{298}(\text{MO})$  would be expected between the dry and moist cases. In one case this was experimentally observed. Had MgO been studied with such a method, the expected difference would have been ~48 kcal. However, values for  $D(\text{MO})$  of CaO and SrO were roughly comparable in both flames which would infer that the dihydroxide formation of Ca

and Sr is less pronounced than for Ba. This would appear to be at odds with conclusions that can be drawn later from two other flame studies (39, 85). Reported values are listed in Table V, all recalculated and corrected to common  $f$  values. In the case of BaO, values are listed without and with corrections for dihydroxide formation so that the extent of the correction is apparent.

#### B. MASS SPECTROMETRIC STUDIES

The difficulty in obtaining reliable data from mass spectrometric work revolves around two major factors: (a) the absolute pressure calibration of the instrument and (b) the ionization cross-sections of the species and associated problems of ion fragmentation. The study of equilibria, for which the equilibrium constant is dimensionless, has the advantage of eliminating the first problem because an absolute calibration is unnecessary. Little ionization cross-section data exist for the alkaline earth elements and their oxides. Those generally used (68) are the relative cross-sections calculated at their maxima. However, two mass spectrometric studies (19, 25) used ionization potentials well below this. Therefore, in the recalculation of the data it has been assumed that the ionization cross-section varies linearly with the energy above the ionization threshold up to its maximum value. For atomic and molecular oxygen, the use of experimental values has

been preferred (53) to the data of Otvos and Stevenson (68).

Table VI lists recalculated experimental values for  $D^{\circ}_{298}(\text{MO})$ . Colin, Goldfinger, and Jeunehomme (22) studied an equilibrium reaction involving the reduction of SO to S. The necessary thermodynamic data in this case were taken from the JANAF Tables (48). The resulting value depends on  $D(\text{SO})$ , which appears to be established to within  $\pm 2.5$  kcal mole<sup>-1</sup>.  $D^{\circ}_0(\text{SO}) = 123.5$  kcal mole<sup>-1</sup> has been used.

## V. DISCUSSION

A study of Tables I, III, V, and VI shows that discrepancies are still apparent in the estimates of  $D^{\circ}_{298}(\text{MO})$ . However, closer inspection has made it possible to pick out what appear to be the most reliable data. This data evaluation is considered for the oxides in turn, starting with BaO.

### A. BaO

This oxide has been considered first, through the reliance which can be placed on its thermochemical cycle value.  $\Delta H_{\text{sub}}^{\circ}(\text{BaO})$  appears well established (8, 46, 66) and the resulting  $D^{\circ}_{298}(\text{BaO}) = 127.5 \pm 7$  kcal mole<sup>-1</sup> carries such a large error through unfortunate uncertainties in  $\Delta H_{\text{sub}}^{\circ}(\text{Ba})$  and  $\Delta H_f^{\circ}(\text{BaO}(c))$ . There is, however, substantial agreement between this and the only direct mass spectrometric result, 124.2 kcal mole<sup>-1</sup> (22). Of the flame values, four are of this order. One, 126.0 kcal mole<sup>-1</sup> (35), was obtained using a high-temperature CO-O<sub>2</sub> flame of very low water content and, consequently, should be reliable. Assessing these values it would appear reasonable to recommend  $D^{\circ}_{298}(\text{BaO}) = 125.9 \pm 2$  kcal mole<sup>-1</sup>. Flame evaluations differing from this by more than 5 kcal mole<sup>-1</sup> would appear generally questionable and cast doubt on the values obtained for the other oxides.

