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THERMODYNAMICS OF CHEMICAL LASER AND HIGH TEMPERATURE SPECIES

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Physical Chemistry Division
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National Bureau of Standards
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) This report (covering July 1974 through June 1975) gives summaries (a) for high-speed thermophysical measurements on hafnium, iron, tantalum, and molybdenum and (b) for an interpretation of the Raman spectra of PF ₅ , AsF ₅ , and VF ₅ . Details of these activities have been or are in the publishing process. In addition, this report includes two articles which are current and have not started the publication process. One is a study on the chemiluminescence of the Pb(g) + O ₃ (g) reaction, and the		

20. other is a review of the literature for dissociation energies of diatomic oxides and fluorides relevant to chemical lasers in the visible region. Finally, some related bibliographies on chemical kinetics are indicated.

FOREWARD

Structure, propulsion, and guidance of new or improved weapons delivery systems are dependent in crucial areas of design on the availability of accurate thermodynamic data. Data on high-temperature (including exhaust ions) are, in many cases, lacking or unreliable. A broad integrated research program at the National Bureau of Standards has supplied new or more reliable thermodynamic properties essential in several major phases of current propulsion development and application. Measured were compounds of those several chemical elements important in efficient propulsion fuels; those substances most affecting ion concentrations in such advanced propulsion concepts as ion propulsion; and the transition and other refractory metals (and their pertinent compounds) which may be suitable as construction materials for rocket motors, rocket nozzles, and nose cones that will be durable under extreme conditions of high temperature and corrosive environment. The properties determined extend in temperature up to 6000 degrees Kelvin. The principal research activities were experimental, and involved developing new measurement techniques and apparatus, as well as measuring heats of reaction, of fusion, and of vaporization; specific heats; equilibria involving gases; several properties from fast processes at very high temperatures; infrared spectra, matrix-isolation, microwave, and electronic types; and mass spectra. Some of these techniques, by relating thermodynamic properties to molecular or crystal structures, make it possible to tabulate reliably these properties over far wider ranges of temperature and pressure than those actually employed in the basic investigations. Additional research activities of the program have involved the critical review of published chemical-thermodynamic (and some chemical-kinetic) data, and the generation of new thermochemical tables important in current chemical-laser research.

ABSTRACT

This report (covering July 1974 through June 1975) gives summaries (a) for high-speed thermophysical measurements on hafnium, iron, tantalum, PF_5 , AsF_5 , and VF_5 . Details of these activities have been or are in the publishing process. In addition, this report includes two articles which are current and have not started the publication process. One is a study on the chemiluminescence of the $\text{Pb}(\text{g}) + \text{O}_3(\text{g})$ reaction, and the other is a review of the literature for dissociation energies of diatomic oxides and fluorides relevant to chemical lasers in the visible region. Finally, some related bibliographies on chemical kinetics are indicated.

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1. HIGH-SPEED THERMOPHYSICAL MEASUREMENTS

Summary

Investigations performed during FY 75 using the millisecond-resolution pulse calorimeter are summarized in the following paragraphs.

(a) Measurements were performed of heat capacity, electrical resistivity, and hemispherical total emittance of hafnium (containing 3.12 wt. % zirconium) in the temperature range 1500 to 2400 K. Also, measurements were made of the temperature and energy of solid-solid (hexagonal close-packed to body-centered cubic) phase transformation in hafnium. The transformation temperature was measured to be 2012 K (hafnium has the highest temperature for known solid-solid phase transformations in metals). The transformation energy was measured to be $5900 \text{ J}\cdot\text{mol}^{-1}$. The measurements indicated decreases in heat capacity (by about 13%) as the result of solid-solid phase transformation. The results on heat capacity are published, Reference [1]; a paper on transformation data is in preparation.

(b) Measurements were performed of the radiance (brightness) temperature (at $0.65 \mu\text{m}$) of iron and tantalum at their respective melting points. The results yielded the values 1670 K for iron and 2846 K for tantalum. These data in conjunction with the melting points are used to obtain normal spectral emittance (at $0.65 \mu\text{m}$) of the two metals: 0.36 for iron, 0.37 for tantalum. A paper describing the work on iron is in press, Reference [2]; a paper on tantalum is in preparation.

(c) Heat capacity of molybdenum in the range 1500 to 2800 K was measured as a part of the Standard Reference Materials Program. The results are in good agreement (within 1%) with those obtained earlier by drop calorimetry in the overlapping temperature range (1500 to 2100 K). The combination of the drop and pulse calorimetry results in the range 300 to 2800 K will yield the certification of molybdenum as a heat capacity standard reference material.

References:

- [1] Cezairliyan, A. and McClure, J. L. Simultaneous measurements of specific heat, electrical resistivity, and hemispherical total emittance by a pulse heating technique: hafnium-3 (wt. %) zirconium, 1500 to 2400 K. J. Res. Nat. Bur. Stand. (U.S.), 79A (Phys. and Chem.), 431 (1975).
- [2] Cezairliyan, A. and McClure, J. L. Radiance temperature (at 653 nm) of iron at its melting point. J. Res. Nat. Bur. Stand. (U.S.), 79A (Phys. and Chem.), in press.

2. POTENTIAL FUNCTIONS FOR THE ν_7 VIBRATION OF PENTAFLUORIDES

Stanley Abramowitz, Lawrence S. Bernstein^{**},
Janice J. Kim^{*}, Kenneth S. Pitzer^{*}, Ira W. Levin^{***}

This collaborative approach to the interpretation of the high resolution Raman spectra of some pentafluorides has resulted in the estimation of barriers to fluorine atom interchange for PF_5 , AsF_5 , and VF_5 . A two dimensional harmonic oscillator basis set and a potential of the form

$$V(\rho, \theta) = (1/2)a^2 - b \cos(3 \theta)\rho^3 + c\rho^4$$

was used to interpret the observed spectra. The work on PF_5 has been published (3). A complete paper on AsF_5 and VF_5 containing more of the methodology and theory as well as parametric tables for other workers in the field is being prepared.

Our estimates of the barriers for fluorine atom interchange range between 995 to 1139 cm^{-1} , 755 and 864 cm^{-1} , and 478 and 539 cm^{-1} for PF_5 , AsF_5 , and VF_5 respectively (1 $\text{cm}^{-1} = 11.96 \text{ J/mol}$).

Reference:

L. S. Bernstein, J. J. Kim, K. S. Pitzer, S. Abramowitz, I. W. Levin, J. Chem. Phys. 62, 3671 (1975).

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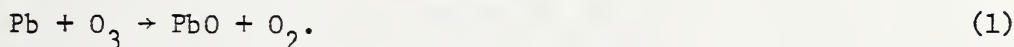
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3. A STUDY ON THE CHEMILUMINESCENCE OF THE $\text{Pb}(\text{g}) + \text{O}_3(\text{g})$ REACTION

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Introduction

The results of our recent studies on laser enhanced reactions have shown that vibrational energy in a reactant molecule can reappear as excitation in a product species. For example, emissions from both NO_2^* and SO_2^* produced in the reactions of NO and SO with O_3 were observed² to shift to shorter wavelength when the O_3 was vibrationally excited using a CO_2 laser^{1,2}. Because of the spectroscopic complexities of the triatomic molecules, NO_2 and SO_2 , our intention in the present study was to investigate a chemiluminescent reaction producing a diatomic product which would be, in principle, easier to characterize spectroscopically. The metal atom-oxidant systems represent a class of such reactions. A significant number of these have been investigated to date because of their potential as chemical lasers. We report herein some observations on the reaction



While the information obtained from studying the infrared laser enhanced reaction component is minimized by the overall reaction complexity, it does nevertheless provide some additional insight into this reaction system. This information coupled with new high pressure spectroscopic results complement the detailed low pressure investigation by Oldenborg, Dickson, and Zare (ODZ)³.

Experimental

The furnace, reaction cell, fast flow pumping system, CO_2 laser, and spectrometer are shown schematically in Fig. 1. Lead vapor, produced from a resistively heated crucible containing lead metal enters the glass reaction chamber in an Ar diluent stream. The 4% O_3 in O_2 effluent from a commercial O_3 generator is mixed with Ar and flows past the cell windows (to eliminate window deposits) into the cell. There it diffusively mixes with the lead-argon flow. The temperature of the crucible (as measured by a thermocouple probe) ranges from 900-1000 K while the temperature in the flame reaction zone varies from 500-600 K. The total pressure in the cell varies from 1 to 5 torr with the flow through the furnace being anywhere from 20 to 50% of the total flow.

