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A THERMODYNAMIC STUDY OF GASEOUS OXIDES

Richard Francis Porter

(Thesis)

December, 1953

Berkeley, California

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A THERMODYNAMIC STUDY OF GASEOUS OXIDES

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December, 1953

ABSTRACT

This thesis is primarily a study of the gaseous state of magnesium oxide. Vapor pressure measurements on the solid oxide show that the solid vaporizes mainly into molecular species. Spectroscopic experiments have been conducted and have shown that the known gaseous $^1\Sigma$ electronic state of MgO is not the principal vaporizing specie. A study of the ultraviolet bands, produced by magnesium burning in air, prove the ground electronic level of the molecule involved in this transition is more important than the $^1\Sigma$ state of MgO. Within experimental uncertainty the heat of sublimation obtained from vapor pressure measurements agrees with a spectroscopically determined heat of sublimation of the unknown specie involved in the ultraviolet transition.

The dissociation energy of SnO has been determined by combining the heat of formation of SnO and a redetermined value of the heat of sublimation of tin. The dissociation energy obtained thermochemically agrees with a linear Birge-Sponer extrapolation to the ground state atoms.

INTRODUCTION

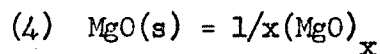
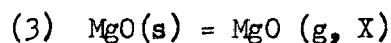
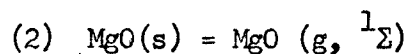
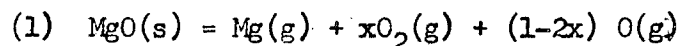
Recent reviews¹⁻³ of the thermochemical and spectroscopic data of the gaseous alkaline earth oxides have revealed several discrepancies in the dissociation energies of these molecules. In general, heats of dissociation obtained from vapor pressure measurements do not agree with spectroscopically obtained values. These reviewers point out that where thermochemical data are available, with the exception of BaO, the spectroscopic value is much lower than the thermochemical value. The spectroscopic values obtained from Birge-Sponer extrapolations of the vibrational levels of the lowest known $^1\Sigma$ states are in some cases as much as three electron volts lower than the thermochemical values. Vapor pressure measurements will give erroneous heats when the principal vaporizing specie is unknown and an incorrect one is assumed. On the other hand, spectroscopic values may be for an excited state of the molecule and since thermochemical data refers to ground states, agreement would not be expected.

With a flame technique Huldt and Lagerqvist¹ obtained independent values which in most cases agreed with values based on vapor pressure measurements. If one accepts the high values for the thermochemical dissociation energy and the low value for the spectroscopic dissociation energy of the $^1\Sigma$ states, then some molecule other than the $^1\Sigma$ must be the principal gaseous specie. Since vapor pressure data do not eliminate the possibility of a complex molecule, the principal vaporizing specie must be another electronic state of the monomer or a polyatomic molecule. In their flame work Huldt and Lagerqvist considered only the monomer to be important and do not indicate whether or not their results were sufficient to eliminate the possibility of other molecules.

If a monomer were suspected of being the main specie, the problem of establishing the true ground state would still remain. A further study of the spectra in a hope of finding transitions involving the ground state would be necessary. Other systems such as the unanalyzed bands obtained in absorption in flames by Barrow and Crawford⁴ may involve a lower state of MgO. Brewer³ has pointed out that the ground states of these molecules may be triplet instead of singlet states. Correlation rules allow only triplet states to be produced from the ground states of the free atoms.

Evidence for the existence of polymers has been shown by Aldrich.⁵ He was able to produce ions such as $Ba_2O_2^+$ in a mass spectrograph, and hence the existence of oxide dimers cannot arbitrarily be discounted. Brewer and Mastick⁶ have shown from theoretical bonding considerations, however, that such molecules as Mg_2O should have no chemical importance.

In a hope of explaining the nature of the gaseous state of these oxides, a specific investigation of MgO was initiated. The following equations show the various possible modes of vaporization:



X and $(\text{MgO})_x$ represent possible gaseous electronic states of MgO and polymers respectively, $\text{MgO(g, } ^1\Sigma)$ refers to the gaseous $^1\Sigma$ state of MgO and MgO(s) refers to the solid standard state. The basic problem is to determine which of these is the principal vaporization process. The essential phases to be considered then are:

(1) Does MgO(s) vaporize mainly to the elements or to molecules?

(2) If MgO(s) does vaporize into molecules, is $\text{MgO(g, } ^1\Sigma)$ the most important specie?

(3) If $\text{MgO} (g, {}^1\Sigma)$ is not the principal specie, is there another electronic state of MgO which is important or does the solid vaporize into polyatomic molecules?

I. VAPOR PRESSURE DETERMINATIONS

Direct vapor pressure data for MgO have not been reported and the significant thermochemical data for the vapor is that reported by Huldt and Lagerqvist.¹ The vapor pressure of MgO was therefore measured by the Knudsen effusion technique. The method measures the rate at which a gas enclosed in a crucible effuses out through a small orifice into a vacuum and is based on the fact that the rate of effusion of a particular specie is proportional to its partial pressure. For vapor pressure determinations the solid or liquid is heated in a Knudsen cell to the desired temperature and the vapor effuses out the orifice into a vacuum. As long as the hole in the crucible cover is small as compared to the cross sectional area of the crucible, the gas inside will approach the true equilibrium pressure. The observed rate of effusion is the sum of the rates of the individual atoms and molecules, and hence the weight loss per unit time is an integral quantity. For MgO, however, it is possible from known thermodynamic data to calculate the equilibrium concentrations of Mg(g), O(g), and O₂(g). Furthermore, if these are the only important species, the observed pressure should be in agreement with the calculated pressure.

Experimental

In the initial runs the Knudsen cells consisted of tungsten crucibles with tungsten covers. In every case the empty crucibles and the MgO were weighed separately before and after heating. The crucibles were heated inductively in a vacuum, the same technique as that used by Brewer and Searcy.⁷ Pressures within the vacuum system varied from .1 to .05 microns, increasing slightly at the beginning of a run and then rapidly decreasing. In later experiments the same procedure was used when BeO and ZrO₂ crucibles were used as containers,

except that tungsten shields were used as heating elements. Crucibles containing the MgO were placed inside slightly larger ones to prevent them from being attacked by contact with tungsten radiation shields. The MgO used was the Reagent Special grade of Baker and Adamson.

Temperatures were read with a calibrated optical pyrometer and the proper window corrections were added. The uncertainties in the temperatures are not more than ten degrees.

Results of Vapor Pressure Measurements

The tungsten crucibles proved to be undesirable as containers for MgO. The results are shown in Table 1.

Table 1

Run	Temp. °K	Time (sec)	Area of Effusion Hole in cm ²	Total Weight Loss of Cell in gr.	Weight Loss of Crucible Alone in gr.
1	1970	3600	.0314	.010	.060
2	2110	3600	.0314	.146	.186
3	1960	5200	.0314	.110	.058

As is seen in Table 1, there is considerable attack of the crucible. The reduction of MgO follows the general equation: $W + xMgO = WO_x + xMg(g)$. If one assumes a value of x, the weight loss due to effusion of Mg(g) can be calculated from the weight loss of the crucible alone. X-ray analysis showed that collected portions of the effusate contained free tungsten and the only explanation is that there is appreciable volatility of WO_x . There is the possibility that $WO(g)$ is formed, which, when collected on a cool collector plate, disproportionates to W and WO_2 . Phases other than W appeared on the X-ray patterns but were not identifiable. Run 2 shows that WO_x does not completely vaporize, and consequently in Runs 1 and 2 the total volatility cannot be explained as simply the contributions

from WO_x and free $Mg(g)$ even assuming x is 3. The $MgO(s)$ must therefore contribute measurably to the total volatility.

More satisfactory results were obtained when BeO and ZrO_2 crucibles were used as MgO containers. Table 2 shows the comprehensive results of the vapor pressure measurements.