### B. SrO

The thermochemical cycle value depends on a single mass spectrometric determination (72) of  $\Delta H_{\text{sub}}^{\circ}(\text{SrO})$ . Comparison with the two most recent mass spectrometric determinations (22, 25) casts grave doubt on its reliability, a value in the midnineties appearing more reasonable. Unfortunately, through the current lack of thermodynamic data for Sr(OH)<sub>2</sub>(g), the flame values are of little help. That obtained using dry CO-O<sub>2</sub> flames (49) is open in some question through the low value reported for BaO. Consequently, at present, it is necessary to base  $D^{\circ}_{298}(\text{SrO})$  on ref 22 and 25. Giving more weight to ref 22, a value  $D^{\circ}_{298}(\text{SrO}) = 96 \pm 5$  kcal mole<sup>-1</sup> appears the most reasonable. Flame results (39, 85) are compatible with this, providing  $p_{\text{Sr}(\text{OH})_2}/p_{\text{SrO}}p_{\text{H}_2\text{O}} \sim 200$  at 2500°K (cf. Table IV). A value of  $\Delta H_{\text{sub}}^{\circ}_{298}(\text{SrO}) = 145$  kcal mole<sup>-1</sup> is to be expected.

### C. CaO

The evaluation for CaO is identical with that above for SrO since the thermochemical cycle value is based on a sole  $\Delta H_{\text{sub}}^{\circ}(\text{CaO})$  determination (4) which appears unreliable. Based on ref 22 and 25,  $D^{\circ}_{298}(\text{CaO}) = 88 \pm 5$  is the best estimate at present. To be compatible with this, the two apparently reliable flame values (39, 85) require  $p_{\text{Ca}(\text{OH})_2}/p_{\text{CaO}}p_{\text{H}_2\text{O}} \sim 2000$  at 2500°K (cf. Table IV).  $\Delta H_{\text{sub}}^{\circ}_{298}(\text{CaO})$  appears to be 165.6 kcal mole<sup>-1</sup> rather than the value in Table I (4).

### D. MgO

The thermochemical cycle value is based on the mean of two transpiration study determinations (2, 3) of  $\Delta H^{\circ}_{\text{sub}}(\text{MgO})$ . The value  $83 \pm 5$  kcal mole<sup>-1</sup> appears to be the best estimate of  $D^{\circ}_{298}(\text{MgO})$ , as the mass spectrometric determination (25) is most probably about 5 kcal too low and the sole flame estimate (30) is undoubtedly much too high.

### E. BeO

Two reported mass spectrometric investigations (19, 86) are responsible for both the thermochemical cycle and the more direct mass spectrometric values. Substantial agreement between the two similar studies suggests  $D^{\circ}_{298}(\text{BeO}) = 102.5 \pm 2$  (<sup>1</sup>Σ) or  $97.7 \pm 2$  (<sup>3</sup>Σ). The latter is considered the better choice.

Recommended values, with errors illustrating present uncertainties, are summarized for convenience in Table VII. Both oxide bond dissociation energies and their heats of sublimation are listed.

TABLE VII  
RECOMMENDED VALUES FOR  $D^{\circ}_0(\text{MO})$  AND  $\Delta H_{\text{sub}}^{\circ}_0(\text{MO})$

	BeO		MgO	CaO	SrO	BaO
	( <sup>1</sup> Σ)	( <sup>3</sup> Σ)				
$D^{\circ}_0(\text{MO})$	101.5 ±2	96.7 ±2	82 ±5	87 ±5	95 ±5	125.0 ± 2
$\Delta H_{\text{sub}}^{\circ}_0(\text{MO})$	176.7	181.5	155	165	145	110.7 ± 3

Data have become available recently for the heat of dissociation (atomization) of several of the alkaline earth suboxides. Assuming these to have a linear structure and triplet ground electronic state, recalculated values are  $D^{\circ}_{298} = 211 \pm 10$  (86) for Be<sub>2</sub>O and  $188 \pm 6$  (25) for Sr<sub>2</sub>O; and  $D^{\circ}_{1750} = 209 \pm 15$  kcal mole<sup>-1</sup> (46, 66) for Ba<sub>2</sub>O. The values indicate that the energy required to remove successive alkaline earth elements from the suboxide is either approximately the same or a little less for the first removal.

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