The 0.5 cm diameter beam from a CO₂ laser tuned to the 9.6 μm P(30) transition is square wave chopped and traverses the flame exciting ν₃, the asymmetric stretching mode of O₃ (1043 cm⁻¹). The chemiluminescence from the Pb + O₃ reaction is monitored through a spectrometer-photomultiplier assembly. The photomultiplier output is fed through a series of pulse amplifiers and voltage discriminator into a dual counter, one channel of which records the "laser-on" signal and the other the "laser-off". A printout from these counters is synchronized with the spectrometer wavelength-scan-drive thereby facilitating the recording of the modulation spectrum vs wavelength. The normal spectral ("laser-off") emission is automatically obtained from the "laser-off" counter.

Results

In contrast to the spatially sharp diffusion flame observed for the Ba + O₃ (or N₂O) reaction, the Pb - O₃ flame is quite diffuse (apparently reaction limited). It is brightest in the high temperature zone at the furnace nozzle, diminishes with decreasing temperature (increasing distance from the nozzle), and persists for some two to three feet into the pumping system. These observations suggest a reaction rate for Pb + O₃ which is considerably slower than gas kinetic. The spectrum which we observe at several torr total pressure partly resembles the low pressure spectrum obtained by ODZ and reproduced by us in a similar quasi-beam apparatus. The short wavelength end of the more complete spectrum (Fig. 2) can be identified from the low (submicron) pressure spectrum in that it is less diffuse. The long wavelength portion between 480 nm and 595 nm is almost entirely the new a state recently characterized by ODZ. At still longer wavelengths, our spectrum differs from that of ODZ in that we observe a series of strong lines which do not agree with a → X, A → X, or B → X, but rather appear to originate from a new state observed via six weak lines by ODZ and identified as b by them. This b state is seen more intensely in our high pressure spectrum. This series of lines in our spectrum can be fit to the expression:

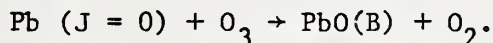
$$\nu(\nu', \nu'') = 16315 + 441.0 \nu' - \{717.7 \nu'^2 - 3.53 \nu''^2\}$$

where the lower state constants have been taken from Rosen's compendium.⁴

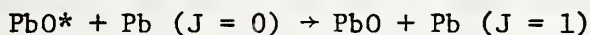
A definite vibrational assignment for an electronic state, for which a rotational analysis has not been observed, requires the measurement of a vibrational isotope shift. Lacking data of this type one tries to assign band heads such that both (0,ν'') and (ν',0) levels are observed. The assignment hypothesized by ODZ on the basis of six observed transitions in a (ν',0) transition has placed T₀₀ of the b state about one vibrational quanta above T₀₀ of the a state. In this study 20 band heads have been observed that can be assigned to b state. In addition to the (ν',0) band heads, other bands have been

observed with $v'' = 1, 2, 3, 4, 5$. The hypothesis regarding the separation of the a and b states is supported by arguments given later.

Although considerable emission intensity is observed for the $B \rightarrow X$ transition, the production of this state lies above the thermodynamic threshold for the reaction



Oldenberg and Zare have suggested that production of this state results from reaction of Pb (J = 1) present in their experiments due to an electric discharge in their furnace. The strong $B \rightarrow X$ emission observed in our high pressure experiment was found to vary markedly with the oven temperature. The observed $B \rightarrow X$ emission increase over that emission from either a or $b \rightarrow X$ with increasing temperature obeyed an Arrhenius-type formulation with an activation energy of some 10 kcal (i.e. nearly equal to the energy difference between $J = 0$ and $J = 1$ multiplet components of Pb). This observation suggests that Pb (J = 1) is produced thermally in our furnace as opposed to its possible production via secondary processes, eg.



If PbO(B) is indeed produced through reaction of Pb (J = 1) with ozone, the rate of this reaction must be extremely fast to compete with the deactivation process



since the deactivation proceeds with a high rate constant and the O_2 pressure is twenty times that of O_3 under our usual experimental conditions.

Part of the modulation spectrum is reproduced in Fig. 3. This spectrum represents only that component of the chemiluminescent emission which varies with the laser excitation of O_3 (i.e. only that component which either increases or decreases due to a change in reaction rate with reactant vibrational excitation). Thus, if the emission originated only from a single electronic state, the modulation spectrum would appear as a quasi-continuum with possibly some small structure due to sharp changes in population of one vibrational line relative to an adjacent one. The large amount of structure in Fig. 3 indicates the presence of emission from at least two electronic states. One might speculate that at the longer wavelength, where the normal spectrum consists mainly of a and b emission lines, this modulation structure could reveal an increase or decrease of b emission lines relative to a emission lines (or vice versa). However, the peaks (or valleys) in the modulation spectrum do not agree well with either a or b state emission lines. More surprisingly, they agree much better with $A \rightarrow X$ transitions. We therefore tentatively identify the modulation spectrum as a quasi continuum due to $a \rightarrow X$ and $b \rightarrow X$ emissions at long wavelengths

(possibly some $B \rightarrow X$ at short wavelength) with structure due to $A \rightarrow X$ emission lines superimposed throughout the entire wavelength range. This suggests that vibrational excitation in O_3 increases the production of the a, b, and possibly the B state of PbO all to some small degree, while increasing A state production most significantly. We must emphasize, however, that the assignment of A state responsibility for structure in the modulation spectrum is tentative since the modulation data are difficult to obtain, require long integration times, and should be obtained in the low (submicron) pressure region where only the a and B states have been observed. Nevertheless, we can speculate on the production of PbO (A) in the laser excited reaction. It is possible that as a result of laser excitation of O_3 forming O_3^+ the reaction with Pb ($J = 1$) now produces PbO (B) in higher vibrational levels. These can then be collisionally transferred to the A state which is seen in emission. A second equally likely possibility is that the vibrational energy in O_3 increases the rate of A state production directly at the expense of one or more of the other reaction channels.

From the numerical value of the percent modulation in the laser experiments (i.e. the continuum region assigned to a and b state enhancement) we can calculate a rate constant enhancement of approximately a factor of two. This is obtained by comparing the percent modulation of both the $Pb + O_3^+$ and $NO + O_3^+$ reactions in this apparatus under identical experimental conditions.

We can obtain a very rough estimate of the quantum yield of a and b state production in the following manner. First we assume the reaction of O_3 with Pb ($J = 1$) funnels entirely into PbO (B), (i.e. quantum yield of unity). From Fig. 2 we see that the a + b emission intensity is comparable to the intensity of PbO (B). However, at the oven temperature of 1000 K only 1 part in 10^5 of the Pb atoms are in $J = 1$. This would imply a quantum yield of a + b due to Pb ($J = 0$) of about 10^{-5} assuming Pb ($J = 0$) and Pb ($J = 1$) reacted with O_3 with the same rate constant. The observation of the decay of chemiluminescence over several feet in our flow tube points to a slow rate of reaction for Pb ($J = 0$) while the fact that the reaction of Pb ($J = 1$) must compete favorably with its deactivation channels speaks for a very fast (collision frequency) rate of reaction for Pb ($J = 1$). Assuming a reaction efficiency of 10^{-2} for the Pb ($J = 0$) reaction in the spectrometer observation zone increases the quantum yield for a + b state production by a factor of 100 to 10^{-3} . We compare this to the ODZ upper limit of 10^{-2} obtained under the assumption of a fast reaction rate for Pb ($J = 0$). A slower reaction rate would unfortunately raise their quantum yield (in greater disagreement with our 10^{-3} estimate). However our observation of a large luminescent region is not necessary contradictory to ODZ's estimate of a fast reaction rate because of the different temperature regions of the two studies. In the quasi-beam configuration, Pb exits the furnace at very high temperature (>1000 K) and collides with O_3 with much higher kinetic energy than in our high pressure experiments

(kinetic energy of 600 K at the nozzle tip and decreasing rapidly to 400 K downstream of the mixing zone).

