sions above, the following quadratic equation is obtained which can be solved for the concentration of unassociated "free" fluoride ion, $[F^-]$, if the total added fluoride concentration, the pH and the ionization constants are known.[16]

$$\Sigma F = [F^-] + [H^+][F^-]/K_1 + 2[H^+][F^-]^2/K_1K_2$$

The results from the polarograms obtained with acidic fluoride solutions are presented in Table III along with results from neutral fluoride solutions.

The reversibility test slopes show that in neutral fluoride solutions the anodic reaction is definitely irreversible. However, in the acidic fluoride solutions the slopes approach the theoretical value of 0.0296 (for a two-electron reaction) much more closely. If it is assumed that the observed $E_{1/2}$ values in the acidic solutions correspond to the reversible values, or very nearly so, then the data from the polarograms in the fluoride solutions of low pH can be used in the calculation of the formula and dissociation constant of the tin(IV) complex.

When the $E_{1/2}$ values for the anodic waves obtained with the acidic solutions are plotted against the logarithm of the "free" fluoride ion concentration, the experimental points fall closely along a line of slope −0.089, indicating a difference of three in the number of fluoride ions complexed by the tin(II) and the tin(IV). This is an entirely reasonable result and indicates that the oxidation reaction occurring at the electrode in acidic fluoride solutions is

$$SnF_3^- + 3F^- \longrightarrow SnF_6^{--} + 2e^-$$

Taking the standard potential of the reaction $Sn^{+2} \rightarrow Sn^{+4} + 2e^-$ to be −0.092 volt (*vs.* S.C.E.)[12] and considering this to represent the oxidation potential of tin(II) in a non-complexing medium, then from the shift in $E_{1/2}$ values in acidic fluoride solutions the ratio of the dissociation constant of the tin(IV) complex to that of the tin(II) complex is calculated to be 3×10^{-15}. From this ratio and the previously calculated value of 10^{-10} for the dissociation constant of SnF_3^-, an over-all dissociation constant of about 10^{-25} is calculated for the complex ion SnF_6^{-2}.

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BLOOMINGTON, INDIANA

(16) The accuracy of this equation was tested by comparing the $E_{1/2}$ values for the reversible cathodic waves obtained with fluoride solutions of low pH, for which the concentration of the "free" fluoride ion was calculated by means of this equation, wth the $E_{1/2}$ values obtained with approximately neutral fluoride solutions for which no correction for association was needed. The values of the half-wave potentials for solutions of corresponding fluoride ion concentration agreed within several millivolts. Furthermore a plot of the $E_{1/2}$ values (for the cathodic waves in the acidic fluoride solutions) *versus* the logarithm of the free fluoride ion concentration (calculated with this equation) gave a straight line, the slope of which again corresponded closely to that expected for a coördination number of three, *i.e.*, the reaction, $SnF_3^- + 2e^- \rightarrow Sn(Hg) + 3F^-$.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

Determination of Molecular Weights of Vapors at High Temperatures. I. The Vapor Pressure of Tin and the Molecular Weight of Tin Vapor[1]

BY ALAN W. SEARCY[2] AND ROBERT D. FREEMAN

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An apparatus is described with which molecular weights of vapors can be determined at temperatures of 1200 to 2200°K. and at pressures of 10^{-6} to 10^{-4} atm. The molecular weight of a vapor is calculated from simultaneous measurements of the vapor pressure by the Knudsen effusion method and by direct determination of the force resulting from effusion of the vapor. The molecular weight of tin vapor is found to be 91 ± 29 in the range 1600–1900°K., confirming the fact that tin vapor is essentially monatomic. The heat of sublimation of tin at 298°K. is calculated to be 71.9 ± 2.0 kcal.

Recent investigations which have established the existence of such unexpected gaseous molecules as $(Al_2S)_x$,[3] $BeO \cdot (H_2O)_x$[4] and Ge_4[5] attract attention to the meagerness of our knowledge of the compositions and structures of gaseous molecules at high temperatures. Most techniques for obtaining information about gaseous species are unreliable or prohibitively difficult to apply at temperatures much above 1000°. As a result, investigators of reactions at higher temperatures are usually forced to assume, with little supporting evidence, that gaseous reaction products are atoms, spectroscopically familiar diatomic molecules, or simple molecules with stoichiometries of known condensed phases. Uncertainty about the composition of reaction products imposes a severe limitation on the usefulness of thermodynamic data for high temperature calculations.