Table 2

Run	Temp. °K	Time in Sec.	Area of Hole in cm ²	Weight Loss in gr.	P_{Mg} (From Rate Eq.) in atm.	K_1	K_2	P_{Mg} (Calculated Theoretically) in atm.
1	2040	3900	.0177	.025	4.5×10^{-5}	1.1×10^{-11}	9.8×10^{-4}	6.6×10^{-6}
2	2040	3900	.0177	.018	3.3×10^{-5}	1.1×10^{-11}	9.8×10^{-4}	6.6×10^{-6}
3	2140	9300	.0177	.184	1.4×10^{-4}	1.6×10^{-10}	2.0×10^{-3}	2.4×10^{-5}
4	2200	3600	.0177	.145	3.0×10^{-4}	7.7×10^{-10}	2.8×10^{-3}	5.6×10^{-5}

Runs 1, 2 and 3 were with BeO crucibles while Run 4 was with a ZrO₂ crucible. In all four runs BeO covers were used. The holes in the covers were ground as close as possible to knife edges. In Runs 1 and 2 the MgO charge was removed from the crucible and weighed separately. The reported values are the weight losses of the MgO itself. The total weight losses of the cells were found to be slightly less than those of the MgO itself. In Runs 3 and 4 the total loss of the crucible plus MgO is reported as the MgO melted at the points of surface contact with the crucibles and could not be removed upon cooling.

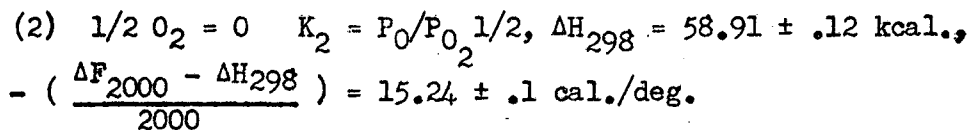
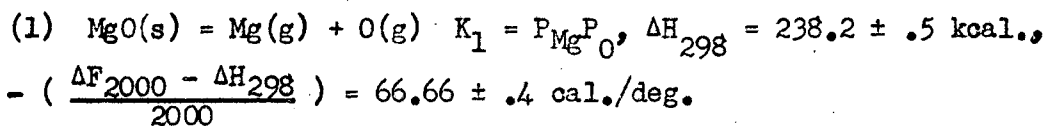
The initial assumption is that only Mg(g), O(g) and O₂(g) are important, and the rate of effusion of Mg(g) is simply the gram atoms of magnesium vaporized per second. The partial pressures of Mg(g) were calculated from the rate equation

$$R = \frac{P (44.383) a}{(MT)^{1/2}}$$

where R is the number of gram atoms or moles effusing per second, a is the area of effusion hole in cm², T the absolute temperature, M the atomic or molecular weight of the effusing specie, and P its partial pressure in atoms. Pressures calculated on this assumption are shown in Column 6.

Comparison of Experimental and Theoretical Values

From known values of $-\left(\frac{\Delta F_T - \Delta H_{298}}{T}\right)$ and ΔH_{298} it is possible to calculate the equilibrium constants for the following reactions:



Knowing K_1 and K_2 together with the auxiliary condition that the rate of effusion of magnesium must equal the total rate of effusion of oxygen (as O_2 and O), we can calculate the true theoretical pressures of magnesium inside the Knudsen cell.

The value of $-\left(\frac{F_{2000} - H_{298}}{2000}\right)$ for $MgO(s)$ was calculated from Kelley's tables^{8,9} and the values for $Mg(g)$, $O(g)$ and $O_2(g)$ were obtained from tabulated values.¹⁰ The best accepted value of $-143.7 \pm .1$ kcal.¹¹ for the heat of formation of MgO , and the most recent value¹² for the heat of dissociation of O_2 were used in the calculations. For the heat of sublimation of magnesium several sources of vapor pressure data were treated. Using Kelley's free energy functions¹³ together with the vapor pressure data we obtained $\Delta H_{298} = 35.3 \pm .2$ kcal from the measurements of Coleman and Egerton,¹⁷ and $\Delta H_{298} = 35.4 \pm .5$ kcal from the measurements of Baur and Brunner.¹⁸ Combining these results with the value of $\Delta H_{298} = 35.9$ kcal, calculated by Kelley¹³ from measurements of Hartmann and Schneider,¹⁹ we take a value of $\Delta H_{298} = 35.6 \pm .3$ kcal. Since $-\left(\frac{\Delta F_T - \Delta H_{298}}{T}\right)$ is not strongly dependent on temperature, the values at $T = 2000^\circ K$ were considered constant over a 200° range.

The three necessary relationships are:

$$(1) P_{Mg} P_O = K_1$$

$$(2) P_O / P_{O_2}^{1/2} = K_2$$

and $R_{Mg} = 2R_{O_2} + R_O$, which expressed in terms of pressures is

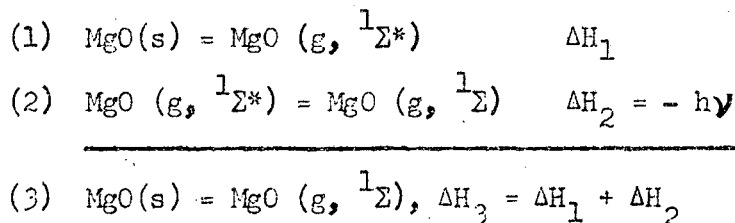
$$(3) \frac{P_{Mg}}{M_{Mg}^{1/2}} = \frac{2P_{O_2}}{M_{O_2}^{1/2}} + \frac{P_O}{M_O^{1/2}}$$

Partial pressures of Mg , O and O_2 were calculated by successive approximations until two place accuracy was achieved. The values for Mg are shown in Column 9.

Comparison of Columns 6 and 9 shows the observed pressures are consistently a factor of five or six times higher than the theoretical pressures. With the widest limits of uncertainty in the thermochemical data the error in ΔF for reaction 1 at 2000°K is 1.3 kcal. This corresponds to an error in K_1 of about 40% and an error of 20% in the calculated pressures in Column 9. On the other hand the vapor pressure measurements are reproducible to better than a factor of two. The discrepancy therefore between the observed and calculated pressures in Columns 6 and 9 is not just accidental. The initial assumption is consequently false and we are not permitted to assume that only $Mg(g)$, $O(g)$ and $O_2(g)$ are the important vapor species. Molecular species must contribute appreciably to the vapor and the solid does not vaporize simply to the elements.

II. THE HEAT OF SUBLIMATION OF $\text{MgO} (g, {}^1\Sigma)$

Having shown from the vapor pressure measurements that $\text{MgO} (s)$ vaporizes principally into molecular species, the next problem is to consider the importance of the lowest known ${}^1\Sigma$ state of $\text{MgO} (g)$. The method to be used is similar to that used by Brewer, Gilles and Jenkins.¹⁴ If an electronic state of the gaseous molecule in equilibrium with the solid emits a measurable amount of radiation, the heat of sublimation of that particular state can be determined from the variation of intensity with temperature. The transition to be treated is the well-known ${}^1\Sigma^* \longrightarrow {}^1\Sigma$ transition of MgO lying in the green region of the spectrum. The desired heat is the heat of sublimation of $\text{MgO} (g, {}^1\Sigma^*)$ minus the excitation energy of the ${}^1\Sigma^*$ as shown by the following equations:



ΔH_1 is to be obtained graphically, and this value together with the known excitation energy gives us ΔH_3 .

Experimental

To obtain a heat of sublimation with variation of intensity with temperature the two following conditions are necessary:

- (1) The gas must be in equilibrium with the solid.
- (2) The temperature must be high enough to populate the upper electronic level sufficiently to produce an observable amount of emission.

The King type resistance furnace as described by Brewer, Gilles and Jenkins was used as the heating unit for MgO . The same type of

graphite tubes was used except that the MgO could not be placed directly into the tubes as it is reduced rapidly by the graphite at higher temperatures. Instead the graphite tubes were lined with a .002" sheet of tantalum and a .002" sheet of tungsten was placed inside this tantalum lining. The MgO was therefore only in contact with the tungsten. Graphite reacting with the tantalum formed a TaC layer and the carbon could not readily penetrate the tungsten. Consequently, except for some attack by the tungsten, rapid reduction of the MgO was prevented. After evacuating the furnace, argon was passed in to decrease diffusion of MgO vapor out the ends of the tube. An argon pressure of .1 to .2 atm. was sufficient. A 22 K.V.A. power source, producing 800 amps or more in the graphite tubes, was required to produce the desired temperatures. All temperatures were read with a calibrated optical pyrometer. Twenty grams of pressed MgO placed inside the tungsten lining would last for about an hour at temperatures around 2500°K.