Conclusions

The low lying valence states of the Group IV oxides can be represented by the following molecular orbital configurations:

$$\sigma^2 \pi^4, 1_{\Sigma}^+ \quad (1)$$

$$\sigma \pi^4 \pi^*, 3_{\pi}, 1_{\pi} \quad (2)$$

$$\sigma^2 \pi^3 \pi^*, 3_{\Sigma}^+, 3_{\Delta}, 3_{\Sigma}^-, 1_{\Sigma}^-, 1_{\Delta}, 1_{\Sigma}^+ \quad (3)$$

The 3_{π} and 3_{Σ}^+ are the lowest energy states resulting from configurations 2 and 3 respectively. Oldenberg et. al. have determined that (unlike CO where the order is reversed) the 3_{Σ}^+ is lower in PbO. For Hund's case c coupling the 3_{Σ}^+ has an 0^- and 1_{Σ} component while the 3_{π} has 0^- , 0^+ , 1 and 2 components and the 1_{Σ}^+ has an 0^+ configuration. Only the 0^+ and 1 are dipole permitted transitions to the 0^+ ground state.

The splitting of the 0^- and 1 components is due to the second order spin-orbit interaction and therefore proportional to the square of the spin-orbit integrals. Assuming molecular integrals will scale with the atomic spin-orbit parameters, the splitting in the case of SnO would be an order of magnitude less than the value for PbO while GeO is about two orders of magnitude less.

Oldenberg et. al. identify the two (0^- , 1) components of the 3_{Σ}^+ as b and a respectively. This identification which can be made by the relative intensity of the a and b transitions is also consistent with theoretical considerations. Theory predicts that the 0^- component of the 3_{Σ}^+ state is at a somewhat higher energy than the 1 component. There are two mechanisms which could give intensity to the dipole forbidden $b \rightarrow X$. As J increases the rotational coupling between the a and b state increases and one expects to see the Q branches of the $b \rightarrow X$ transition in addition to the P, Q, and R branches of the $a \rightarrow X$ transition. However it turns out that for large spin-spin splitting the coupling has only a slight effect even for J as large as 100 (one expects the most probable value of J to be 24 for T = 500 K).

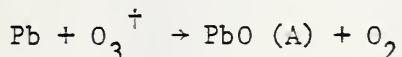
The intensity of the b transition may also arise from electronic-rotation coupling with the 1 component of the 3_{π} state. This effect goes as $8 B J (J + 1) / \Delta E$ where ΔE is the difference in the electronic energies of the two states and B is the rotational constant. Since $\Delta E \sim 5000 \text{ cm}^{-1}$ and $T \sim 500 \text{ K}$ this effect is expected to be large and the states are significantly mixed. In order to treat this problem correctly all states arising from the 3_{Σ}^+ and 3_{π} representations

have to be considered. It seems likely that the b state transition probability would increase with temperature.

In this connection one should also consider the ${}^3\Pi \rightarrow {}^3\Sigma^+$ transitions. These are allowed transitions for both Hund's cases a and c and should have significant intensity even though they are in the infrared ($\sim 5000 \text{ cm}^{-1}$). One might expect that their intensity would be about the same as the observed $a \rightarrow X$ and $b \rightarrow X$ transitions.

Our observations at high pressures are somewhat different from those of Oldenberg et. al. In particular, we find more intensity in the b state than they did. Their experiment was done under beam conditions. The spectral observations were made before collisions took place. In our case many collisions can occur before the observation of the emitted light. We also observed that the B state emission (the l component of the ${}^3\Pi$) is more intense at high Pb temperatures.

Several tentative explanations of the differences between the Oldenberg et. al. and our results can be advanced. It is possible that under beam conditions only the lower (or even lowest) J state of PbO is formed. This would lead to very small mixing of the b (${}^3\Sigma^+$) state with the B (${}^3\Pi$) state and would lead to a low observed intensity. Another possibility is pressure induced emission. The a state may couple more strongly to the b state at the high pressures used in our experiments, or alternatively pressure may enhance B - b transitions which would result in a greater observed intensity for the b state. The observation of the apparent formation of the A state from the reaction of



is also not easy to explain. In order to further unravel these questions, additional experiments must be carried out in conjunction with a more extensive theoretical investigation of the Group IV oxides.

Table 1. Observed Band Heads and Assignments

v(obs)	v(calc)	assignment
24143	24116	B (4,0)
23590	23640	B (3,0)
22392	23402	B (4,1)
23170	23157	B (2,0)
22957	22926	B (3,1)
22636	22665	B (1,0)
22457	22443	B (2,1)
22178	22166	B (0,0)
21954	21951	B (1,1)
21636	21660	b (12,0)
21474	21452	B (0,1)
21169	21211	b (11,0)
]1079	21065	B (5,5)
20877	20870	a (11,0)
20721	20745	B (0,2)
20614	20616	B (4,5)
20442	20445	a (10,0)
20338	20314	b (9,0)
20149	20156	a (11,1)
20024	20014	a (9,0)
19904	19867	b (8,0)
19743	19731	a (10,1)
19585	19578	a (8,0)
19467	19449	a (11,2)
19128	19138	a (7,0)
19015	19023	a (10,2)
18688	18692	a (6,0)
18515	18530	b (5,0) Sh.
18305	18323	a (10,3)
18238	18241	a (5,0)
17986	17978	a (6,1)
17790	17785	a (4,0)
17615	17630	a (10,4)
17535	17527	a (5,1)
17319	17325	a (3,0)
17212	17199	b (2,0)
17108	17052	b (8,4)
17033	17108	b (5,2)
16915	16853	b (6,3)
16858	16859	a (2,0)

v(obs)	v(calc)	assignment
16773	16757	b (1,0)
16614	16664	b (4,2)
16488	16485	b (2,1)
16434	16367	b (10,5)
16297	16315	b (0,0)
16215	16220	b (3,2)
16108	16160	b (6,4)
15773	15778	b (2,2)
15623	15601	b (0,1)
15672	15715	b (5,4)
15363	16335	b (1,2)

The calculated ν have been generated from a least squares treatment of the observed data using Rosen's constants for the X state. The generating equations are:

$$a. \nu_{(\nu', \nu'')} = 15912 + 478.4 \nu' - 2.5 \nu'^2 - \{717.7 \nu''^2 - 3.53 \nu''^2\}$$

$$b. \nu_{(\nu', \nu'')} = 16315 + 414.0 \nu' - \{717.7 \nu''^2 - 3.53 \nu''^2\}$$

$$B. \nu_{(\nu', \nu'')} = 22166 + 502 \nu' - 3.8 \nu'^2 - \{717.7 \nu''^2 - 3.53 \nu''^2\}$$

Table 2. Observed Band Heads for the Modulated Spectrum

$\nu(\text{obs.})$	$\nu(\text{calc})$	ν'	ν''
17592	17599.3	0	3
18319	18299.3	0	2
19015	19006.4	0	1
19708	19720.6	0	0
18005	18041.	1	3
18748	18741.	1	2
17765	17789.3	2	4
18470.	18482.3	2	3
19216	19182.4	2	2
19885	19889.5	2	1
20644	20603.6	2	0
18925	18923.2	3	3
19611	19623.3	3	2
20350	20330.4	3	1
17972	17984.9	4	5
18642	18670.8	4	4
19384	19363.8	4	3
20064	20063.8	4	2
20773	20770.9	4	1
21463	21485.1	4	0
19826	19803.9	5	3
20517	20504.	5	2
21191	21211.1	5	1
18783	18864.8	6	5
19554	19550.7	6	4
20226	20243.7	6	3
20947	20943.8	6	2
21737	21650.9	6	1
20024	19990.1	7	4
18493	18392.5	8	7
19015	19064.3	8	6
20434	20429.1	8	4
18854	18831.	9	7
19497	19502.9	9	6
17940	17946.8	10	9
18573	18604.5	10	8
19271	19269.2	10	7
19964	19941.1	10	6
20584	20619.9	10	5
21350	21305.9	10	4

