THE VAPORIZATION AND THERMODYNAMICS OF THORIUM DICARBIDE

Thesis for the Degree of Ph. D.

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Richard A. Kent

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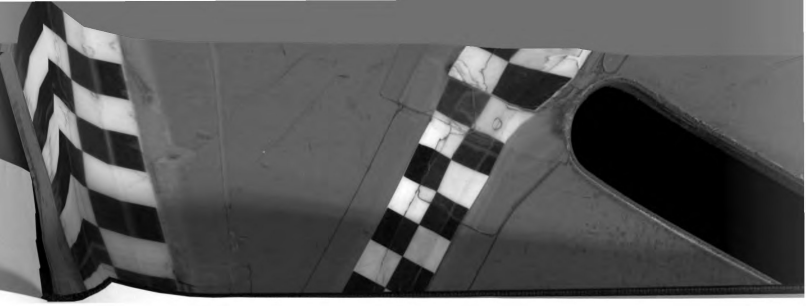

ABSTRACT

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OF THORIUM DICARBIDE

by Richard A. Kent

Quantitative investigations of the vaporization of refractory inorganic compounds are basic to the study of systematic trends in the thermodynamics of vaporization processes and of chemical bonding in gaseous molecules in part because of the comparisons which can be made between their results and those for the corresponding oxides. The characterization of the fundamental properties of thorium dicarbide is of interest both from this basic standpoint, and from its evaluation for possible applications in nuclear technology.

Thorium dicarbide of high purity was prepared by the reaction of graphite either with thorium metal or thorium dioxide and the subsequent homogenization of the crude product by heating at approximately 2400°K in a graphite crucible in high vacuum.

The vaporization of thorium dicarbide over the temperature range 2100 to 2500°K was investigated by the Knudsen effusion method. Samples were evaporated from inductively heated graphite or tungsten effusion crucibles and known fractions of the total effusate were collected on fused silica targets which were assayed for thorium by a neutron activation technique. Chemical and X-ray diffraction analyses of both starting materials and residues were performed.

The rate of effusion of thorium-containing species measured in the target experiments was expressed in terms of an "effective vapor pressure" P_E, which, when combined with the molecular weight of 256.06,

gave directly the rate of evaporation of thorium dicarbide. An empirical equation, fitted to the data by the method of least squares, gave

$$\log P_{E(atm)} = -\frac{40,736(\pm 717)}{T} + 8.742(\pm 0.304).$$

The observed volatility varied by a factor of 10^3 over the 400 degree temperature range and at 2360°K was about 0.025 per cent that of thorium dioxide and about 0.006 per cent that of thorium metal.

Combination of the published mass spectrometric data for the vaporization of thorium dicarbide and the target data measured in this investigation, yielded the data requisite to a linear treatment of the individual vapor species as a function of reciprocal temperature. By means of the second law of thermodynamics the following values were obtained:

For the reaction

$$ThC_{2(s)} = Th_{(g)} + 2C_{(graphite)} \qquad (I)$$

$$\Delta H^{o}_{298} = 176.92 \pm 3.30 \text{ kcal/mole},$$

$$\Delta S^{o}_{298} = 34.49 \pm 0.64 \text{ e.u.}$$

For the reaction

$$ThC_{2(s)} = ThC_{2(g)} \qquad (II)$$

$$\Delta H^{o}_{298} = 196.24 \pm 3.30 \text{ kcal/mole},$$

$$\Delta S^{o}_{298} = 42.81 \pm 0.72 \text{ e.u.}$$

Values were estimated for the free energy functions of $ThC_{2(s)}$ and $ThC_{2(g)}$ and these were combined with the published data for graphite and $Th_{(g)}$ to yield the following values calculated from the third law of thermodynamics:

For the reaction

$$ThC_{2(s)} = Th_{(g)} + 2C_{(graphite)} \qquad (I)$$

$$\Delta H^{o}_{298} = 175.82 \pm 0.68 \text{ kcal/mole.}$$

For the reaction

$$ThC_{2(s)} = ThC_{2(g)} \qquad (II)$$

$$\Delta H^{o}_{298} = 204.96 \pm 1.25 \text{ kcal/mole.}$$

The enthalpies obtained for the dissociation reaction (I) were combined with the published value for the enthalpy of vaporization of thorium metal and the following values for the standard enthalpy of formation of $ThC_{2(s)}$ were calculated:

From the second law,

$$\Delta H^{o}_{298} = -40.32 \pm 3.33 \text{ kcal/mole.}$$

From the third law,

$$\Delta H^{o}_{298} = -39.22 \pm 0.84 \text{ kcal/mole.}$$

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ERRATUM

After this thesis was accepted, it was found that pyrometer No. 1572579, which was used in this work, no longer conformed to the calibration data obtained from the National Bureau of Standards. The implication of this observation is that the temperatures reported herein vary from seventeen degrees too low at 1900°C, to twenty-five degrees too low at 2200°C.

