Measurement of Enthalpies of Evaporation of Bi and Bi₂ by an Optical Absorption Technique*·†

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The enthalpies of evaporation of Bi and Bi₂ were determined by the second-law method using an optical absorption technique to measure the change of vapor density with temperature for each species. The 3067-Å line was used for Bi and the band head at 2731 Å was used for Bi₂. The enthalpy of dissociation of Bi₂ is the difference between the two enthalpies of evaporation. The evaporation values obtained were

$$\text{Bi(l)} = \text{Bi(g)} \qquad \Delta H^\circ_{298} = 49\ 600 \pm 1100 \text{ cal,}$$

$$\text{Bi(l)} = \tfrac{1}{2}\text{Bi}_2\text{(g)} \qquad \Delta H^\circ_{298} = 24\ 700 \pm 1000 \text{ cal,}$$

$$\tfrac{1}{2}\text{Bi}_2\text{(g)} = \text{Bi(g)} \qquad \Delta H^\circ_{298} = 24\ 900 \pm 2100 \text{ cal.}$$

The optical absorption technique was checked on lead, using the 2833-Å line. For lead, the $\Delta H^\circ_{v,298}$ measured was 47 240±850 cal, as compared with an accepted value of 46 600±300 cal.

INTRODUCTION

SEVERAL elements have multiple gaseous species in equilibrium with the condensed phase. These include carbon, phosphorous, sulfur, antimony, bismuth, and others. In order to determine the enthalpy of evaporation of the individual species by the second-law method, it is necessary to measure the temperature dependences of the vapor pressures of the individual species. This can be done by mass-spectrometric methods, by a combined Knudsen-torsion–effusion method in the case where only two important vapor species exist, or by optical absorption techniques. In this work, the temperature dependences of the vapor densities of Bi and Bi₂ in equilibrium with liquid bismuth were determined as a function of temperature using an optical absorption method. From these values, the enthalpy of dissociation of Bi₂ was determined. The measurements were made on the 3067-Å absorption line for Bi and on the band head at 2731 Å for Bi₂.

Since it is not necessary to know the *absolute* pressures of the species to use the second-law method, a knowledge of the optical absorption coefficient, or f value, was not required in this study. It was necessary, however, to know the optical absorption law applicable, that is, the relationship between the vapor density and the optical absorption parameter being measured.

With this knowledge, ΔH_v could be determined by an extension of the second-law method, viz., by plotting the appropriate absorption parameter versus the reciprocal of the absolute temperature and relating the slope to the enthalpy of evaporation.

SYMBOLS AND NOMENCLATURE

B	A constant $= \Delta C_p / R$
b	Dispersion half-breadth $= b_n + b_s + b_c$
C_I	A constant $= (\sigma_I^2 / \pi c k)[2\pi R(M_1^{-1} + M_2^{-1})]^{\frac{1}{2}}$
ΔC_p	Difference in heat capacity between vapor species and liquid
d	Spacing of lines in an absorption band
g_1, g_2	Statistical weights of normal and excited states, respectively
$\Delta H_{v,298}$	Enthalpy of evaporation at 298°K
I_0	Incident intensity at wavenumber ω
I_s	Transmitted intensity
I_ω	Transmitted intensity at wavenumber ω
k	Boltzmann's constant
L	A constant $= (\Delta H_{v,298} - 298\Delta C_p)/R$
l	Optical path length
M_1, M_2	Masses of absorbing species and inert-gas species, respectively
N	Concentration of absorbing species
n	Number of lines in an absorption band
P	Pressure of absorbing species
P_I	Pressure of inert gas
P_ω	Absorption coefficient at ω; $dI_\omega/I_\omega = -P_\omega dX$
R	Gas constant
S	Integrated absorption is

$$\int_0^\infty P_\omega d\omega = \frac{\lambda_0^2}{8\pi c \tau} \frac{g_2}{g_1}$$

T Absolute temperature
T_r Fractional transmittance
X Optical density $= Nl$
β Total absorption
β_1 Total absorption at low optical density
β_2 Total absorption at high optical density
λ_0 Wavelength at center of absorption line
τ Lifetime in excited state
Φ Integration constant
ω Wavenumber
ω_0 Wavenumber at center of absorption line