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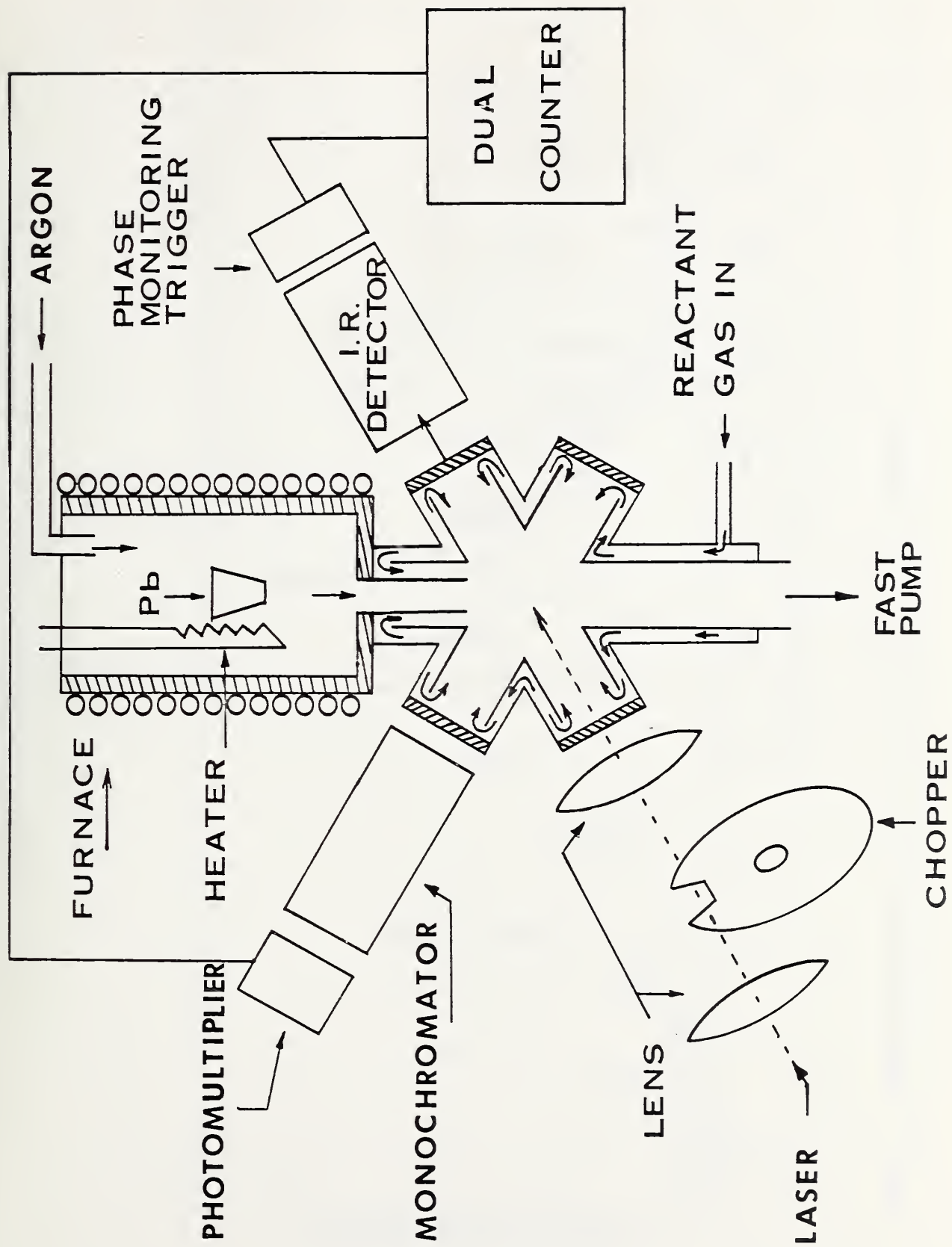


Figure 1. Schematic of the chemiluminescence flow reaction apparatus.

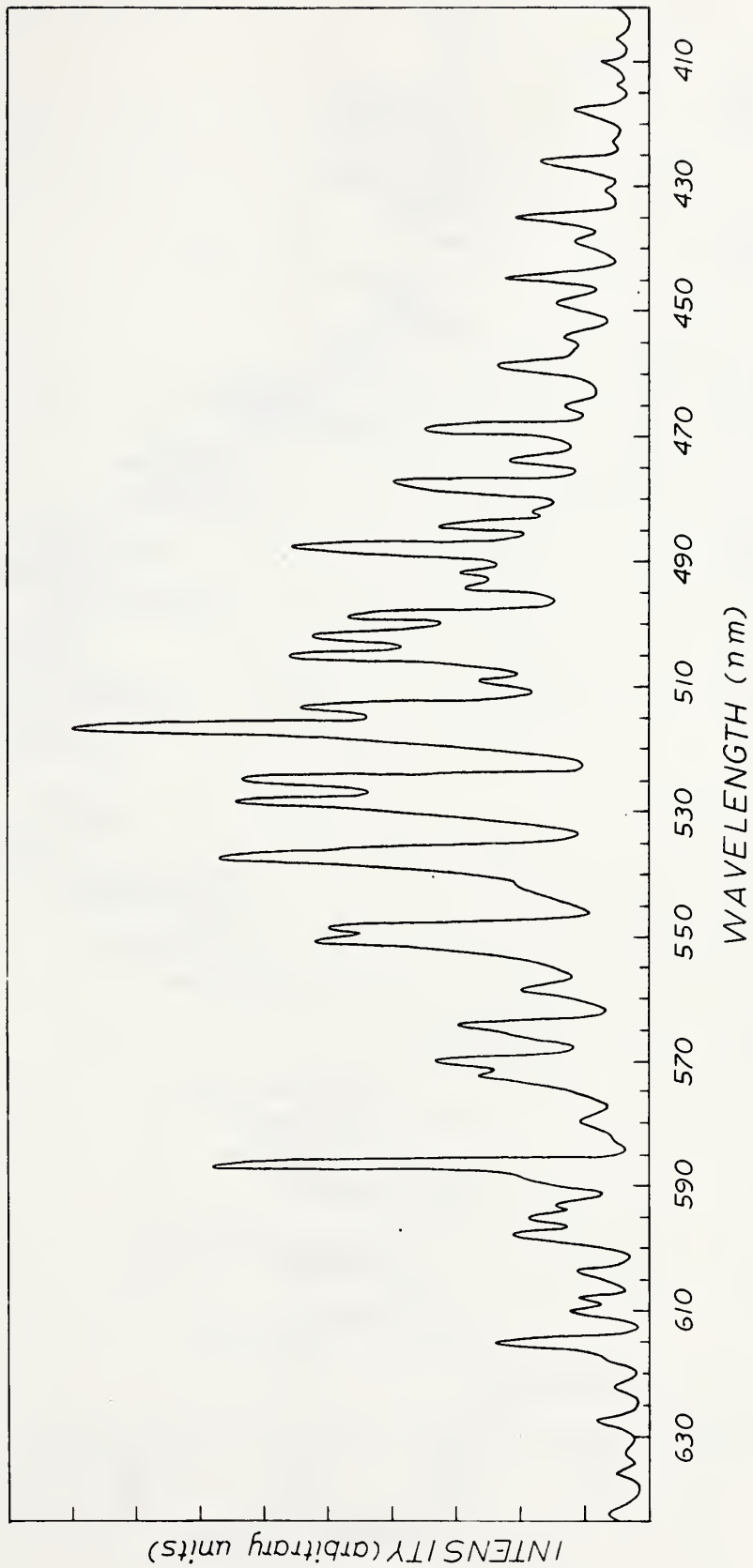


Figure 2. Chemiluminescence Spectrum from the $\text{Pb(v)} + \text{O}_3$ reaction.

