

pendence whereas second-order dependences are observed only in the case of essentially nonacidic reducing agents such as I^- and Br^- .²³ Apparently the same maximum requirement for two H^+ in the activated complex obtains for both VO_2^+ and NpO_2^{3+} in reductions by nonacidic species.

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Registry No. Am(III), 2541-46-4; AmO_2^+ , 22878-02-0; AmO_2^{2+} , 12323-66-9; NpO_2^{3+} , 33702-71-5; Br^- , 24959-67-9; H^+ , 12408-02-5.

References and Notes

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Temperature Dependence of the Extinction Coefficient of Mercuric Iodide Vapor. Heat of Sublimation and Vapor Pressure of Solid HgI_2

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The temperature dependence of the extinction coefficient of HgI_2 vapor has been determined at a single wavelength of 342 nm where the data can be represented by the equation $\epsilon(\lambda, T) = (0.803 \pm 0.008)T/K - (273.1 \pm 4.1)$. Measurements of the absorbance of the vapor in equilibrium with the solid as a function of temperature yielded the following vapor pressure equation, where the pressure is in millimeters of Hg (reduced to 273.15 K and standard gravity) and the temperature is in Kelvins: $\ln P = -(9959 \pm 71)K/T + (23.28 \pm 0.16)$, $417 \leq T \leq 509$. The heat of sublimation calculated from this equation is $82.80 \text{ kJ mol}^{-1}$. The linear dependence of $\ln P$ vs. $1/T$ also establishes Beer's law for the vapor.

Introduction

It is possible in practice as well as in principle to thermally decompose water well below 3500 K by means of a properly selected sequence of chemical reactions.¹⁻³ The sequence may be regarded as a machine,⁴ powered by heat, which does work on water to decompose it into the elements. Since the reagents are components of the machine, they must be regenerated essentially without loss on traversing the cycle. One such sequence, designated ANL-4, is currently under investigation in the Chemistry Division of the Argonne National Laboratory.⁵

The hydrogen product in the cycle ANL-4 is generated by the reaction of mercury vapor with vaporized ammonium iodide. In preparing to study the kinetics of this reaction, spectroscopically, we found it necessary to reexamine the temperature dependence of the extinction coefficient of HgI_2 vapor. During the course of these measurements we have also been able to determine the vapor pressure of solid HgI_2 and the heat of sublimation. It is these results we report at this time.

The absorption spectrum of HgI_2 vapor has been found by several investigators^{6,7} to be continuous with a band commencing at about 400 nm and rising to a maximum at 265 nm. It has also been established that HgI_2 does not thermally decompose in the temperature range of interest to us, viz., up to 775 K.⁸ A complicating feature, however, is the temperature dependence of the extinction coefficient.⁹ This would present no problem if an experiment were conducted at constant temperature provided Beer's law is obeyed. Herczog and

Wieland⁹ determined the temperature dependence of the extinction coefficient of HgI_2 , but they did not, at the same time, establish the validity of Beer's law for the vapor; they assumed that

$$\log(I_0/I) = \epsilon(\lambda, T)Cl \quad (1)$$

where C is the concentration of HgI_2 in moles/liter, l is the optical path length in centimeters, and $\epsilon(\lambda, T)$ is the wavelength-temperature-dependent extinction coefficient. Although there is little reason to doubt the soundness of this procedure, it was essential for our purposes to establish experimentally that the monitored species (HgI_2) does indeed follow Beer's law.

Experimental Section

A schematic diagram of the optical train and ancillary equipment, which were assembled to perform these measurements, is presented in Figure 1. Both the xenon arc and the single monochromator were Bausch and Lomb units; the monochromator covered the spectral range 300-700 nm in 5-nm scale graduations. To reduce any long wavelength light which may have been scattered through the exit slit of the monochromator, a UV filter (λ_{\max} 360 nm, $fwhm = 50$ nm) was positioned at the exit slit. The two aspheric condensing lenses produced a nearly parallel beam which was chopped at 325 Hz. This beam was then split into a reference, I_0 , and a sample beam, I , by the optically flat quartz plate. The reference beam was directed to a silicon photodetector as was the sample beam after it had traversed the furnace (sample region). The voltage generated by the respective detectors was amplified and phase detected by the PAR lock-in amplifiers and finally fed into a Hewlett-Packard digital voltmeter operating in the ratio mode. The voltmeter output yielded the ratio

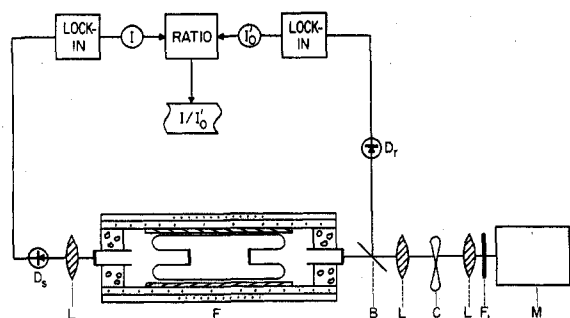


Figure 1. Schematic diagram of the high-temperature spectrometer: M, monochromator and source; F_1 , filter; L, lenses; C, chopper; B, beam splitter; F, furnace and absorption cell; D_1 , D_2 , reference and sample detectors.