EXPERIMENTAL METHOD

A schematic diagram of the absorption apparatus is shown in Fig. 1. A parallel beam of light from a continuous source is passed through a cell containing the vapor to be studied. The light is then passed through a 1% mirror and focused on the grating of a spectrometer. The output is recorded as the ratio of the intensity in a very narrow range of frequencies (the resolution of the spectrometer) to the integrated intensity of the total beam. The details of the apparatus were given in a previous publication.[1]

OPTICAL ABSORPTION LAWS AND THE SECOND-LAW METHOD

The optical absorption parameter used in this investigation is β, the total absorption,

$$\beta = \int_0^\infty \frac{I_0 - I_\omega}{I_0}\, d\omega. \qquad (1)$$

It is a measure of the total energy removed from the light beam by the vapor in the wavenumber region surrounding the particular absorption line of interest. The quantity is experimentally determined by a procedure discussed in Ref. 1. Also in this reference, the total absorption is related to the features of the absorption line such as natural line breadth, collision line breadth, hyperfine structure, etc.

For measurements on atomic absorption lines it is shown that when a line is "fully absorbed," the addition of an inert gas can be used to make the collision line breadth much larger than the natural breadth or the self-collision breadth and yield a simple relationship between the total absorption (β_2) and the pressure of the species being measured [Eq. (2)]:

$$\beta_2 = (4SC_I P_I l P / kT^{\frac{1}{2}})^{\frac{1}{2}}. \qquad (2)$$

The combination of Eq. (2) with the form of the Clapeyron equation in Eq. (3) yields the relationship in Eq. (5),

$$\ln P = -(L/T) + B \ln T + \Phi, \qquad (3)$$

where

$$L = (\Delta H_{v,298} - 298\Delta C_p)/R, \qquad (4)$$

$$\ln(\beta_2 T^{\frac{1}{2}(3-2B)}) = -(L/2T) + \tfrac{1}{2}\Phi + \tfrac{1}{2}\ln(4SP_I C_I l/k). \qquad (5)$$

[1] P. A. Rice and D. V. Ragone, J. Chem. Phys. 42, 701 (1965).

Thus, if a constant inert-gas pressure is kept in the cell during optical absorption measurements, a plot of $\ln(\beta_2 T^{\frac{1}{2}(3-2B)})$ vs $1/T$ will be linear, with a slope related to the enthalpy of evaporation.

For molecular absorption bands, this treatment has been extended to cover absorption bands made up of an infinite number of equally spaced, equally intense, dispersion-broadened lines,[2] and also the case of an absorption band made up of a large number of absorption lines having random spacings.[3] A series of limiting absorption laws is derived for the fractional transmittance of the band, T_r, as a function of optical density X. The fractional transmittance is defined as the ratio of the transmitted intensity to the incident intensity over a wavenumber range $\Delta\omega$:

$$T_r = (\Delta\omega)^{-1} \int_{\Delta\omega} \frac{I_\omega}{I_0}\, d\omega. \qquad (6)$$

In particular it is shown that if the line breadth b is very much greater than the line spacing d, then

$$T_r = \exp(-SX/d). \qquad (7)$$

In this case, the transmittance is independent of the line breadth and is thus unaffected by the addition of an inert gas. The measurements on absorption bands in this study correspond to the conditions for Eq. (7). Hence