Emitted light from the MgO vapor was passed on to the slit of a 3 meter concave grating spectrograph and reflected directly on to an RCA 1P 21 photomultiplier tube. Stray light emitted from the sides of the furnace tube was cut out of the beam to prevent high backgrounds. The photo tube, amplifying unit, and recording device was that described by Phillips.¹⁵ The photo tube was part of the scanning device and could be set immediately at the desired wave length. Several tracings of each spectral feature were made at each temperature until it was sure that equilibrium within the furnace had been attained. A characteristic tracing of the 0;0 sequence of the ${}^1\Sigma^* \longrightarrow {}^1\Sigma$ system is shown in Figure 1. The actual dispersion of the grating is about 4A/mm in the first order whereas the scanner was set to a slow enough speed to produce a spread of 10.6A/inch on the tracing.

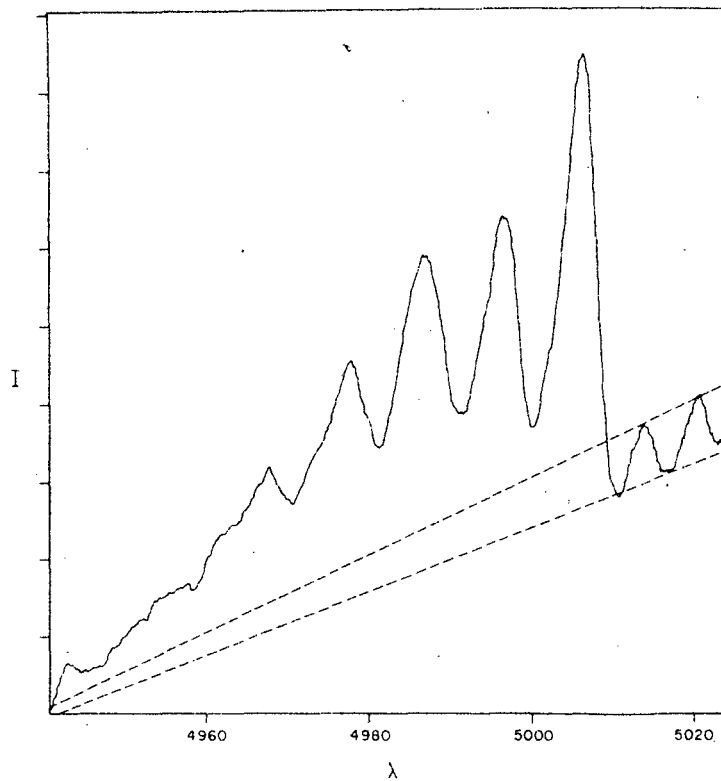


Fig 1 - Frission tracing of the C_0 sequence of the green bands of MgO produced from MgO vapor in equilibrium with MgO solid at $T = 2550^\circ\text{K}$. Dotted lines represent limits of the true background.

Calculations and Results

Tracings of the 0,0 sequence of the $^1\Sigma^* \rightarrow ^1\Sigma$ transition of MgO in equilibrium with the solid were made at various temperatures. The heights of the 0,0 band heat at 5007.3A, as seen in Figure 1, were measured from the lowest dotted line representing the lowest extrapolated background. The heights multiplied by the proper amplification factor are proportional to the intensity of emitted radiation. The intensities presented in Table 3 are the heights in centimeters.

Table 3

T°K	Relative Intensity of 0,0 Band
2498	13.6
2488	11.3
2488	10.2
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2533	23.0
2533	21.2
2528	21.8
<hr/>	
2598	74.0
2598	66.0
2593	70.0
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2648	128.0
2653	104.0
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The upper dotted line in Figure 1 is an extrapolation of MgH rotational structure, the MgH appearing as an impurity in the furnace. The variation in heights measured from the upper dotted line is about 10% of the reported values. The true background lies somewhere between the two dotted lines. At temperatures above 2650°K the intensities diminish rapidly since the solid disappears at a rapid

rate and equilibrium is not maintained.

Determination of ΔH_1 for reaction (1), $\text{MgO}(s) = \text{MgO}(g, {}^1\Sigma^*)$.

To obtain the heat of sublimation of the ${}^1\Sigma^*$ state, a \sum plot, which includes the variation in heat capacity with temperature, was made instead of a simple $\Delta F/T$ vs. $1/T$ plot.

From thermodynamics we have the relationship:

$$d(\Delta F/T)/dT = -\Delta H/T^2 \quad (1)$$

and since the intensity of emitted radiation is proportional to the concentration of ${}^1\Sigma^*$, we have a second relationship: $\Delta F = -RT \ln P_{{}^1\Sigma^*} = -RT \ln kT$, k being the proportionality constant. From the relationship: $\Delta H - \Delta H_{298} = \int_{298}^T \Delta C_p dT$, and from known heat capacities of the solid and gas we obtain for reaction (1):

$$\Delta H = \Delta H_{298} - 5.21T - .87 \times 10^{-3}T^2 - 1.48/T \times 10^5 + 2100.$$

The heat capacity for $\text{MgO}(s)$ was taken from Kelley's Table.⁸ For the gas we are considering a single vibrational level of a particular electronic state, and hence vibrational and electronic terms do not contribute to the total heat capacity. A rotational contribution should be included but, since only a few rotational levels are involved in forming the heat of the band, is small as compared to the translational term. Therefore a C_p of $5/2R$ was taken for the gas.

Substituting ΔH into the equation (1) and integrating we obtain:

$$\Delta F/T = (\Delta H_{298} + 2100)/T + 5.21 \ln T + .87 \times 10^{-3}T - \frac{.74 \times 10^5}{T^2} + \text{const.}$$

$$\text{Setting } \Delta F \text{ equal to } -RT \ln k T \text{ and letting } - \left(\frac{\Delta H_{298} + 2100}{T} \right) + \text{const.}$$

be \sum , we get:

$$\sum = - \left(\frac{\Delta H_{298} + 2100}{T} \right) + \text{const.} = 4.575 \log I + 16.55 \log T + .87 \times 10^{-3}T - \frac{.74 \times 10^5}{T^2}$$

The slope of a Σ vs. $1/T$ plot gives us ΔH_{298} . The values of Σ calculated from the averaged sets of data presented in Table 3 are shown in Table 4.

Table 4

T°K	Σ
2488	63.08
2533	64.67
2598	67.20
2648	68.58

The Σ vs. $1/T$ plot is given in Figure 2 in which the same weight is given to each point. From the slope of the line we obtain $\Delta H_{298} = 230$ kcals. To obtain ΔH_3 for reaction (3), $\text{MgO}(s) = \text{MgO}(g, {}^1\Sigma)$, we subtract the sum of the electronic and rotational energies of the ${}^1\Sigma^*$. The electronic energy calculated from the band origin is 57 kcals. The band head forms approximately at the rotational level $J = 40$ giving a rotational contribution of 2.7 kcals. We therefore obtain for the heat of sublimation of $\text{MgO}(g, {}^1\Sigma)$ a value of 170 kcals.

Uncertainties in the heat of sublimation.

In general with a limited number of points it is difficult to obtain accurate heats. A small uncertainty in the slope of the line will produce a large uncertainty in the heat. In this case there is an uncertainty of 10 kcals. alone in establishing the best position of the curve.

