By expressing $R(t)$ from (38) and substituting it back into (37), we obtain the following relationship between a and v:

$$a = v^{2/3}\frac{3^{2/3}\int_{\phi}\int_{\theta}\sigma^{2}\sin\theta\,d\theta\,d\phi}{\left[\int_{\phi}\int_{\theta}\sigma^{3}\sin\theta\,d\theta\,d\phi\right]^{2/3}} \equiv v^{2/3}f \qquad (39)$$

The quotient appearing in the above equation is constant for a given shape, and abbreviated by f. Assuming that all crystals are of the equual size, one obtains

$$v = nM/(N\rho), \quad A = Na \qquad (40)$$

From eq 39 and 40 one reproduces eq 8 for $\nu = 3$.

$$A = N^{1/3}f(M/\rho)^{2/3}n^{2/3} \qquad (41)$$

An analogous procedure (using the cylindrical coordinates) can be applied to the growth of platelike crystals. In this way one derives the relation equivalent to (8) for $\nu = 2$. For $\nu = 1$, i.e., for one-dimensional growth, eq 8 obviously holds.

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High-Purity Iron(II) Iodide: Preparation, Vapor Pressure, and Vapor Composition, 792 to 1138 K

S. A. Mucklejohn,* N. W. O'Brien,

THORN EMI Lighting Limited, Research and Engineering Division, Leicester LE7 4PD, U.K.

and T. R. Brumleve

Anderson Physics Laboratories, Urbana, Illinois 61801 (Received: September 17, 1984; In Final Form: February 4, 1985)

The preparation of high-purity iron(II) iodide from metallic iron and elemental iodine is described. The product is shown to have extremely low levels of hydrogen- and oxygen-containing impurities and is primarily intended for use in discharge lamps. The results of a high-temperature mass spectrometric study of iron(II) iodide are outlined. The vapor pressure above iron(II) iodide has been measured in the range 792–1138 K by the quasistatic method. The partial pressures of I_2, FeI_2, and Fe_2I_4 were derived from the vapor pressure and the corresponding mole fractions. The molar enthalpies of sublimation and evaporation for the vaporization of iron(II) iodide to $FeI_2(g)$ and $Fe_2I_4(g)$ are calculated by the second-law and third-law methods. The uncertainties associated with these quantities are discussed. From the second-law treatment: $FeI_2(s) = FeI_2(g)$, $\Delta H_m°(298.15\ K) = 209 \pm 6$ kJ·mol^{-1}; $2FeI_2(s) = Fe_2I_4(g)$, $\Delta H_m°(298.15\ K) = 321 \pm 12$ kJ·mol^{-1}; $FeI_2(l) = FeI_2(g)$, $\Delta H_m°(298.15\ K) = 150 \pm 2$ kJ·mol^{-1}; $2FeI_2(l) = Fe_2I_4(g)$, $\Delta H_m°(298.15\ K) = 201 \pm 2$ kJ·mol^{-1}.

Introduction

Iron iodides and metal halide systems containing iron iodides are of considerable interest as sources of UV radiation in medium-pressure discharge lamps. The exploitation of such systems has, to date, been limited. Reiling[1] first investigated the properties of a discharge lamp containing mercury and iron(II) iodide. Iron has strong emission lines in the UV A region of the spectrum,[2] 315–400 nm. Gardner et al.[3] and Dobrusskin et al.[4] have developed UV sources containing iron(II) iodide. More recently Kondo[5,6] used a mixture of gallium and iron iodides in a lamp designed for use in photoetching and photoengineering processes. Page[7] has developed a lamp, containing FeI_2 and GaI_3, which is used in skin therapy, lithographic printing plate manufacture, and silk screen imaging.

By employing a suitable phosphor to convert UV radiation to visible radiation, Page and Wharmby[8] have shown that use of the FeI_2 + NaI system in a discharge lamp provides an interesting white light source.

If satisfactory performance and lamp life are to be obtained from lamps dosed with iron(II) iodide, the material must be introduced with very low levels of oxygen-, hydrogen-, and carbon-containing impurities. To this end a synthesis of high-purity iron(II) iodide has been developed together with analytical techniques for the determination of low levels of impurities.

The vapor pressure, vapor phase composition, and the thermodynamics of evaporation of iron(II) iodide are required for a detailed model of the discharge arc containing FeI_2 to be developed.

There are several reports of the measurement of the vapor pressure above solid iron(II) iodide but only one report concerning the vapor pressure of liquid iron(II) iodide. The majority of previous studies of FeI_2 have been carried out by transpiration methods on the $FeI_2 + I_2$ system. Measurement of vapor pressure by the quasistatic method of Rodebush and Dixon[9] is acknowledged to give high precision. There are no detailed reports of the determination of the vapor pressure above FeI_2 by this method.

We have measured the vapor pressure above iron(II) iodide in the range 792–1138 K using the quasistatic method and the results have been analyzed in terms of eq 1 and 2 to yield the partial

$$FeI_2(s\ or\ l) = Fe(s) + I_2(g) \qquad (1)$$

$$Fe_2I_4(g) = 2FeI_2(g) \qquad (2)$$

pressures of I_2, FeI_2, and Fe_2I_4. Equilibrium constants for reactions 1 and 2, $K_p(1)$ and $K_p(2)$, respectively, were based on the work of Zaugg and Gregory.[10,11] Thermodynamic quantities for the vaporization of iron(II) iodide to $FeI_2(g)$ and $Fe_2I_4(g)$ have been

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[1] G. H. Reiling, *J. Opt. Soc. Am.*, **54**, 532 (1964).

[2] "Wavelengths and Transition Probabilities for Atoms and Atomic Ions", *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.*, No. **68** (1980).

[3] P. J. Gardner, J. C. Morris, W. R. Watson, H. G. Silver, and J. A. Scholz, *J. Illum. Eng. Soc.*, **5**, 45 (1975).

[4] A. Dobrusskin, H. Leyendecker, and G. Schmid, *Int. Kongr. Reprog. Inf. 4th*, 9 (1975).

[5] S. Kondo, *J. Light Visual Environ.*, **3**, 5 (1979).

[6] S. Kondo and J. Yuasa, *GS News Tech. Rep.*, **39**, 48 (1980).

[7] R. B. Page, Third International Symposium on the Science and Technology of Light Sources, Toulouse, 1983.

[8] R. B. Page and D. O. Wharmby, unpublished results.

[9] W. H. Rodebush and A. L. Dixon, *Phys. Rev.*, **26**, 851 (1925).

[10] W. E. Zaugg and N. W. Gregory, *J. Phys. Chem.*, **70**, 486 (1966).

[11] W. E. Zaugg and N. W. Gregory, *J. Phys. Chem.*, **70**, 490 (1966).

0022-3654/85/2089-2409$01.50/0

calculated by the second-law and third-law methods.

The results of a mass spectrometric study of iron(II) iodide under Knudsen conditions are also outlined.

Preparation of Iron(II) Iodide. Previous approaches to the synthesis of iron(II) iodide have included high-temperature reaction of iron metal with HI or I_2,[12] high-temperature reaction of iron(II) oxide with AlI_3,[13] reaction of the metal with aqueous HI or with iodine in organic solvents,[14,15] and electrochemical oxidation of an Fe metal electrode in an iodine/organic solvent mixture.[16]

Since we are most concerned here with material for use in discharge lamps and vapor-phase studies, we have taken the approach of direct reaction of Fe with I_2. This eliminates potential contamination from organic solvents, in particular hydrogen- and oxygen-containing impurities. Increased levels of these species are detrimental to lamp life by causing the acceleration of electrode erosion.