I. INTRODUCTION

A. General Incentives for this Research

Thermochemical and mass spectrometric investigations in recent years have shown that previously unsuspected gaseous molecules containing heavy metal atoms are rather common in the vapor phases of refractory compounds in equilibrium with their solid phases.

The study of vaporization processes not only provides for the measurement of vapor pressures and the preparation of new substances, but also served to help establish the nature and kinetics of high temperature reactions. Moreover, much of the data required for the testing of the theories of chemical bonding come from high temperature vaporization experiments. Good thermochemical measurements on a large number of refractory systems of heavy metals are necessary both to provide stepping stones to the simplification of the theory of chemical bonding and to enable formulation of empirical treatments for technological purposes.

To date, systemization of vaporization behavior and detection of trends, for example, of dissociation pressures, have been hindered, not only by the considerable absence of pertinent data, but also by the poor reliability of much of the data available.

While no single experimental investigation can provide more than a small contribution to these goals, each accurate characterization of a particular molecule is a definite advance in this direction. This study of the vaporization and dissociation of thorium dicarbide was undertaken with these thoughts in mind.

B. Previous Investigations of the Thorium-Carbon System

1. General

The preparation of thorium dicarbide in an electric arc furnace was first reported by Troost (1) and confirmed by Moissan and Etard (2). The existence of the monocarbide was established by Wilhelm, Chiotti, Snow, and Daane (3). Wilhelm and co-workers (3,4) investigated the system thorium-carbon and constructed, on the basis of X-ray diffraction and melting point data, a tentative phase diagram in which they assume that a continuous series of solid solutions crystallizes from melts between thorium monocarbide and thorium dicarbide. Further, they assume that at some lower temperature these solid solutions decompose into a thorium-rich phase and a phase based on thorium monocarbide, on the one hand, and into two phases nearly corresponding to the compositions ThC and ThC_2, respectively, on the other. Accordingly, their phase diagram shows two miscibility gaps with critical points at approximately two weight percent carbon and 1975°, and between about six and seven weight percent carbon at about 2300°. At approximately 12.5 weight percent carbon and 2500° thorium dicarbide forms an eutectic with graphite.

It is unlikely that such a constitution exists since a continuous transition from the structure of thorium via that of the monocarbide to that of the dicarbide cannot occur. Hansen (5), using the data of Wilhelm and co-workers, has constructed a more amenable phase diagram which is shown in Figure 1. This diagram should, of course, be regarded only as a rough approximation and is presented here only to give a conception of what the phase relationships could be. Although there is no evidence as yet as to the existence of the carbide Th_2C_3, this phase