Errors may also be due to temperature gradients along the graphite tube. In order to minimize this uncertainty the MgO was placed in the central uniformly heated portion of the tube. In making the temperature measurements the optical pyrometer was focused directly onto the hot surface of the MgO and the temperature was observed to be constant over

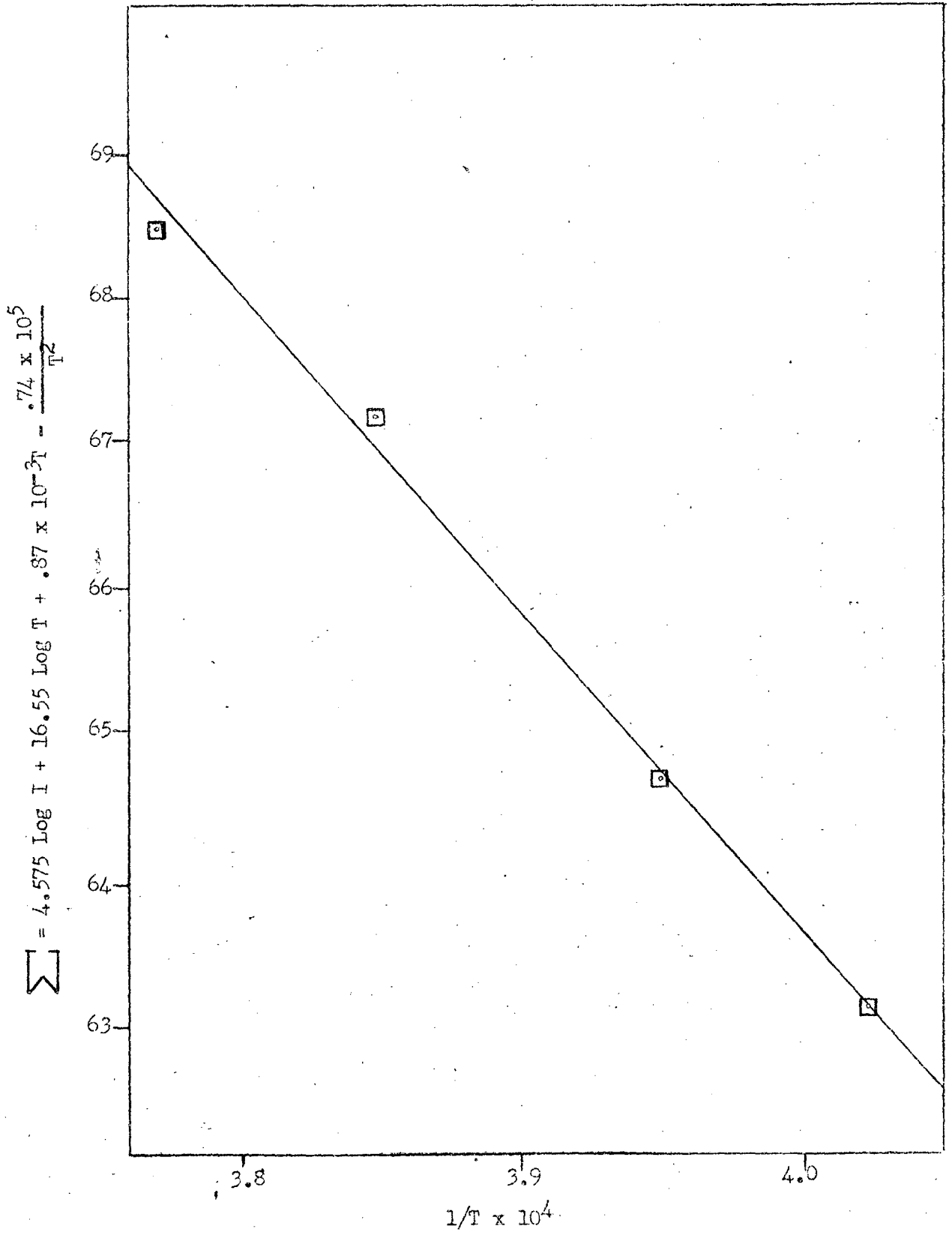


Figure 2

the total surface area. Temperatures read on an exposed central portion of the graphite tube agreed with readings on the surface of the MgO; and since the hot graphite approaches a black body radiator, it was presumed that the MgO was also radiating as a black body.

Reduction of the MgO by tungsten produces a solid oxide of tungsten and eventually the MgO will be completely reduced. As long as solid MgO is still present, however, the true equilibrium pressure of MgO vapor will be maintained. At lower temperatures the reduction is slow enough to allow time for several tracings at each temperature.

The temperature range which can be studied is limited since at lower temperatures the amount of emission is too small to observe while at higher temperatures the gas will not reach its true equilibrium pressure and the observed intensities will be too small. A plot of this type will therefore tend to give low results if the points at high temperatures are treated equally with points at lower temperatures. Consequently we shall take the ΔH_{298} of 170 kcals. as a lower limit.

Conclusions

The heat of sublimation of MgO (g, $^1\Sigma$) has been obtained graphically and found to be: $\Delta H_{298} \gg 170$ kcals.

From Kelley's tables^{8,9} we obtain for the reaction,

$$\text{MgO}(g) = \text{MgO}(g, ^1\Sigma), - \left(\frac{\Delta F_{2000} - \Delta H_{298}}{2000} \right) = 41.7.$$

Using $\Delta H_{298} \gg 170$ kcals. and setting ΔF equal to $-RT \ln P_{1\Sigma}$ we calculate $P_{1\Sigma} \ll 10^{-10}$ atms. at 2000°K. Comparing this value with the pressure of Mg(g) in Column 9 of Table 2, we see that MgO (g, $^1\Sigma$) is even less important than Mg(g) and also cannot be the principal vaporizing specie.

III. THE ULTRAVIOLET BAND SYSTEM

The 3700A band system appearing in emission from magnesium burning in air and also in absorption in flames containing magnesium⁴ will now be considered. Although the bands are complex and have not been analyzed, there are good reasons to suspect from the various ways they have been produced that they either involve electronic states of MgO or states of a more complex molecule containing magnesium and oxygen. If this transition occurs with equal or greater intensity than the ${}^1\Sigma^* \longrightarrow {}^1\Sigma$ transition, we ought to observe it in King furnace as we did the green bands and further ought to be able to study the states involved in the transition. Experiments were therefore undertaken to obtain the 3700A bands both in emission and absorption under equilibrium vapor conditions and to study the importance of the lowest electronic state of the transition relative to MgO (g, ${}^1\Sigma$).

Experimental

The technique used to produce the ${}^1\Sigma^* \longrightarrow {}^1\Sigma$ bands was also successful in studying the ultraviolet system. Light from the MgO vapor in equilibrium with the solid was passed on to the slit of the 3 meter grating and reflected onto a 1P28 photomultiplier tube. Slit widths of .1 mm were required to give a reasonable response by the phototube. A quartz optical system was used throughout the ultraviolet experiments. Several tracings at temperatures about 2600°K between wave lengths of 3800 and 3600 Angstroms were made in order to locate the bands. Several molecules and atomic features appeared on the emission tracings; and after identifying the important atomic lines, the bands were definitely shown to be the ones observed by Barrow and Crawford.⁴ Figure 3a is a reproduction of tracings made at two different temperatures. The recording device was set to

produce a dispersion of 42.3 Å/inch on the tracing paper.

For absorption experiments a xenon lamp with a high effective arc temperature in this wave length region was used as a source. Parallel light from the source was passed through the calcium fluoride windows of the furnace and on to the slit of the spectrograph. Figure 4 shows tracings of the transmitted light from the xenon lamp with absorption by the MgO vapor at two different furnace temperatures. The absorption features in Figure 4 are seen to be just the reverse of the emission features in Figure 3a. On this low dispersion the tracings show only an integrated shape of absorption features, and small fluctuations in the lamp intensity are also present.

Intensity Comparison of the Two Band Systems

From a comparison of rates of rise in intensities with temperature for the two band systems we can qualitatively establish which of the lower states involved in the transitions has the smaller heat of sublimation.