Experimental Section

Preparation of Iron(II) Iodide. Starting materials were Fe metal containing less than 100-ppm total metallic impurities, 18-ppm carbon, 30-ppm oxygen, and less than 1-ppm nitrogen and hydrogen, and resublimed iodine (reagent ACS). The Fe metal rods, contained in a tungsten crucible, are slipped into a fused silica tube (closed at one end) with the top of the crucible at the closed end. Under a flowing argon cover, a depression is made in the wall of the silica tube to provide a shelf. A neck is then attached concentrically to the open end of the vessel, and the vessel is rinsed with deionized water followed by reagent-grade ethanol. It is then evacuated on a rough vacuum system and heated to between 425 and 475 K to remove solvent residues.

The reaction vessel is then evacuated to less than 10^{-3} Pa and the main body heated to approximately 675 K. The metal and crucible are further heated to orange heat, 1050 to 1170 K. A high vacuum is then rapidly established in the vessel and maintained until the metal has cooled. This high vacuum procedure is then repeated.

Iodine is introduced through the neck, and the vessel is again attached to the rough vacuum system, rinsed three times with inert gas, and evacuated to an ultimate pressure of approximately 30 Pa. The neck of the vessel is then sealed off with a glass-blowing torch.

The vessel is placed vertically into two independent tube furnaces. The top furnace (containing the crucible) is heated to 1173 K and the bottom furnace (containing the iodine) is held at 393 K. The product eventually begins to condense in a ring or plug in the air gap between the furnaces.

The final step in the preparation consists of melting the product under inert gas and filtering the salt through a porous silica frit. The details of this process have been described in the literature for other metal iodides.[17,18] This procedure thus removes insoluble material and avoids potential decomposition at the melting point by rapidly quenching the filtered liquid. This provides particles with a small surface area to mass ratio, and consequently reduces potential H_2O and O_2 contamination.

Vapor-Pressure Measurements. The details of our procedure and apparatus have been reported previously.[19]

A series of five experiments were carried out requiring 15 g of sample for each. All handling operations were carried out in an argon-filled drybox.

TABLE I: Determination of the Total Iron Content in FeI_2 Samples

	calcd	found 1[a]	found 2[b,c]	found 3[b,c]
% Fe	18.0	18.2 ± 0.2	18.0 ± 0.2	18.2 ± 0.2

[a] Varian 1475 instrument at Anderson Physics Laboratories. [b] Perkin-Elmer 306 instrument at THORN EMI Lighting Laboratories. [c] Sample 2 before vapor-pressure measurements, sample 3 from material after vapor-pressure measurements had been made.

The vapor pressure was measured with a Baratron Model 170 capacitance gauge with a precision of 0.1 Pa in the range up to 1.3 kPa and 1 Pa in the range from 1.3 to 13.3 kPa. The sample was heated by a platinum wound vertical furnace, regulated by a Stanton Redcroft LVP controller. The temperature could be maintained within ±0.2 K over the temperature range employed. The temperature of the sample was monitored independently by a platinum—platinum–13 mass % rhodium thermocouple and the potential difference monitored by a Thurlby 1905a voltmeter with a resolution of 1 μV.

The sample cell was fabricated from Thermal Syndicate grade four electrically fused silica. There was no evidence for interaction between FeI_2 and this material, either in the form of attack on the surface of the fused silica or the appearance of volatile byproducts in the apparatus. Similarly, in lamps containing FeI_2 prepared in the manner described here, there was no evidence for reaction between the lamp body and the dose. Electrically fused silica used in this work has a surface hydroxyl concentration of less than 5 ppm; this low level is responsible for the passive nature of the containers.

Subsequent determination of the iron content of the sample by atomic absorption spectrometry indicated that no change had taken place in the iron to iodide ratio during the course of the experiments.

Mass Spectrometry. Mass spectrometric studies were carried out on a Vacuum Generators Micromass 1201 magnetic sector instrument fitted with a high-temperature furnace assembly. The iron(II) iodide samples were held in sintered alumina buckets which were contained in a molybdenum Knudsen-effusion cell similar to the quadcell described by Johnston.[20] The orifice was cylindrical, 0.25 mm diameter × 1 mm. The temperature of the sample was measured by a three-junction platinum—platinum–13 mass % rhodium thermocouple.

Variation in the response of the mass spectrometer was taken into account by calibration with argon before each experiment. Ions were identified by comparison with the theoretical isotope patterns. Spectra were recorded at 20 eV.

Differential Thermal Analysis (DTA). DTA studies were carried out with a Stanton Redcroft Model 67-4 instrument. The iron(II) iodide samples were contained in sealed nickel-coated stainless steel capsules. The details of this technique for the study of volatile and/or air-sensitive materials will be described elsewhere. The melting point of iron(II) iodide was found to be 833 ± 3 K.

Results

Characterization of Iron(II) Iodide. The iron(II) iodide obtained from the synthesis described above was analyzed for total iron content by atomic absorption spectrophotometry at 248.3 nm using standard conditions[21] for the Varian 1475. A similar determination was carried out on the material (from the original batch) that was used for vapor-phase studies using a Perkin-Elmer 306 instrument. The results for the total iron content of the iron(II) iodide samples are listed in Table I.

The product was also analyzed for trace H_2O and OH^- by coulometric Karl Fischer titration, employing a specially constructed solid sample inlet. This apparatus and technique have recently been described in detail.[22] The technique has been found to be sensitive down to approximately 1 μg of H_2O. The results

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(12) G. Brauer, "Handbook of Preparative Inorganic Chemistry", 2nd ed, Vol. 2, Academic Press, New York, 1965.

(13) M. Chaigneau, *Bull. Soc. Chim. Fr.*, 886 (1957).

(14) G. Winter, *Inorg. Syn.*, **14**, 101 (1973).

(15) R. Job and R. Earl, *Inorg. Nucl. Chem. Lett.*, **15**, 81 (1979).

(16) J. J. Habeeb, L. Neilson, and D. G. Tuck, *Inorg. Chem.*, **17**, 306 (1978).

(17) S. Anderson and R. B. Page, *J. Light Visual Environ.*, **5**, 1 (1981).

(18) S. Anderson, U. S. Patents, 3 676 534, 3 948 793, 4 010 000 and 4 201 739.

(19) S. A. Mucklejohn and N. W. O'Brien, *J. Chem. Thermodyn.*, **16**, 767 (1984).

(20) G. R. Johnston, *Dyn. Mass Spectrom.*, **5**, 206 (1978).

(21) "Analytical Methods for Flame Spectroscopy", Varian Techtron Pty. Ltd., Springvale, Australia, 1979.

(22) T. R. Brumleve, *Anal. Chim. Acta*, **155**, 79 (1983).