$$\ln T_r = -SX/d = -SlP/dkT. \qquad (8)$$

Combining Eq. (17) with the Clapeyron relationship [Eq. (10)] yields

$$\ln[T^{(1-B)} \ln(1/T_r)] = -(L/T) + \Phi + \ln(Sl/dk). \qquad (9)$$

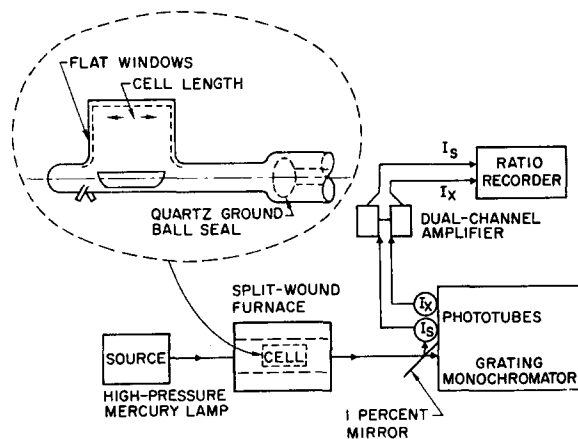This, a plot of $\ln[T^{(1-B)} \ln(1/T_r)]$ versus $1/T$, is a

FIG. 1. Schematic diagram of the absorption apparatus.

[2] W. M. Elasser, Harvard Meteorological Studies, (Harvard University Press, Cambridge, Mass., 1942), No. 6.
[3] S. S. Penner, Quantitative Molecular Spectroscopy and Gas Emissivities (Addison–Wesley Publ. Co., Inc., Reading, Mass., 1959).

straight line with slope L which is related to the enthalpy of evaporation of the diatomic species.

MEASUREMENTS

Optical absorption measurements were made on the Bi 3067-Å line, the Pb 2833-Å line, and the Bi$_2$ band starting at 2731 Å. Measurements on Bi were made from 770° to 1280°K (corresponding approximately to 2×10^{-8} to 10^{-3} atm); on Pb from 780° to 1280°K (3×10^{-8} to 2×10^{-3} atm); and on Bi$_2$ from 1010° to 1280°K (approximately 10^{-5} to 10^{-3} atm).

The atomic absorption lines were treated as outlined in Ref. 1. The measure of absorption for diatomic absorption was the ratio of transmitted intensity I_e, to incident intensity I_0, both extrapolated to the frequency where the band head shows half its maximum value.

Absorption measurements were made with and without helium present. When it was used, pressure was maintained at 746 mm Hg. The optical absorption β of monatomic species (lines) increased with the introduction of helium in the higher temperature regions (Fig. 2) because at these higher temperatures the center of the line is fully absorbed. The addition of helium increases the breadth of the line by collision. The transmittance of the absorption bands was not affected by the introduction of helium, which indicates
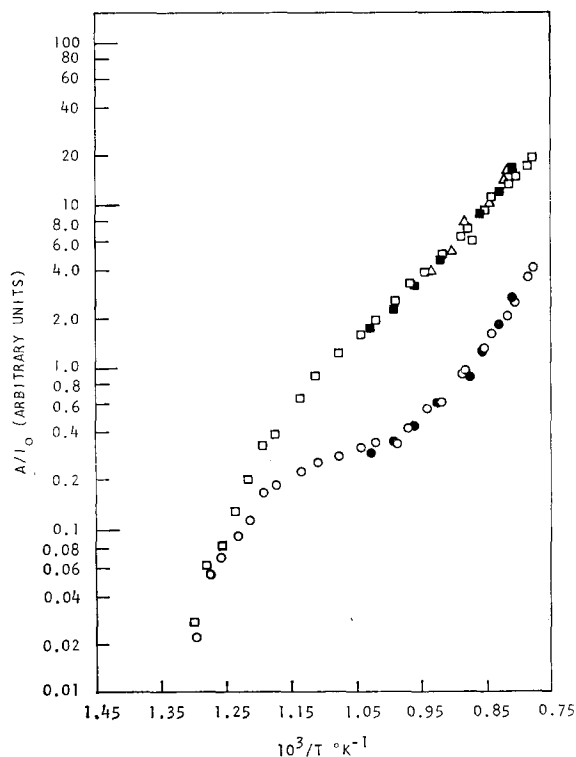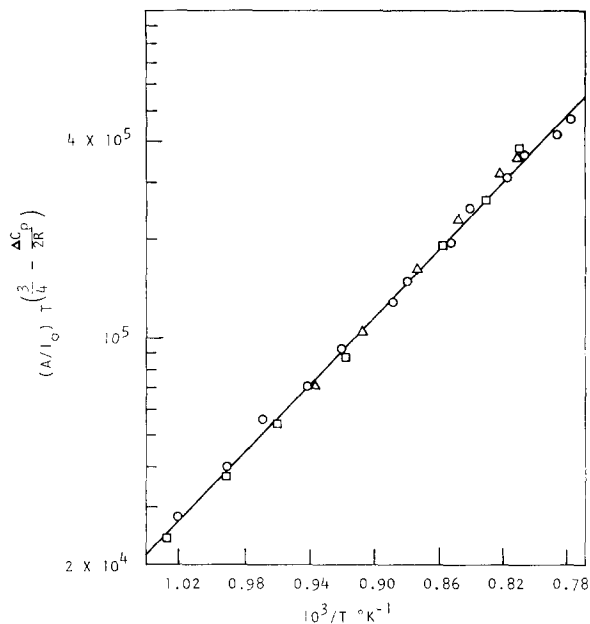