Simultaneous tracings were made for both the green and ultraviolet systems. The furnace was first brought to the desired temperature and held constant to allow the MgO vapor to equilibrate with the solid. The spectrograph was adjusted to permit study of both regions with one setting. The scanner was first set at approximately λ 5000 and a tracing of the green system was made. The scanner was then set at approximately λ 3700 and a tracing of the ultraviolet region was taken. Several tracings of each system were made at a particular temperature until equilibrium was established and tracings of each system were reproduced with the same shape and magnitude. The furnace temperature was then changed and another series of tracings were made. Figure 3a is a reproduction of two tracings of the ultra-

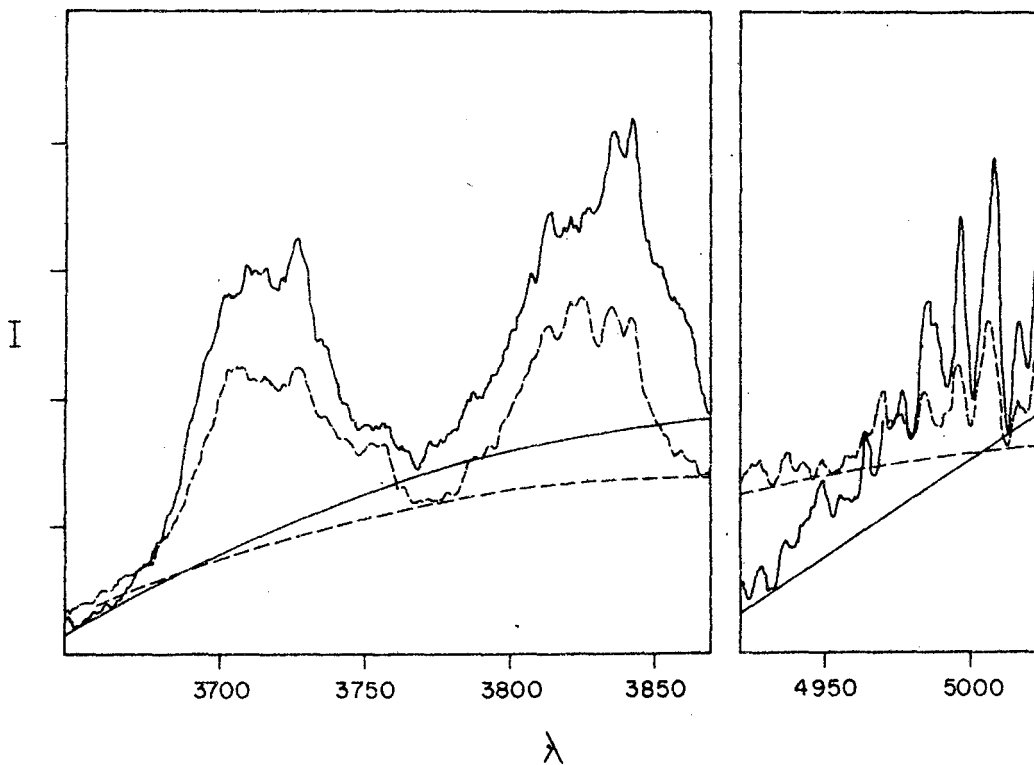


Fig. 3 - (a)

(b)

(a) Thermal emission tracings of the ultraviolet bands

(b) Thermal emission tracings of the green bands.

Solid lines represent tracings made at $T = 2600^{\circ}\text{K}$ while dotted lines represent tracings made at $T = 2550^{\circ}\text{K}$. Extrapolated backgrounds are also indicated

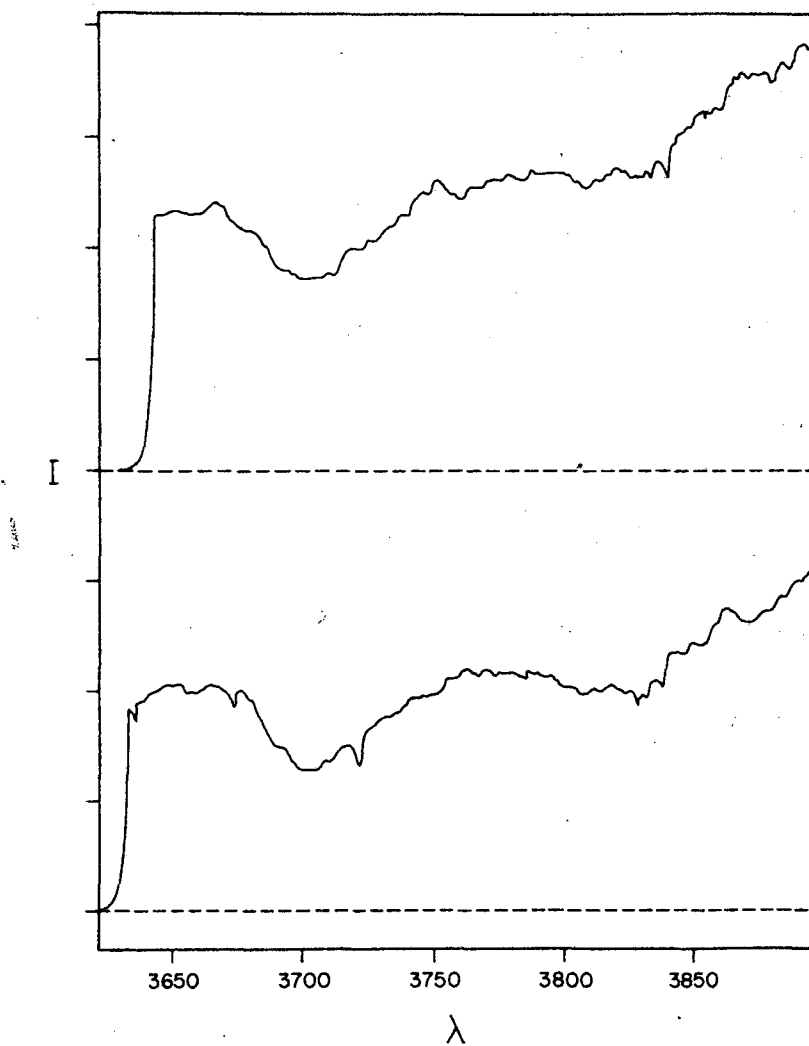
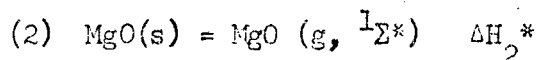
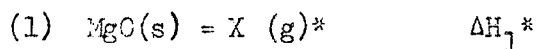


Fig 4 - Intensity tracings of light transmitted from a xenon lamp through MgO vapor showing absorption of radiation by the vapor. The upper tracing is made at $T = 2320^\circ\text{K}$ and the lower at $T = 2420^\circ\text{K}$. Dotted lines are zero light reference lines.

violet region, and Figure 3b shows two tracings of the green system. The solid lines are tracings made at $T = 2600^\circ\text{K}$ while the tracings shown by dotted lines were made at $T = 2550^\circ\text{K}$. The backgrounds are extrapolations of the observed backgrounds.

First we consider the excited states and the reactions:



$X(g)^*$ represents an excited state of the unknown molecular specie.

From thermodynamics we have the relationships:

$$\frac{d\left(\frac{\Delta F_1^*}{T}\right)}{dT} = -\frac{\Delta H_1^*}{T^2} \quad (1)$$

$$\frac{d\left(\frac{\Delta F_2^*}{T}\right)}{dT} = -\frac{\Delta H_2^*}{T^2} \quad (2)$$

Setting ΔF_1^* equal to $-RT \ln k_1 I_1 T$ and ΔF_2^* equal to $k_2 I_2 T$, where I_1 and I_2 are the intensities of the ultraviolet and green systems respectively and k_1 and k_2 are the proportionality constants, we obtain from equations 1 and 2:

$$\frac{d(\ln I_1 T)}{dT} = \frac{\Delta H_1^*}{T^2} \quad (3)$$

$$\frac{d(\ln I_2 T)}{dT} = \frac{\Delta H_2^*}{T^2} \quad (4)$$

For comparison purposes in the ultraviolet system we will consider the strong molecular features in the region of λ 3720 as seen in Figure 3a. The features appearing at approximately λ 3840 contain the strong ${}^3D \longrightarrow {}^3P^0$ transition of magnesium and cannot be used. For the green system we will treat the sequence of bands

beginning at λ 5007.3. Using the areas enclosed by the solid and dotted lines as measures of integrated intensities for both systems, we find

$$\frac{I_{1, T = 2600^\circ\text{K}}}{I_{1, T = 2550^\circ\text{K}}} = 1.6, \quad \frac{I_{2, T = 2600^\circ\text{K}}}{I_{2, T = 2550^\circ\text{K}}} = 2.0$$

We see that the green system is rising more rapidly with temperature than the ultraviolet system. Expressed mathematically,

$$\frac{I_{1, T = 2600^\circ\text{K}}}{I_{1, T = 2550^\circ\text{K}}} < \frac{I_{2, T = 2600^\circ\text{K}}}{I_{2, T = 2550^\circ\text{K}}} \quad \text{or:} \quad \frac{d(\ln I_1 T)}{dT} < \frac{d(\ln I_2 T)}{dT}$$

Therefore, from equations 3 and 4 we may also write:

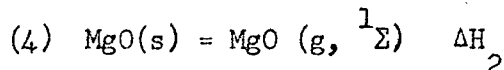
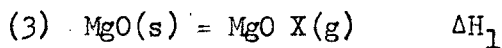
$$\Delta H_1^* < \Delta H_2^*$$

Assuming the ultraviolet bands involve a monomer of MgO we can plot $\log I_1/I_2$ vs. $1/T$ and obtain from the slope the difference in heats of sublimation of the two excited electronic states. A plot of this type was made using the integrated intensities from the tracings shown in Figure 3a, and a difference of roughly 50 kcals. was obtained.