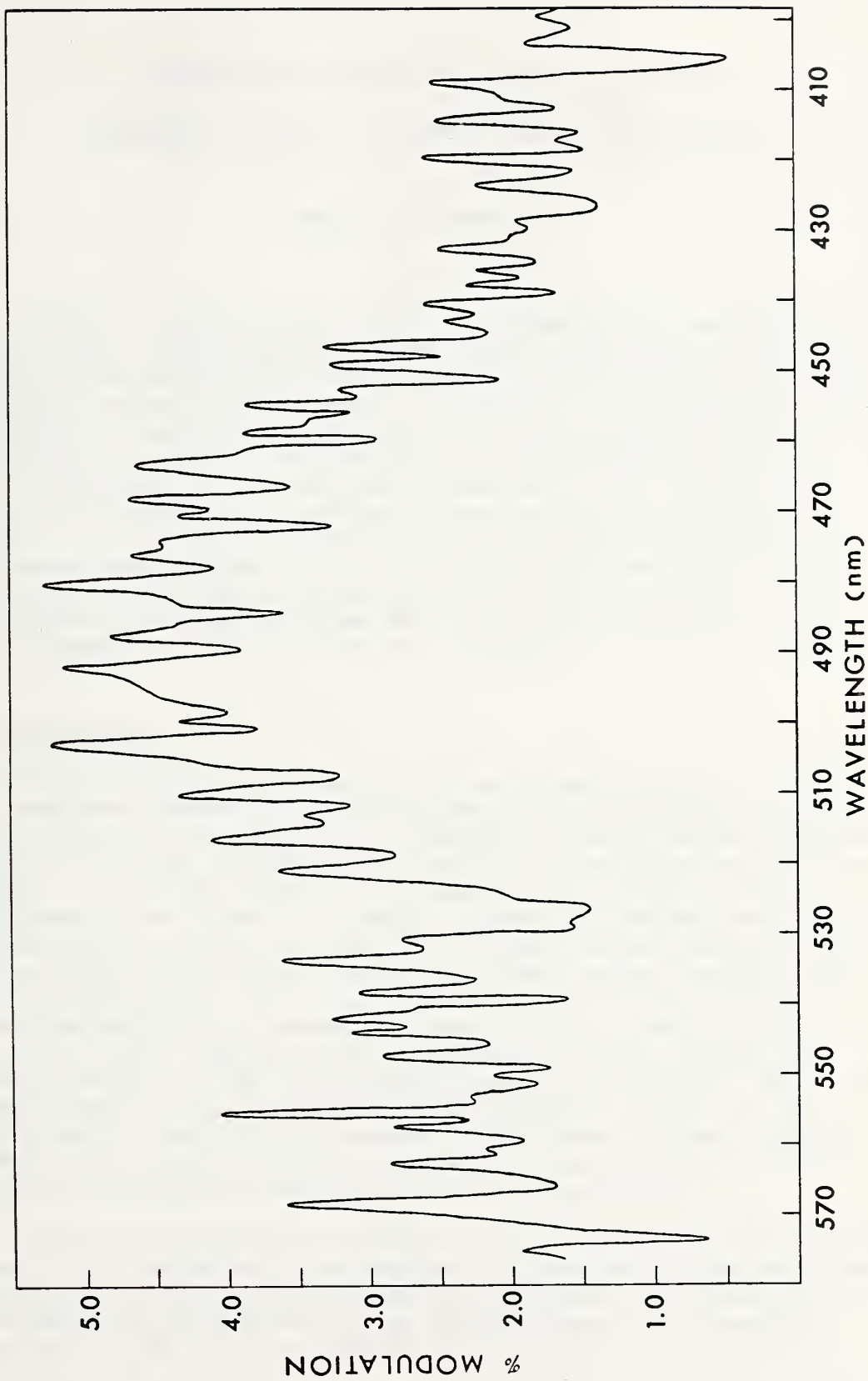


Figure 3. Modulation Spectrum (the component of the emission which varies with laser excitation of O_3). This spectrum has been smoothed.

4. DISSOCIATION ENERGIES OF DIATOMIC MOLECULES RELEVANT TO CHEMICAL LASERS IN THE VISIBLE REGION

Ralph F. Krause, Jr.

Selected values of the ground state dissociation energies of diatomic oxide and fluoride molecules which are relevant to chemical lasers in the visible region are assembled from the literature. When an alkaline-earth, scandium group, rare-earth, or group IVA atom has a bimolecular reaction with a certain oxidizer (O_2 , O_3 , N_2O , or F_2), the enthalpy change to form the corresponding diatomic molecule may be equivalent to an electronic transition in the visible region. Most of these molecules have already been the subject of recent reviews; so no attempt was made to duplicate those reviews which provide established values. The results of equilibrium studies which have subsequently been published are included for comparison. In those cases which appear unclear even previously published studies are examined, and revised values are presented.

I. Introduction

Most of the diatomic oxide and fluoride molecules of interest here have been subject to recent reviews in the literature. In a recent report [1] the dissociation energies of the scandium group and rare-earth diatomic oxides were evaluated from published equilibrium studies. In table 1 values of the dissociation energies of the alkaline-earth and group IVA diatomic oxides are compared among several compilations [2, 3, 4, 5, 6, and 7]. The most recent among these are the new JANAF Tables [7] of the alkaline-earth oxides for which the new assignments [27] of the electronic states have been used. Table 2 covers the selections of several reviews on all of the fluorides of interest here. Again the JANAF Tables [7] seem to provide the latest values, this time for the alkaline-earth fluorides. Most of the values selected by the JANAF Tables and reference 1 appear to be established at least for the present. Since these reviews were performed, some other equilibrium studies have been published. Their results are included in the present work for comparison.

In the case of those molecules which are missing from the JANAF Tables [7] or reference 1, the relevant equilibrium studies are examined, and values of dissociation energies are appropriately documented. These molecules include some of the scandium group and rare-earth fluorides and the group IVA oxides and fluorides.

Table 1. Comparison of Values^a of Dissociation Energies of Alkaline-Earth and Diatomic Oxides Compiled by Various Reviews

Molecule	D_0° (kJ/mol)					JANAF ^b (ref 7)
	Gaydon (ref 2)	Brewer and Rosenblatt (ref 3)	Rosen (ref 4)	Wagman et al. ^b (ref 5)	Suchard (ref 6)	
MgO	396 ± 60	326 ± 30	339.1	376.5	401 ± 13	335.8 ± 25
CaO	415 ± 70	347 ± 30	382.0 ± 5.7	378.5	415 ± 68	380.5 ± 21
SrO	405 ± 60	385 ± 25	415	422.0 ^c	≥550	422.7 ± 17
BaO	555 ± 15	548 ± 25	545.5 ± 25	546.2 ^c	≥550	548.4 ± 10
SiO	781 ± 30	798.7 ± 8	764.8 ± 13	798.7	764.8 ± 13	794.7 ± 9
CeO	654 ± 8	656.5 ± 13	654 ± 6	666.5	654 ± 8	
SnO	521 ± 7	527 ± 8	529.1 ± 8		521 ± 7	
PbO	373 ± 5	370 ± 8	369.8 ± 6		373 ± 5	370.7 ± 7

^aConversion factors are 4.184 J/cal, 96.48 kJ·mol⁻¹·eV⁻¹, or 11.96 J·mol⁻¹·cm.

^bValues of D_0° were calculated from values of ΔH_f° for M(g), O(g), and MO(g) given by source.

^cAt 298.15 K.

Table 2. Comparison of Values of Dissociation Energies of Diatomic Fluorides Compiled by Various Reviews

Molecule	$D_0^{\circ}/(\text{kJ/mol})$					
	Gaydon (ref 2)	Zmbov et al. ^{a,c}	Rosen (ref 4)	Wagman et al. ^b (ref 5)	Suchard (ref 6)	JANAF ^b (ref 7)
MgF	440 ± 10	-	458 ± 22	444.7	440 ± 10	446.2 ± 6
CaF	525 ± 20	-	529 ± 7	525.6	534 ± 11	526.8 ± 9
SrF	526 ± 10	-	538 ± 8	532.1 ^c	526 ± 10	533.9 ± 9
BaF	560 ± 10	-	584 ± 7	582.0	560 ± 10	577.0 ± 10
ScF	480 ± 100	590	585 ± 13	591.	585	-
YF	-	610	596.6 ± 21	634.2	596.6 ± 21	-
LaF	-	(600 ± 50) ^d	-	-	-	-
CeF	-	(580 ± 50)	-	-	-	-
PrF	-	(580 ± 50)	-	-	-	-
NdF	540 ± 10	550	545 ± 12	565.6 ^c	567 ± 13	-
PmF	-	(540 ± 50)	-	-	-	-
SmF	-	530	527 ± 19	549.3 ^c	527 ± 19	-
EuF	-	530	523 ± 17	547.2 ^c	523 ± 17	-
GdF	-	590	586 ± 17	648. ^c	-	-
TbF	-	(560 ± 50)	527 ± 18	-	-	-
DyF	-	530	527 ± 18	549.3 ^c	-	-
HoF	-	550	542.4 ± 12	559.7 ^c	-	-
ErF	-	570	568 ± 17	584.4 ^c	-	-
TmF	-	(570 ± 50)	-	-	-	-
YbF	-	(570 ± 50)	-	-	-	-
LuF	-	(570 ± 50)	-	-	-	-
SiF	480 ± 50	565	541.7 ± 12	524	480 ± 50	544 ± 11
GeF	480 ± 100	502	481.4 ± 19	484.2	480	-
SnF	380 ± 140	477	377	-	461 ± 13	-
PbF	290 ± 50	356	352 ± 8	-	290 ± 50	351.3 ± 11

^aValues for the scandium group and rare-earth fluorides are from ref. 8, and values for the group IVA fluorides are from ref. 25.

