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Mass Spectrometric Determination of Dissociation Energies
of PrS, GdS, and PrO.

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by

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Abstract

The dissociation energies of the gaseous molecules PrS, GdS, and PrO have been determined by means of isomolecular equilibrium studies, using as reference values $D_O^0(YS) = 125.7 \pm 3.0^{(6)}$ and $D_O^0(YO) = 171.8 \pm 4.0 \frac{\text{kcal}}{\text{mole}}^{(8)}$. Ames et al⁽⁸⁾ have previously determined the dissociation energy of PrO, and a comparison of our results with theirs is made in an attempt to arrive at a "best" value. A mass spectrometric study of GdS described within, and an earlier study of Pr_3S_4 ⁽⁴⁾ also allow calculation of the gaseous dissociation energies of GdS and PrS. Results of these various studies are described, and "best" values of the dissociation energies are reported as listed below.

Molecule	Selected "best" value $D_O^0(\frac{\text{kcal}}{\text{mole}})$
PrS	121.8 ± 2.0
GdS	125.5 ± 4.0
PrO	182.2 ± 3.0

Mass Spectrometric Determination of Dissociation Energies of PrS, GdS, and PrO.

Introduction

As part of a systematic survey of the properties of high temperature sulfide and oxide molecules we have previously reported effusion and mass spectrometric vaporization studies of the solid phases US⁽¹⁾, LaS⁽²⁾, PrS⁽³⁾, Pr₃S₄⁽⁴⁾ and YS⁽⁵⁾. In addition the gaseous dissociation energies of ScS, YS, LaS, ZrS, and UO have been reported⁽⁶⁾. The present report describes the current status of the Pr₃S₄ study and describes the mass spectrometric studies of GdS. In addition mass spectrometric studies of the following isomolecular equilibria are described.

By combining the experimental heats of these reactions with the known dissociation energies of YS^(5,6,7), and YO⁽⁸⁾, one can obtain the dissociation energies of the other molecules.

The equilibrium constant for reactions 1-3 above, which are of the general form

can be determined as a function of temperature by measuring the ion current intensities of the gaseous species as they effuse from a Knudsen cell into the mass spectrometer. The equilibrium constant for a gaseous isomolecular reaction at a particular temperature, T , is given by the expression

$$K = P_N P_{MX} / P_{NX} P_M$$

The ion current intensity of a particular species i , is related to the partial vapor pressure in the Knudsen cell by

$$K_i P_i = I_i^+ T \quad (5)$$

where K_i = instrument sensitivity constant

P_i = partial pressure of species i

I_i^+ = ion current of i th species

T = absolute temperature of Knudsen cell.

The constant, K_i , gives the instrumental sensitivity for species i . Included in K_i are the electronic ionization cross section for that species and its relative sensitivity at the detector.

It is probably reasonable to assume that $K_{NX}/K_N = K_{MX}/K_M$.

Then the equilibrium constant can be expressed as

$$K_T = I_{MX}^+ I_N^+ / I_{NX}^+ I_M^+$$

By studying the equilibria over a sufficiently large temperature interval, the so-called "second law" enthalpy can be obtained from the slope of the well known equation

$$\ln K = -\frac{\Delta H_T^0}{RT} + \frac{\Delta S_T^0}{R} \quad (6)$$

The enthalpy at absolute zero may be obtained by use of the appropriate enthalpy functions listed in Table 1.

The so-called "third law" enthalpy of reaction is

obtained from a combination of individual equilibrium constants with the appropriate free energy functions, $f_{ef} = - (G_T^0 - H_O^0)/T$, listed in appendix 2, thus

$$\Delta H_O^0 = - RT \ln K + T \Delta(f_{ef}). \quad (7)$$

Free energy functions can be calculated by the methods of statistical mechanics from molecular constants which are either obtained spectroscopically or are estimated. Molecular parameters used in this report are listed in Table 2.

The dissociation energies of YO and PrO have been reported previously by Ames et al.⁽⁸⁾ The value of the dissociation energy of YO obtained by Ames et al.⁽⁸⁾, seems well substantiated, and was used as a standard in our calculation of the dissociation energy of PrO. Our results are compared with theirs and an attempt is made herein to obtain a "best" value for the dissociation energy of PrO.

The dissociation energies of PrS and GdS obtained from various studies conducted in this laboratory are compared and "best" values are reported.

Table 1

Enthalpy Functions

Species	Temp($^{\circ}$ K)	$H_T^0 - H_0^0 (\frac{\text{cal}}{\text{mole}})$	Species	Temp($^{\circ}$ K)	$H_T^0 - H_0^0 (\frac{\text{cal}}{\text{mole}})$
Y(18)	2100	11,277	YS*	2150	18,538
	2150	11,544	PrS*	2100	18,148
Pr(13)	2100	13,094		2150	18,595
	2150	13,421	GdS*	2150	18,545
Gd(13)	2150	13,121	GdS** _(s)	2150	31,175
YO(8)	2100	17,685	S(14)	2100	10,926
PrO(8)	2100	17,720		2150	11,182

*Estimated via method in Davidson.(15)

**Estimated via method of Kubeschewski(19)

Table 2

Molecular Parameters

Species	$\omega_e (\text{cm}^{-1})$	$r_e^0 (\text{\AA})$	Ground State Degeneracy
YS	511	2.19	2
PrS	466	2.29	4
GdS	505	2.23	9
YO	852	1.79	2
PrO	777	1.87	4

Isomolecular Studies

Mass Spectrometric Techniques

The mass spectrometric equipment and general techniques have been adequately described elsewhere^(1,2,3,5). Briefly, mixtures of the solid phases of interest were placed in a Knudsen cell fabricated from single-crystal tungsten, and heated by electron bombardment. The effusing molecular beam was directed upward into the ionization region of a time-of-flight mass spectrometer. Temperatures were measured by sighting a calibrated optical pyrometer directly on the orifice. The mass spectrometer was fitted with two scanner-recorder pairs, so that the ion currents from two species could be measured simultaneously.

In the studies of the YS-PrS and YO-PrO systems, ion currents were measured by using a wide gate setting and continuously recording the ion current. In the case of YS-GdS however, it was necessary to scan the Gd and GdS peaks. There are six naturally occurring isotopes of Gd, and complete resolution of the isotope peaks was not possible. For each data point several scans were taken and the average peak heights of the best resolved peaks, corresponding to m/e ratios of 160 and 192 for Gd^+ and GdS^+ respectively, were used as the reported ion currents. The same scanner-recorder pair was used for measuring both the metal ion and its corresponding oxide or sulfide. This should cancel any dif-

ference in the sensitivities of the two scanner-recorder pairs, as only ratios of M^+/MX^+ are used in calculating the equilibrium constants.

Initial studies of the YS-GdS system were carried out at a nominal electron energy of 12eV. However ionization efficiency experiments indicated the individual ion currents would be less sensitive to small electron energy fluctuations at 13eV. Therefore experiments 4 and 5 on YS-GdS, as well as YS-PrS and YO-PrO experiments were done at 13eV. Only very minor differences were noted in the equilibrium constants for the YS-GdS system at the two electron energies. Reported results have been normalized.

Ionization efficiency curves for all species indicate that no appreciable fragmentation occurs at these low voltages. The M^+/MS^+ or M^+/MO^+ ratios were found within experimental uncertainty to be equal in all cases to their ratios at plateau energies.

The solid samples of YS(5), PrS(3), and GdS(9) were taken from batches prepared during earlier studies. The PrS sample used had been partially oxidized. Initially the oxide peaks were as intense as the sulfide peaks, which allowed the determination of equilibrium constants for the oxygen exchange reaction

Experimental Details and Results.

YO-PrO

A 1:1 molar ratio of 57 mg YS and 83 mg PrS was crushed and mixed together in a Knudsen cell. The PrS sample had been stored in a vacuum desiccator for several months and had oxidized slightly. This initial oxygen contamination allowed the observation of the oxygen exchange equilibrium constant. After each change in the power setting and temperature, one-half hour was allowed for equilibrium to be established before any measurements were taken. A series of five equilibrium constants were obtained before the oxide peak intensities began to decrease drastically.