TABLE II: Vapor Pressures, p, above Solid FeI_2, Partial Pressures $x(I_2)p$, $x(FeI_2)p$, $x(Fe_2I_4)p$, and Equilibrium Constants $K_p = \{x(FeI_2)p\}^2/x(Fe_2I_4)p$

T/K	p/Pa obsd	p/Pa calcd	$x(I_2)p$/Pa	$x(FeI_2)p$/Pa	$x(Fe_2I_4)p$/Pa	K_p/Pa
792	46.5	42.7	0.9	19.6	22.2	17.3
808	87.6	89.0	1.4	34.8	52.8	22.9
815	114.5	119.9	1.7	43.8	74.4	25.7
827	172.9	198.9	2.3	64.3	132.2	31.3
836	290.1	301.9	3.0	88.0	210.9	36.7
855	706.6	634.3	4.9	152.7	476.7	48.9

TABLE III: Vapor Pressures, p, above Liquid FeI_2, Partial Pressures $x(I_2)p$, $x(FeI_2)p$, $x(Fe_2I_4)p$, and Equilibrium Constants $K_p = \{x(FeI_2)p\}^2/x(Fe_2I_4)p$

T/K	p/kPa obsd	p/kPa calcd	$x(I_2)p$/kPa	$x(FeI_2)p$/kPa	$x(Fe_2I_4)p$/kPa	K_p/kPa
872	1.1599	1.1543	0.0075	0.2400	0.9068	0.0635
882	1.403	1.430	0.009	0.288	1.133	0.073
899	1.973	2.041	0.014	0.392	1.635	0.094
904	2.253	2.253	0.016	0.426	1.811	0.100
921	3.014	3.158	0.024	0.570	2.564	0.127
926	3.388	3.469	0.026	0.618	2.825	0.135
945	5.040	4.988	0.040	0.845	4.103	0.174
949	5.336	5.354	0.043	0.898	4.413	0.183
963	6.999	6.816	0.057	1.106	5.653	0.216
968	7.503	7.483	0.064	1.198	6.221	0.240
978	8.801	8.867	0.078	1.388	7.401	0.260
986	10.403	10.106	0.091	1.554	8.461	0.286
987	10.596	10.274	0.093	1.577	8.604	0.288
1005	14.145	13.662	0.130	2.018	11.514	0.354
1031	20.692	20.262	0.208	2.842	17.212	0.469
1061	29.558	30.958	0.346	4.111	26.501	0.638
1088	42.223	44.496	0.538	5.646	38.312	0.832
1111	60.288	59.651	0.771	7.111	51.769	1.034
1138	81.073	82.120	1.146	9.673	71.301	1.312

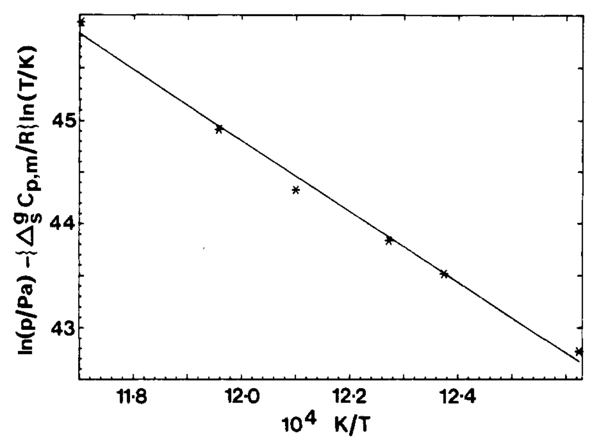

Figure 1. Plot of [ln $(p/\mathrm{Pa}) - \{\Delta_s^g C_{p,m}/R\}$ ln (T/K)] against K/T for solid FeI_2.

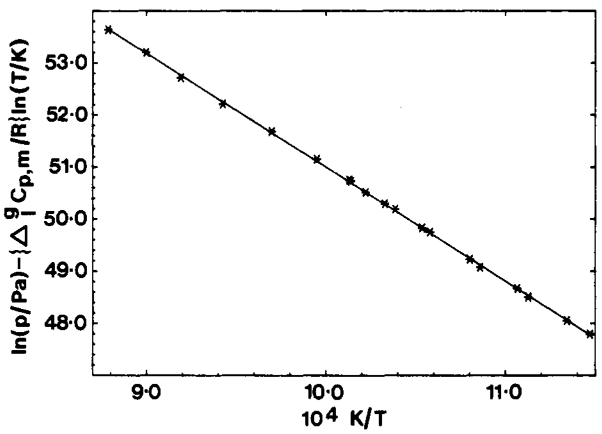

Figure 2. Plot of [ln $(p/\mathrm{Pa}) - \{\Delta_l^g C_{p,m}/R\}$ ln (T/K)] against K/T for liquid FeI_2.

for two replicate 1-g samples were 1 and 0 ppm of H_2O.

The Cl and Br content of the iron(II) iodide was determined by using a Dionex 2000i ion chromatograph. The sample was found to contain 53 ± 5 ppm of Cl and 10 ± 1 ppm of Br (mass:mass).

Vapor-Pressure Measurements. Throughout this work uncertainties quoted refer to 95% confidence limits; this corresponds to two standard deviations.

Tables II and III list the total vapor pressure above solid and liquid iron(II) iodide, respectively. A linear regression analysis of [ln $(p/\mathrm{Pa}) - \Delta_s^g C_{p,m}/R$ ln (T/K)] against K/T enables the vapor pressure above solid FeI_2 to be represented as

$$\ln (p/\mathrm{Pa}) = -3.4101 \times 10^4(\mathrm{K}/T) - 5.83 \ln (T/\mathrm{K}) + 85.7228 \quad (3)$$

where $\Delta_s^g C_{p,m}$ is the difference between the molar heat capacities of the vapor and solid. The value of $\Delta_s^g C_{p,m}/R = -5.83$ is taken from the JANAF tables.[23] Similarly, the vapor pressure above liquid FeI_2 can be represented by

$$\ln (p/\mathrm{Pa}) = -2.1868 \times 10^4(\mathrm{K}/T) - 6.02 \ln (T/\mathrm{K}) + 72.8641 \quad (4)$$

where $\Delta_l^g C_{p,m}/R = -6.02$ is the difference between the molar heat capacities of the vapor and liquid; this value is also derived from the JANAF tables.[23] Figures 1 and 2 show plots of [ln $(p/\mathrm{Pa}) - \Delta_s^g C_{p,m}/R$ ln (T/K)] and [ln $(p/\mathrm{Pa}) - \Delta_l^g C_{p,m}/R$ ln (T/K)] against K/T, respectively.

The $\Delta C_{p,m}/R$ terms in eq 3 and 4 consider the molar heat capacity of the vapor as a weighted average of the molar heat capacities of the components at the midpoint temperature.

The vapor phase above iron(II) iodide is considered to contain $I_2(g)$, $FeI_2(g)$, and $Fe_2I_4(g)$. Zaugg and Gregory[10] have studied the decomposition of FeI_2, eq 1, over the range 771–858 K using a transpiration method. The equilibrium constant for eq 1 can be expressed by

$$\ln \{K_p(1)/\mathrm{Pa}\} = -1.8721 \times 10^4(\mathrm{K}/T) + 23.4913 \quad (5)$$

Equation 5 allows calculation of the iodine partial pressure above iron(II) iodide. Subtraction of the iodine partial pressure from the total pressure leaves the sum of the monomer and dimer partial pressures. Use of the mole fractions for the monomer + dimer equilibrium, eq 2, together with the FeI_2 + Fe_2I_4 pressure allows the calculation of the partial pressures of FeI_2 and Fe_2I_4. Zaugg and Gregory[11] have also studied the monomer + dimer equilibrium above liquid FeI_2 by the transpiration technique. The temperature variation of the equlibrium constant for eq 2, $K_p(2)$, is given by

$$\ln \{K_p(2)/\mathrm{Pa}\} = -1.1283 \times 10^4(\mathrm{K}/T) + 17.0922 \quad (6)$$

this equation is obtained from the results listed in ref 11.

The uncertainties associated with this analysis are discussed in a later section.

Table II lists the partial pressures of I_2, FeI_2, and Fe_2I_4 above solid iron(II) iodide; these values have been derived by use of eq 3 to calculate the total pressure and eq 5 and 6 to determine $K_p(1)$ and $K_p(2)$, respectively. Similarly, the partial pressures of I_2, FeI_2, and Fe_2I_4 above liquid iron(II) iodide have been calculated by use of eq 4 to give the total pressure. These results are listed in Table III.