FIG. 3. Optical absorption versus inverse temperature for Bi 3067-Å line, with helium pressure of 746 mm Hg, corrected for self-broadening and hyperfine structure. O, Run 69; □, Run 72; △, Run 73. $\frac{3}{4}-(\Delta C_p/2R)=1.4115$.

that the breadth of the lines was greater than the spacing. This justifies the use of the simple absorption law given in Eq. (7).

In order to use the method represented by Eqs. (5) and (9) for monatomic and diatomic species, respectively, heat capacities of the liquids and particular vapor species have to be known. The values chosen were from the compilation by Stull and Sinke.[4] Monatomic absorption values were corrected for hyperfine structure. A least-squares line was fitted to $\ln(\beta T^{\frac{1}{4}(3-2B)})$ vs $1/T$ (Fig. 3). Only the higher-temperature points were used $(1/T<1.07\times10^{-3})$ to ensure that the points were all in the fully absorbed region.

For the Bi$_2$ data, the line was fitted (Fig. 4) to $\ln[T^{(1-B)}\ln(1/T_r)]$ versus $1/T$. In this case the data points taken between 970° and 1150°K were used to fit the least-squares line. The data points at higher temperatures deviated from the straight-line relationship shown in Eq. (9) and were not used in the calculation of the enthalpy. From the values obtained, the enthalpies of evaporation in Table I were calculated. These were extrapolated to 298°K using the heat-capacity values of Stull and Sinke.[4]

DISCUSSION

The accurate determination of enthalpies of evaporation by the second-law method requires that measurements be made over a long temperature range and that systematic temperature-dependent errors be elimi-

FIG. 2. Uncorrected optical absorption versus reciprocal temperature for Bi 3067-Å line for various helium pressures. Run 69: □, helium pressure=746 mmHg; O, helium pressure=0. Run 72: ■, helium pressure =746 mm Hg; ●, helium pressure= 0. Run 73: △, helium pressure =746 mm Hg.

[4] D. R. Stull and G. C. Sinke, Advan. Chem. Ser. 18, 55 (1956).
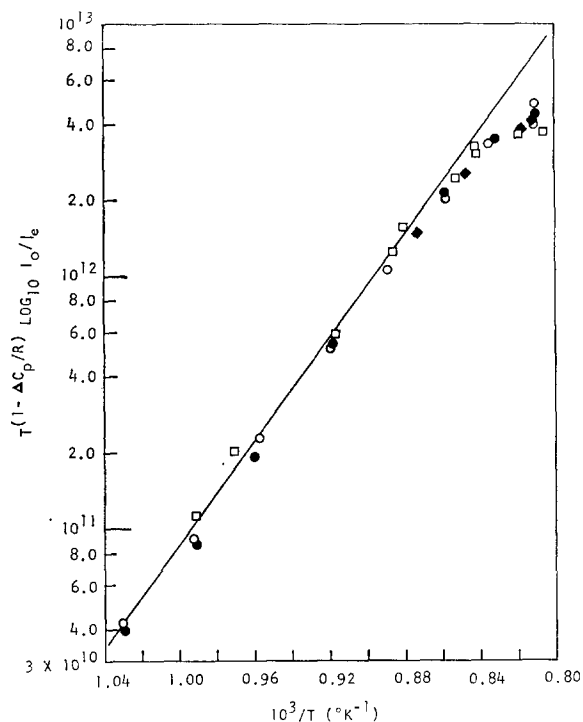
FIG. 4. Fractional transmittance versus inverse temperature for the Bi_2 band head at 2731 Å. Run 69: □, $P_{He}=0$ mm; ■, $P_{He}=746$ mm. Run 72: ○, $P_{He}=0$ mm; ●, $P_{He}=746$ mm. Run 73: ◇, $P_{He}=0$ mm; ◆, $P_{He}=746$ mm. $1-(\Delta C_p/R)=4.15$