For the reaction

ion current equilibrium constants $K = \frac{I_{YO}^+ I_{Pr}^+}{I_Y^+ I_{PrO}^+}$ are plotted in figure 1 as $\log K$ versus $10^4/T$. The equation, with standard derivations, for the least squares line plotted in figure 1 is

$$\log K = - (0.297 \pm 0.065) 10^4/T - (0.388 \pm 0.308) \quad (9)$$

The slope corresponds at the mean temperature 2150°K to a heat for reaction (8) of $\Delta H_{2150}^O = 13.6 \pm 3.0 \frac{\text{kcal}}{\text{mole}}$.

The intercept corresponds to $\Delta S_{2150} = 1.77 \pm 1.41 \text{ e.u.}$

Reducing the heat to 0°K by means of the appropriate thermal functions listed in Table 1 yields $\Delta H_O^O = 11.83 \pm 3.0 \text{ kcal/}$

mole. Combined with the $D_O^O(YO_{(g)}) = 171.8 \pm 4.0 \text{ kcal/mole}^{(8)}$,

this value gives $D_O^O(PrO_{(g)}) = 183.6 \pm 4.0 \text{ kcal/mole}$ or $7.96 \pm 0.17 \text{ eV.}$

MASS SPECTROMETRIC EQUILIBRIUM CONSTANTS

Figure 1

Third law calculations based on the individual equilibrium constants and free energy functions gave an average heat for reaction (8) of $\Delta H_O^\circ = 10.00 \pm 0.4$ kcal/mole. (Appendix 2 and Figure 2). However, the estimated standard deviations in the free energy functions increase this uncertainty by about 3 kcal/mole. The ground state degeneracies were taken to be 2 for $YO_{(g)}$ and 4 for $PrO_{(g)}$, as calculated by Ames et al⁽⁸⁾, using a model proposed by Carlson et al⁽¹⁰⁾. The average third law heat gives $D_O^\circ(PrO_{(g)}) = 181.8 \pm 4.0$ kcal/mole or 7.88 ± 0.17 ev. The second and third law heats agree within their standard deviations.

Ames et al⁽⁸⁾ have obtained an average $D_O^\circ(PrO) = 181.7 \pm 4.6$ kcal/mole or 7.88 ± 0.2 ev from isomolecular studies of the Tb - PrO and PrO-La systems. Their second law value was 178.7 ± 4.6 kcal/mole and their third law value was 184.7 ± 4.6 kcal/mole.

These values are in excellent agreement with the present determination. The average of these results is herein reported as a "best" value for the $D_O^\circ(PrO_{(g)}) = 182.2 \pm 4.0$ kcal/mole or 7.90 ± 0.17 ev.

The dissociation energy data are summarized in Table 3.

YS-PrS

The YS-PrS sample mixture used in the study of the YO-PrO system was annealed until the oxide peaks were negligible. Then 22 equilibrium constants were measured in the range 1970 to 2280°K. After the experiment the residue was a metallic gold with a NaCl-type lattice parameter $a_o = 5.5881 \pm 0.0007$ Å at

Figure 2

Table 3

Dissociation Energies of MX

Molecule	Dissociation Energy (kcal/Mole)			Reference
	Second Law	Third Law	Average	
PrS	120.5 $\pm$ 3.0 120.7 $\pm$ 3.0	123.1 $\pm$ 3.0 123.0 $\pm$ 6.0 121.7 $\pm$ 6.0	121.8	This work Fries and Cater ⁽⁴⁾ Holler ⁽³⁾
GdS	125.0 $\pm$ 4.0 128.8 $\pm$ 5.0	122.7 $\pm$ 4.0 ---	125.5	This work GdS study
PrO	178.7 $\pm$ 4.6 183.6 $\pm$ 4.0	184.7 $\pm$ 4.6 181.8 $\pm$ 4.0	182.2	Ames et al ⁽⁸⁾ This work

Molecule	Selected "best" value D_0^0
PrS	121.8 $\pm$ 2.0 kcal/mole
GdS	125.5 $\pm$ 4.0 kcal/mole
PrO	182.2 $\pm$ 3.0 kcal/mole

room temperature. Apparently a solid solution of YS ($a_0 = 5.4873 \pm 0.0005\text{\AA}$) and PrS ($a_0 = 5.7331 \pm 0.0003\text{\AA}$) had formed. For the reaction

ion current equilibrium constants $K = \frac{I^+(\text{YS}) I^+(\text{Pr})}{I^+(\text{Y}) I^+(\text{PrS})}$ are plotted in Fig. 1 as $\log K$ vs $10^4/T$. The data are listed in Appendix 1. A linear least squares treatment yields

$$\log K = (0.074 \pm 0.012) 10^4/T - (0.107 \pm 0.057) \quad (10)$$

The slope corresponds at the mean temperature 2150°K to $\Delta H_{2150}^\circ = -3.40 \pm 0.56$ kcal/mole, and the intercept to $\Delta S_{2150}^\circ = -0.491 \pm 0.263$ e.u. Reducing the heat to 0°K by means of enthalpy functions collected in Table 1 gives $\Delta H_0^\circ = -5.22 \pm 3.0$ kcal/mole where the uncertainty includes the uncertainty in the estimated functions. Combined with $D_0^\circ(\text{YS}) = 125.7 \pm 3.0$ kcal/mole⁽⁶⁾ this value yields $D_0^\circ(\text{PrS}_{(g)}) = 120.5 \pm 3.0$ kcal/mole.

A third law treatment using estimated free energy functions for $\text{YS}_{(g)}$ and $\text{PrS}_{(g)}$ and tabulated values for $\text{Y}_{(g)}$ ⁽¹⁸⁾ and $\text{Pr}_{(g)}$ ⁽¹³⁾ yields a $D_0^\circ(\text{PrS}_{(g)}) = 123.1 \pm 3.0$ kcal/mole. Here the ground state degeneracies for $\text{YS}_{(g)}$ and $\text{PrS}_{(g)}$ are taken to be 2 and 4 respectively, the same as those used for $\text{YO}_{(g)}$ and $\text{PrO}_{(g)}$ ⁽⁸⁾. The results are listed in appendix 2 and are plotted in figure 2.

The dissociation energy of $\text{PrS}_{(g)}$ has previously been determined by B. Holler⁽³⁾; J. A. Fries and E. D. Cater⁽⁴⁾. In these calculations a ground state degeneracy of 2 was used for $\text{PrS}_{(g)}$. If a value of 4 is used, the studies of the vaporization of solid PrS by Holler yield a third law $D_{\text{O}}^{\circ}(\text{PrS}_{(g)}) = 121.7 \pm 6.0 \frac{\text{kcal}}{\text{mole}}$. The study of $\text{Pr}_3\text{S}_4(s)$ by Fries and Cater⁽⁴⁾ yields a second law value of $120.7 \pm 3.0 \text{ kcal/mole}$ and a third law value of $123.0 \pm 6.0 \text{ kcal/mole}$. It may be seen that all of these values are in excellent agreement. The average of these results is taken as the "best" value for the $D_{\text{O}}^{\circ}(\text{PrS}_{(g)}) = 121.8 \pm 2.0 \text{ kcal/mole}$. (Table 3)

YS-GdS

A mixture of 67.9 mg GdS and 37.2 mg YS was placed in the mass spectrometer and heated for 8 hours at 1940°C obs. The sample was removed, weighed, and x-rayed. Approximately 15% of the sample had been lost. A single phase solid solution with a cubic lattice parameter $a_0 = 5.5280 \pm 0.0003 \text{ \AA}$ remained. The sample was then returned to the mass spectrometer where a series of five runs and a total of 41 equilibrium constants were measured. The final lattice parameter was $a_0 = 5.5237 \pm 0.0004$, indicating a shift in composition toward a higher percentage YS in the solid mixture. ($a_0(\text{YS}) = 5.4873 \text{ \AA}$; $a_0(\text{GdS}) = 5.5626 \text{ \AA}$). Despite this apparent shift in solid composition, there was no detectable shift in the equilibrium

constants measured.