In most reactions yielding gaseous products, knowledge of the molecular weight of the products would permit almost certain identification of the molecular species formed. A promising method for simultaneous determination of the vapor pressure of a substance and of the molecular weight of its vapor has been developed by Mayer[6] and Volmer.[7] However, they and later workers[8–10] have employed the method only at temperatures at-

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(2) Division of Mineral Technology, University of California, Berkeley, Cal.

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tainable with resistance heating. This paper describes an adaptation of the method to measurements in the 1200–2200°K. range using radio frequency induction heating.

The method consists of simultaneous determination of the vapor pressure of a substance by the Knudsen method[11] and by what we shall call the Torsion method. In a Knudsen determination the weight of vapor ω effusing in unit time through a unit area is related to the pressure P_K by

$$P_K = \omega(2\pi RT/M)^{1/2}/k \qquad (1)$$

where R is the gas constant, T is the absolute temperature and M is the molecular weight of the effusing species. The Clausing factor[12] k is the probability that a molecule, having entered one end of a hole of finite length, will escape from the opposite end.

In the Torsion method the torque F resulting from the effusion of vapor from a cell through holes of area a_1 and a_2 at distances q_1 and q_2 from the axis of suspension of the cell is determined from the angle φ through which the torque twists the fine wire of torsion constant D by which the cell is suspended. The torque is related to φ and to the pressure P_T in the cell by

$$F = D\varphi = (q_1a_1 + q_2a_2)fP_T/2 \qquad (2)$$

The factor f is the ratio of the force resulting from the effusion of vapor through a hole of finite length to the force expected if the hole had an infinitesimal length.[13] The torsion constant D is calculated from the period of oscillation t of the suspension system alone and the period t_w with a weight of known moment of inertia I added

$$D = 4\pi^2 I/(t_w^2 - t^2) \qquad (3)$$

If the results of the simultaneous vapor pressure determinations disagree by more than experimental error, the molecular weight M assumed for equation 1, and therefore P_K, which is calculated from the assumed value of M, is incorrect. Since P_K is inversely proportional to the square root of the value assumed for M, the correct value for the molecular weight M^* of the effusing vapor is related to the actual pressure P_T by

$$M^* = M(P_K/P_T)^2 \qquad (4)$$

If more than one species is effusing, M^* is a kind of average molecular weight which is related to the molecular weights of the effusing species by the equation $M^* = 1/(m_1M_1^{-1/2} + m_2M_2^{-1/2} + \cdots + m_nM_n^{-1/2})^2$ in which m_n and M_n, for example, are the mass fraction and molecular weight of the nth species.

Experimental

Apparatus.—The effusion cell for simultaneous determination of vapor pressures by the Knudsen and Torsion methods was made from a 3.2 cm. length of $^5/_8$ in. graphite rod. In each end of the rod was drilled a hole 0.95 cm. in diameter and 1.3 cm. in length. This left a solid center section about 0.6 cm. long. The rod was then machined to a 1.15 cm. square cross-section.

Through the solid center section hole b (0.13 cm. in diameter) was drilled so that its axis was perpendicular to the top and bottom of the cell and parallel to its sides. The axis of hole *b* coincided as nearly as possible with the vertical axis of the cell. Two more holes, c and d, were drilled into the bottom of the cell so that the axis of the three holes, b, c and d, lay in a plane parallel to the ends of the cell. Hole d was 0.13 cm. in diameter, hole c was 0.24 cm.; both were 0.7–0.8 cm. in depth.

In one of the vertical sides of the cell a hole a_1 was drilled so that its axis was perpendicular to the side and was 1.0 cm. from the axis of hole b, *i.e.*, the axis of rotation of the cell. In the opposite vertical side another hole a_2 was drilled so that with respect to holes a_1 and a_2 the axis of hole b had twofold symmetry. Holes a_1 and a_2 were 0.24 cm. in diameter.

The ends of the cell were sealed with machined graphite plugs. A radiation shield in the form of a closely fitting box of 0.0025 cm. molybdenum sheet encased the cell. There were holes in the shield concentric with, and slightly larger than, the holes in the cell.