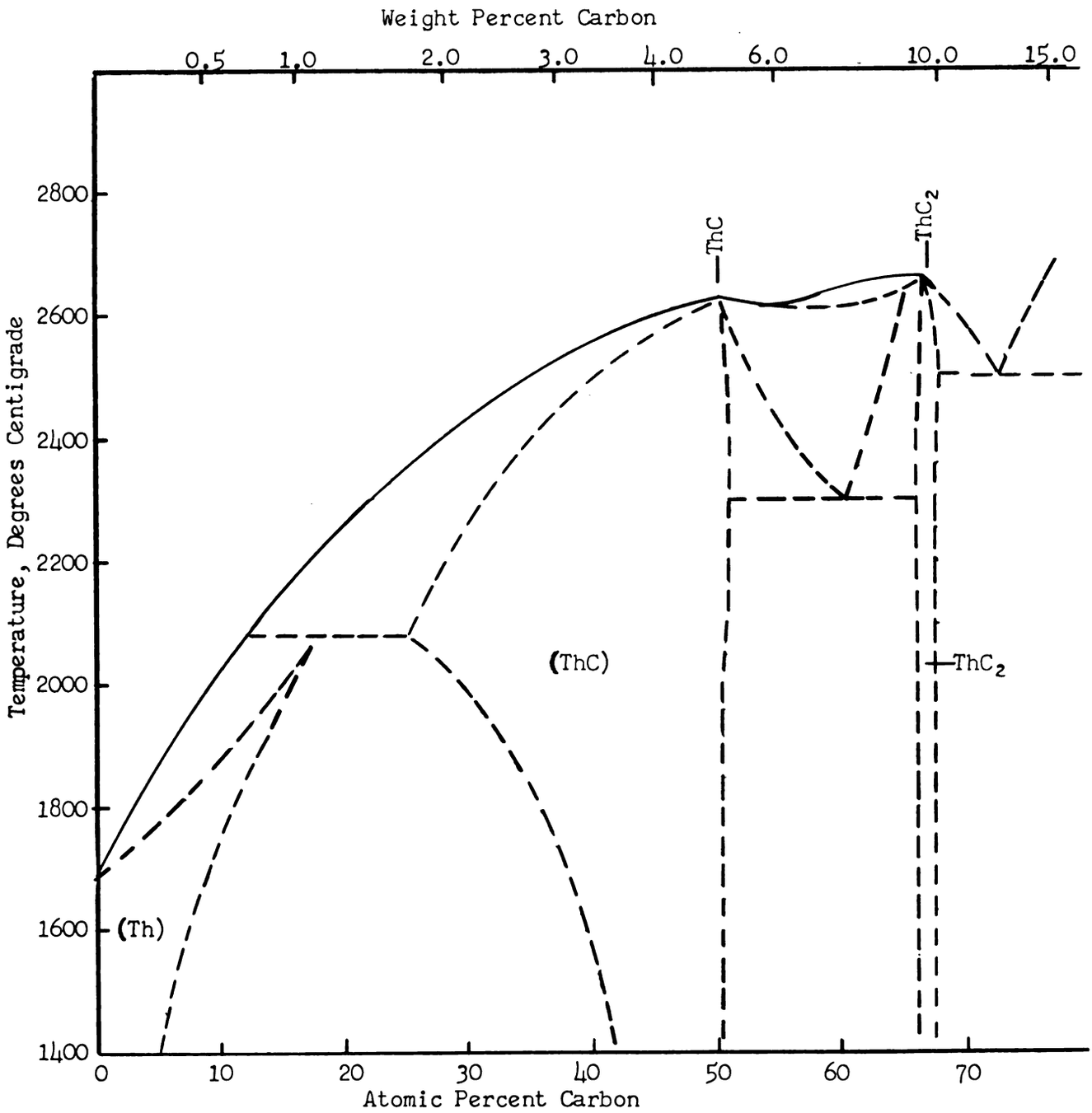


Figure 1. Tentative phase diagram for the thorium-carbon system.

may exist in analogy to U_2C_3. Wilhelm and Chiotti (4) report the monocarbide to be cubic (NaCl-type) with the lattice parameter $a_0 = 5.34\mathring{A}$, corresponding to a density of 10.67 g per cm^3.

The crystal structure of the dicarbide was first investigated by von Stackelberg (6), who reported a tetragonal structure involving pairs of carbon atoms which he assumed to be acetylene ions. This structure has also been reported for calcium carbide and the rare earth dicarbides. However, by using X-ray and neutron diffraction techniques, Hunt and Rundle (7) established that thorium dicarbide crystallizes as a monoclinic structure, space group C2/c, with $a_0 = 5.53\mathring{A}$, $b_0 = 4.24\mathring{A}$, $c_0 = 6.56\mathring{A}$, $\beta = 104^o$, and with four ThC_2 molecules per unit cell. As in the structure suggested by von Stackelberg, the monoclinic structure contains groups of carbon pairs. However, the carbon-carbon bond distance is $1.5\mathring{A}$, a distance close to the accepted single bond value, which would seem to eliminate acetylene ions. The arrangement of the thorium atoms about the C_2 groups combines single-, double-, and triple bond character and, according to Hunt and Rundle, covalent character for the thorium-carbon bonds is indicated. The electron structure suggested by the authors is closely related to that proposed by Rundle (8) for interstitial compounds of the type MX, including thorium monocarbide. Hunt and Rundle assume that both the mono- and dicarbide of thorium have metallic character.

Reports in the literature on the hydrolysis of thorium dicarbide are sparse and often contradictory. Moissan and Etard (2) reported the hydrolysis to yield 47.74 % acetylene, 29.37 % methane, 5.76 % ethylene, and 17.12 % hydrogen. Modic (9) reported that the major hydrolysis product was methane. Lebeau and Damiens (10) found the hydrolysis to

yield 15 % acetylene, 3.1 % methane, 2.8 % ethylene, 10.7 % ethane, 59.6 % hydrogen, 2.4 % higher paraffins, and 6.4 % higher olefins. One of the major difficulties inherent in these investigations is obtaining samples of a single phase. The early work on the hydrolysis of thorium dicarbide probably suffers most in this regard.

Engle, Goeddel, and Luby (11) who studied the hydrolysis of thorium dicarbide in moist air propose the following reaction:

$$ThC_2 + H_2O = ThO_2 \cdot XH_2O + H_2 + \text{aliphatic hydrocarbons.}$$

They report the hydrocarbons to consist of methane and ethane gases and C_4- and C_5 condensed hydrocarbons--no acetylene was observed. An increase in temperature or decrease in sample size increases the reaction rate and thorium dicarbide was observed to hydrolyze about ten times as fast as uranium dicarbide, the reaction going to completion in one to five hours. The authors also observed that the rate was affected by carbon content, carbon deficient samples having lower reaction rates.