For the reaction

ion current equilibrium constants $K = \frac{I^+(YS) I^+(Gd)}{I^+(Y) I^+(GdS)}$

are plotted in figure 1 as $\log K$ versus $10^4/T$. Experimental results are listed in appendix 1. A linear least squares treatment yields

$$\log K = (-0.019 \pm 0.017) 10^4/T + (0.279 \pm 0.081) \quad (11)$$

The slope corresponds at a mean temperature of 2150°K to $\Delta H_{2150}^0 = 0.88 \pm 0.80 \frac{\text{kcal}}{\text{mole}}$, and the intercept corresponds to $\Delta S_{2150}^0 = 1.27 \pm 0.37$ e.u. Using the appropriate thermal functions listed in Table 1, the heat reduced to 0°K becomes $\Delta H_0^0 = -0.695 \pm 0.80 \frac{\text{kcal}}{\text{mole}}$. This combined with the dissociation energy of $YS(g)$ $125.7 \pm 3.0 \text{ kcal/mole}^{(8)}$ yields a second law value $D_0^0(GdS(g)) = 125.0 \pm 4.0 \text{ kcal/mole}$.

For reaction (11) third law calculations using the 41 individual values of K and free energy functions from appendix 2 yield an average heat $\Delta H_0^0 = -3.00 \pm 0.22 \frac{\text{kcal}}{\text{mole}}$ (Figure 2). Ground state degeneracies of 2 for $YS(g)$ and 9 for $GdS(g)$ were used. The average third law dissociation energy is $D_0^0(GdS(g)) = 122.7 \pm 4.0 \frac{\text{kcal}}{\text{mole}}$, where the uncertainty includes possible errors in the estimated free energy functions.

Fries and Cater⁽⁴⁾ have looked at the vaporization of $\text{GdS}_{(g)}$ using mass spectrometric techniques. This work is also discussed later in this report. As yet no total effusion studies have been done so only a second law value $D_0^{\circ}(\text{GdS}_{(g)}) = 128.8 \pm 5.0 \frac{\text{kcal}}{\text{mole}}$ is as yet available. This is somewhat higher than the isomolecular results, but still lies within experimental uncertainty of the isomolecular second law value we obtained. The isomolecular values are probably more reliable since the ionization cross sections should tend to cancel in the equilibrium constant. As a "best" value for the dissociation energy of $\text{GdS}_{(g)}$ we report the average of these studies to be $D_0^{\circ}(\text{GdS}_{(g)}) = 125.5 \pm 4 \frac{\text{kcal}}{\text{mole}}$.

Mass Spectrometric Study of GdS

The mass spectrometric study of GdS was performed with the same equipment and techniques reported earlier^(1,2,3,5). Since our preliminary report⁽⁴⁾ last year on the vaporization study of GdS, much additional data has been obtained. Four additional experimental runs have been made in the mass spectrometer, as well as additional ionization efficiency curves. The x-ray lattice parameter was determined after each run; and, on this basis, it would appear that $\text{GdS}_{(g)}$ vaporizes congruently. The lattice parameters are tabulated in Table 4.

In the mass spectrometric study of GdS it was necessary to use a narrow gate setting, and to scan the Gd and GdS peaks because Gd has the naturally occurring isotopes 154,

Table 4

Lattice Parameters

Film#	Sample	Sample History	Parameter (Å)
30	YS-GdS	Solid mixture annealed 8 hr 1950°C	5.5280 ± 0.0003
33	YS-GdS	Mass spec residue from run 5	5.5237 ± 0.0004
35	YS-PrS	Mass spec residue from run 2	5.5881 ± 0.0007
10	GdS	Annealed at 1950°C ⁽⁹⁾ ; Stored 1½ years.	5.5662 ± 0.0003
11	GdS	Mass spec residue from run 3	5.5620 ± 0.0004
17	GdS	Mass spec residue from run 5	5.5623 ± 0.0003
23	GdS	Mass spec residue from run 6	5.5619 ± 0.0002
24	GdS	Mass spec residue from run 7	5.5629 ± 0.0002

155, 156, 157, 158 and 160, and the gate width of the detector in the mass spectrometer is too narrow to record all these peaks simultaneously. After each temperature change, no measurements were made for $\frac{1}{2}$ hour to allow the system to reach equilibrium. The peaks were then scanned a number of times in succession. In each case the ion currents were calculated by averaging the peak heights of the highest mass isotope. Corrections were then applied for natural isotopic abundance and slight differences between the two scanner-recorder pairs. Sulfur intensities were taken only during run 6.

In ionization efficiency studies no fragmentation was detected at energies below 15 eV. The first ionization potential of Gd is reported to be 6.7 volts⁽¹¹⁾. Extrapolation to zero current yielded an uncorrected appearance potential of 5.8 eV for Gd^+ , and 6.6 eV for GdS^+ . This indicates that Gd^+ and GdS^+ were primary species and were not formed by fragmentation. A nominal energy of 12 eV was used in these studies to avoid fragmentation; the ratio of ion currents $I^+(\text{Gd})/I^+(\text{GdS})$ was constant in this voltage range.

Experiments 1-3

This work has been reported previously⁽⁴⁾. A total of 30 experimental measurements of $I^+(\text{Gd})$ and $I^+(\text{GdS})$ were obtained in the temperature interval 2097 to 2257°K. The

sample was not examined until after run 3. Of an initial 141 mg sample only 20 mg remained. The sample had been vapor deposited on the lid of the Knudsen cell. However, this should not affect the experimental intensities if a true solid-vapor equilibrium was attained. After each temperature change, one-half hour was allowed for equilibrium before any measurements were made. The data appear to be in agreement with later studies in which the sample remained on the Knudsen cell bottom.

After experiment three the sample was x-rayed and a sulfur analysis⁽³⁾ carried out. A lattice parameter of $5.5620 \pm 0.0004\text{\AA}$ was obtained as compared to $5.5662 \pm 0.0003\text{\AA}$ obtained prior to heating in the mass spectrometer. A sulfur to gadolinium ratio of 1.05 ± 0.05 was obtained. In the sample as initially prepared this ratio was found to be $0.97^{(9)}$. This difference is due in part at least to the presence of some oxide in the initial sample. The intensities from the three experiments have been normalized with the other experimental intensities tabulated in appendix 3 and plotted in figure 3.

Experiment 5.

An additional 88 mg of GdS was added to the residue from experiment 3. After experiment 4 which was plagued by instrumental difficulties, experiment 5 was carried out

over a temperature range of 2037 to 2229°K. After the series of 19 measurements, the sample was removed and x-rayed. The sample, which was found to be still in the bottom of the Knudsen cell, had a lattice parameter $a_0 = 5.5623 \pm 0.0003\text{\AA}$. The data were normalized with data from the other experiments and may be found in appendix 3.

Experiment 6

The residue from experiment 5 was studied over the temperature range 2005 to 2254°K. A series of 23 intensity measurements of Gd^+ and GdS^+ were made, as well as 18 intensity measurements of S^+ . The $\text{I}^+(\text{S})$ measurements were obtained by scanning the peak using a narrow gate setting. At such a low voltage, only a small percentage of the S is ionized. This, in conjunction with large background problems, introduced a large amount of scatter and experimental uncertainty into these measurements. The $\text{I}^+(\text{S})$ data are listed in appendix 3, but have not been used in any thermodynamic calculations. The $\text{I}^+(\text{Gd})$ and $\text{I}^+(\text{GdS})$ data were normalized with the other data and also appear in appendix 3. The lattice parameter, after run 6, was $5.5619 \pm 0.0002\text{\AA}$.

Experiment 7.

An additional 219 mg of GdS was added to the residue of experiment 6. After initial annealing to remove GdO,

a series of 21 intensity measurements were made over a temperature range of 2022 to 2288°K. No measurements of $I^+(S)$ were made. The lattice parameter of the residue was $5.5629 \pm 0.0002\text{\AA}$. These data are also included in the normalized data listed in appendix 3 and plotted in figure 3.

Results of GdS Mass Spec. Studies

The data from experiments 1 through 7, with the exception of experiment 4 which were discarded because of instrumental difficulties, were normalized together at 2150°K, and a single linear least squares line was computed for each species. These data are plotted in figure 3 and tabulated in appendix 3. The least squares equations for these lines are as follows:

$$\log IT(Gd^+) = - (29,873 \pm 182)/T + (15.248 \pm 0.084) \quad (12)$$

$$\log IT(GdS^+) = - (30,343 \pm 221)/T + (15.176 \pm 0.102) \quad (13)$$

$$\log IT(S^+) = - (26,453 \pm 1,188)/T + (11.868 \pm 0.548) \quad (14)$$

At this time only second law calculations may be carried out for this system. The uncertainty in the sulfur data is quite large, and these data have not been used in any further calculations. Since the lattice parameters (Table 4) after each run are all equal within experimental error, (and are different from that of the initial sample), it seems logical to assume the composition changed from the initial value until in all these experiments congruent vaporization occurred. In such a case the ratio of partial pres-

Figure 3

tures of Gd and S must be constant and according to the chemical analysis, the ratio is $1.05 \pm .05$. We choose therefore to assume the slopes of $\log I^+T$ vs. $1/T$ for both Gd^+ and S^+ are equal to the slope of equation (12). The slopes in terms of kcal/mole are for Gd^+ and S^+ , 136.7 ± 0.83 ; and for GdS^+ , 138.8 ± 1.01 . The sulfur slope which has not been used is $121.0 \pm 5.44 \frac{\text{kcal}}{\text{mole}}$.