With an estimated uncertainty of 20 kcals. we have:

$$\Delta H_1^* = \Delta H_2^* - 50 \text{ kcals.}$$

To obtain a relation between the heats of sublimation of the lower levels we subtract from ΔH_1^* and ΔH_2^* the electronic energies. The reactions are:



$X(2)$ represents the lower state of the unknown molecular specie. The energy for the 1Σ is 57 kcals. For X^* we shall take the origin of the system at λ 3700 giving an electronic energy of 77 kcals.

We have then the following relations:

$$\Delta H_1 = \Delta H_1^* - 77 \text{ kcals.}$$

$$\Delta H_2 = \Delta H_2^* - 57 \text{ kcals.}$$

Since $\Delta H_1^* = \Delta H_2^* - 50 \pm 20$ kcals., we obtain the relation:

$$\Delta H_1 = \Delta H_2 - 70 \pm 20 \text{ kcals.}$$

Showing the lower level of ultraviolet system lies significantly lower than the lower level of the green system.

Conclusion and Discussion

The 3700A bands, originally produced in emission from burning magnesium and in absorption in flames containing magnesium, have been produced in absorption and emission in equilibrium with solid MgO. A comparison of intensities of the ultraviolet and green systems has shown the lower state of the ultraviolet system to have a smaller heat of sublimation than the 1Σ state by approximately 70 kcals. These results show the pressure of the unknown molecule to be significantly greater than that of the 1Σ and suggest the possibility that the unknown molecule is the principal vapor specie.

On the tentative assumption that a monomer is the principal vaporizing specie, we can calculate a heat of sublimation from the vapor pressure data shown in Table 2, taking the weight loss due mainly to MgO(g). Table 5 gives results of such calculations. An electronic contribution should also be included in the free energy functions in Table 5 if the vaporizing specie is a multiplet electronic state. If the molecule is a 3Σ state of MgO, the quantity $RT \ln 3$ should be added to the tabulated values of ΔH_{298} .

Table 5

T°K	P _{MgO} in Atms. (Calculated from Rate Eq.)	$-\left(\frac{\Delta F_T - \Delta H_{298}}{T}\right)$	
		MgO(s) = MgO(g)	ΔH_{298} in Kcals. MgO(s) = MgO(g)
2040	5.84×10^{-5}	41.66	123.5
2040	4.20×10^{-5}	41.66	124.8
2140	1.84×10^{-4}	41.33	125.2
2200	3.81×10^{-4}	41.13	125.1

Averaging the results of Table 5 we obtain a heat of sublimation of 124 ± 2 kcals. Comparing this with the experimentally obtained value of $\gg 170$ kcals. for the heat of sublimation of the $^1\Sigma$ state of MgO we see the principal vaporizing specie must be at least 45 kcals. lower than the $^1\Sigma$ state. The ground level of the ultraviolet transition has been shown to be 70 ± 20 kcals. lower than the $^1\Sigma$ state. The thermochemically obtained heat of sublimation and the heat of sublimation of the unknown molecule determined spectroscopically, therefore, are the same within the experimental uncertainties, and it is reasonable to conclude that the unknown molecule is the principal vaporizing specie. Even if the spectrum pertained to a polyatomic molecule, the same general conclusions could be drawn.

Huldt and Lagerqvist⁴ obtained a thermochemical value of 5.2 e.v. for the dissociation energy of MgO. With the same heats of reaction used previously and with this value for the dissociation energy we calculate a heat of sublimation of 118 kcals. This is 4 kcals. from the uncertainty limit of the value obtained here.

The Ultraviolet Bands on High Dispersion

Further investigation of the ultraviolet band system is necessary in order to identify the molecular states involved in the transition. On low dispersion the bands are too complex to permit a vibrational or rotational analysis. Barrow and Crawford⁴ measured many band heads but did not have sufficient resolution to attempt a vibrational analysis. Verhaeghe¹⁶ has classified the bands into distinct sets of sequences, but over-all little work has been done on the ultraviolet system. In a hope of obtaining further information about the electronic states involved in this transition we have obtained the bands again under higher dispersion.

Experimental

All spectrograms were made with a 21-foot grating, ruled with 30,000 lines/inch, giving a linear dispersion of .67Å/mm at λ 3700 in the second order. An eighteen-inch photographic plate was placed on the Rowland circle with the center of plate at approximately λ 3750 so as to include a range between λ 3600 and λ 3900. Eastman Kodak II a-o plates were used and found to give sharp contrast. The three following methods of excitation were used:

(1) Burning Magnesium

Light from the burning end of a thin piece of magnesium ribbon fed through a quartz tube was focused directly onto the slit. The height of the quartz tube could be adjusted to allow only selective portions of the flame to focus on the slit, but the erratic burning of the ribbon would not allow complete exclusion of continuous radiation from the glowing mass. Slit widths of .05 mm with an exposure time of ten minutes were required to give observable spectral features. In some cases burning pellets of magnesium, which give a

brighter instantaneous source, were used; but in all cases backgrounds were too high. On the best plates several sequences of bands appeared with partially resolved rotational structure, but overlapping of many vibrational bands forbid a vibrational analysis.

(2) Magnesium Arc

Magnesium electrodes of one-half inch diameter and approximately 3" long were fastened to the clamps of a conventional iron arc. The arc was powered by a 220 volt DC source. The green portion of the arc was focused onto the slit, and the position of the arc could be adjusted to allow only a certain portion to be exposed to the slit. The arc could be run for only 30 seconds at a time as the electrodes became overheated. In some cases the arc went out by itself after a few seconds because of MgO formation at the surface of the electrodes. Slit widths were 0.05 mm and the total exposure times were about 10 minutes. Backgrounds on the plates were considerably reduced and rotational structure was more obvious than on the exposures with burning magnesium. Many impurity lines and bands also appeared. Bands of CN were particularly strong, and presence of these impurities would not permit an analysis.

(3) Thermal Excitation

The bands were obtained in emission and absorption in the manner previously described.

(a) For emission the MgO was brought to temperatures of about 2550°K, and light from the vapor was focused onto the slit. With a slit width of 0.03 mm an exposure time of 35 minutes was required.

(b) For absorption a xenon lamp was used as a source of continuum. An MgO temperature of 2550°K was found to be the most ideal for reversal of the bands. This temperature is lower than the

effective lamp temperature and still high enough to produce a large concentration of vapor. The slit width was again 0.03 mm. At this temperature the solid MgO lasted about 40 minutes which was a sufficient exposure time.

Description of the Ultraviolet Bands

Spectrograms of the bands obtained under high excitation as in the case of burning magnesium and magnesium arcs are too complex to permit a vibrational analysis by themselves. The spectrograms obtained under equilibrium vapor conditions, however, are considerably less complex since only lower vibrational levels are populated and only a few of the principal bands appear. In our analysis of the bands we will treat them as we would a simple diatomic spectrum, assuming a monomer of MgO is involved in the transition. From the vibrating frequencies of the singlet state of MgO we would expect this molecule to have a vibrating frequency between 800 and 900 cm^{-1} . The spacing between the 0,0 band and the 0,I band would therefore be of the order of 100 Angstroms. Close examination of all the plates shows, not one, but several sets of sequences separated by approximately this distance. If the molecule is a simple monomer, the only conclusion is that more than two electronic states are involved in the transition. The splittings are too great to be simply multiplet splittings. Three measured sets of sequences are shown in Table 6.