The components of the suspension system, in order from bottom to top, are: the shielded cell; 40 cm. of carefully straightened 0.127 cm. tantalum wire the lower end of which is pushed through hole b, bent 180°, and stuck into hole d; a 14.0 × 0.48 cm. diameter aluminum rod to which are attached, near the lower end, a small mirror, and, near the upper end and concentric with the rod, a 0.48 × 5.55 cm. diameter aluminum disc; 24.5 cm. of 0.0051 cm. tungsten wire, the torsion filament; and a 0.152 cm. tungsten wire which was sealed coaxially in a test-tube-end cap made from a 71/60 ground Pyrex joint.

This cap formed the top of a vertical 70 mm. vacuum line approximately 125 cm. tall. The lower half of the vacuum line was a removable, water-jacketed, 70-mm. Pyrex tube in which the cell was centered. An optical window was attached to the bottom of this tube by a 42/29 ground joint. Oscillation of the suspension was damped by interaction of the field of an Alnico horseshoe magnet with the aluminum disc. Orientation of the cell was determined by viewing with a telescope the image of a 50-cm. radius circular scale in the mirror.

During vapor pressure runs, the residual pressure in the vacuum line was 2 × 10^{-5} mm. or less. The cell was heated by an induction coil of $^1/_4$ in. copper tubing placed concentrically about the water-jacketed tube. The temperature of the cell was measured with an optical pyrometer which was sighted through a right-angled prism and the optical window into hole c. An automatically controlled variometer[14] held the temperature constant within ±3°.

Procedure.—The principal difficulty in adapting induction heating to this method of molecular weight determination was that the electromagnetic field induced by the radio frequency current caused the cell to rotate. Thus, the observed rotation was caused by combined action of the effusing vapor and of the induced field, and bore no direct relationship to the pressure in the cell. It seemed probable that the field-induced cell rotation resulted from movement of the electromagnetic center of the cell around the center of gravity of the cell toward the electromagnetic center of the induced field. If this were the cause of the rotation, there should be no rotation when the center of gravity of the cell and the electromagnetic centers of the cell and of the field are in a vertical plane with the electromagnetic center of the cell between the other two centers. An orientation of the cell that gave no field-induced rotation was found; it will be referred to as the null position.

Any deflection of the cell when power was first turned on was caused solely by the action of the field on the cell. The null position was located by rotating the cap to which the suspension was attached until the position was found from which the cell was not deflected when the power was first turned on. When the power was then left on to allow the cell to become hot, the cell was rotated from the null position to a new position determined by the sum of three forces: the force resulting from the effusion of vapor, the force of the field on the cell, and the restoring force of the torsion wire. Approximately 15 minutes was allowed for the system to reach equilibrium. Then the cap was rotated to return the cell to its null position where it was no longer subject to the field-cell force. The angle through which the cap was rotated was just the angle φ through which the cell

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would have been turned by the force of effusion in the absence of the force exerted by the field. This angle of rotation was determined from the movement of a plumb line which was suspended from a rod attached securely to the cap. The position of the plumb line could be determined with a precision of ± 0.03 cm. on a 50-cm. radius scale.

The weight of vapor effusing from the cell during heating was determined by weighing as a unit the cell, its radiation shield and the tantalum wire.

Application of the Method to Tin.—Approximately 1.5 g. of C.P. "Baker Analyzed" tin with a purity of 99.99% was placed in each end of an effusion cell which had dimensions: a_1 = 0.04453 cm.^{2}, a_2 = 0.04490 cm.^{2}, q_1 = 1.045 cm., q_2 = 1.069 cm. The average length to radius ratio of the effusion holes was 0.796. About 0.5% of the tin was vaporized from the cell before measurements were started. X-Ray diffraction photographs of the material remaining in the cell after the measurements and of sublimate scraped from the water-jacketed tube yielded the pattern of tin only. There was no evidence of contamination by carbon.

Temperatures were measured with an optical pyrometer which had been checked against a standard lamp. All temperatures were corrected for the reflectivity and absorptivity of the right-angled prism and the optical window. Comparison of optical pyrometer readings on holes of various depths indicated that within experimental error the temperature obtained from hole b was the true black body temperature.

Results of Knudsen and Torsion determinations of the vapor pressure of tin are listed in Table I. The Knudsen pressures were calculated on the assumption that tin vaporizes as atoms. Figure 1 presents a plot of the logarithm of the vapor pressures *vs.* $1/T$. The lines shown are from least squares solutions for the data.