The resultant heats for the following reactions are listed in Table 5.

In order to calculate the heats at zero degrees, tabulated enthalpy functions for $Gd^{(13)}$ and $S^{(14)}$ were used, along with a value for $GdS_{(g)}$ calculated from estimated molecular parameters from equations given by Davidson.⁽¹⁵⁾ These functions are listed in Table 1. The heats at zero degrees are listed in Table 5.

In order to obtain third law values it will be necessary to obtain total effusion data. A vacuum balance study of GdS has been initiated, but is not yet complete. This is particularly important since the values for the dissociation energy of $GdS_{(g)}$ obtained in this study and in the isomolecular studies, discussed elsewhere in this report, are not in good agreement. Third law results are

Table 5
Second Law Enthalpies

Reaction	$\Delta H_{2150}^{\circ} \frac{\text{kcal}}{\text{mole}}$	$\Delta H_0^{\circ} \frac{\text{kcal}}{\text{mole}}$
15) $\text{GdS}_{(s)} \rightleftharpoons \text{GdS}_{(g)}$	138.8 ± 4.0	151.4 ± 4.0
16) $\text{GdS}_{(s)} \rightleftharpoons \text{Gd}_{(g)} + \text{S}_{(g)}$	275.5 ± 4.0	282.4 ± 4.0
17) $\text{GdS}_{(g)} \rightleftharpoons \text{Gd}_{(g)} + \text{S}_{(g)}$	134.6 ± 4.0	128.8 ± 4.0

Table 6
The Dissociation Energy of Gaseous PrS

System Investigated	Second Law Value	Third Law Values			
		1.5-2*	1.5-4*	.343-2*	.343-4*
PrS(3)	154.9 ± 3.2	---	---	124.5 ± 6.0	121.7 ± 6.0
YS-PrS	120.5 ± 3.0	126.1	123.1	126.1	123.1 ± 3.0
Pr ₃ S ₄	120.7 ± 2.0	117.8	114.9	125.9	123.0 ± 6.0

* Values assumed for (sensitivity constant ratio PrS/Pr)-(ground state degeneracy of PrS)

not as sensitive to small changes in stoichiometry or instrumental sensitivities as are second law results. It is hoped that third law heats will better agree with the $D_o^0(\text{GdS}(\text{g}))$ obtained in our isomolecular work.

Status of Pr_3S_4 Study

The study of Pr_3S_4 was quite completely outlined in last years report⁽⁴⁾. No additional experiments have been done on the Pr_3S_4 system. However a re-evaluation of the data is currently in progress; in an attempt at better correlation with the general literature and results of the isomolecular experiment.

At the time of our earlier report⁽⁴⁾ a ground state degeneracy 2 was assumed for $\text{PrS}(\text{g})$ in agreement with a value assumed by B. Holler⁽³⁾. However it seems more logical to assume $\text{PrS}(\text{g})$ to have the same ground state degeneracy as $\text{PrO}(\text{g})$. Therefore a value of 4 has been assumed in line with the value of Ames et al.⁽⁸⁾ for $\text{PrO}(\text{g})$. This results in much better agreement in the value of $D_o^0(\text{PrS}(\text{g}))$ as obtained in the $\text{PrS}^{(3)}$, $\text{Pr}_3\text{S}_4^{(4)}$ and isomolecular studies.

Additionally, it was assumed⁽⁴⁾ that the cross section ratio for PrS/Pr was 1.5. There is an increasing volume of data^(8,17) which suggests that a ratio less than 1.0 may be closer to the true value. In the study of

PrS, B. Holler⁽³⁾ used the same instrument used in our studies. A treatment of her results via the method of Cater and Thorn⁽¹⁶⁾ resulted in an instrumental sensitivity ratio $K_{\text{PrS}}/K_{\text{Pr}} = 0.343$. Use of this value rather than the more arbitrarily selected value previously used, results in better agreement between second and third law heats from the vaporization study of Pr_3S_4 . The various values for $D_{\text{O}}^{\circ}(\text{PrS}_{(\text{g})})$ are tabulated in Table 6 for comparative purposes. A "best" value $D_{\text{O}}^{\circ}(\text{PrS}_{(\text{g})}) = 121.8 \pm 2.0 \frac{\text{kcal}}{\text{mole}}$ is reported.

New third law calculations are not yet complete for the remainder of the thermodynamic quantities reported previously⁽⁴⁾. Second law values will not be affected and it is expected that better second and third law agreement will result.

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Appendix I

Tables of equilibrium constants and least squares calculations of heats and entropies of reaction for the gaseous equilibria

SECOND LAW DATA

YS-PRS RUNS 1-2 NORMALIZED AT 2150. DEG K 13 EV

SPECIES 1 IS YS, 2 IS Y, 3 IS PRS, 4 IS PR

	TEMP(K)	10000/T	I(1)	I(2)	I(3)	I(4)	K	LOG K	NORM LOG K
1	2190.5	4.3835	162.40	280.80	551.00	1560.00	1.6374	0.21416	0.22506
	2127.2	4.4621	61.80	90.00	233.20	540.00	1.5901	0.20141	0.21231
	2053.6	4.5521	20.04	27.36	72.60	176.00	1.7757	0.24936	0.26026
	2093.6	4.6640	33.50	47.00	127.80	303.60	1.6932	0.22872	0.23962
	2161.0	4.7934	105.40	153.40	368.00	890.00	1.6617	0.22056	0.23146
2	2281.3	4.3835	555.00	732.00	1660.00	3600.00	1.6443	0.21598	0.20508
	2241.1	4.4621	292.00	353.00	900.00	1792.00	1.6470	0.21670	0.20580
	2196.8	4.5521	148.00	156.00	480.00	906.00	1.7907	0.25302	0.24212
	2144.1	4.6640	71.80	72.00	256.00	435.00	1.6945	0.22904	0.21814
	2086.2	4.7934	30.30	30.00	111.20	201.20	1.8274	0.26184	0.25094
	2026.3	4.9352	10.80	10.94	40.00	75.30	1.8584	0.26914	0.25824
	1971.7	5.0718	4.38	3.86	15.92	27.76	1.9786	0.29636	0.28546
	2038.9	4.9047	14.64	13.80	55.60	89.20	1.7020	0.23095	0.22005
	2103.0	4.7550	38.40	38.20	140.40	248.00	1.7756	0.24935	0.23845
	2158.8	4.6321	88.20	95.00	301.00	570.00	1.7581	0.24505	0.23415
	2209.5	4.5260	174.80	188.00	580.00	1060.00	1.6993	0.23026	0.21936
	2254.9	4.4349	335.00	405.00	1000.00	2008.00	1.6609	0.22035	0.20945
	2278.1	4.3896	446.00	606.00	1276.00	2860.00	1.6496	0.21738	0.20648
	2245.3	4.4537	264.00	303.00	780.00	1456.00	1.6264	0.21123	0.20033
	2196.8	4.5521	126.00	132.80	404.00	750.00	1.7614	0.24585	0.23495
	2145.1	4.6617	60.20	60.60	213.20	361.00	1.6821	0.22584	0.21494
	2089.3	4.7862	25.00	25.00	92.60	162.00	1.7495	0.24290	0.23200
	2027.3	4.9326	9.26	8.86	34.80	59.90	1.7990	0.25503	0.24413
	1972.7	5.0691	3.62	3.30	13.42	21.80	1.7820	0.25090	0.24000
	2069.4	4.8324	19.72	18.08	70.60	116.00	1.7921	0.25336	0.24246
	2179.9	4.5873	103.40	102.60	347.00	594.00	1.7252	0.23683	0.22593
	2274.9	4.3958	420.00	495.00	1214.00	2392.00	1.6718	0.22319	0.21229
SLOPE A =			0.076437+ OR -		0.011794				
PARAMETER B =			-0.127658+ OR -		0.055225				