^bSee footnote b of Table 1.

^cAt 298.15 K.

^dParentheses denote an estimate.

II. Sources and Evaluation of Data

1. BaO

Two independent groups of investigators [28, 29] have recently studied the vaporization of BaO(s). They both used mass-spectrometry on the vapor effusing from Knudsen cells. Using JANAF Tables [7], comparable results were obtained as follows:

Temperature Range	$\Delta H_0^\circ(\text{subl})/(\text{kJ/mol})$		$D_0^\circ/(\text{kJ/mol})$		Reference
	2nd law	3rd law	2nd law	3rd law	
1332-1681	439.3 ± 16	432.6	537.0	543.7	28
1643-1803	436.3 ± 8	428.7	540.0	547.6	29

The third law value of $D_0^\circ(\text{BaO})$ from reference 29 confirms the selection made earlier by JANAF [7], but all of the values agree within their uncertainties. Farber and Srivastava [29] took the close agreement between their 2nd and 3rd law values as proof of the assignment of electronic states [27] which were adopted by JANAF [7] for the derivation of the Gibbs free energy functions of BaO(g).

2. CaF, SrF, and BaF

Menzinger [30] calculated lower limits to the ground state dissociation energies from his electronic chemiluminescent studies on alkaline-earth atoms reacting with fluorine. He obtained $D_0^\circ \geq 537, 533,$ and 592 kJ/mol , respectively, for CaF, SrF, and BaF. These results indicate that the values selected by JANAF [7] for $D_0^\circ(\text{CaF})$ and $D_0^\circ(\text{BaF})$ may be a little low.

3. YO

Liu and Wahlbeck [31] measured the vapor pressure of $\text{Y}_2\text{O}_3(\text{s})$ from 2342 to 2614 K by Knudsen rate of effusion and mass spectrometry. They calculated values for $D_0^\circ(\text{YO})$ from these methods to be (716.7 ± 5) and $(712.5 \pm 8) \text{ kJ/mol}$, respectively, which confirm within their uncertainties the value selected by reference 1.

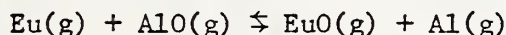
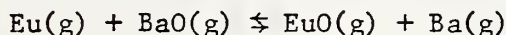
4. NdO

Tetenbaum [32] studied the vaporization of $\text{Nd}_2\text{O}_3(\text{s})$ from 2155 to 2485 K by transpiration, using controlled partial pressures of oxygen. He determined ΔH_0° for the assumed reaction, $\text{Nd}_2\text{O}_3(\text{s}) \rightleftharpoons 2 \text{NdO}(\text{g}) + 1/2 \text{O}_2(\text{g})$, to be $(1510.8 \pm 4.6) \text{ kJ/mol}$. Using the thermofunctions cited in reference 1 gives $D_0^\circ(\text{NdO})$ to be 721 kJ/mol which is about 3 kJ/mol less than that obtained earlier [1] for the above assumed reaction,

but the value 695 kJ/mol was adopted [1] as a compromise on the ambiguous presence of NdO₂(g) in the vapor phase.

5. EuO

Hildenbrand [33] has studied the vapor equilibrium for the following two reactions from 2000 to 2250 K by mass spectrometry:



He determined 2nd and 3rd law values of ΔH_0° to be (92 ± 10) and (77 ± 11) kJ/mol, respectively, for the first reaction, and (43 ± 12) and (50 ± 11) kJ/mol, respectively, for the second reaction. Using 548 kJ/mol [7] for $D_0^\circ(\text{BaO})$ and 508 kJ/mol [38] for $D_0^\circ(\text{AlO})$ gives an average value for $D_0^\circ(\text{EuO})$ of (462 ± 11) kJ/mol, considerably lower than the 544 kJ/mol adopted earlier [1]. Dickson and Zare [34] calculated $D_0^\circ(\text{EuO}) \geq 550$ kJ/mol from their chemiluminescent study of the reaction between Eu(g) and F₂(g), but Hildenbrand [33] reported that this data [34] could be interpreted to yield a lower limit of 473 kJ/mol. For the present the value for $D_0^\circ(\text{EuO})$ is ambiguous.

6. ScF, YF, NdF, SmF, EuF, GdF, DyF, HoF, ErF, SiF, GeF, and SnF

Values of D° for these diatomic fluorides were calculated from published enthalpy changes as shown in Table 3. Mass spectrometry has been used to study the vapor equilibria of various isomolecular reactions [9, 14, 15, 19, 24, 25, and 26]. In these studies the ratio of ion-intensities (I^+/T) have been plotted versus $1/T$, and 2nd law values of ΔH° were obtained from $-R[d(\ln K_p)/d(1/T)]^*$, for which the ratio of cross sections were assumed to cancel. Only in the cases of SiF and GeF were 3rd law values directly available. Relative enthalpy changes of gases were generally calculated from molecular constants provided by Rosen [4], but in some cases were estimated from C_p/R assumed to be 5/2, 9/2, 15/2, and 10 for the gases M, MF, MF₂, and MF₃, respectively. Values of $D^\circ(\text{CaF})$ and $D^\circ(\text{F}_2)$ which are needed in several of the calculations are given at the bottom of the table.

Because Spedding and Henderson [13] have shown that the ΔH° for a solid transition of YF₃ at 1350 K is 32.4 kJ/mol, a revised value for the ΔH° of sublimation was calculated from the mass spectrometric data [12] which had been obtained from 1256 to 1434 K. A least squares fit of the data, excluding the points above 1350 K, yielded the 2nd law value of (437.6 ± 8.7) kJ/mol for $\Delta H_{1299}^\circ(\text{subl})$ while the earlier value was (418 ± 13) kJ/mol.

* $R = 8.3143 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$

Table 3. Derivation of Dissociation Energies of Some Scandium Group, Rare-Earth, and Group IVA Diatomic Fluorides.

Molecule	Reaction	No.	T/K	ΔH° in kJ/mol	Method	Ref.
ScF	$\text{Ca(g)} + \text{ScF(g)} \rightleftharpoons \text{CaF(g)} + \text{Sc(g)}$	1	1410	66.1	mass-spect. (2nd law)	9
	$\Delta(\text{H}_{1410}^\circ - \text{H}_{298}^\circ)$ for reaction 1			0.8	mol. constants	4,10
	$\Delta(\text{H}_{298}^\circ - \text{H}_0^\circ)$ for reaction 2			4.6	review	5
	$\text{ScF(g)} \rightleftharpoons \text{Sc(g)} + \text{F(g)}$	2	0	590.8		
YF	$2\text{CaF(g)} + \text{YF(g)} \rightleftharpoons 2\text{Ca(g)} + \text{YF}_3(\text{g})$	3	1337	-239.7	mass-spect. (2nd law)	9
	$\Delta(\text{H}_{1337}^\circ - \text{H}_0^\circ)$ for reaction 3			17.0	estimate	
	$\text{YF}_3(\text{s}) \rightleftharpoons \text{YF}_3(\text{g})$	4	1299	437.6	mass-spect. (2nd law) ^a	12
	$\Delta(\text{H}_{1299}^\circ - \text{H}_0^\circ)$ for reaction 4			-19.8	drop calor. of solid	13
	$\text{Y(s)} + 3/2 \text{F}_2(\text{g}) \rightleftharpoons \text{YF}_3(\text{s})$		298	-1718.4	bomb calor.	11
	$\text{Y(s)} \rightleftharpoons \text{Y(g)}$		298	424.7	review	10
	$\Delta(\text{H}_{298}^\circ - \text{H}_0^\circ)$ for reaction 5			4.3	review	5
	$\text{YF(g)} \rightleftharpoons \text{Y(g)} + \text{F(g)}$	5	0	605.2		
NdF	$2\text{Ba(g)} + \text{NdF}_2(\text{g}) \rightleftharpoons 2\text{BaF(g)} + \text{Nd(g)}$	6	1428	12.6	mass-spect. (2nd law)	14
	$\text{BaF(g)} + \text{NdF(g)} \rightleftharpoons \text{NdF}_2(\text{g}) + \text{Ba(g)}$	7	1428	-24.3	mass-spect. (2nd law)	14
	$\text{Ba(g)} + \text{NdF(g)} \rightleftharpoons \text{BaF(g)} + \text{Nd(g)}$	8	1428	-8.2	mass-spect. (2nd law)	14
	$\Delta(\text{H}_{1428}^\circ - \text{H}_0^\circ)$ for reaction 8			7.1	elements only	10
	$\text{BaF(g)} \rightleftharpoons \text{Ba(g)} + \text{F(g)}$		298	580.3	review	7
	$\text{NdF(g)} \rightleftharpoons \text{Nd(g)} + \text{F(g)}$		298	{ 561.5 565.0	using no. 6 and 7 using no. 8	
SmF	$\text{Ho(g)} + \text{SmF(g)} \rightleftharpoons \text{HoF(g)} + \text{Sm(g)}$	9	1401	-11.3	mass-spect. (2nd law)	19
	$\Delta(\text{H}_{1401}^\circ - \text{H}_0^\circ)$ for reaction 9			10.4	elements only	10
	$\text{SmF(g)} \rightleftharpoons \text{Sm(g)} + \text{F(g)}$		298	544.0		
EuF	$\text{Ho(g)} + \text{EuF(g)} \rightleftharpoons \text{HoF(g)} + \text{Eu(g)}$	10	1321	-14.6	mass-spect. (2nd law)	19
	$\Delta(\text{H}_{1321}^\circ - \text{H}_0^\circ)$ for reaction 10			0	elements only	10
	$\text{EuF(g)} \rightleftharpoons \text{Eu(g)} + \text{F(g)}$		298	551.5		