TABLE I

THE VAPOR PRESSURE OF TIN

Temp., °K.	Wt. loss of cell, g.	Duration of experiment, sec.	Torsion constant D, dyne/rad.	Deflection φ, radian	Pressure (atm. × 10^5) PK	PT
1424	0.0065	3136	2.334	...	0.252	...
1434	.0105	2409	2.334	0.045	...	0.282
1456	.0108	2671	3.965	...	0.496	...
1472	.0149	2768	2.334	.136	.665	.851
1487	.0207	3155	2.334	.130	.814	.813
1488	.0221	3453	3.856	...	.795	...
1497	.0238	3370	4.169	.100	.879	1.12
1528	.0386	3426	4.169	.152	1.42	1.70
1565	.0387	1748	4.169	.300	2.82	3.36
1573	.0409	1846	4.169	.252	2.83	2.81
1604	.0486	1408	4.169	.414	4.44	4.62
1633	.0847	1662	4.169	.695	6.63	7.77
1638	.0811	1314	4.169	.777	8.04	8.68

Discussion

This study of the molecular weight of tin vapor was undertaken primarily as a means of determining the characteristics of the apparatus and its reliability for molecular weight and vapor pressure determinations. A mass spectrometric investigation by Honig[5] leaves little doubt that tin vapor is predominately monatomic. The Sn^+ peak accounted for over 99% of the ion current produced when tin vapor was introduced into the mass spectrometer. It is possible, of course, that polyatomic tin molecules were present in a concentration greater than 1%, but were dissociated by collision with the high energy electrons of the spectrometer. It is very unlikely, however, that such collisions with triatomic, or more complex, molecules would produce only Sn^+ charged fragments. The data appear, therefore, to preclude the presence in tin vapor of more than 1% of molecular species other than atoms or diatomic molecules. The presence of a high concentration of diatomic molecules cannot be ruled out, but is improbable.

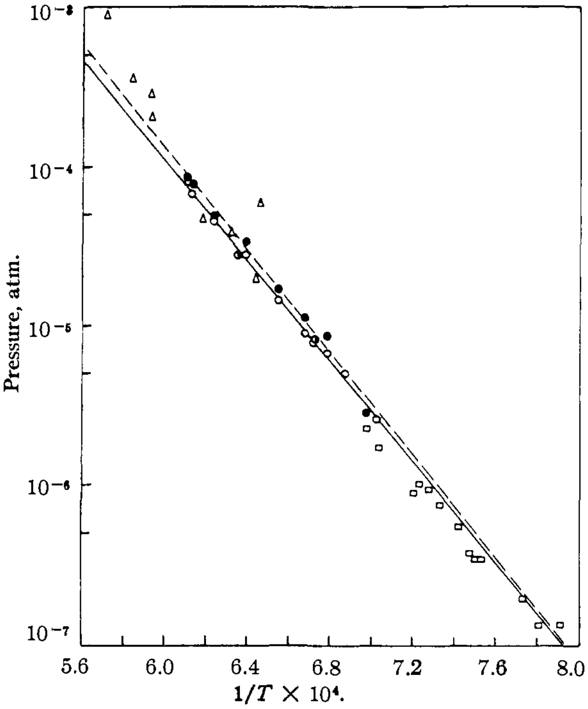

Fig. 1.—The vapor pressure of tin: □, Harteck; △, Brewer and Porter; ○ (—), this work, P_K; ● (---), this work, P_T.

Vapor density determinations[15] by an adaptation of the Victor Meyer method yielded a vapor molecular weight for tin of 740 ± 50. This molecular weight, however, was termed "only apparent" by the investigator, who noted special difficulty in applying his method to the study of tin vapor.