HEAT OF VAPORIZATION = -3.50 + OR - 0.54 KCAL/MOLE

ENTROPY OF VAPORIZATION = -0.58 + OR - 0.25CAL/DEG-MOLE

NORMALIZATION TEMP = 2150.00000

SECOND LAW DATA

YO-PRO RUN 1 Y + PRO = YC + PR 13 EV 12/17/68

SPECIES 1 IS YO, 2 IS Y, 3 IS PRO, 4 IS PR

TEMP(K)	10000/T	I(1)	I(2)	I(3)	I(4)	K	LOG K
2190.5	4.5652	17.20	280.80	900.00	1560.00	0.1062	-0.97399
2127.2	4.7009	6.80	90.00	426.00	540.00	0.0958	-1.01875
2053.6	4.8695	2.37	27.36	182.00	176.00	0.0838	-1.07693
2093.6	4.7766	4.15	47.00	270.00	303.60	0.0993	-1.00311
2161.0	4.6276	8.44	153.40	476.00	890.00	0.1029	-0.98770

SLOPE A = -0.297428+ OR - 0.065475

PARAMETER B = 0.387858+ OR - 0.308333

HEAT OF VAPORIZATION = 13.61 + OR - 3.00 KCAL/MOLE

ENTROPY OF VAPORIZATION = 1.77 + OR - 1.41CAL/DEG-MOLE

PRISM WINDOW CORRECTION = 0.1230

SECOND LAW DATA

YS-GDS RUNS 1-5 NORMALIZED AT 2150 DEG K 1-3 AT 12 EV, 4-5 AT 13

SPECIES 1 IS YS, 2 IS Y, 3 IS GDS, 4 IS GD

	TEMP(K)	10000/T	I(1)	I(2)	I(3)	I(4)	K	LOG K	NORM LOG K
	2267.5	4.4101	152.00	174.00	42.10	76.40	1.5853	0.20011	0.19316
	2236.9	4.5303	96.00	115.00	25.60	47.90	1.5620	0.19367	0.18672
	2204.2	4.6755	64.60	72.80	17.20	30.20	1.5580	0.19258	0.18563
	2170.4	4.8496	41.00	46.30	11.08	19.08	1.5249	0.18324	0.17630
1	2135.7	4.7574	25.32	28.16	6.70	11.62	1.5594	0.19296	0.18602
	2059.9	4.7718	6.80	7.36	1.71	3.07	1.6617	0.22056	0.21362
	2014.7	4.6366	3.25	3.60	0.89	1.54	1.5566	0.19217	0.18523
	2041.0	4.5303	5.30	5.80	1.48	2.46	1.5123	0.17964	0.17270
	2084.1	4.4307	11.10	12.12	2.80	5.04	1.6509	0.21771	0.21077
	2266.5	4.4101	129.40	147.60	35.00	62.70	1.5705	0.19605	0.19578
	2230.6	4.5303	81.00	90.40	20.00	35.00	1.5680	0.19535	0.19509
	2189.4	4.6755	44.00	46.80	10.90	18.16	1.5664	0.19490	0.19463
	2150.4	4.8496	25.40	29.60	5.53	10.74	1.6666	0.22182	0.22155
2	2105.1	4.7574	13.00	14.00	3.18	5.16	1.5067	0.17304	0.17777
	2058.9	4.7718	7.10	7.40	1.83	2.62	1.3701	0.13674	0.13647
	2090.4	4.6366	12.70	14.12	2.92	5.04	1.5524	0.19102	0.19075
	2135.7	4.5303	24.52	25.00	5.74	9.42	1.6096	0.20672	0.20645
	2264.4	4.4101	114.40	117.00	27.00	45.60	1.6514	0.21784	0.18707
	2242.2	4.5303	75.40	80.00	19.00	32.28	1.6013	0.20446	0.17369
	2220.0	4.6755	55.00	55.00	13.24	21.20	1.6012	0.20445	0.17367
	2191.5	4.8496	37.20	36.00	8.60	14.24	1.7110	0.23325	0.20248
3	2162.0	4.7574	27.00	26.60	5.91	10.24	1.7587	0.24519	0.21442
	2136.7	4.7718	16.60	16.20	3.97	6.78	1.7500	0.24303	0.21226
	2107.2	4.6366	10.72	10.02	2.38	3.88	1.7471	0.24231	0.21154
	2076.7	4.5303	6.54	6.34	1.50	2.33	1.6010	0.20438	0.17360
	2039.9	4.4307	3.48	4.22	0.66	1.23	1.5368	0.18663	0.15585
	2265.4	4.4142	110.40	110.00	23.92	40.60	1.7035	0.23134	0.20057
	2267.5	4.4101	166.40	167.40	33.60	52.50	1.5532	0.19122	0.20453
	2221.1	4.5303	83.00	80.00	17.56	23.80	1.4062	0.14804	0.16135
	2167.3	4.6755	40.00	38.00	8.08	11.28	1.4695	0.16717	0.18049
	2112.5	4.8496	18.00	15.40	3.56	4.29	1.4085	0.14876	0.16207
	2044.1	4.7574	6.10	5.54	1.17	1.65	1.5509	0.19059	0.20390
4	2095.7	4.7718	13.80	12.20	2.68	3.59	1.5152	0.18048	0.19379
	2156.7	4.6366	34.52	30.20	6.72	9.60	1.6329	0.21297	0.22628
	2207.3	4.5303	71.00	65.00	13.34	18.00	1.4739	0.16846	0.18177
	2257.0	4.4307	133.00	133.00	24.80	37.00	1.4919	0.17375	0.18706
	2267.5	4.4101	218.80	222.40	31.90	47.70	1.4711	0.16764	0.19232
	2207.3	4.5303	95.20	94.00	13.80	20.40	1.4971	0.17526	0.19994
	2138.8	4.6755	36.20	35.50	4.94	7.38	1.5234	0.18281	0.20749
	2062.0	4.8496	10.64	10.40	1.52	2.05	1.3798	0.13982	0.16449
5	2102.0	4.7574	21.00	20.20	2.90	4.04	1.4483	0.16085	0.18553

SLOPE A = -0.019154+ OR - 0.017457

PARAMETER B = 0.273787+ OR - 0.081069

HEAT OF VAPORIZATION = 0.88 + OR - 0.80 KCAL/MOLE

ENTROPY OF VAPORIZATION = 1.28 + OR - 0.37CAL/DEG-MOLE

NORMALIZATION TEMP = 2150.00000

Appendix II

Tables of heats of reaction calculated from
 $\Delta H^{\circ}_0 = -RT \ln K + T \Delta(fef)$ for the gaseous equilibria

THIRD LAW DATA

YS-PRS RUN 1 PRS + Y = YS + PR 13 EV 12/16/68

SPECIES 1 IS YS, 2 IS PRS, 3 IS PR, 4 IS Y

TEMP	LOG K	FEF(1)	FEF(2)	FEF(3)	FEF(4)	FEFDIF	ENTHALPY
2190.5	0.21416	67.4230	70.4014	51.4324	48.5162	-0.06216	-2.283
2127.2	0.20141	67.1703	70.1479	51.2489	48.3580	-0.08670	-2.145
2053.6	0.24936	66.8671	69.8438	51.0308	48.1647	-0.11053	-2.570
2093.6	0.22872	67.0332	70.0103	51.1508	48.2727	-0.09904	-2.398
2161.0	0.22056	67.3061	70.2842	51.3469	48.4425	-0.07362	-2.340

AVE HEAT OF REACTION = -2.347 + OR - 0.156 KCAL/MOLE

QUOTED UNCERTAINTY IS STANDARD DEVIATION.