A linear regression analysis of ln $\{x(FeI_2)p/\mathrm{Pa}\}$ against K/T enables the pressure of FeI_2 to be represented as

$$\ln \{x(FeI_2)p/\mathrm{Pa}\} = -2.2099 \times 10^4(\mathrm{K}/T) + 30.8915 \quad (7)$$

for temperatures below the melting point and for temperatures above the melting point as

$$\ln \{x(FeI_2)p/\mathrm{Pa}\} = -1.3803 \times 10^4(\mathrm{K}/T) + 21.3332 \quad (8)$$

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[23] "JANAF Thermochemical Tables", *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.*, No. 37 (1971).

TABLE IV: Comparison of Second-Law Sublimation Thermodynamics of Iron(II) Iodide to $FeI_2(g)$ and $Fe_2I_4(g)$[a]

	this work	Zaugg and Gregory[b]
$\{H_m^\circ(\mathrm{FeI_2,g,824\ K}) - H_m^\circ(\mathrm{FeI_2,s,298.15\ K})\}/(\mathrm{kJ\cdot mol^{-1}})$	184 ± 5	161 ± 6
$\{H_m^\circ(\mathrm{FeI_2,g,298.15\ K}) - H_m^\circ(\mathrm{FeI_2,s,298.15\ K})\}/(\mathrm{kJ\cdot mol^{-1}})$	209 ± 6	186 ± 7
$\{S_m^\circ(\mathrm{FeI_2,g,824\ K}) - S_m^\circ(\mathrm{FeI_2,s,298.15\ K})\}/(\mathrm{J\cdot K^{-1}\cdot mol^{-1}})$	161 ± 5	131 ± 7
$\{S_m^\circ(\mathrm{FeI_2,g,298.15\ K}) - S_m^\circ(\mathrm{FeI_2,s,298.15\ K})\}/(\mathrm{J\cdot K^{-1}\cdot mol^{-1}})$	210 ± 6	180 ± 10
$\{H_m^\circ(\mathrm{Fe_2I_4,g,824\ K}) - 2H_m^\circ(\mathrm{FeI_2,s,298.15\ K})\}/(\mathrm{kJ\cdot mol^{-1}})$	274 ± 9	223 ± 3
$\{H_m^\circ(\mathrm{Fe_2I_4,g,298.15\ K}) - 2H_m^\circ(\mathrm{FeI_2,s,298.15\ K})\}/(\mathrm{kJ\cdot mol^{-1}})$	321 ± 12	269 ± 4
$\{S_m^\circ(\mathrm{Fe_2I_4,g,824\ K}) - 2S_m^\circ(\mathrm{FeI_2,s,298.15\ K})\}/(\mathrm{J\cdot K^{-1}\cdot mol^{-1}})$	277 ± 10	215 ± 4
$\{S_m^\circ(\mathrm{Fe_2I_4,g,298.15\ K}) - 2S_m^\circ(\mathrm{FeI_2,s,298.15\ K})\}/(\mathrm{J\cdot K^{-1}\cdot mol^{-1}})$	367 ± 12	305 ± 6

[a] p^0 = 101325 Pa. [b] Reference 11.

TABLE V: Second-Law Evaporation Thermodynamics of Iron(II) Iodide[a]

$\{H_m^\circ(\mathrm{FeI_2,g,1005\ K}) - H_m^\circ(\mathrm{FeI_2,l,298.15\ K})\}/(\mathrm{kJ\cdot mol^{-1}})$	115 ± 1
$\{S_m^\circ(\mathrm{FeI_2,g,1005\ K}) - S_m^\circ(\mathrm{FeI_2,l,298.15\ K})\}/(\mathrm{J\cdot K^{-1}\cdot mol^{-1}})$	81 ± 1
$\{H_m^\circ(\mathrm{FeI_2,g,298.15\ K}) - H_m^\circ(\mathrm{FeI_2,l,298.15\ K})\}/(\mathrm{kJ\cdot mol^{-1}})$	150 ± 2
$\{S_m^\circ(\mathrm{FeI_2,g,298.15\ K}) - S_m^\circ(\mathrm{FeI_2,l,298.15\ K})\}/(\mathrm{J\cdot K^{-1}\cdot mol^{-1}})$	142 ± 2
$\{H_m^\circ(\mathrm{Fe_2I_4,g,1005\ K}) - 2H_m^\circ(\mathrm{FeI_2,l,298.15\ K})\}/(\mathrm{kJ\cdot mol^{-1}})$	136 ± 1
$\{S_m^\circ(\mathrm{Fe_2I_4,g,1005\ K}) - 2S_m^\circ(\mathrm{FeI_2,l,298.15\ K})\}/(\mathrm{J\cdot K^{-1}\cdot mol^{-1}})$	117 ± 1
$\{H_m^\circ(\mathrm{Fe_2I_4,298.15\ K}) - 2H_m^\circ(\mathrm{FeI_2,l,298.15\ K})\}/(\mathrm{kJ\cdot mol^{-1}})$	201 ± 2
$\{S_m^\circ(\mathrm{Fe_2I_4,g,298.15\ K}) - 2S_m^\circ(\mathrm{FeI_2,l,298.15\ K})\}/(\mathrm{J\cdot K^{-1}\cdot mol^{-1}})$	193 ± 2

[a] Uncertainties quoted are derived from a linear regression of ln (p/Pa) against K/T. p^0 = 101325 Pa.

Similarly the partial pressure of Fe_2I_4 above solid iron(II) iodide is represented by

$$\ln\{x(\mathrm{Fe_2I_4})p/\mathrm{Pa}\} = -3.3005 \times 10^4(\mathrm{K}/T) + 44.7982 \quad (9)$$

and above the liquid by

$$\ln\{x(\mathrm{Fe_2I_4})p/\mathrm{Pa}\} = -1.6310 \times 10^4(\mathrm{K}/T) + 25.5587 \quad (10)$$

In view of the uncertainties associated with this analysis, particularly in the determination of $K_p(2)$, the authors consider that the partial pressures of the monomer and dimer are adequately represented by equations of the type $\ln(p/\mathrm{Pa}) = -A/T + B$.

The molar enthalpies and entropies of sublimation and evaporation for the monomer and dimer, calculated from a second-law analysis, are listed in Tables IV and V, respectively. Values of these quantities at 298.15 K were determined from the measured values at 824 (sublimation) and 1005 K (evaporation) by using the molar heat capacities for $FeI_2(s)$, $FeI_2(l)$, $FeI_2(g)$, and $Fe_2I_4(g)$ listed in the JANAF tables.[23] The uncertainties quoted in Tables IV and V are derived from a linear regression analysis of ln (p/Pa) against K/T.

The molar enthalpies of vaporization for the monomer and dimer can also be calculated by using the third-law method whereby each experimental measurement gives a value for ΔH_m°(298.15 K). The third-law treatment for evaporation can be expressed as[24]

$$\Delta_l^g H_m^\circ(298.15\ \mathrm{K})/T = -\Delta_l^g\{G_m^\circ(T) - H_m^\circ(298.15\ \mathrm{K})\}/T - R\ln(p/p^\circ) \quad (11)$$

Values of $\{G_m^\circ(T) - H_m^\circ(298.15\ \mathrm{K})\}/T$ for $FeI_2(s)$, $FeI_2(l)$, $FeI_2(g)$, and $Fe_2I_4(g)$ are listed in the JANAF tables.[23]

Table VI lists values ΔH_m°(298.15 K) for the sublimation and evaporation of iron(II) iodide to $FeI_2(g)$ and $Fe_2I_4(g)$.