nated. The optical absorption techniques used here were fortunately able to provide measurements over reasonably long temperature ranges. For example, the absorption for Bi was measured from 770° to 1280°K (roughly a variation of five decades in pressure). Only the data in the higher-temperature region (970° to 1250°K) were used in the calculation, but this was still a reasonably long temperature span (280°K). As assurance that systematic temperature-dependent errors had been eliminated, the technique was used to measure the enthalpy of evaporation of lead, which is reasonably well established. The value obtained, 47.24±0.85 kcal/mole at 298°K, agrees within experimental error

TABLE I. Enthalpies of evaporation (this study).

Species	$\Delta H°$ (cal/g-atom)	Temp range (°K)
Bi	48 100−2.63T±1100[a]	970–1250
½Bi₂	23 400−3.13T±1000[a]	970–1150
Pb	46 700−2.0T±850[a]	930–1200

[a] 95% confidence limits.

with the established value[5] of 46.60±0.30. The data, calculations, and plots for lead are given elsewhere.[6]

There have been some previous measurements on bismuth vapor that take atomicity into account. These include the torsion-effusion work of Yoshiyama[7] and the vapor velocity distribution work of Ko.[8] The results of these measurements were re-evaluated using the third-law method by Brackett and Brewer[9] and are listed in Table II. More recently, Aldred and Pratt[10] have published some torsion-effusion work on bismuth. A mass-spectrometric determination of vapor atomicity has been reported by Martynovitch[11] and quoted in a recent compilation by Nesmeyanov.[12]

The value of enthalpy of evaporation for monatomic bismuth determined in this study agrees very well with the third-law value calculated by Brackett and Brewer[9] and with the value of Aldred and Pratt.[10] The latter is a third-law value calculated from Bi pressures using

TABLE II. Enthalpy changes at 298°K (kilocalories per gram-atom).

Reaction	This study	Bracket and Brewer[a]	Aldred and Pratt[b]
Bi(l) =Bi(g)	49.6±1.1	49.5±1.0	50.13±0.92
Bi(l) =½Bi₂(g)	24.7±1.0	26.2±2.0	26.36±0.35
½Bi₂(g) =Bi(g)	24.9±2.1	23.3±1.0	23.93±1.36
Pb(l) =Pb(g)	47.24±0.85[c]		

[a] Reference 11.
[b] Reference 12.
[c] Hultgren et al.[7] give 46.60±0.30.

the free-energy function from Stull and Sinke. The enthalpy for Bi₂ overlaps the values cited in Refs. 9 and 10 when experimental error is taken into account. However, the values cannot be considered as being in good agreement. The value obtained in this study is probably a little low. Evidence for this can be obtained by calculating the equilibrium Bi₂ pressure using the third law. Using the free-energy functions of Stull