WINDOW-PRISM CORRECTION = 0.1230

THIRD LAW DATA

YS-PRS RUN 2 PRS + Y = YS + PR 13 EV 12/18/68

SPECIES 1 IS YS, 2 IS PRS, 3 IS PR, 4 IS Y

TEMP	LOG K	FEF(1)	FEF(2)	FEF(3)	FEF(4)	FEFDIF	ENTHALPY
2281.3	0.21598	67.7735	70.7530	51.6876	48.7351	-0.02695	-2.316
2241.1	0.21670	67.6200	70.5990	51.5751	48.6386	-0.04256	-2.318
2196.8	0.25302	67.4478	70.4263	51.4507	48.5320	-0.05977	-2.675
2144.1	0.22904	67.2385	70.2163	51.2979	48.4002	-0.08014	-2.419
2086.2	0.26184	67.0027	69.9798	51.1286	48.2527	-0.10118	-2.711
2026.3	0.26914	66.7521	69.7283	50.9489	48.0910	-0.11832	-2.735
1971.7	0.29636	66.5173	69.4927	50.7794	47.9407	-0.13678	-2.943
2038.9	0.23095	66.8054	69.7818	50.9867	48.1250	-0.11472	-2.389
2103.0	0.24935	67.0717	70.0490	51.1787	48.2975	-0.09607	-2.602
2158.8	0.24505	67.2974	70.2753	51.3405	48.4370	-0.07443	-2.581
2209.5	0.23026	67.4975	70.4761	51.4866	48.5628	-0.05479	-2.449
2254.9	0.22035	67.6730	70.6522	51.6137	48.6718	-0.03722	-2.357
2278.1	0.21738	67.7614	70.7408	51.6787	48.7274	-0.02820	-2.330
2245.3	0.21123	67.6362	70.6152	51.5868	48.6487	-0.04092	-2.262
2196.8	0.24585	67.4478	70.4263	51.4507	48.5320	-0.05977	-2.603
2145.1	0.22584	67.2425	70.2203	51.3008	48.4027	-0.07977	-2.388
2089.3	0.24290	67.0155	69.9926	51.1379	48.2611	-0.10028	-2.532
2027.3	0.25502	66.7563	69.7325	50.9519	48.0937	-0.11801	-2.605
1972.7	0.25090	66.5216	69.4971	50.7826	47.9435	-0.13638	-2.534
2069.4	0.25336	66.9331	69.9099	51.0782	48.2074	-0.10599	-2.618
2179.9	0.23683	67.3812	70.3595	51.4017	48.4897	-0.06628	-2.507
2274.9	0.22319	67.7493	70.7286	51.6697	48.7198	-0.02940	-2.390

AVE HEAT OF REACTION = -2.512 + OR - 0.169 KCAL/MOLE

QUOTED UNCERTAINTY IS STANDARD DEVIATION.

WINDOW-PRISM CORRECTION = 0.1230

Third Law Data

YO-PrO Run 1 $\text{PrO} + \text{Y} \rightleftharpoons \text{YO} + \text{Pr}$ 13 eV
 Species 1 is YO, 2 is PrO, 3 is Pr, 4 is Y

Temp	Log K	fef(1)	fef(2)	fef(3)	fef(4)	fefdif	Enthalpy
2190.5	-0.9740	64.312	67.142	51.436	48.506	0.100	9.982
2127.2	-1.0187	64.059	66.885	51.252	48.344	0.082	10.090
2053.6	-1.0769	63.764	66.587	51.032	48.157	0.052	10.226
2093.6	-1.0031	63.924	66.749	51.153	48.259	0.069	9.754
2161.0	-0.9877	64.194	67.022	51.351	48.431	0.092	9.966

Average Heat of Reaction = $10.000 \pm 0.4 \frac{\text{kcal}}{\text{mole}}$

Window - Prism Correction = 0.1230

THIRD LAW DATA

YS-GDS RUNS 1-5 Y + GDS = YS + GD 1-3 AT 12 EV, 4-5 AT 13 EV

SPECIES 1 IS YS, 2 IS GDS, 3 IS GD, 4 IS Y

TEMP	LOG K	FEF(1)	FEF(2)	FEF(3)	FEF(4)	FEFDIF	ENTHALPY
2267.5	0.20011	67.7211	72.3649	52.8590	48.7020	-0.48677	-3.180
2236.9	0.19367	67.6039	72.2476	52.7733	48.6285	-0.49893	-3.098
2204.2	0.19258	67.4768	72.1205	52.6817	48.5501	-0.51199	-3.071
2170.4	0.18324	67.3436	71.9872	52.5871	48.4660	-0.52246	-2.954
2135.7	0.19296	67.2047	71.8482	52.4899	48.3792	-0.53281	-3.024
2059.9	0.22056	66.8935	71.5369	52.2697	48.1817	-0.55537	-3.223
2014.7	0.19217	66.7027	71.3460	52.1341	48.0597	-0.56886	-2.918
2041.0	0.17964	66.8142	71.4575	52.2130	48.1307	-0.56099	-2.823
2084.1	0.21771	66.9940	71.6375	52.3423	48.2471	-0.54817	-3.219
2266.5	0.19605	67.7173	72.3611	52.8562	48.6996	-0.48715	-3.137
2230.6	0.19535	67.5795	72.2232	52.7557	48.6134	-0.50145	-3.112
2189.4	0.19490	67.4187	72.0623	52.6403	48.5135	-0.51678	-3.084
2150.4	0.22182	67.2638	71.9073	52.5311	48.4160	-0.52841	-3.319
2105.1	0.17804	67.0804	71.7238	52.4043	48.3027	-0.54193	-2.856
2058.9	0.13674	66.8894	71.5327	52.2667	48.1790	-0.55566	-2.432
2090.4	0.19102	67.0200	71.6635	52.3612	48.2641	-0.54634	-2.969
2135.7	0.20672	67.2047	71.8482	52.4899	48.3792	-0.53281	-3.158
2264.4	0.21784	67.7093	72.3531	52.8503	48.6945	-0.48798	-3.362
2242.2	0.20446	67.6243	72.2680	52.7881	48.6413	-0.49681	-3.212
2220.0	0.20445	67.5384	72.1821	52.7260	48.5880	-0.50566	-3.199
2191.5	0.23325	67.4270	72.0706	52.6462	48.5187	-0.51614	-3.470
2162.0	0.24519	67.3102	71.9537	52.5636	48.4450	-0.52492	-3.561
2136.7	0.24303	67.2087	71.8522	52.4928	48.3817	-0.53247	-3.514
2107.2	0.24231	67.0889	71.7324	52.4102	48.3080	-0.54129	-3.477
2076.7	0.20438	66.9634	71.6068	52.3201	48.2271	-0.55037	-3.085
2039.9	0.18663	66.8096	71.4529	52.2097	48.1277	-0.56134	-2.887
2265.4	0.23134	67.7131	72.3569	52.8531	48.6969	-0.48763	-3.503
2267.5	0.19122	67.7211	72.3649	52.8590	48.7020	-0.48677	-3.088
2221.1	0.14804	67.5427	72.1864	52.7291	48.5906	-0.50523	-2.627
2167.3	0.16717	67.3312	71.9748	52.5784	48.4582	-0.52341	-2.792
2112.5	0.14876	67.1106	71.7541	52.4250	48.3212	-0.53975	-2.578
2044.1	0.19059	66.8273	71.4706	52.2223	48.1391	-0.56010	-2.928
2095.7	0.18048	67.0418	71.6852	52.3771	48.2784	-0.54471	-2.872
2156.7	0.21297	67.2890	71.9325	52.5488	48.4317	-0.52652	-3.237
2207.3	0.16846	67.4889	72.1326	52.6904	48.5575	-0.51074	-2.829
2257.0	0.17375	67.6811	72.3248	52.8296	48.6768	-0.49094	-2.902
2267.5	0.16764	67.7211	72.3649	52.8590	48.7020	-0.48677	-2.843
2207.3	0.17526	67.4889	72.1326	52.6904	48.5575	-0.51074	-2.898
2138.8	0.18281	67.2172	71.8607	52.4986	48.3870	-0.53185	-2.927
2062.0	0.13982	66.9023	71.5456	52.2760	48.1874	-0.55475	-2.463
2102.0	0.16085	67.0677	71.7111	52.3956	48.2950	-0.54283	-2.688

AVE HEAT OF REACTION = -3.037 + OR - 0.277 KCAL/MOLE

QUOTED UNCERTAINTY IS STANDARD DEVIATION.

WINDOW-PRISM CORRECTION = 0.1230

Appendix III

Tables of mass spectrometric intensity measurements and linear least squares calculations of the slope and intercept for the vapor species observed over solid GdS.

MASS SPEC INTENSITY DATA

NORM GD+ DATA GDS RUNS 1-7, EXCEPT 4

Y = IT/10000.