I/I_0' ; to obtain transmittance, I/I_0 , the normalizing value, I_0/I_0' , was obtained with the sample tube in place before and after the furnace was heated (a separate experiment indicated that I_0/I_0' was independent of furnace temperature).

The fused quartz vessel which was used for both the vapor pressure and extinction coefficient measurements was 4.1 cm in diameter and 18 cm long. A 1.7 cm diameter reentrant tube was sealed into each end of the vessel; the inner end of each of these tubes was sealed by an optically flat quartz plate. The optical path lengths of the two cells used were 4.96 and 10.20 cm as determined with a cathetometer. A filling-evacuation tube was also sealed to one end of the vessel so as not to obstruct the light beam.

The furnace indicated in the diagram, Figure 1, was 46 cm long by 5.2 cm in diameter. The core of the furnace was wound with 16 gauge Nichrome heating wire. The winding was uniform except for a section 4 cm each side of the center of the core, where the interval between adjacent windings was doubled. This first winding was then wrapped with four layers of "Refrasil" glass tape. A second winding, approximately 12 cm in length, was positioned about the center of the furnace. Three additional layers of glass tape and then asbestos tape were wrapped over the windings. Finally, a magnesium oxide cylinder was made to fit snugly over the entire assembly.

A rolled nickel tube of 30-cm length and 3-mm wall thickness was centered within the furnace. The quartz vessel was centered within the nickel tube by means of three quartz tubes attached symmetrically to the outside of the vessel. Chromel-alumel thermocouples were inserted in the guide tubes. Firebrick endplugs for the furnace were drilled out and 17 mm diameter quartz tubes with an optically flat quartz plate sealed on one end inserted.

The power delivered to the primary winding was supplied by a Barber-Coleman proportioning unit; a chromel-alumel thermocouple inserted in the furnace acted as a temperature monitor for this device. A Variac supplied power to the auxiliary winding. At a given furnace temperature, the optimum Variac setting was found by trial and error. The average temperature was found to vary by no more than 0.8 °C across the length of the quartz vessel at the highest temperature reported here (757 K).

The HgI_2 used for this work was precipitated from a solution of reagent grade $\text{Hg}(\text{NO}_3)_2$ by adding the stoichiometric amount of dissolved reagent grade KI. The precipitate was washed with water and acetone then dried in an oven at 110 °C. The dried HgI_2 was sublimed and then resublimed. The resublimed material melted sharply at 254 °C. Literature values¹⁰ range from 248.5 to 258 °C. After careful evaluation of the various values, we accept that of Eade and Hartshorne,¹¹ 255.5 °C, as the correct one.

For the temperature dependence of the extinction coefficient, an amount of HgI_2 was chosen such that all would be in the vapor phase at the lowest temperature of interest. The weighed HgI_2 was introduced through the filling tube and the vessel was then attached to a vacuum line. The vessel was evacuated, and, while pumping, the HgI_2 was again sublimed. The filling tube was then collapsed and sealed close to the end of the vessel, which was removed from the line. The vessel was then centered in the furnace.

The normalization value, I_0/I_0' , was determined. The controller was then set for a temperature and after the system had come to thermal equilibrium as shown by a constant temperature reading for ~0.75 h, I/I_0' values were recorded for a period of time to be certain that the vapor also was in equilibrium. In this way values of I/I_0 were

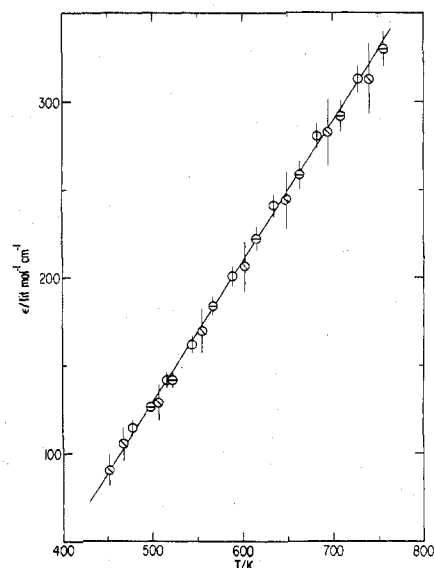


Figure 2. Molar extinction coefficient of HgI_2 vapor at 342 nm as a function of temperature: \odot , $C(\text{HgI}_2) = 9.82 \times 10^{-5}$ mol/L; \square , $C(\text{HgI}_2) = 2.92 \times 10^{-4}$ mol/L; \triangle , $C(\text{HgI}_2) = 6.32 \times 10^{-4}$ mol/L.