Kempter and Krikorian (12) have studied the hydrolysis of thorium monocarbide and dicarbide at 25° using a mass spectrograph. The reaction products are listed in Table I. Since thorium monocarbide yields mainly methane on hydrolysis, it seems likely that Modic hydrolyzed the monocarbide rather than the dicarbide.

Palenik and Warf (13) studied the hydrolysis of lanthanum and cerium dicarbides. For purposes of comparison, the results, along with those of Kempter and Krikorian are listed in Table II. Hydrogen and methane are not included in the totals since Palenik and Warf used liquid nitrogen to condense the hydrolysis products and did not collect these gases. On runs made at 25° they obtained about five mole percent non condensables.

Table I. Hydrolysis products of thorium monocarbide and thorium dicarbide.

Species[a]	H_2	CH_4	C_2H_2	C_2H_4	C_2H_6	C_3H_4	C_3H_8	C_4H_6	C_4H_8	C_4H_{10}	Above C_4H_x
ThC	9.3	86.4	---	0.75	2.35	1.2	---	---	---	---	---
ThC_2	27.2	2.35	9.5	2.45	29.8	1.5	1.5	8.6	11.3	3.8	2.0

[a]All totals expressed in mole percent.

Table II. Distribution of hydrocarbon hydrolysis products of some inner transition metal dicarbides.

Species[a]	LaC_2	CeC_2	ThC_2	UC_2
Alkanes	25.07	20.56	49.80	68.90
Alkenes	11.30	10.00	19.50	28.30
Alkynes	61.50	67.30	27.80	2.80
Unidentified	2.20	2.10	2.80[b]	----

[a]All totals expressed in mole percent of total hydrocarbons produced during hydrolysis at 25°.

[b]Hydrocarbons above C_4H_x.

It is apparent that the prediction of Palenik and Warf concerning thorium and uranium dicarbides, "the two electron oxidation in the hydrolysis reaction is expected to produce more hydrogen and hydrogenated hydrocarbons than in the case of the rare earth dicarbide", is consistent with the hydrolysis data for thorium and uranium dicarbides. A simple representation of the overall reaction might be something like the following:

$$ThC_2 + 2H_2O = Th(OH)_2 + C_2H_2$$

$$Th(OH)_2 + 2H_2O = Th(OH)_4 + H_2$$

$$C_2H_2 + H_2 = C_nH_{2n+2} + C_nH_{2n}.$$

2. Thermodynamic Investigations

The melting point of thorium monocarbide is reported by Wilhelm and Chiotti (4) as 2625°, and that of the dicarbide as 2655°.

Prescott and Hincke (14) studied the reaction

$$ThO_{2(s)} + 4C_{(graphite)} = ThC_{2(s)} + 2CO_{(g)}$$

in the temperature range 2057 to 2494°K by measuring the pressure of the carbon monoxide produced and found the enthalpy of reaction to be ΔH^0_{298} = 194.8 kcal/mole. From this, they calculated the heat of formation of solid thorium dicarbide to be ΔH^0_{298} = -78.9 kcal/mole. Rath and Becker (15) recalculated this quantity using their determination of the heat of formation of thorium dioxide and found the enthalpy of formation of the dicarbide to be ΔH^0_{298} = -45.7 kcal/mole. Krikorian (16), using Prescott and Hincke's data and estimated free energy functions, obtained an enthalpy of formation ΔH^0_{298} = -33 ± 8 kcal/mole. Meslan (17) on the basis of emf measurements on the cell

$$Th_{(s)}/LiCl\text{-}KCl_{(eutectic)} + 5\%\ ThCl_{4(l)}/ThC_2,C$$

found the free energy of formation of thorium dicarbide to be -36.4 kcal/mole at 800°. Brewer and co-workers (18) have estimated -45.6 kcal/mole to be the standard enthalpy of formation of solid thorium dicarbide.

Lonsdale and Graves (19) have studied the dissociation of thorium dicarbide over the temperature range 2300 to 2900°K using the Knudsen effusion method. The effusate was collected on cooled graphite targets which were assayed for thorium by means of neutron activation analysis. They report that, in the temperature range studied, the vapor pressure of thorium gas over solid thorium dicarbide may be represented by the equation:

$$\log P_{(atm)} = -\frac{37,600 \pm 1,000}{T} + 7.39 \pm 0.39.$$

They obtained a second law heat of dissociation of 172.0 ± 4.6 kcal/mole from which they calculated the heat of formation of thorium dicarbide to be $\Delta H^{o}_{298} = -46 \pm 6$ kcal/mole.