^aRecalculated from data.

Table 3 (continued)

Molecule	Reaction	No.	T/K	ΔH° in kJ/mol	Method	Ref.	
GdF	$\text{HoF(g)} + \text{GdF}_2(\text{g}) \rightleftharpoons \text{GdF}_3(\text{g}) + \text{Ho(g)}$	11	1428	-92.5	mass-spect. (2nd law)	19	
	$\text{HoF}_2(\text{g}) + \text{GdF(g)} \rightleftharpoons \text{GdF}_2(\text{g}) + \text{HoF(g)}$	12	1428	-25.5	mass-spect. (2nd law)	19	
	$\Delta(\text{H}_{1428}^\circ - \text{H}_{298}^\circ)$ for sum of reactions 11 and 12			4.7	estimate		
	$2\text{HoF(g)} \rightleftharpoons \text{HoF}_2(\text{g}) + \text{Ho(g)}$	13	1369	-13.0	mass-spect. (2nd law)	15	
	$\Delta(\text{H}_{1369}^\circ - \text{H}_{298}^\circ)$ for reaction 13			9.0	estimate		
	$2\text{HoF(g)} + \text{GdF(g)} \rightleftharpoons 2\text{Ho(g)} + \text{GdF}_3(\text{g})$	14	1428	-136.4	mass-spect. (2nd law)	19	
	$\Delta(\text{H}_{1428}^\circ - \text{H}_{298}^\circ)$ for reaction 14			14.2	estimate		
	$\text{GdF}_3(\text{s}) \rightleftharpoons \text{GdF}_3(\text{g})$	15	1456	377.8	mass-spect. (2nd law)	8	
	$\Delta(\text{H}_{1456}^\circ - \text{H}_{298}^\circ)$ for reaction 15			-25.1	drop calor. of solid	13	
	$\text{Gd(s)} + 3/2 \text{F}_2(\text{g}) \rightleftharpoons \text{GdF}_3(\text{s})$		298	-1700.8	bomb calor.	17	
DyF	$\text{Gd(s)} \rightleftharpoons \text{Gd(g)}$		298	397.5	review	10	
	$\text{GdF(g)} \rightleftharpoons \text{Gd(g)} + \text{F(g)}$		298	655.1	using no. 11, 12, and 13		
			298	649.2	using no. 14		
	$\text{Ho(g)} + \text{DyF(g)} \rightleftharpoons \text{HoF(g)} + \text{Dy(g)}$	16	1460	-11.3	mass-spect. (2nd law)	15	
	$\Delta(\text{H}_{1460}^\circ - \text{H}_{298}^\circ)$ for reaction 16			0.5	elements only	10	
	$\text{DyF(g)} \rightleftharpoons \text{Dy(g)} + \text{F(g)}$		298	554.3			
	HoF	$3\text{HoF}_2(\text{g}) \rightleftharpoons 2\text{HoF}_3(\text{g}) + \text{Ho(g)}$	17	1369	-95.0	mass-spect. (2nd law) ^b	15
		$3\text{HoF(g)} \rightleftharpoons 2\text{Ho(g)} + \text{HoF}_3(\text{g})$	18	1369	-63.6	mass-spect. (2nd law) ^b	15
		$\Delta(\text{H}_{1369}^\circ - \text{H}_{298}^\circ)$ for reaction 18			13.9	mol. constants	10,16,20
		$\text{HoF}_3(\text{s}) \rightleftharpoons \text{HoF}_3(\text{g})$	19	1366	441.8	mass spect. (2nd law)	18
$\Delta(\text{H}_{1366}^\circ - \text{H}_{298}^\circ)$ for reaction 19				-23.9	drop calor. of solid	13	
$\text{Ho(s)} + 3/2 \text{F}_2(\text{g}) \rightleftharpoons \text{HoF}_3(\text{s})$			298	-1705.8	mol. constants	16	
$\text{Ho(s)} \rightleftharpoons \text{Ho(g)}$			298	300.8	bomb calor.	17	
$\text{HoF(g)} \rightleftharpoons \text{Ho(g)} + \text{F(g)}$			298	565.6	review	10	
		298	566.7	using no. 13 and 17			
				using no. 18			

^bObtained from author's graph.

Table 3 (continued)

Molecule	Reaction	No.	T/K	ΔH° in kJ/mol	Method	Ref.
ErF	$\text{Ho(g)} + \text{ErF(g)} \rightleftharpoons \text{HoF(g)} + \text{Er(g)}$	20	1460	25.1	mass-spect. (2nd law)	15
	$\Delta(\text{H}_{1460}^\circ - \text{H}_0^\circ)$ for reaction 20 $\text{ErF(g)} \rightleftharpoons \text{Er(g)} + \text{F(g)}$		298	0 591.2	estimate	
SiF	$\text{Si(g)} + \text{SiF}_2(\text{g}) \rightleftharpoons 2\text{SiF(g)}$	21	298	98.3	review	7
	$2\text{CaF(g)} + \text{Si(g)} \rightleftharpoons 2\text{Ca(g)} + \text{SiF}_2(\text{g})$	22	298	-140.6	review	7
	$\text{Ca(g)} + \text{SiF}_2(\text{g}) \rightleftharpoons \text{CaF(g)} + \text{SiF(g)}$	23	298	100.4	mass-spect. (3rd law)	25
	$\text{SiF}_4(\text{g}) + 2\text{Ca(g)} \rightleftharpoons \text{SiF}_2(\text{g}) + 2\text{CaF(g)}$	24	298	154.8	mass-spect. (3rd law)	25
	$\text{Si(s)} + 2\text{F}_2(\text{g}) \rightleftharpoons \text{SiF}_4(\text{g})$	298	298	-1614.9	review	7
	$\text{Si(s)} \rightleftharpoons \text{Si(g)}$	298	298	455.6	review	10
	$\Delta(\text{H}_{298}^\circ - \text{H}_0^\circ)$ for reaction 25 $\text{SiF(g)} \rightleftharpoons \text{Si(g)} + \text{F(g)}$	25	0	4.6 546.6 { 536.0	review using no. 21 and 22 using no. 23 and 24	7
GeF	$\text{CaF(g)} + \text{Ge(g)} \rightleftharpoons \text{GeF(g)} + \text{Ca(g)}$	298	298	{ 31.4 } { 22.2 }	mass-spect. (3rd law)	{ 24 } { 25 }
	$\Delta(\text{H}_{298}^\circ - \text{H}_0^\circ)$ for reaction 26 $\text{GeF(g)} \rightleftharpoons \text{Ge(g)} + \text{F(g)}$	26	0	4.8 493.9 { 493.1	review using ref. 24 using ref. 25	5
SnF	$\text{Ca(g)} + \text{SnF(g)} \rightleftharpoons \text{CaF(g)} + \text{Sn(g)}$	27	1350	-50.2	mass-spect. (2nd law) ^b	26
	$\Delta(\text{H}_{1350}^\circ - \text{H}_0^\circ)$ for reaction 27 $\text{SnF(g)} \rightleftharpoons \text{Sn(g)} + \text{F(g)}$		0	9.5 467.1	{ mol constants } review	4 10
CaF	$\text{CaF(g)} \rightleftharpoons \text{Ca(g)} + \text{F(g)}$	298	298	530.1	review	7
F ₂	$1/2 \text{F}_2(\text{g}) \rightleftharpoons \text{F(g)}$	298	298	78.9	review	7

^b Obtained from author's graph.