Mass Spectrometry. The relative abundances of the ions detected above a sample of solid iron(II) iodide are listed in Table VII.

TABLE VI: Third-Law Vaporization Thermodynamics of Iron(II) Iodide[a]

$\{H_m^\circ(\mathrm{FeI_2,g,298.15\ K}) - H_m^\circ(\mathrm{FeI_2,s,298.15\ K})\}/(\mathrm{kJ\cdot mol^{-1}})$	194 ± 19
$\{H_m^\circ(\mathrm{Fe_2I_4,g,298.15\ K}) - 2H_m^\circ(\mathrm{FeI_2,s,298.15\ K})\}/(\mathrm{kJ\cdot mol^{-1}})$	206 ± 20
$\{H_m^\circ(\mathrm{FeI_2,g,298.15\ K}) - H_m^\circ(\mathrm{FeI_2,l,298.15\ K})\}/(\mathrm{kJ\cdot mol^{-1}})$	146 ± 15
$\{H_m^\circ(\mathrm{Fe_2I_4,g,298.15\ K}) - 2H_m^\circ(\mathrm{FeI_2,l,298.15\ K})\}/(\mathrm{kJ\cdot mol^{-1}})$	125 ± 12

[a] The uncertainties are discussed in the text. p^0 = 101325 Pa.

TABLE VII: Relative Abundances of Ions Detected above $FeI_2(s)$ at 722 K[a]

ion	rel abundance	ion	rel abundance
Fe^+	0.047	$Fe_2I_3^+$	0.505
FeI^+	1.000	$Fe_2I_4^+$	0.119
FeI_2^+	0.910	$Fe_2I_5^+$	<0.001
FeI_3^+	0.012	$Fe_2I_6^+$	<0.001

[a] The energy of the ionizing electrons was 20 eV.

TABLE VIII: Second-Law Sublimation Thermodynamics of Iron(II) Iodide and Dissociation Enthalpy of $Fe_2I_4(g)$[a]

$\{H_m^\circ(\mathrm{FeI_2,g,693\ K}) - H_m^\circ(\mathrm{FeI_2,s,298.15\ K})\}/(\mathrm{kJ\cdot mol^{-1}})$	168 ± 14
$\{H_m^\circ(\mathrm{Fe_2I_4,g,693\ K}) - 2H_m^\circ(\mathrm{FeI_2,s,298.15\ K})\}/(\mathrm{kJ\cdot mol^{-1}})$	218 ± 13
$\{2H_m^\circ(\mathrm{FeI_2,g,693\ K}) - H_m^\circ(\mathrm{Fe_2I_4,g,693\ K})\}/(\mathrm{kJ\cdot mol^{-1}})$	130 ± 11

[a] p^0 = 101325 Pa.

The variation of the ion currents of FeI^+, $I(FeI^+)$, and $Fe_2I_3^+$, $I(Fe_2I_3^+)$, were monitored over the range 664–724 K. The molar enthalpies of sulimation for $FeI_2(g)$ and $Fe_2I_4(g)$ were derived from the slopes of plots of $\ln\{I(\mathrm{FeI^+})T/(\mathrm{A\ K})\}$ against K/T and $\ln\{I(\mathrm{Fe_2I_3^+})T/(\mathrm{A\ K})\}$ against K/T, respectively. $\{I(\mathrm{FeI}_n^+)T/(\mathrm{A\ K})\}$ is the product of the ion current from FeI_n^+ and the absolute temperature. The molar enthalpy of dissociation of $Fe_2I_4(g)$, eq 2, was derived from a plot of $\{\ln K_p(2')/p^\circ\}$ against K/T. The equilibrium constant, $K_p(2')$, was calculated from

$$K_p(2') = [\sigma_1 k_1\{I(\mathrm{FeI^+})T\}]^2/[\sigma_2 k_2\{I(\mathrm{Fe_2I_3^+})T\}] \quad (12)$$

where σ_1 and σ_2 are the ionization cross sections for reaction 13 and 14, respectively; $\sigma_1{:}\sigma_2$ = 1:1.50. The constants for the conversion of the product of ion current and temperature to pressure are represented by k_1 and k_2.

$$\mathrm{FeI_2(g) + e^- = FeI^+ + I + 2e^-} \quad (13)$$

$$\mathrm{Fe_2I_4(g) + e^- = Fe_2I_3^+ + I + 2e^-} \quad (14)$$

Thermodynamic quantities determined from the mass spectrometric study are listed in Table VIII.

Discussion

It has been established that use of metal halides which contain more than 10 ppm of H_2O and O_2 in discharge lamps can lead to unacceptably short lamp lives.[25] Failure of such lamps is brought about by continuous removal of tungsten from the electrode shank and deposition on the arc tube wall. Oxygen, introduced into the lamp during dosing and processing, plays a vital role in these reactions. The presence of hydrogen within the discharge lamp inhibits the striking of the arc.

Iron(II) iodide, prepared in the manner described in this paper, has proved suitable for use in a variety of medium-pressure lamps. The extremely low concentrations of hydrogen and oxygen have meant that lamp life has not been limited by erosion of the electrode assemblies.

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(24) L. Brewer and E. Brackett, *Chem. Rev.*, 61, 425 (1961).

(25) M. A. Cayless and A. M. Marsden, "Lamps and Lighting", 3rd ed, Edward Arnold, London, 1983, p 236.

The mass spectrum recorded above solid iron(II) iodide shows that the major iron-containing species in the vapor are FeI_2 and Fe_2I_4. The mass spectrum from iron(II) iodide was first reported by Schoonmaker et al.[26] This group found FeI_2^+ to be the most abundant ion in the spectrum; this is in contrast to our work, Table VI, where FeI^+ was the most abundant species. FeI_3 was detected in low abundance in the spectrum above samples of iron(II) iodide. Detailed appearance potential measurements were not carried out during the course of this work and consequently the precursors of FeI_3^+ cannot be uniquely defined. Possible precursors of FeI_3^+ are FeI_3, Fe_2I_4, and products of ion–molecule reactions within the ion-source region. Of these, the largest contribution is expected to come from FeI_3. Calculation of the partial pressure of FeI_3 formed from the gas-phase reaction of FeI_2 and I_2 using the limited information available[28] shows the expected partial pressure to be less than 0.02 Pa (total pressure 1.1 Pa) at 722 K.

The ions $Fe_2I_5^+$ and $Fe_2I_6^+$ were found in extremely low abundance relative to FeI^+ and are considered to be derived from Fe_2I_6. Another candidate for the precursor of $Fe_2I_5^+$ is the mixed valence compound Fe_2I_5, considered by Gregory[27] to be a possible trace species in the vapor above iron(II) iodide. The very low ion currents of $Fe_2I_5^+$ and $Fe_2I_6^+$ precluded any appearance potential measurements for these species.

Comparison of Tables IV and VIII shows that values for the molar enthalpy of sublimation of iron(II) iodide to $FeI_2(g)$ and $Fe_2I_4(g)$ derived from the mass spectrometric study are considerably lower than the corresponding values derived from vapor-pressure measurements. Although the uncertainties associated with the derivation of the molar enthalpies of sublimation from the latter method are large (see below), it is considered that these values are more reliable than those calculated from the mass spectrometric study.

The molar enthalpy of dissociation of $Fe_2I_4(g)$ measured in this work is 130 ± 11 kJ·mol^{-1} at 693 K; this compares with 96 kJ·mol^{-1} at 945 K[11] and 157 kJ·mol^{-1} at 714 K[26] from previous studies.