No calculation of the standard enthalpy of formation by the third law technique is reported; their calculations are based on the assumption that the gaseous species consist only of thorium gas and polymeric carbon. However, a previous mass spectrometric investigation of the carbon-rich end of the Lanthanum-carbon system by Chupka and co-workers (20) showed that both lanthanum and lanthanum dicarbide are important gaseous species. The ratio of pressures, $P(LaC_2)/P(La)$, was found to increase from 0.2 at 2200°K to 0.8 at 2600°K.

Jackson, Barton, Krikorian and Newbury (21) have completed a mass spectrometric investigation of the vaporization process and thermodynamics of solid thorium dicarbide. They report that the vapor species

consist of both thorium and thorium dicarbide. The presence of gaseous thorium monoxide in the system was found to be dependent on sample preparation techniques. The ratio of gaseous thorium dicarbide to gaseous thorium over solid thorium dicarbide was found to vary from about 1.2 at 2400°K to about 1.8 at 2600°K. By means of a second law treatment of the data, Jackson and co-workers calculated the following enthalpies:

$$ThC_{2(s)} = ThC_{2(g)} \quad ; \Delta H^{o}_{298} = 188.1 \pm 3.4 \text{ kcal/mole}$$

$$ThC_{2(s)} = Th_{(g)} + 2C_{(graphite)} \quad ; \Delta H^{o}_{298} = 160.3 \pm 3.2 \text{ kcal/mole.}$$

From a least squares calculation, assuming ΔC_P to be zero, they obtain the following expressions for the vapor pressure of each species over solid thorium dicarbide:

$$\text{for } ThC_{2(g)}, \quad \log P_{(atm)} = -\frac{39{,}364 \pm 163}{T} + 7.20 \pm 0.65,$$

$$\text{for } Th_{(g)}, \quad \log P_{(atm)} = -\frac{36{,}025 \pm 144}{T} + 5.74 \pm 0.57.$$

In addition they calculated the enthalpies by a third law method:

$$ThC_{2(s)} = ThC_{2(g)} \quad ; \Delta H^{o}_{298} = 212.8 \pm 1.5 \text{ kcal/mole,}$$

$$ThC_{2(s)} = Th_{(g)} + 2C_{(graphite)} \quad ; \Delta H^{o}_{298} = 184.7 \pm 1.5 \text{ kcal/mole.}$$

Using the reported value (22) of the enthalpy of sublimation of thorium metal, $\Delta H^{o}_{298} = 136.6 \pm 0.5$ kcal/mole and the enthalpies given above, the authors calculated the following standard enthalpies of formation for thorium dicarbide.

Second Law, $\Delta H^{o}_{298} = -23.7 \pm 3.5$ kcal/mole,

Third Law, $\Delta H^{o}_{298} = -48.1 \pm 2.0$ kcal/mole.

The third law result agrees well with the second law result obtained by Lonsdale and Graves and with the value estimated by Brewer.

However, the large discrepancy between the second and third law results indicates the probable presence of systematic errors. A possible

explanation, as given by the authors, may be that the thorium dicarbide phase has a variable solid solubility of carbon as this behavior is not uncommon in carbides. The most common causes for such a discrepancy, however, are errors in temperature measurement. Also, the enthalpies determined by Jackson and co-workers by the third law method are somewhat temperature dependent, indicating a systematic error.

C. The Specific Purpose of This Research

Various workers in the past have experimentally determined the enthalpy of formation of thorium dicarbide. The values obtained range from about - 20 kcal/mole to about -50 kcal/mole. Recently, two attempts involving the Knudsen effusion method have been made to determine this quantity--the mass spectrometric investigation by Jackson and co-workers and the study of Lonsdale and Graves. While the second law results obtained by Lonsdale and Graves are reasonably close to the third law results of Jackson and co-workers, their failure to take into account the species $ThC_{2(g)}$ and the discrepancy between the second and third law values determined by Jackson and co-workers seem to justify further investigation of the vaporization and dissociation of thorium dicarbide.

This project was undertaken to prepare pure thorium dicarbide; to repeat the investigation by Lonsdale and Graves of the vaporization and dissociation of thorium dicarbide employing the Knudsen effusion method; and, taking into account the findings of Jackson and co-workers regarding the gaseous species involved, to compare the measured values of the entropy and enthalpy of vaporization and dissociation and the standard enthalpy of formation determined by this method with the values determined by Jackson and co-workers in their mass spectrometric investigation.