[5] R. Hultgren, R. L. Orr, P. D. Anderson, and K. K. Kelley, Selected Values of Thermodynamic Properties of Metals and Alloys (John Wiley & Sons, Inc., New York, 1963).
[6] P. A. Rice, "Thermodynamic Measurements Using Optical Absorption in Metal Vapors," Doctoral dissertation, University of Michigan, 1962.
[7] S. Yoshiyama, J. Chem. Soc. Japan 62, 204 (1941).
[8] C. Ko, J. Franklin Inst. 217, 173 (1934).
[9] E. Brackett and L. Brewer, University of California Radiation Laboratory Rept. UCRL-3712, March 1957.
[10] A. T. Aldred and J. N. Pratt, J. Chem. Phys. 38, 1085 (1963).
[11] G. N. Martynovitch, Vestn. Mosk. Univ. Ser. Mat. Mekhan. Astron. Fiz. i. Khim. 13, 67 (1958).
[12] A. N. Nesmeyanov, Vapor Pressure of the Chemical Elements (Elsevier Publ. Co., Amsterdam, 1963).

and Sinke[4] and our value of $\Delta H°_{298}$ given in Table II, one obtains a pressure of 1.1×10^{-4} atm at 1000°K. This value is higher than the total pressure 3.9×10^{-5} atm at this temperature measured by Aldred and Pratt.[10] There was, however, a considerable scatter in the Bi₂ data, as can be seen in Fig. 4. If the Bi₂ value

is low, then the enthalpy of dissociation of Bi₂ given in Table II would be high.

Vacuum-Ultraviolet Photolysis of Ethane Films

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The vacuum-ultraviolet photolysis of films of solid ethane has been studied both at 1470 and 1236 Å. The product distributions have been measured and evidence is presented for the quenching of excited ethane and ethylene. The over-all mechanism, with the exception of quenching reactions, appears to be the same as in the gas-phase photolysis.

IN a previous study[1] of the solid-phase photolysis at 1236 A it was concluded that a molecular mechanism was responsible for the formation of hydrogen and that the quantum yields were of the same order of magnitude as in the gas phase. These conclusions were based upon the observations that little HD was formed in the photolysis of either CH₃CD₃ or C₂H₆–C₂D₆ mixtures and that the estimated hydrogen quantum yield was roughly the same in both phases.

A more recent publication[2] on the gas-phase photolysis of ethane at 1236 A shows that in addition to the primary process corresponding to the molecular elimination of hydrogen, an equally important primary process is the elimination of two hydrogen atoms. It is doubtful whether isotopic analysis in the solid phase can distinguish between these two mechanisms since cage recombination of hydrogen atoms will also appear to be a molecular process. Any differences that occur between the two phases should be reflected in the product distributions. The purpose of the present work is to extend the 1236 A results to include product distributions and to study the effect of energy on these distributions.

I. EXPERIMENTAL

A. Materials

Phillips research-grade ethane and ethane-d₆ obtained from Merck and Company were purified by

gas chromatography. The purified ethanes were passed through Ascarite and P₂O₅ in order to remove any CO₂ and water that might have been present. The ethanes were then degassed by repeated freezing and pumping in vacuo. Following the above treatment the ethane was found by gas chromotography to contain less than one part of ethylene in 10⁵ parts of ethane and one part of butane in 10⁶ parts of ethane. No other higher hydrocarbons were detected.

B. Apparatus

The apparatus used for the photolysis experiments at 77°K consisted of a glass finger filled with liquid N₂ on the outside of which ethane was deposited. A nozzle which was out of the light path but directed toward the finger was used to deposit the ethane. For the photolysis experiments at 20°K, an Air Products Joule–Thomson cryostat was used and ethane frozen onto a copper disk. In each apparatus the lamps were attached to the system directly through a ground glass joint using Apiezon wax. The Xe and Kr lamps were fabricated according to the techniques described by Okabe,[3] and a check of the purity of the Xe lamps with a 1-m vacuum-ultraviolet monochromator indicated only the expected resonance lines. The isotopic analysis of the products were performed with a C.E.C. 620 mass spectrometer.

C. Procedure

Each of the systems were evacuated to 10⁻⁶ torr or better before the surfaces were cooled to the appropriate temperature. A known quantity of ethane

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[1] M. D. Scheer, J. R. McNesby, and R. Klein, J. Chem. Phys. 36, 3504 (1962).

[2] R. F. Hampson, Jr., and J. R. McNesby, J. Chem. Phys. 42, 2200 (1965).

[3] H. Okabe, J. Opt. Soc. Am. 54, 478 (1964).