T OBS	TEMP(K)	10000/T	I	LOG Y	NORM LOG Y	Run
1927.0	2257.4	4.4300	552.5	2.09594	2.08366	
1903.0	2232.1	4.4801	354.8	1.89869	1.88641	
1876.0	2203.7	4.5378	253.0	1.74622	1.73394	
1850.0	2176.4	4.5948	158.0	1.53636	1.52409	
1823.0	2148.0	4.6555	109.6	1.37180	1.35952	
1921.0	2251.0	4.4424	474.0	2.02814	2.01586	
1890.0	2218.4	4.5077	273.5	1.78302	1.77075	1
1864.0	2191.1	4.5640	188.6	1.61616	1.60388	
1833.0	2158.5	4.6328	126.9	1.43775	1.42547	
1807.0	2131.2	4.6922	79.5	1.22873	1.21645	
1775.0	2097.6	4.7673	46.1	0.98560	0.97332	
1812.0	2136.4	4.6807	84.0	1.25406	1.24179	
1840.0	2165.9	4.6171	136.1	1.46940	1.45712	
1867.0	2194.2	4.5574	207.3	1.65789	1.64562	
1925.0	2255.3	4.4341	468.0	2.02347	1.99827	
1903.0	2232.1	4.4801	337.0	1.87632	1.85112	
1872.0	2199.5	4.5465	242.5	1.72697	1.70177	
1848.0	2174.3	4.5993	156.2	1.53089	1.50569	2
1822.0	2147.0	4.6578	109.1	1.36977	1.34457	
1792.0	2115.5	4.7271	63.5	1.12797	1.10277	
1923.0	2253.1	4.4382	381.3	1.93403	2.00595	
1906.0	2235.3	4.4738	284.9	1.80407	1.87598	
1883.0	2211.1	4.5227	209.6	1.66597	1.73789	
1857.0	2183.7	4.5793	145.2	1.50118	1.57310	
1829.0	2154.3	4.6419	97.7	1.32327	1.39519	
1797.0	2120.7	4.7154	54.8	1.06522	1.13713	
1840.0	2165.9	4.6171	113.2	1.38964	1.46155	3
1869.0	2196.3	4.5530	165.3	1.55996	1.63188	
1897.0	2225.8	4.4928	242.0	1.73131	1.80323	
1921.0	2251.0	4.4424	338.8	1.88234	1.95426	
1891.0	2223.2	4.4981	413.7	1.96366	1.84834	
1873.0	2204.2	4.5368	298.6	1.81838	1.70306	
1853.0	2183.1	4.5807	209.6	1.66044	1.54512	
1835.0	2164.1	4.6208	171.7	1.57002	1.45470	
1811.0	2138.8	4.6755	120.9	1.41265	1.29733	
1791.0	2117.8	4.7220	89.9	1.27946	1.16414	
1767.0	2092.5	4.7790	49.3	1.01364	0.89832	
1742.0	2066.2	4.8398	37.1	0.88429	0.76896	
1715.0	2037.8	4.9072	22.1	0.65357	0.53825	
1897.0	2229.5	4.4853	264.4	1.77044	1.85932	5
1872.0	2203.1	4.5390	183.1	1.60574	1.69462	
1843.0	2172.5	4.6029	137.0	1.47364	1.56253	
1830.0	2158.8	4.6321	98.3	1.32662	1.41550	
1792.0	2118.8	4.7196	58.0	1.08945	1.17833	
1771.0	2096.7	4.7694	32.0	0.82619	0.91507	
1727.0	2050.4	4.8770	18.6	0.58206	0.67094	
1781.0	2107.2	4.7455	44.1	0.96780	1.05668	
1809.0	2136.7	4.6801	68.1	1.16307	1.25195	
1852.0	2182.0	4.5829	128.8	1.44866	1.53755	
1920.0	2253.8	4.4370	402.7	1.95794	1.95617	
1895.0	2227.4	4.4895	285.8	1.80393	1.80210	
1859.0	2189.4	4.5674	179.5	1.59428	1.59245	
1829.0	2157.8	4.6344	119.2	1.41020	1.40838	

1796.0	2123.0	4.7103	74.3	1.19816	1.19634
1761.0	2086.2	4.7934	39.4	0.91442	0.91259
1725.0	2048.3	4.8820	21.9	0.65220	0.65037
1684.0	2005.3	4.9869	10.7	0.33169	0.32986
1704.0	2026.3	4.9352	16.1	0.51452	0.51269
1744.0	2068.3	4.8349	31.6	0.81590	0.81408
1781.0	2107.2	4.7455	56.5	1.07599	1.07416
1817.0	2145.1	4.6617	99.0	1.32707	1.32524
1845.0	2174.7	4.5984	163.1	1.54986	1.54803
1880.0	2211.6	4.5217	248.9	1.74065	1.73882
1908.0	2241.1	4.4621	360.3	1.90710	1.90527
1918.0	2251.7	4.4411	428.3	1.98426	1.98244
1891.0	2223.2	4.4981	274.9	1.78612	1.78430
1871.0	2202.1	4.5412	212.8	1.67077	1.66894
1848.0	2177.8	4.5918	154.8	1.52777	1.52595
1809.0	2136.7	4.6801	90.4	1.28597	1.28414
1768.0	2093.6	4.7766	46.3	0.98648	0.98465
1708.0	2030.5	4.9250	18.2	0.56704	0.56521
1833.0	2162.0	4.6253	129.2	1.44620	1.44437
1953.0	2288.7	4.3694	787.2	2.25567	2.24950
1928.0	2262.2	4.4204	547.9	2.09328	2.08710
1904.0	2236.9	4.4705	348.9	1.89229	1.88612
1872.0	2203.1	4.5390	219.2	1.68384	1.67766
1842.0	2171.5	4.6051	135.6	1.46907	1.46290
1808.0	2135.7	4.6824	87.1	1.26967	1.26349
1778.0	2104.1	4.7527	50.1	1.02322	1.01705
1738.0	2062.0	4.8496	28.1	0.76342	0.75725
1700.0	2022.1	4.9454	14.1	0.45390	0.44773
1721.0	2044.1	4.8920	20.0	0.61055	0.60437
1758.0	2083.0	4.8007	38.8	0.90767	0.90150
1795.0	2122.0	4.7126	75.5	1.20483	1.19866
1828.0	2156.7	4.6366	117.6	1.40430	1.39812
1860.0	2190.5	4.5652	193.6	1.62746	1.62128
1891.0	2223.2	4.4981	307.8	1.83519	1.82902
1918.0	2251.7	4.4411	454.8	2.01032	2.00415
1945.0	2280.2	4.3856	650.2	2.17104	2.16487
1951.0	2286.5	4.3734	737.9	2.22718	2.22100
1881.0	2212.6	4.5195	256.2	1.75342	1.74725
1849.0	2178.9	4.5895	155.7	1.53054	1.52437
1750.0	2074.6	4.8202	31.4	0.81408	0.80791
SLOPE A =		-2.987265+	OR -	0.018176	
PARAMETER B =		15.247687+	OR -	0.084096	

6

7

HEAT OF VAPORIZATION = 136.69 + OR - 0.83 KCAL/MOLE

ENTROPY OF VAPORIZATION = 69.771 + OR - 0.385 CAL/DEG-MOLE

NORMALIZATION TEMP = 2150.0

Gd⁺

MASS SPEC INTENSITY DATA

NORM GDS+ DATA GDS RUNS 1-7, EXCEPT 4

Y = IT/10000.