II. VAPORIZATION STUDIES

A. General

When we investigate the vaporization process of a given substance we can obtain, in addition to the vapor pressure, information concerning the thermodynamic nature of both the condensed phase or phases and of the gaseous species produced. By studying the temperature dependence of the vapor pressure or partial pressures of individual species we can determine the values of the enthalpy and entropy changes accompanying the vaporization (or dissociation) process, commonly termed the heat and entropy of vaporization (or dissociation). In addition, we can determine the standard enthalpies of formation of solid compounds and gaseous molecules.

The phase rule

$$\underline{F} = \underline{C} - \underline{P} + 2$$

expresses the relationship between the number of degrees of freedom $\underline{F}$ (the variance) which must be specified in order to completely define a system in a thermodynamic sense, and $\underline{C}$ and $\underline{P}$, respectively the number of components and the number of phases in equilibrium in the system.

Consider, for example, a two component system in a closed container in which condensed material is in equilibrium with vapor. There are two ways for the pressure to be temperature dependent. One way is if there are three phases present. Since the vapor constitutes one phase, there must be two condensed phases, solid or liquid or both. The other way is if some additional restriction is imposed on the system, i.e., if the overall composition of the vapor is the same as that of the condensed

phase. The latter case is defined as a congruent vaporization process. Both situations are said to be invariant because a change in one variable, e.g., the temperature, to a new fixed value uniquely redefines the total pressure.

The congruence of a vaporization process can be demonstrated by examining the residue after successive evaporation experiments. In a congruent process the overall composition of the residue will not change during the evaporation.

For three component systems the number of degrees of freedom is 5 - P and the number of additional phases or restrictions must be increased by one to make the pressure a function of temperature only.

A study of the vapor pressure or related rate of evaporation of a given substance with time at a given temperature, combined with chemical and X-ray diffraction analyses before and after the evaporation, permits a deduction of the behavior of the condensed phase involved and thus renders meaningful any thermodynamic values obtained from further evaporation studies with the same substance.

B. Thermodynamic Relationships in Vaporization Studies

1. Second Law Determination of Vapor Pressure

Consider the reaction at T°K,

$$M_{(s \text{ or } l)} = M_{(g)}.$$

For this reaction

$$\Delta F_T^0 = \Delta H_T^0 - T\Delta S_T^0 = - RT\ln K. \qquad (1)$$

The equilibrium constant for this reaction is expressed in the usual manner as the product of partial pressures raised to appropriate powers; in this case K is $P_{M(g)}$. If we consider ΔC_P to be a constant for the

reaction,

$$\Delta H_T^0 = \Delta H_\Theta^0 + \int_\Theta^T \Delta C_p \, dT = \Delta H_\Theta^0 + \Delta C_p(T - \Theta) \qquad (2)$$

and

$$\Delta S_T^0 = \Delta S_\Theta^0 + \Delta C_p \ln(T/\Theta) \qquad (3)$$

where Θ is the reference temperature, usually 298.16°K. If we combine equations (1), (2), and (3) we have

$$-RT \ln P_{M(g)} = \Delta F_T^0 = \Delta H_\Theta^0 + \Delta C_p(T-\Theta) - T\Delta S_\Theta^0 - T\Delta C_p \ln(T/\Theta) \qquad (4)$$

This gives rise to two cases of interest:

(a) <u>ΔC_p is approximately zero</u>

If we assume that ΔC_p is zero for the reaction, equation (4) reduces to

$$-RT \ln P_{M(g)} = \Delta H_\Theta^0 - T\Delta S_\Theta^0 \qquad (5)$$

or

$$\log P_{M(g)} = -\frac{\Delta H_\Theta^0}{2.303RT} + \frac{\Delta S_\Theta^0}{2.303R} \qquad (6)$$

which is the familiar Clausius-Clapeyron equation in which R is the molar gas constant and 2.303 is the natural logarithm of ten.

After $P_{M(g)}$ has been measured, we graph $\log P_{M(g)}$ against $1/T$ over the temperature range studied; ΔH_Θ^0 is obtained from the slope and ΔS_Θ^0 from the intercept.

The assumption that ΔC_p is zero for the reaction implies that the heat capacities of the gaseous products are equal to those of the condensed phases, a situation which is virtually never true for non-ideal systems. If heat capacity data are available or can be estimated for both reactants and products, it is possible to obtain values of ΔH_T^0 and

ΔS_T^0 for each temperature, and to extrapolate them, for tabulation purposes, to a suitable reference temperature Θ.