obtained for several different temperatures. Extinction coefficient measurements were carried out for three different concentrations of HgI_2 .

For the measurement of vapor pressure of solid HgI_2 , an 8 mm diameter quartz-to-Pyrex graded seal extension tube was attached to the vessel. A sufficient amount of HgI_2 to maintain a condensed phase was introduced into the cell, which was then evacuated. After subliming the material, the extension tube was sealed off so that a 4 cm length of Pyrex tube remained, to serve as a reservoir for the HgI_2 . A copper cylinder was machined to fit snugly over the end of this tube. Copper tubing, long enough to project out of the furnace, was soldered to the end of the cylinder to provide a "cold-leak". An inner groove along the copper cylinder wall accommodated a thermocouple to monitor the reservoir temperature. The cylinder was wrapped with a layer of glass tape and then with 30-gauge resistance wire. The portion of the extension tube between the reservoir and quartz vessel not surrounded by copper was also wound with resistance wire and the entire tube assembly was covered with Sauereisen porcelain cement. This arrangement enabled the number density of the HgI_2 in the vapor to be varied independently of the main furnace temperature, which determined the value of the extinction coefficient.

The thermocouples used in these measurements were standardized against a Pt-Pt-10% Rh couple with calibration traceable to the NBS.

All of the data reported here were taken with the monochromator set at the nominal wavelength of 340 nm. Since the resetability was no better than ± 1 nm and from the work of Herczog and Wieland⁹ it was estimated that $(d\epsilon/d\lambda)_T = -14 \text{ L mol}^{-1} \text{ cm}^{-1} \text{ nm}^{-1}$, the wavelength scale was locked in position. Calibration of the wavelength scale showed that 340 nm nominal was actually 342 nm.

Results and Discussion

Extinction coefficients, $\epsilon(342 \text{ nm}, T)$, were calculated from the raw data, using eq 1. The results are displayed in Figure 2, where $\epsilon(342 \text{ nm}, T)$ is plotted against the temperature in Kelvins. The effect of a finite slit width on the observed transmittances, and hence extinction coefficients, was found to be negligible for the slit width employed here.¹⁵ The vertical bar on each data point represents the propagated errors in ϵ .

It may be seen from this plot that within experimental errors, HgI_2 vapor does indeed follow Beer's law over the temperature and concentration range employed.

A least-squares line through the points gives the equation

$$\epsilon(342, T) = (0.803 \pm 0.008)T/K - (273.1 \pm 4.1) \quad (2)$$

In the temperature range considered here, the data of Herczog and Wieland⁹ are ~7% higher than those represented by eq

Table I. Vapor Pressures of HgI₂^a

I ^b			II ^c		
T/K	P/mmHg	ΔP ^d	T/K	P/mmHg	ΔP
416.5	0.51	0.09	504.6	33.2	1.2
424.8	0.82	0.09	494.0	22.9	0.8
434.7	1.32	0.10	481.7	13.4	0.5
443.2	2.26	0.12	472.8	9.17	0.34
453.4	3.88	0.17	460.5	5.22	0.21
465.2	6.80	0.26	450.9	3.43	0.15
476.2	11.1	0.4	438.4	1.90	0.11
485.9	16.8	0.6	428.7	1.08	0.10
499.2	26.9	1.0	420.2	0.66	0.09
509.1	40.6	1.5			

^a 1 mmHg = 133.3224 N m⁻². ^b Increasing reservoir temperature. ^c Decreasing reservoir temperature. ^d Error in derived vapor pressure as propagated from experimental uncertainties.

2. Since the errors (estimated from their graph) in their data are ~10%, we consider the two sets of data to be in satisfactory agreement.

A series of measurements was now made with the reservoir side arm attached to the cell. For these measurements, the furnace temperature was set at some value and the reservoir containing the HgI₂ was heated to a series of temperatures but always lower than the furnace temperature. At the single furnace temperature of 569.3 K, the reservoir temperature was varied from 415 to 510 K. I/I_0' values were recorded for both increasing and decreasing reservoir temperatures.