Unfortunately there are inconsistencies in reference 15 between the text and the plotted data involving HoF. Many of the D° 's calculated in Table 3 depend upon a value for $D^\circ(\text{HoF})$, but the sign and the assignment of the values given in the text [15] for the ΔH° 's of reactions 17 and 18 of Table 3 appear to be in error. The values given in Table 3 for these reactions were obtained from the plotted data [15] and appear to be more reasonable. Incidentally a sign error is believed to exist also for the value given in another text [26] which deals with the ΔH° of reaction 27 of Table 3; here again the value obtained from the plotted data [26] was chosen.

Dickson and Zare [34] calculated $D_0^\circ(\text{SmF}) \geq 517$ kJ/mol and $D_0^\circ(\text{EuF}) \geq 542$ kJ/mol from their chemiluminescent studies of the reactions between $\text{F}_2(\text{g})$ and $\text{Sm}(\text{g})$ and $\text{Eu}(\text{g})$, respectively. These values are consistent with those derived in Table 3.

7. SiO

An average value and its standard error for $\Delta H_f^\circ[\text{SiO}(\text{g})]$ may be deduced as (-103.0 ± 3.7) kJ/mol from an analysis in the JANAF Tables [7] of 15 independent published studies. When the value for $\Delta H_f^\circ[\text{Si}(\text{g})]$ is taken to be 451.3 kJ/mol from Hultgren et al. [10], $D_0^\circ(\text{SiO})$ becomes 801.1 kJ/mol.

Hildenbrand [35] used mass spectrometry to study the equilibrium for $\text{Ge}(\text{g}) + \text{SiO}(\text{g}) \rightleftharpoons \text{GeO}(\text{g}) + \text{Si}(\text{g})$ and obtained ΔH_{298}° as (134.7 ± 8) kJ/mol, which corresponds to $D_0^\circ(\text{SiO})$ being (788.7 ± 8) kJ/mol when the revised average for $D^\circ(\text{GeO})$ found below is used.

Zmbov, Ames, and Margrave [37] studied the reaction $\text{Si}(\text{s}) + \text{SiO}_2(\text{quartz}) \rightleftharpoons 2 \text{SiO}(\text{g})$, from 1267 to 1487 K by mass spectrometry and obtained a 3rd law value and standard deviation, (694.1 ± 5.4) kJ/mol, for ΔH_{298}° . When this value is combined with the selected values of ΔH_f° for $\text{Si}(\text{g})$ [10], $\text{O}(\text{g})$ [7], and $\text{SiO}_2(\text{quartz})$ [7], the result is 807.5 kJ/mol for $D_0^\circ(\text{SiO})$. Supporting this value which is higher than the average deduced from the JANAF analysis [7] is the recent ab initio quantum mechanical calculation performed by Heil and Schaefer [36] who predicted $D_0^\circ(\text{SiO})$ to be 804 kJ/mol.

When the values deduced from Hildenbrand [35] and Zmbov et al. [37] are combined with the above average from the JANAF Tables [7], the revised average value for $D_0^\circ(\text{SiO})$ is 800.7 kJ/mol.

8. GeO

Drowart et al. [22] studied the vaporization of $\text{GeO}_2(\text{hex})$, $\text{GeO}(\text{amorph})$, and a mixture of $\text{GeO}_2(\text{hex})$ and $\text{Ge}(\text{s})$ by mass spectrometry. Correcting for the presence of $(\text{GeO})_n(\text{g})$ polymers in the vapor phase, they reinterpreted other vaporization data published earlier. The average $D_0^\circ(\text{GeO})$ from their analysis of nine independent experiments

is (653.5 ± 7.9) kJ/mol. Brewer and Rosenblatt [3] report that the transpiration studies of Belton (1968) on $\text{Ge(s)} + \text{H}_2\text{O(g)} \rightleftharpoons \text{GeO(g)} + \text{H}_2\text{(g)}$ yield (200.8 ± 0.4) kJ/mol for ΔH_{298}° by the 3rd law method, which corresponds to $D_0^\circ(\text{GeO})$ being 659.3 kJ/mol, according to the values of the ΔH_f° for $\text{H}_2\text{O(g)}$ [7], $\text{O}_2\text{(g)}$ [7], and Ge(g) [10]. When the value from Belton (1968) is included in the average from Prowart et al. [22], the revised value for $D_0^\circ(\text{GeO})$ is 654.1 kJ/mol.

9. SnO

Colin et al. [23] studied the vaporization of $\text{SnO}_2\text{(s)}$ by mass spectrometry. Correcting for the presence of $[\text{SnO}]_2\text{(g)}$ in the vapor phase, they also reinterpreted the data from five other independent studies published before their work and deduced the average value, (529.3 ± 8) kJ/mol, for $D_0^\circ(\text{SnO})$. Later, Hoenig and Searcy [39] studied the vaporization of $\text{SnO}_2\text{(s)}$ from 1315 to 1660 K by Knudsen rate of effusion and obtained (600.0 ± 4.6) kJ/mol for the ΔH_{298}° of $\text{SnO}_2\text{(s)} \rightleftharpoons \text{SnO(g)} + 1/2 \text{O}_2\text{(g)}$. When this value is combined with the values of ΔH_f° for Sn(g) [10] and $\text{SnO}_2\text{(s)}$ [23], $D_0^\circ(\text{SnO})$ becomes 524.3 kJ/mol. Combining this with the average value from Colin et al. [23] gives the revised average value, 528.6 kJ/mol, for $D_0^\circ(\text{SnO})$.

III. Selected Values

Selected values of the dissociation energies which are discussed in section II are compiled in Table 4. Values which are believed to be established from earlier reviews and some estimates are also included to provide a complete list.

Table 4. Selected Values^a of Dissociation Energies of Diatomic Molecules

Oxides			Fluorides		
Molecule	D ₀ ^o in kJ/mol	Reference ^d	Molecule	D ₀ ^o in kJ/mol	Reference ^d
MgO	336	7	MgF	446	7
CaO	380	7	CaF	527	7
SrO	423	7	SrF	534	7
BaO	548	7	BaF	577	7
ScO	674	1	ScF	591	
YO	711	1	YF	605	
LaO	799	1	LaF	(600 ± 50)	8
CeO	795	1	CeF	(580 ± 50) ^c	8
PrO	745	1	PrF	(580 ± 50)	8
NdO	695 ^b	1	NdF	563	
PmO	(670) ^b	21	PmF	(540 ± 50)	8
SmO	590	1	SmF	544	
EuO	544	1	EuF	552	
GdO	707	1	GdF	652	
TbO	711	1	TbF	(560 ± 50)	8
DyO	628	1	DyF	554	
HoO	644	1	HoF	566	
ErO	644	1	ErF	591	
TmO	565	1	TmF	(570 ± 50)	8
YbO	420	1	YbF	(570 ± 50)	8
LuO	678	1	LuF	(570 ± 50)	8
SiO	801		SiF	541	
GeO	654		GeF	494	
SnO	529		SnF	467	
PbO	371	7	PbF	351	7

^aConversion factors are 4.184 J/cal, 96.48 kJ·mol⁻¹·eV⁻¹, or 11.96 J·mol⁻¹·cm.

^bParentheses denote an estimated value.

^cValues of rare-earth fluorides are at 298.15 K.

^dSee Table 3 and text for derivation of values without references.

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b) NBS Technical Note 866 - Chemical Kinetic and Photochemical Data for Modelling Atmospheric Chemistry.

c) Rate of reaction, and activation energy for; $O + H_2O \rightarrow OH + OH$ and $O + H_2 \rightarrow OH + H$, where O is $O(^3P)$, $O(^1D)$, $O(^1S)$; chemi-ionization reaction, $Ba + OH \rightarrow BaOH^+ + e^-$; energy transfer reactions $H_2O + H_2O \rightarrow H_2O^* + H_2O$ where * denotes vibrational excitation.

d) Short list on kinetics rate data for metallic species.

e) Chemical Kinetics of Reactions of Nitrogen Fluorides in Gas Phase.