Each pair of the simultaneously obtained Knudsen and Torsion vapor pressure values listed in Table I could be substituted into equation 4 for calculation of the molecular weight of tin vapor, and the resultant molecular weights then averaged. However, since the ratio M^*/M depends on the square of most of the quantities measured in obtaining P_K and P_T, this method gives too great weight to P_K/P_T ratios larger than the average. A more valid value for M^* can be obtained from least squares equations for log P_K and log P_T as functions of $1/T$ fitted to the experimental data. For our data, log P_K = 5.471 − (15730/T) and log P_T = 5.810 − (16160/T). Combination of these equations gives $(P_K/P_T)^2 = 0.209e^{1980/T}$ which, when substituted into equation 4, yields 91 ± 29 as the average value of M^*, compared to the atomic weight of 118.70. The uncertainty quoted is based on the estimated maximum error of 18% in the torsion pressure determinations. All errors in both pressure determinations are estimated to be less than 2%, except for the errors in the torsion constant D and in the angle of rotation φ. The torsion constant varies by as much as 10% in the course of a series of runs; the accuracy with which

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(15) H. v. Wartenberg, *Z. anorg. Chem.*, **56**, 320 (1908).

the null point can be located is not greater than ±0.01 radian, or about 7% of a typical deflection.

Calculations of the heat of sublimation of tin at 298°K. from both Knudsen and Torsion measurements of the vapor pressure are summarized in Table II. Entropy, enthalpy and heat capacity data for gaseous tin were calculated from spectroscopic data[16]; data for solid and liquid tin were obtained from Kelley.[17] The value obtained for $\Delta H°_{298}$ for sublimation of tin from the Knudsen pressure determinations is 72.0 ± 0.2 kcal.; the value from the torsion determinations is 71.7 ± 0.4 kcal. The uncertainties given are average deviations. In computing these average values one Knudsen and three Torsion measurements, which were felt at the time of the determination to be unreliable, were rejected. Inclusion of these rejected values would give even closer agreement between the heats of sublimation calculated from Knudsen and Torsion data. Taking into account probable error in pressure, entropy and heat capacity data, the weighted average for the heat of sublimation for tin at 298°K. is 71.9 ± 2.0 kcal.

TABLE II

CALCULATION OF $\Delta H°_{298}$ FOR SUBLIMATION OF TIN

Temp., °K.	$-(\Delta F - \Delta H°_{298})/T$, cal. mole^{-1} deg.$^{-1}$	$\Delta F/T$, cal. mole^{-1} deg.$^{-1}$		$\Delta H°_{298}$, kcal. mole^{-1}	
		Knudsen	Torsion	Knudsen	Torsion
1424	25.16	25.61	...	72.30	...
1434	25.15	...	25.39	...	72.47
1456	25.14	24.27	...	71.94	...
1472	25.13	23.69	23.20	71.86	71.14
1487	25.11	23.28	23.29	71.96	71.97
1488	25.11	23.34	...	72.09	...
1497	25.10	23.13	22.65	72.20	71.48
1528	25.07	22.18	21.82	72.20	71.65
1565	25.05	20.82	20.47	71.79	71.24
1573	25.04	20.81	20.82	72.12	72.14
1604	25.03	19.91	19.83	72.08	71.96
1633	25.01	19.12	18.80	72.06	71.54
1638	25.00	18.73	18.53	71.63	71.38

In a review of determinations of the vapor pressure of tin, Baughan[18] rejected the data of Harteck,[19] which yield 72.6 ± 1.0 kcal. for $\Delta H°_{298}$. Baughan gave as the average value from results of other workers 62.4 ± 2.0 kcal. However, Brewer and Porter[20] have since obtained 70 ± 2 kcal. and have suggested that SnO was the vaporizing species in experiments that yielded lower heats of sublimation. It would be highly desirable to have new static measurements of the vapor pressure of tin in which the presence of reactive gases is rigorously excluded.

Evaluation of the Method.—It is clear from the results obtained here that the Torsion method provides a means for determining vapor pressures at high temperatures at accuracy comparable to the accuracy of the Knudsen[11] and the Langmuir[21] methods. The Torsion method has two significant advantages over the other two: It requires no knowledge of the molecular weight of the vapor, and it is the most rapid of the three methods for determining pressures at a series of temperatures.

The Knudsen–Torsion method for molecular weight determinations is very sensitive to error because the calculated molecular weight depends on the square of most measured quantities. On the other hand it has two very important advantages for studies of high temperature species: it can be applied at lower pressures, and therefore at lower temperatures for any given substance, than other methods for determining molecular weights. Because all necessary data are obtained simultaneously in a single apparatus, several possible sources of systematic errors are eliminated. For example, equilibrium pressure need not be established inside the cell for the molecular weight determination to be valid.

LAFAYETTE, INDIANA

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