With the absorbance defined by $A \equiv \log(I_0/I)$, then at constant furnace temperature, T_f , eq 1 becomes

$$A(T_r) = \epsilon(\lambda, T_f)lC(T_r) = \epsilon(\lambda, T_f)lP_v(T_r)/RT_f \quad (3a)$$

Solving for $P_v(T_r)$

$$P_v(T_r) = A(T_r)RT_f/\epsilon(\lambda, T_f)l \quad (3b)$$

where $P_v(T_r)$ is the vapor pressure of HgI₂ in millimeters of mercury pressure at 273.15 K and standard gravity of 980.665 cm s⁻², R is the gas constant in appropriate units, l is the optical path length in centimeters, T_f is the furnace temperature and $\epsilon(\lambda, T_f)$ is the extinction coefficient corresponding to T_f , calculated from eq 2, and T_r is the reservoir temperature. Equation 3a implies ideal gas behavior for HgI₂. At constant T_f , a plot of $\ln(P_v(T_r))$ vs. $1/T_r$ will be a straight line if the absorption of HgI₂ vapor follows Beer's law.¹⁶ In addition, the slope of the line will, in this case, be the heat of sublimation divided by the gas constant. The results are presented in Table I and displayed in Figure 3. A linear least-squares line through the points is also displayed in the figure; this line is represented by

$$\ln(P_v(T)) = -(9959 \pm 71)K/T + (23.28 \pm 0.16) \quad (4)$$

The propagated errors in $\ln P_v$ are also shown as vertical bars centered on the data points; at high $\ln P_v$ values, the error does not exceed the circle size of the datum. Literature values^{12,13} on the vapor pressure of HgI₂ in this temperature range are also displayed in Figure 3. It may be seen that except for the low-pressure region, where the uncertainties in our derived vapor pressures are the largest, the different measurements are in good agreement. The least-squares line of eq 4 yields, for the heat and entropy of sublimation, 82.80 ± 0.59 kJ mol⁻¹ and 193.6 ± 1.3 J K⁻¹ mol⁻¹, respectively, which may be compared to the values of 84.51 ± 0.42 kJ mol⁻¹ and 196.7 ± 0.9 J K⁻¹ mol⁻¹ determined by a similar least-squares analysis of the results presented by Rinse.¹²

The value for the entropy change on sublimation may be combined with the tabulated¹⁷ entropy of solid HgI₂ to give the entropy of the vapor. At both 400 and 500 K, the "experimental" values differ from the tabulated¹⁷ entropy of

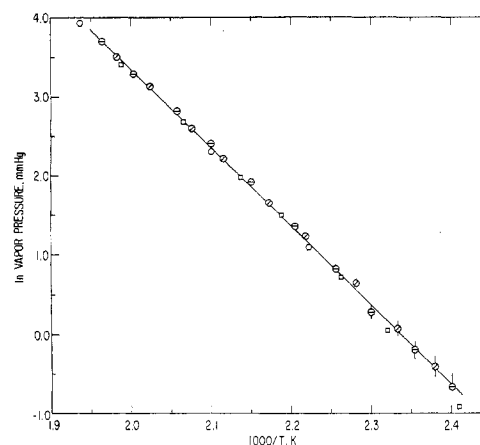


Figure 3. Natural logarithm of the vapor pressure of solid HgI₂ in millimeters of mercury as a function of reciprocal Kelvin temperature: ref 12, square; ref 13, hexagon; this work, Θ (increasing reservoir temperature) and \odot (decreasing reservoir temperature).

the ideal gas, corrected to the actual vapor pressure, by 30 J K⁻¹ mol⁻¹. This difference is well outside the experimental error for the entropy change on sublimation but is easily accounted for by a 15% uncertainty in the solid entropy.

Both the extinction coefficient and vapor pressure measurements establish that HgI₂ vapor adheres to Beer's law over a wide range of concentration and temperature: the former measurements were restricted to about a 10-fold change in the concentration while the latter provided nearly a 100-fold change in concentration.

Although the present method of vapor pressure determination does not require that the extinction coefficient be known for more than one temperature, previous work¹⁴ in which the material under study and its vapor were in the same chamber requires that each vapor pressure determination be corrected for the varying extinction coefficient. Although the rate of change of extinction coefficient with temperature may be small, there is no reason, a priori, to assume it is zero.

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Registry No. HgI₂, 7774-29-0.

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- (16) This assumption would imply that the heat of sublimation is independent of temperature over the range of temperatures employed so that $\ln P_v$ is expressible by the equation $\ln P_v = A + B/T$.
- (17) "JANAF Thermochemical Tables".