There have been only three reports published on the measurement of the vapor pressure of solid iron(II) iodide. Schäfer and Hönes[28] determined the vapor pressure of solid and liquid iron(II) iodide using a transpiration method to study the $FeI_2 + I_2$ system. The results were calculated by assuming the only species containing Fe(II) was FeI_2. Sime and Gregory[29] measured the vapor pressure above solid iron(II) iodide by the torsion effusion method. This technique did not require the average molar mass of the vaporization species to be known. The results were similar to those reported by Schäfer and Hönes;[28] this was taken to be justification for the assumption that FeI_2 was the dominant species in the vapor above solid iron(II) iodide. Shortly before the publication of the paper by Sime and Gregory,[29] Schoonmaker et al.[26] reported their mass spectrometric study of iron(II) iodide showing that at comparatively low temperatures the dimer, Fe_2I_4, made a substantial contribution to the vapor phase. The mole fraction of the dimer was found to be 0.16 at 714 K. It had been appreciated for some time prior to the work of Schoonmaker et al.[26] that the vapor above iron(III) iodide contained monomeric and dimeric species.

Zaugg and Gregory[10,11] deduced the vapor pressures above iron(II) iodide by refining the results from previous studies.[28,29] They did not, however, measure the vapor pressure of iron(II) iodide by an independent technique.

Barin and Knacke[30] have estimated the standard Gibbs free energies of $FeI_2(s)$, $FeI_2(l)$, $FeI_2(g)$, and $Fe_2I_4(g)$ from which the vapor pressures of solid and liquid iron(II) iodide can be calculated.

Vapor-pressure measurements above solid iron(II) iodide are compared in Figure 3 by means of a plot of ln (p/Pa) against K/T. In Figure 3 the results from ref 28 are not corrected for the presence of the dimer. Figure 4 compares the total vapor pressure above liquid iron(II) iodide from this work and from that of Schäfer and Hönes.[28] Again, the latter results have been calculated on the assumption that FeI_2 is the only iron-containing species in the vapor. Measurements from our study cover a considerably larger temperature range than those reported previously. The intersection of the solid and liquid vapor-pressure curves from this work gives a melting point of 865 K, in excellent agreement with that found in our DTA studies, 866 ± 3 K.

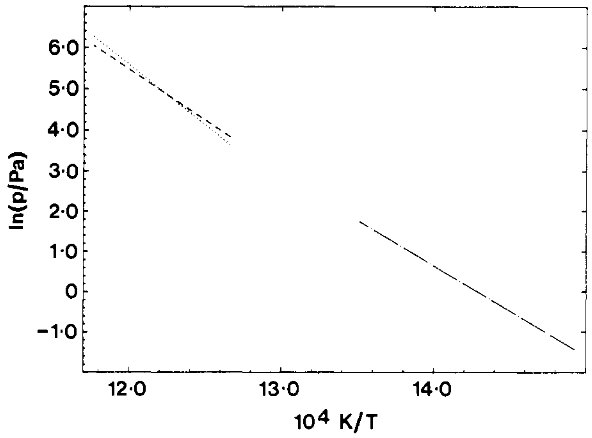

Figure 3. Plot of ln (p/Pa) against K/T for solid iron(II) iodide: (···) this work; (- - -) ref 28; (- · · ·) ref 29.

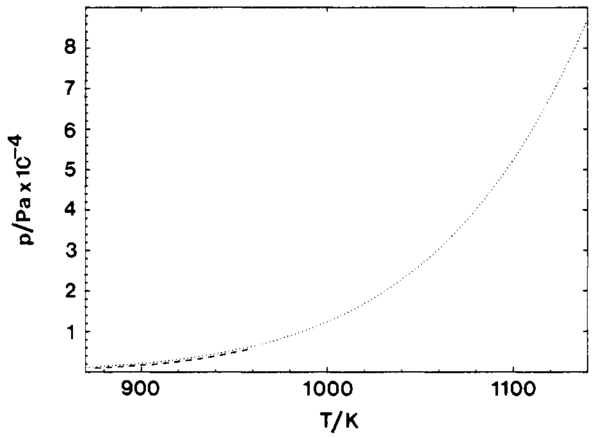

Figure 4. Plot of p/Pa against temperature for liquid iron(II) iodide: (···) this work; (- - -) ref 28.

In order to calculate the partial pressures of I_2, FeI_2, and Fe_2I_4 above iron(II) iodide we have extrapolated the results of Zaugg and Gregory[10] for the decomposition of solid iron(II) iodide, eq 1, into the liquid range. Subtraction of the iodine partial pressure from the total pressure leaves the sum of the partial pressures of FeI_2 and Fe_2I_4. Zaugg and Gregory[11] are the only workers to have reported a study of the monomer + dimer equilibrium above liquid iron(II) iodide. The equilibrium constant was derived from a complex series of experiments using a transpiration method to study the $FeI_2(l) + I_2(g)$ system. Inspection of their results shows that there is a large uncertainty associated with $K_p(2)$. Gregory[27] in a subsequent paper draws attention to the large uncertainty in $K_p(2)$ and attempted to refine values of the equilibrium constant by a spectrophotometric method. This approach, however, proved unsuccessful.

Six points are listed in ref 11 for the variation of $K_p(2)$ with temperature, 865–1025 K. One of these points seems to be inconsistent with the remainder; a linear regression analysis of ln $\{K_p(2)/\text{Pa}\}$ against K/T omitting this point gives a statistically better fit than when all six points are included. We have therefore used these five points to give the variation of $K_p(2)$ with temperature, eq 6.

In his attempt to improve the characterization of the monomer + dimer equilibrium, Gregory[27] employed four different expressions for the variation of the equilibrium constant with tem-

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[26] R. C. Schoonmaker, A. H. Friedman, and R. F. Porter, *J. Chem. Phys.*, **31**, 1586 (1959).

[27] N. W. Gregory, *J. Phys. Chem.*, **83**, 692 (1979).

[28] H. Schäfer and W. J. Hönes, *Z. Anorg. Allg. Chem.*, **288**, 62 (1956).

[29] R. J. Sime and N. W. Gregory, *J. Phys. Chem.*, **64**, 86, (1960).

[30] I. Barin and O. Knacke, "Thermochemical Properties of Inorganic Substances", Springer, Berlin, 1973.

TABLE IX: Comparison of Second-Law and Third-Law Values for the Vaporization of Iron(II) Iodide to $FeI_2(g)$ and $Fe_2I_4(g)$[a]

	this work		ref 11	
	2nd law	3rd law	2nd law	3rd law
Sublimation				
$\{H_m^\circ(FeI_2,g,298.15\ K) - H_m^\circ(FeI_2,s,298.15\ K)\}/(kJ\cdot mol^{-1})$	209	194	186	195
$\{H_m^\circ(Fe_2I_4,g,298.15\ K) - 2H_m^\circ(FeI_2,s,298.15\ K)\}/(kJ\cdot mol^{-1})$	321	206	269	206
Evaporation				
$\{H_m^\circ(FeI_2,g,298.15\ K) - H_m^\circ(FeI_2,l,298.15\ K)\}/(kJ\cdot mol^{-1})$	150	146		
$\{H_m^\circ(Fe_2I_4,g,298.15\ K) - 2H_m^\circ(FeI_2,l,298.15\ K)\}/(kJ\cdot mol^{-1})$	201	125		

[a] $p^0 = 101325$ Pa.