(b) ΔC_p is not zero but is constant

If we make the assumption, not that the heat capacities of the gaseous and condensed phases are equal, but that the difference between them, ΔC_p, is constant, we have, from equation (4),

$$\log P_{M(g)} = -\frac{\Delta H_\theta^0}{2.303RT} - \frac{\Delta C_p(T - \Theta)}{2.303RT} + \frac{\Delta C_p \ln(T/\Theta)}{2.303\ R} + \frac{\Delta S_\theta^0}{2.303R} \quad (7)$$

which is of the form

$$\log P_{M(g)} = -A/T + B \ln T + C. \quad (8)$$

2. Third Law Determination of Vapor Pressure

Because the slopes of the various experimental plots are sensitive to small errors in temperature measurement it is advisable if possible, to check the values for enthalpy and entropy determined by the second law method against a method based on the third law of thermodynamics. When this third law method is employed, the heats and entropies of vaporization or dissociation so obtained may be more reliable than the second law values because of a decreased sensitivity to errors in the measured temperatures.

The third law method makes use of the free energy function, fef, defined by

$$\text{fef} = \left(\frac{F_T^0 - H_\theta^0}{T}\right) = \left(\frac{H_T^0 - H_\theta^0}{T}\right) - S_T^0 \quad (9)$$

where, as above, Θ is the reference temperature. For convenience in calculations the free energy functions are often tabulated relative to 298.16°K, thus the relation

$$\left(\frac{F_T^0 - H_{298}^0}{T}\right) = \left(\frac{H_T^0 - H_{298}^0}{T}\right) - S_T^0 \qquad (10)$$

is employed with standard heats of formation ΔH_{298}^0. Equation (10) can be related to the 0^oK free energy function by the relation

$$\left(\frac{F_T^0 - H_{298}^0}{T}\right) = \left(\frac{F_T^0 - H_0^0}{T}\right) - \left(\frac{H_{298}^0 - H_0^0}{T}\right). \qquad (11)$$

For the vaporization reaction

$$M_{(s \text{ or } 1)} = M_{(g)}$$

$$\Delta fef = \left(\frac{F_T^0 - H_{298}^0}{T}\right)_{(g)} - \left(\frac{F_T^0 - H_{298}^0}{T}\right)_{(s \text{ or } 1)} = \frac{\Delta F_T^0}{T} - \frac{\Delta H_{298}^0}{T} \qquad (12)$$

but,

$$\Delta F_T^0 = -RT\ln K = -RT\ln P_{M(g)} \qquad (13)$$

so that

$$\Delta fef = -R\ln P_{M(g)} - \frac{\Delta H_{298}^0}{T} \qquad (14)$$

thus

$$\Delta H_{298}^0 = -T\Delta fef - RT \ln P_{M(g)} \qquad (15)$$

or

$$\Delta H_{298}^0 = -T\left[\Delta\left(\frac{F_T^0 - H_{298}^0}{T}\right)\right] - 2.303\ RT \log P_{M(g)}. \qquad (16)$$

Thus, provided that the free energy functions are tabulated, an independent value of the heat of vaporization (or dissociation) may be calculated for each pressure measurement.

The free energy function may be evaluated for a given substance if measured heat capacities are available. In the case of a gas, the free energy function may be evaluated from spectroscopic data if such are available.

Unfortunately, heat capacity and spectroscopic data are not always available, and the standard tabulations of free energy functions [see for example, references (23) and (24)] and those found in individual publications for substances at high temperatures often do not contain data applicable to the problem at hand, and we must often accept the second law values of enthalpy without third law confirmation. It is possible, however, to estimate free energy functions for a given compound with fair accuracy, if those for related compounds are known. Such semi-empirical estimates are frequently used to provide a third law check of the second law heats and entropies.

C. The Knudsen Effusion Method

1. Some Principles of Molecular Effusion from a Knudsen Crucible

Consider a closed inert container which is at a fixed uniform temperature and is located in a vacuum. If this container or crucible contains a condensed phase which is in equilibrium with its vapor, the pressure inside the crucible will be the equilibrium vapor pressure and, if the vapor behaves ideally, we can show from kinetic theory that the number of each kind of molecule striking a unit area of the crucible wall in unit time is $n\bar{c}/4$ where n is the density of the gas in molecules per unit volume and $\bar{c}$ is the average molecular speed. In 1909 Knudsen (25,26) demonstrated that if the wall were thin and contained a small orifice of known area the number of molecules which would effuse through this opening in unit time would be the same as the number which would strike an equal area of the wall in the same time. Thus, by determing the number of molecules which effuse through this orifice in a given time we can measure the vapor pressure of the substance in the crucible.