All of the band heads presented in Table 6 were observed in thermal absorption. If the bands were distinguishable on other plates, the other methods of excitation are also listed. The measurements in general agree with those of Barrow and Crawford.⁴

	1st Sequence Q Heads		Methods of Excitation	Direction of Degradation	2nd Sequence Q Heads		Methods of Excitation	Direction of Degradation
	λ	ν			λ	ν		
System I	3721.41	26863.9	1,2,3a,3b	V	3626.73	27565.2	3b	V
	3731.75	26789.5	1,2,3a,3b	V	3659.95	27315.0	3b	R
	3742.27	26714.2	3a,3b	V				
	3751.33	26649.7	3a,3b	V	3rd Sequence			
	3759.38	26592.6	3a,3b	V	Q Heads			
	3766.50	26542.3	1,2,3a,3b	R	λ	ν		
	3772.36	26497.6	1,2,3a,3b	R	3846.84	25988.0	3a,3b	?
	3773.3	26459	1,2,3a,3b	R	3854.81	25934.3	3a,3b	?
P Head								
	3725.7	26833	1,2,3a,3b	V				

	1st Sequence Q Heads				2nd Sequence Q Heads			
	λ	ν			λ	ν		
System II	3704.2	26988.7	3b	V	3802.4	26291	3a,3b	V
	3695.2	27053.7	3b	V	3792.8	26358	3a,3b	V
	3686.5?	27118.3	3b	V	3784.5	26416	3a,3b	V

	1st Sequence Heads Undesignated				2nd Sequence Heads Undesignated			
	λ	ν			λ	ν		
System III	3793.3	26319	1,2,3a,3b	R	3684	27137	3b	R
	3804.4	26278	1,2	R	3691.2?	27084	3b	?
	3805.4	26271	1,2,3a,3b	R				
	3810.2	26237	1,2,3a	R				
	3815.7	26200	1	R?				
	3816.3	26192	1	R?				

Table 6. Methods of Excitation are: (1) Burning Magnesium, (2) Magnesium Arc, (3a) Thermal Emission, (3b) Thermal Absorption.

The most outstanding sequence begins at $\lambda 3721$. On the absorption spectrograms several members of the sequence appear. The members converge off toward the red while the first members are obviously shaded toward the violet. The third and fourth members of the sequence are barely visible on the emission spectrograms obtained by burning magnesium. We see, therefore, a sequence of bands initially shaded to the violet, becoming headless, and finally shading toward the red. The sixth member of the sequence appears quite intense on the emission spectrograms and indeed is shaded to the red. From this we can conclude nearly equal rotational constants for the two states, $B_1' \approx B_1''$. From the direction in which the bands are progressing we can also conclude: $W_1' < W_1''$. Another interesting feature is that the band heads at $\lambda 3721.49$, $\lambda 3725.7$ and $\lambda 3731.75$ each have multiple components, an indication of multiplet states with Hund's case (b) coupling.

The second system has two sequences of comparable intensity both degrading and progressing toward the violet, $B_2' > B_2''$, $W_2' > W_2''$.

A third system has one intense sequence of bands at $\lambda 3798$ shaded and progressing toward the red and a second weaker sequence at $\lambda 3684$ also shading and progressing to the red. This shows us:

$$B_3' < B_3'' \text{ and } W_3' < W_3''.$$

Other weaker bands also appear in thermal absorption but were not measured. Some of these may be members of the systems already mentioned or may be part of another system. In order to explain the presence of so many band systems as part of a simple diatomic spectrum we are forced to recognize the existence of several electronic states. One explanation is that there are two upper electronic states lying close together and two lower states lying close together. Correlation rules allow a 3Σ and 3Π state to form from the ground state magnesium

and oxygen atoms. An alternate explanation is that the molecule is polyatomic and we are observing more than one mode of vibration. Considering all aspects of the spectrum, however, the former solution appears to be the more feasible. Verhaeghe¹⁶ is also of the opinion that several states are involved.

A provisional vibrational scheme is given for system I in Table 7. We have taken the intense band at λ 3721 as the beginning of the 0,0 sequence. This scheme must be taken tentatively until the numbering of the bands is definitely established.

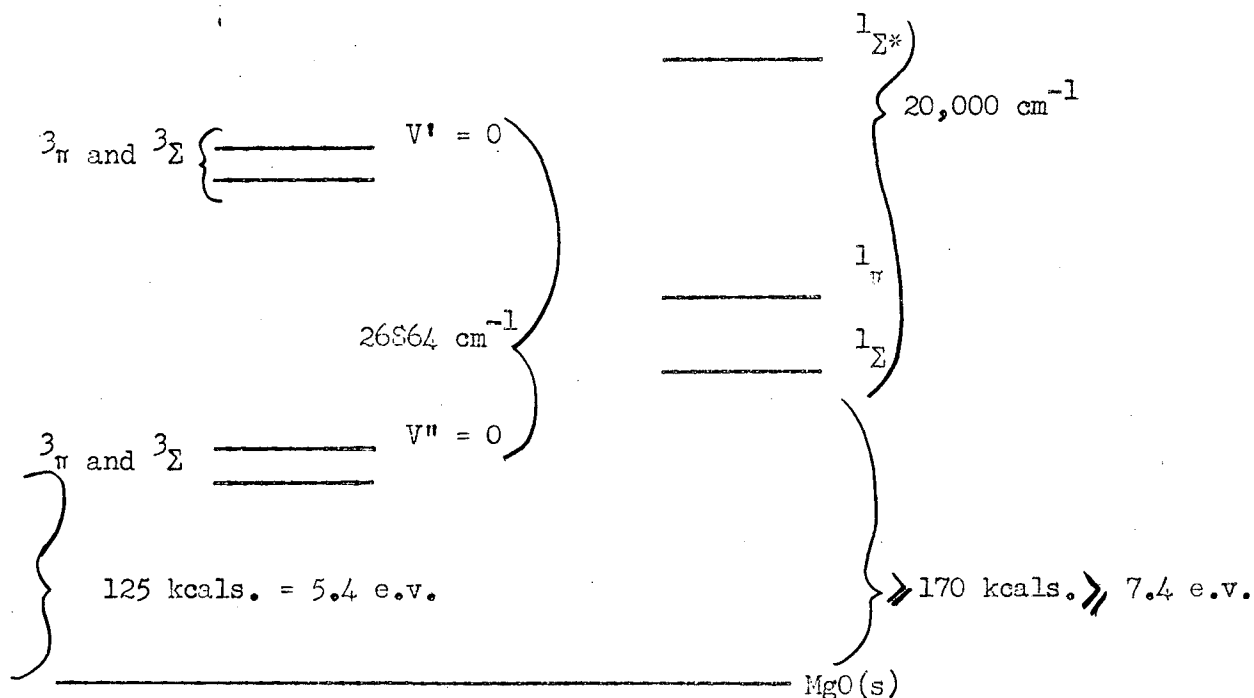
$V' \backslash V''$	0	1	2	3	4	5	6	7
0	26863.9 (875.9)	25988.0 (801.5)						
1		26789.5 (855.2) (775.7)	25934.3 (779.9)					
2		27565.2 (851)	26714.2					
3				26649.7				
	$\omega_{e''} \approx 902, X_{e''} \omega_{e''} \approx 13$ $\omega_{e'} \approx 817, X_{e'} \omega_{e'} \approx 9.5$							
4					26592.6 (722.4)			
5					27315.0 (772.7)	26542.3		
6							26497.6	
7								26459

Table 7

III. DISCUSSION

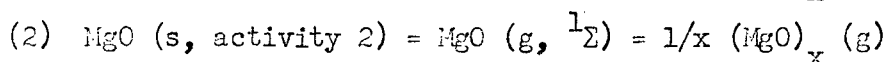
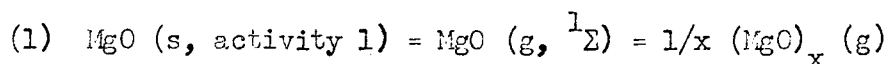
Experiments on the vaporization of solid MgO have shown that the solid vaporizes principally in c molecules. The ground electronic specie involved in the ultraviolet transition has been shown to be more important than the known ${}^1\Sigma$ state of MgO, and there is strong evidence indicating this unknown electronic specie is the principal vaporizing molecule. The spectrum of the ultraviolet bands is not inconsistent with a simple diatomic spectrum if we recognize the possibility that several electronic levels are involved in the transition.