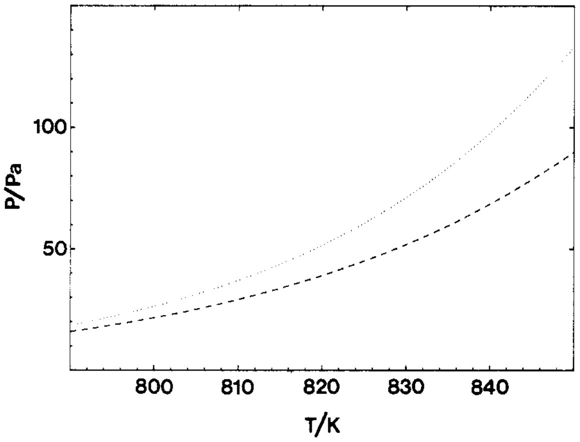

Figure 5. Plot of $x(FeI_2)p/Pa$ against temperature for solid iron(II) iodide: (···) this work; (- - -) ref 11.

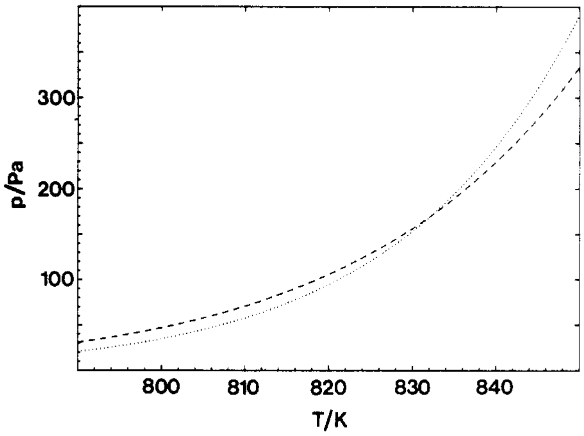

Figure 6. Plot of $x(Fe_2I_4)p/Pa$ against temperature for solid iron(II) iodide: (···) this work; (- - -) ref 11.

perature. Values of $K_p(2)$ calculated from eq 6 are similar to those derived from the expression preferred by Gregory.[27]

The partial pressures above solid iron(II) iodide were also calculated by using $K_p(2)$ from eq 6.

The uncertainty in the partial pressures derived from the analysis described above must take into account contributions from the vapor pressure (eq 3 and 4) and from the equilibrium constants (eq 5 and 6). The limitations associated with the determination of partial pressure from vapor-pressure measurements and the equilibrium constant for the monomer + dimer equilibrium have been described in detail elsewhere.[19]

Zaugg and Gregory[11] only report the partial pressure of FeI_2 above solid iron(II) iodide; they do not list the partial pressure of Fe_2I_4. We have determined the partial pressure of Fe_2I_4 from their work by subtracting $p(FeI_2+I_2)$ from the total pressure measurements of Schäfer and Hönes.[28] The partial pressures of FeI_2 above solid iron(II) iodide from this work and from ref 11 are compared in Figure 5. The corresponding curves for Fe_2I_4 are shown in Figure 6.

Table IV lists the second-law molar enthalpies and entropies of sublimation derived from these two studies. The uncertainties quoted refer to a linear regression analysis of ln (p/Pa) against K/T. Thermodynamic quantities at 298.15 K were calculated from the experimental values by using molar heat capacities for $FeI_2(s)$, $FeI_2(g)$, and $Fe_2I_4(g)$ listed in the JANAF tables.[23]

The uncertainty associated with a value of $\Delta H_m^\circ(298.15\ K)$ calculated by the third-law method is not straightforward to evaluate. Experimental scatter in values of ln (p/Pa) will be taken into account when the statistical analysis is carried out on the values of $\Delta H_m^\circ(298.15\ K)$ obtained from a third-law calculation. Uncertainties in $\{G_m^\circ(T) - H^\circ(298.15\ K)\}/T$, however, would not be reflected in such an analysis and these should be considered separately. The values for the standard Gibbs free energies listed in the JANAF tables[23] for the iron(II) iodides are based on estimated molecular parameters. We have assigned an overall uncertainty of 10% to all third-law values in this work, although the statistical variation in values of $\Delta H_m^\circ(298.15\ K)$ is much lower.

Table IV compares the second-law and third-law molar sublimation enthalpies of FeI_2 and Fe_2I_4 from this work and that of Zaugg and Gregory.[11] The second-law and third-law values for the molar enthalpies of evaporation of FeI_2 and Fe_2I_4 are also shown in Table IX. There is satisfactory agreement between the second-law and third-law calculations in this work for the molar enthalpies relating to the monomer. Similarly, the agreement between our work and that of Zaugg and Gregory[11] is close. Comparison of second-law values of $\{H_m^\circ(FeI_2,g,298.15\ K) - H_m^\circ(FeI_2,s,298.15\ K)\}$ for these two studies shows a difference of 23 $kJ\cdot mol^{-1}$; the corresponding third-law values are almost identical.

Second-law and third-law values for the molar enthalpy of sublimation to the dimer from our work are disparate. Third-law treatment of the partial pressures of Fe_2I_4 from this work and ref 11 are identical, yet the corresponding second-law values differ by 52 $kJ\cdot mol^{-1}$. This highlights the point illustrated by recent studies on sodium iodide[19,31] that third-law treatments are much more sensitive to the values of $S_m^\circ(298.15\ K)$ used than to the vapor pressures. Gregory[27] has recently shown that data listed in the JANAF tables[23] for $FeI_2(g)$ and $Fe_2I_4(g)$ lead to $K_p(2)$ values which are not in agreement with results obtained from transpiration experiments.

Values of $S_m^\circ(Fe_2I_4,g,298.15\ K)$ can be calculated from second-law values of $\{S_m^\circ(Fe_2I_4,g,298.15\ K) - 2S_m^\circ(FeI_2,s,298.15\ K)\}$. Using $S_m^\circ(FeI_2,s,298.15\ K) = 349.5\ J\cdot K^{-1}\cdot mol^{-1}$ (JANAF) gives $S_m^\circ(Fe_2I_4,g,298.15\ K) = 701.7\ J\cdot K^{-1}\cdot mol^{-1}$ (this work), 640.0 $J\cdot K^{-1}\cdot mol^{-1}$ (ref 11), and 543.3 $J\cdot K^{-1}\cdot mol^{-1}$ (JANAF). These figures suggest that the values of $S_m^\circ(Fe_2I_4,g,T)$ listed in the JANAF tables[23] are too small.

All third-law values calculated in this work show a marked dependence on temperature. A similar trend was noted by Zaugg and Gregory[10] for the third-law treatment for the decomposition of solid iron(II) iodide, eq 1. This was attributed to the use of an incorrect value for $S_m^\circ(FeI_2,s,298.15\ K)$.

Bartovska and Cerny[32] have recently surveyed published data for the thermodynamic properties of the iron-group metal halides. Their recommended values for $\Delta_f H_m^\circ(FeI_2,s,298.15\ K)$, $\Delta_f G_m^\circ(FeI_2,s,298.15\ K)$, and $S_m^\circ(FeI_2,s,298.15\ K)$ are the same as those listed in the JANAF tables[23] (which are based on ref 10

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(31) D. E. Work, *J. Chem. Thermodyn.* **13**, 491 (1981).

(32) L. Bartovska and C. Cerny, *Sb. Vys. Sk. Chem. Technol. Praze, Fiz. Chem.*, 55 (1979).