T OBS	TEMP(K)	10000/T	I	LOG Y	NORM LOG Y	Run
1927.0	2257.4	4.4300	246.7	1.74576	1.78736	
1903.0	2232.1	4.4801	168.9	1.57625	1.61786	
1876.0	2203.7	4.5378	120.8	1.42505	1.46665	
1850.0	2176.4	4.5948	74.5	1.21004	1.25165	
1823.0	2148.0	4.6555	49.5	1.02688	1.06848	
1921.0	2251.0	4.4424	213.7	1.68214	1.72374	
1890.0	2218.4	4.5077	131.1	1.46375	1.50535	1
1864.0	2191.1	4.5640	94.3	1.31534	1.35695	
1833.0	2158.5	4.6328	56.6	1.08699	1.12859	
1812.0	2136.4	4.6807	35.9	0.88530	0.92691	
1840.0	2165.9	4.6171	61.3	1.12323	1.16483	
1867.0	2194.2	4.5574	95.3	1.32029	1.36189	
1925.0	2255.3	4.4341	159.9	1.55705	1.66792	
1903.0	2232.1	4.4801	134.4	1.47721	1.58809	
1872.0	2199.5	4.5465	93.9	1.31483	1.42570	2
1848.0	2174.3	4.5993	63.2	1.13807	1.24894	
1822.0	2147.0	4.6578	43.8	0.97349	1.08436	
1792.0	2115.5	4.7271	21.4	0.65516	0.76603	
1923.0	2253.1	4.4382	135.8	1.48584	1.67244	
1906.0	2235.3	4.4738	113.7	1.40500	1.59160	
1883.0	2211.1	4.5227	94.8	1.32145	1.50805	
1857.0	2183.7	4.5793	58.0	1.10276	1.28936	
1829.0	2154.3	4.6419	40.6	0.94146	1.12806	3
1797.0	2120.7	4.7154	19.6	0.61818	0.80478	
1840.0	2165.9	4.6171	46.0	0.99829	1.18489	
1869.0	2196.3	4.5530	66.0	1.16148	1.34808	
1897.0	2225.8	4.4928	110.4	1.39036	1.57696	
1921.0	2251.0	4.4424	143.9	1.51034	1.69694	
1891.0	2223.2	4.4981	259.9	1.76178	1.57051	
1873.0	2204.2	4.5368	190.6	1.62328	1.43201	
1853.0	2183.1	4.5807	132.8	1.46236	1.27109	
1835.0	2164.1	4.6208	108.5	1.37066	1.17939	
1811.0	2138.8	4.6755	70.6	1.17876	0.98749	
1791.0	2117.8	4.7220	53.8	1.05644	0.86517	
1767.0	2092.5	4.7790	29.6	0.79228	0.60101	
1742.0	2066.2	4.8398	21.7	0.65159	0.46032	
1715.0	2037.8	4.9072	12.5	0.40443	0.21316	
1897.0	2229.5	4.4853	165.1	1.56593	1.57385	
1872.0	2203.1	4.5390	114.9	1.40337	1.41129	
1843.0	2172.5	4.6029	82.1	1.25117	1.25909	
1830.0	2158.8	4.6321	62.5	1.13042	1.13833	
1792.0	2118.8	4.7196	35.1	0.87132	0.87924	5
1771.0	2096.7	4.7694	20.3	0.62967	0.63759	
1727.0	2050.4	4.8770	11.5	0.37147	0.37938	
1781.0	2107.2	4.7455	27.6	0.76527	0.77318	
1809.0	2136.7	4.6801	42.5	0.95765	0.96556	
1852.0	2182.0	4.5829	78.5	1.23367	1.24158	
1920.0	2253.8	4.4370	257.1	1.76297	1.65619	
1895.0	2227.4	4.4895	190.6	1.62784	1.52106	
1859.0	2189.4	4.5674	124.1	1.43394	1.32717	
1829.0	2157.8	4.6344	78.7	1.22986	1.12309	
1796.0	2123.0	4.7103	48.6	1.01345	0.90668	
1761.0	2086.2	4.7934	26.6	0.74429	0.63752	

1725.0	2048.3	4.8820	14.7	0.47782	0.37105
1684.0	2005.3	4.9869	6.4	0.10809	0.00132
1704.0	2026.3	4.9352	8.9	0.25819	0.15142
1744.0	2068.3	4.8349	20.1	0.61970	0.51293
1781.0	2107.2	4.7455	37.2	0.89445	0.78767
1817.0	2145.1	4.6617	64.1	1.13801	1.03124
1845.0	2174.7	4.5984	104.0	1.35426	1.24749
1880.0	2211.6	4.5217	168.4	1.57102	1.46425
1908.0	2241.1	4.4621	228.8	1.70986	1.60309
1918.0	2251.7	4.4411	277.8	1.79628	1.68951
1891.0	2223.2	4.4981	184.9	1.61392	1.50714
1871.0	2202.1	4.5412	145.0	1.50405	1.39728
1848.0	2177.8	4.5918	104.3	1.35646	1.24969
1809.0	2136.7	4.6801	60.5	1.11129	1.00452
1768.0	2093.6	4.7766	32.0	0.82641	0.71964
1708.0	2030.5	4.9250	10.5	0.32761	0.22083
1833.0	2162.0	4.6253	97.5	1.32406	1.21729
1953.0	2288.7	4.3694	400.9	1.96266	1.91371
1928.0	2262.2	4.4204	296.2	1.82616	1.77721
1904.0	2236.9	4.4705	197.2	1.64448	1.59553
1872.0	2203.1	4.5390	121.3	1.42697	1.37802
1842.0	2171.5	4.6051	75.5	1.21453	1.16559
1808.0	2135.7	4.6824	46.5	0.99707	0.94812
1778.0	2104.1	4.7527	28.3	0.77559	0.72664
1738.0	2062.0	4.8496	16.2	0.52450	0.47556
1700.0	2022.1	4.9454	7.9	0.20269	0.15374
1721.0	2044.1	4.8920	11.1	0.35412	0.30518
1758.0	2083.0	4.8007	23.1	0.68255	0.63360
1795.0	2122.0	4.7126	40.7	0.93590	0.88696
1828.0	2156.7	4.6366	66.0	1.15358	1.10463
1860.0	2190.5	4.5652	115.7	1.40371	1.35476
1891.0	2223.2	4.4981	181.6	1.60609	1.55714
1918.0	2251.7	4.4411	263.2	1.77280	1.72385
1945.0	2280.2	4.3856	376.4	1.93363	1.88469
1951.0	2286.5	4.3734	420.7	1.98320	1.93425
1881.0	2212.6	4.5195	150.9	1.52371	1.47476
1849.0	2178.9	4.5895	96.0	1.32067	1.27172
1750.0	2074.6	4.8202	18.6	0.58719	0.53824

6

7

SLOPE A = -3.034329+ OR - 0.022102
 PARAMETER B = 15.178302+ OR - 0.102213

HEAT OF VAPORIZATION = 138.85 + OR - 1.01 KCAL/MOLE

ENTROPY OF VAPORIZATION = 69.454 + OR - 0.468 CAL/DEG-MOLE

NORMALIZATION TEMP = 2150.0

GdS⁺

MASS SPEC INTENSITY DATA

NORM S+ DATA GDS RUN 6 ONLY

Y = IT/10000.

T OBS	TEMP(K)	10000/T	I	LOG Y	NORM LOG Y
1920.0	2253.8	4.4370	6.0	0.13128	0.13128
1895.0	2227.4	4.4895	4.8	0.02520	0.02520
1859.0	2189.4	4.5674	2.2	-0.31935	-0.31935
1829.0	2157.8	4.6344	2.2	-0.32566	-0.32566
1796.0	2123.0	4.7103	1.2	-0.60939	-0.60939
1761.0	2086.2	4.7934	0.9	-0.70414	-0.70414
1744.0	2068.3	4.8349	0.6	-0.89127	-0.89127
1781.0	2107.2	4.7455	0.8	-0.77321	-0.77321
1817.0	2145.1	4.6617	1.2	-0.58558	-0.58558
1845.0	2174.7	4.5984	2.9	-0.20260	-0.20260
1880.0	2211.6	4.5217	3.8	-0.07194	-0.07194
1908.0	2241.1	4.4621	5.5	0.09040	0.09040
1918.0	2251.7	4.4411	5.3	0.07720	0.07720
1891.0	2223.2	4.4981	4.3	-0.02438	-0.02438
1871.0	2202.1	4.5412	3.6	-0.10599	-0.10599
1848.0	2177.8	4.5918	2.2	-0.31338	-0.31338
1809.0	2136.7	4.6801	1.5	-0.49265	-0.49265
1768.0	2093.6	4.7766	0.7	-0.81175	-0.81175

SLOPE A = -2.645298+ OR - 0.118801
 PARAMETER B = 11.867532+ OR - 0.547898

HEAT OF VAPORIZATION = 121.04 + OR - 5.44 KCAL/MOLE

ENTROPY OF VAPORIZATION = 54.304 + OR - 2.507 CAL/DEG-MOLE

NORMALIZATION TEMP = 2150.0