Treating the unknown molecule as the principal vaporizing monomer, using the heat of sublimation shown in Table 5 and the experimental determined value for the heat of sublimation of the ${}^1\Sigma$ state, employing the correlation rules and using the frequency measurements in Table 6, we can set up the following energy level diagram for the gaseous molecules.



V. PROPOSALS FOR FURTHER WORK

A rotational analysis of the ultraviolet spectrum would give us a moment of inertia which would be more conclusive in identifying the unknown molecule. Even on the high dispersion obtained here, however, the rotational structure was only partially resolved and attempts at a rotational analysis were unsuccessful. A study of the isotope shift would also give us additional information about the molecule. A third method to distinguish a monomer from a polymer is to study the intensities of the ultraviolet and green bands together under equilibrium vapor conditions, at constant temperature, but varying the thermodynamic activity of the solid MgO. The chemical equations are:



The thermodynamic relationship is:

$$\left\{ \frac{P_{^1\Sigma}(\text{activity 1})}{P_{^1\Sigma}(\text{activity 2})} \right\}_T = \left\{ \frac{P_{(\text{MgO})_x}(\text{activity 1})}{P_{(\text{MgO})_x}(\text{activity 2})} \right\}_T^{1/x}$$

or expressed in terms of intensities:

$$\left\{ \frac{I_{^1\Sigma}(\text{activity 1})}{I_{^1\Sigma}(\text{activity 2})} \right\}_T = \left\{ \frac{I_{(\text{MgO})_x}(\text{activity 1})}{I_{(\text{MgO})_x}(\text{activity 2})} \right\}_T^{1/x}$$

Comparing the intensities of the two band systems at different activities of the solid will give a value for x. The method described in previous sections could be used here again except that in this case we would vary the activity of MgO instead of the temperature. The problem would be to find substances which will dissolve solid MgO at higher temperatures but will not chemically react with it.

VI. THE HEAT OF SUBLIMATION OF TIN
AND THE DISSOCIATION ENERGY OF SnO

Introduction

Brewer and Mastick²⁰ have reviewed the data in the literature on the heat of formation of gaseous SnO and have combined this value with a value of the heat of sublimation of tin to obtain the heat of dissociation of the SnO molecules to the gaseous atoms. This value was found to be in close agreement with the linear Birge-Sponer extrapolation²¹ of the vibrational levels of SnO. Barrow and Drummond²² have recently reconsidered these calculations and by use of a lower heat of sublimation of tin have claimed that the data indicate a linear Birge-Sponer extrapolation to an excited tin state rather than to the ground state tin atom.

In an effort to resolve this difference the heat of sublimation of tin was redetermined by measurements of the vapor pressure using the Knudsen method. The vapor pressure of tin has been determined previously by Wartenberg,²³ Greenwood,²⁴ Harteck,²⁵ Ruff and Bergdahl,²⁶ and Granovskaya and Lyubimov.²⁷

Table 8 indicates the temperature ranges used in some of the previous investigations, the method of study, and the average heat of sublimation at 298°K derived from these results using free energy functions. Heats calculated from the vapor pressure data of Ruff and Bergdahl and Granovskaya and Lyubimov are 64 and 65 kcals. respectively. Of these previous determinations, all of the methods used except that by Harteck and Granovskaya and Lyubimov are subject to a very serious error because tin forms a volatile oxide SnO which is much more volatile than the metal.

Table 3

Investigator	Temperature Range °K	Method	Averaged ΔH in Kcal. ²⁹⁸
Von Wartenberg	1400-1640	Flow System	61
Greenwood	2240-2380	Observation of Boiling Point	65
Harteck	1300-1450	Knudsen	73

Thus any method which does not completely eliminate the presence of oxygen in the form of elemental oxygen or water or carbon dioxide is liable to give results which are much too high. Comparison of the results of Table 8 shows that the methods which do not rigorously eliminate oxygen do in fact give much too high vapor pressure. Harteck used an effusion method in vacuum which can avoid this error because the oxygen can be completely removed by evacuation. Since the Knudsen method appears to be the only one which is likely to give reliable results it was used also in this work.

Experimental

The apparatus and procedure described by Brewer and Mastick²⁹ were also used for this work. The Knudsen cell was made of graphite. For the lids, graphite, tantalum carbide and tantalum were used with varying hole sizes. The vapor pressure was determined by measuring the weight loss of the Knudsen cell after diffusion had proceeded for approximately two hours in the average run. The results are tabulated in Table 9.

The crucible covers in Runs 1 and 2 did not have knife-edge holes in them and consequently the flow of gas was restricted and lower pressures were observed with correspondingly higher heats.

The free energy functions used for these calculations were obtained from Brewer.²⁸ It was assumed that monatomic tin was the main gaseous species. The recent study of tin vapor in the mass spectrometer by Honig²⁹ would substantiate the assumption that monatomic tin is the main species. Averaging the results of Table 9 yields $\Delta H_{298}^{\circ} = 70 \pm 2$ kcal. for $\text{Sn}(s) = \text{Sn}(g)$. This new result agrees quite closely with that obtained by Harteck and is the same heat of sublimation of tin as that used by Brewer and Mastick.²⁰ Thus the validity of the

Table 9

Run	Temperature or °C	Head (in si. cu.)	Plate area (in sq. cm.)	Press. (atm.)	$-\left(\frac{\Delta T - \Delta H_{298}}{T}\right)$	ΔH_{298} (kcal.)
1	1556	C	.0314	1.94×10^{-5}	25.32	72.94
2	1601	C	"	4.70×10^{-5}	25.29	73.10
3	1753	TaO	.0377	9.02×10^{-4}	25.23	68.73
4	1720	Ta	"	3.51×10^{-4}	25.26	70.33
5	1543	Ta	"	5.93×10^{-5}	25.32	68.14
6	1683	Ta	"	2.87×10^{-4}	25.27	70.01
7	1582	Ta	.0804	2.83×10^{-5}	25.31	72.0
8	1688	Ta	"	2.05×10^{-4}	25.27	71.14

linear Birge-Sponer extrapolation²¹ for tin oxide is substantiated.

The Knudsen technique will give pressures lower than the equilibrium pressure only when the accommodation coefficient of the vaporizing specie is considerably lower than unity. The relationship between the actual pressure inside the cell and the true equilibrium pressure as given by:

$$P_{eq.} = P (1 + a/\alpha A),$$

where $P_{eq.}$ is the true equilibrium vapor pressure, P is the actual pressure, a the cross sectional area of the orifice, A the cross sectional area of the crucible, and α the accommodation coefficient. In runs 3, 4, 5 and 6, the ratio of hole to crucible area, a/A , was .02. In order to be off by a factor of two or more to the true equilibrium pressure the accommodation coefficient must be equal to or less than .02. The accommodation coefficient was checked by measuring the degree of bouncing of tin atoms off of a platinum collector plate. A negligible amount of tin was observed to bounce off. The accommodation coefficient, therefore, was considered to be close to unity and the actual pressure inside the cell must closely approach the true equilibrium vapor pressure.

Brewer and Mastick²⁰ have pointed out that the fourth group oxides appear to give very satisfactory linear Birge-Sponer extrapolations assuming that the extrapolations go to the ground atomic state. The present work reconfirms this for SnO. Also, as pointed out by Brewer,³⁰ recent work on GeO by Jolly and Latimer and work by Gilles and Wheatley on TiO have confirmed the validity of the linear Birge-Sponer extrapolations for these molecules. In every instance where data are available for fourth group oxides this extrapolation appears to work quite well.

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