J. Phys. Chem. 1985, 89, 2415-2419

and 11). Although Bartovska and Cerny[32] recommend $\Delta_f H_m^\circ(\mathrm{FeI_2},\mathrm{s},298.15\ \mathrm{K}) = -105\ \mathrm{kJ{\cdot}mol^{-1}}$, the average value of the reports surveyed is $-118\ \mathrm{kJ{\cdot}mol^{-1}}$. Separate values for the vaporization to the monomer and dimer are not listed in ref 32.

With data from the JANAF tables[23] for the molar enthalpy of formation of solid iron(II) iodide, the molar enthalpy of formation of $\mathrm{FeI_2(g)}$ and $\mathrm{Fe_2I_4(g)}$ can be determined from the vapor pressures given above. Taking second-law values, we obtain $\Delta_f H_m^\circ(\mathrm{FeI_2},\mathrm{g},298.15\ \mathrm{K}) = 105\ \mathrm{kJ{\cdot}mol^{-1}}$ and $\Delta_f H_m^\circ(\mathrm{Fe_2I_4},\mathrm{g},298.15\ \mathrm{K}) = 111\ \mathrm{kJ{\cdot}mol^{-1}}$.

The standard molar enthalpy change, $\Delta_{\mathrm{dim}} H_m^\circ$, for the gaseous dimerization of iron(II) iodide can be calculated.

$$2\mathrm{FeI_2(g)} = \mathrm{Fe_2I_4(g)} \qquad (15)$$

Use of second-law values gives $\Delta_{\mathrm{dim}} H_m^\circ(298.15\ \mathrm{K}) = -97\ \mathrm{kJ{\cdot}mol^{-1}}$ when calculated from sublimation results and $\Delta_{\mathrm{dim}} H_m^\circ = -99\ \mathrm{kJ{\cdot}mol^{-1}}$ when calculated from evaporation results.

No evidence was found for the reaction of iron(II) iodide with sintered alumina, molybdenum (mass spectrometric studies), or with the type of silica used in vapor-pressure measurements and discharge lamps.

Our work shows that a detailed investigation of the monomer + dimer equilibrium above iron(II) iodide would be desirable; we suggest that the transpiration technique is the most appropriate. Our results also suggest the data listed in the JANAF tables[23] for $\mathrm{Fe_2I_4(g)}$ need to be revised. In this study greater reliability is given to second-law results than to third-law results, particularly for vaporization to the dimer. The vapor pressures measured in this study are similar to those reported previously but cover a much larger temperature range.

The preparative method described herein produces iron(II) iodide with extremely low levels of impurities that is suitable for use in discharge lamps.

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Registry No. $\mathrm{FeI_2}$, 7783-86-0; $\mathrm{Fe_2I_4}$, 92785-63-2; $\mathrm{I_2}$, 7553-56-2.

Photoionization Thresholds of Chlorophyll *a* and *N*,*N*,*N'*,*N'*-Tetramethylbenzidine in Vesicle and Micelle Frozen Solutions

Nobuaki Ohta[†] and Larry Kevan*

Department of Chemistry, University of Houston, Houston, Texas 77004 *(Received: October 24, 1984; In Final Form: January 10, 1985)*

Photoionization of chlorophyll *a* (Chla) and *N*,*N*,*N'*,*N'*-tetramethylbenzidine (TMB) in rapidly frozen vesicle and micelle solutions at 77 K has been studied with detection of the Chla and TMB cation radicals by electron spin resonance. The photoionization threshold of Chla in DL-α-dipalmitoylphosphatidylcholine (DPPC) vesicles is about 0.2 eV less than the threshold in anionic and cationic micelles. The decrease is discussed in terms of differences in the cation polarization energy and the quasi-free electron energy level. The photoionization threshold of TMB is similar in micelles and vesicles. The difference between Chla and TMB may be due to different extents of their penetration into micelles and vesicles.

Introduction

Photosynthesis is a membrane-associated phenomenon which is initiated by photoexcitation of chlorophyll (Chl) with net charge separation. Studies in vesicles and micelles have shown that net charge separation can be achieved by photoinitiated electron-transfer reactions in both liquid and frozen solutions of such molecular aggregates.[1-8] Even though the structures of vesicles and micelles do not reproduce the complexity of natural membranes, photochemical studies of Chl in such organized assemblies give data applicable to photosynthetic systems.[9]

Most studies of photoreactions of Chl incorportated into micelles and vesicles have focused on electron-phototransfer reactions.[10-13] The photoionization thresholds (IP's) of such reactions have been little studied, although the IP's of molecules and solvated electrons in various condensed hydrocarbons have been investigated.[14,15] Recent studies of pyrene[16,17] and Chl[18] in micelles showed considerable decreases in their PI's compared to the values in solvents such as tetramethylsilane. The decreases were explained in terms of changes in the ground-state energies of the quasi-free electrons ejected into the solvent.

Since both micelles and vesicles are formed in aqueous media, the IP's of Chl in micelles and vesicles might be expected to be the same. However, in rapidly frozen solutions we find a significant decrease in the IP of Chl in vesicles compared to micelles. This decrease is discussed in terms of the cation polarization energy and the quasi-free electron energy. In contrast, the photoionization of *N*,*N*,*N'*,*N'*-tetramethylbenzidine (TMB) shows no threshold

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[†] On leave from the Department of Applied Physics and Chemistry, Hiroshima University, Shitami, Saijyo, Higashi-Hiroshima, Japan.

(1) S. C. Wallace, M. Gratzel, and J. K. Thomas, *Chem. Phys. Lett.*, **23**, 359 (1973).

(2) M. Gratzel and J. K. Thomas, *J. Phys. Chem.*, **18**, 2248 (1974).

(3) J. K. Thomas, *Acc. Chem. Res.*, **10**, 133 (1977).

(4) J. H. Fendler, *Acc. Chem. Res.*. **13**, 7 (1980).

(5) P. A. Narayana, A. S. W. Li, and L. Kevan, *J. Am. Chem. Soc.*, **103**, 3603 (1981).

(6) P. A. Narayana, A. S. W. Li, and L. Kevan, *J. Am. Chem. Soc.*, **104**, 6502 (1982).

(7) A. S. W. Li and L. Kevan, *J. Am. Chem. Soc.*, **105**, 5152 (1983).

(8) M. Calvin, *Photochem. Photobiol.*, **37**, 349 (1983).

(9) J. K. Hurley and G. Tollin, *Sol. Energy*, **28**, 187 (1982).

(10) A. Yoshimura and S. Kato, *Bull. Chem. Soc. Jpn.*, **53**, 1877 (1980).

(11) J. K. Hurley, F. Castelli, and G. Tollin, *Photochem. Photobiol.*, **34**, 623 (1981).

(12) W. E. Ford and G. Tollin, *Photochem. Photobiol.*, **35**, 809 (1982).

(13) W. E. Ford and G. Tollin, *Photochem. Photobiol.*, **36**, 647 (1982).

(14) L. Kevan in "Advances in Radiation Chemistry", Vol. 4, M. Burton and J. L. Magee, Ed., Wiley, New York, 1974, p 181.

(15) "Electron-Solvent and Anion-Solvent Interactions", L. Kevan and B. C. Webster, Ed., Elsevier, Amsterdam, 1976.

(16) A. Bernas, D. Grand, S. Hautecloque, and A. Chambaudet, *J. Phys. Chem.*, **85**, 3684 (1981).

(17) D. Grand, S. Hautecloque, A. Bernas, and A. Petit, *J. Phys. Chem.*, **87**, 5236 (1983).

(18) A. Bernas, D. Grand, S. Hautecloque, and T. Myasoedova, *Chem. Phys. Lett.*, **104**, 105 (1984).

0022-3654/85/2089-2415$01.50/0