The number of molecules which are effused by molecular flow per unit time per unit solid angle in a given direction above the plane of the orifice is described, for an ideal "knife-edged" orifice, by the cosine law which may be written as

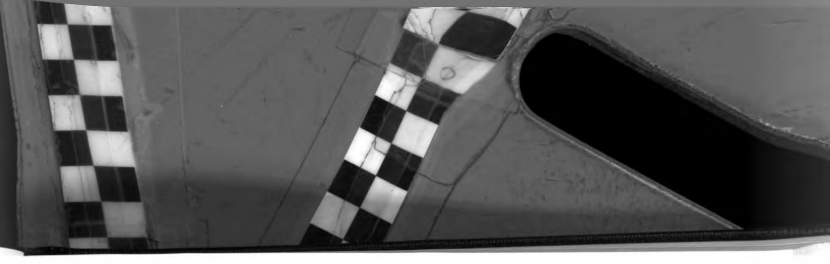
$$dz = Z_0\left(\frac{1}{\pi}\right) dS_0 \cos\theta \, d\omega \, dt. \qquad (17)$$

For a derivation of the cosine law and a discussion of its applications the reader is referred to the work of Carlson (27). In equation (17) dz represents the number of molecules leaving the orifice in time t from the element of area dS_0 in an elementary solid angle $d\omega$ at the angle θ to the normal to the orifice plane at dS_0. The total rate of emission from the entire orifice is $Z_0 = n\bar{c}/4$ molecules per cm^2 per unit time. Integration of equation (17) shows that in a given time equal numbers of molecules pass through equal areas located anywhere on a large sphere tangent to the orifice thus, if the orifice is ideally thin, it is necessary only that we know the distance to and the angular orientation of a target anywhere above the orifice in order to calculate the fraction of the total effusate that strikes the target.

2. Vapor Pressure Equations

There are several ways in which we can determine the number of molecules which leave the crucible through the orifice in a given time. The simplest method is to determine the weight lost by the crucible during the vaporization by weighing the crucible before and after the experiment. We can relate the partial pressure P of the vapor species of molecular weight M to the weight W of that species effusing in time t through an orifice of area S_0 by the equation

$$P = \frac{W}{S_0 t}\left(\frac{2\pi RT}{M}\right)^{1/2} \qquad (18)$$



where T is the absolute temperature inside the crucible and R is the molar gas constant. This result corresponds to an expression of the pressure in terms of the rate of effusion, Z moles, of vapor as

$$P = \frac{Z}{S_0 t}(2\pi MRT)^{1/2}. \tag{19}$$

In the high temperature investigation of a very slightly volatile substance it is often more convenient to condense a known fraction of the actual weight loss of the crucible. If a circular target of radius r is placed at a distance d from the orifice and is coaxial to it, it can be shown (27,28) that the pressure P is related to the weight w gained by the target according to the equation:

$$P = \frac{w}{S_0 t}\left(\frac{2\pi RT}{M}\right)^{1/2}\left(\frac{r^2 + d^2}{r^2}\right) \tag{20}$$

or

$$P = \frac{0.022557\ w}{S_0 t}\left(\frac{T}{M}\right)^{1/2}\left(\frac{r^2 + d^2}{r^2}\right). \tag{21}$$

When the units on w , S_0, t, and T are grams, cm^2, seconds and degrees Kelvin, respectively, equation (21) gives the pressure in atmospheres.

3. Two fundamental Requirements in Effusion Studies

(a) Free molecular flow

The pressure inside the effusion crucible must be low enough that collisions between gaseous molecules are so infrequent that each molecule leaves through the orifice without affecting the trajectories of the others. Knudsen (26) in his experiments on the flow of gases through thin-edged orifices observed that hydrodynamic flow effects caused the mass of gas effusing from a region at a known pressure to be greater than that expected when the pressure was above certain values. The

values corresponded to a ratio of mean-free path (λ) to orifice diameter (D), λ/D, of about ten and this value has often been quoted in the literature as the upper limit of molecular effusion and thus of the effusion method.

Subsequent experimental investigations (29,30,31,32) give mutually inconsistent information on the upper limit. Unfortunately the problem is a complex one and no theoretical treatment has yet been presented which accurately predicts the pressure at which departure from molecular flow should occur for a given species.

(b) Orifice shape

The second fundamental limitation to the validity of pressure measurements by the effusion method is the shape of the orifice. If the orifice has the form of a tube of finite length, the distribution of molecules effusing through it will no longer be given by the cosine law because reflections from the orifice wall will change the distribution of molecules at large angles to the normal. Also, there is a corresponding probablility that a molecule which has struck the wall will, as a result of such a collision, be returned to the cavity, resulting in a decrease in the measured vapor pressure.

Clausing (33,34) has investigated the flow of gases through orifices of finite length and obtained integral equations whose approximate numerical solutions yield dimensionless correction factors which take into account the length of the orifice. When these correction factors, W_o, which range from zero to unity are applied, equation (21) becomes

$$P = \frac{0.022557\,w}{W_o S_o t} \left(\frac{T}{M}\right)^{1/2} \left(\frac{r^2 + d^2}{r^2}\right). \qquad (22)$$

Further discussions of this correction factor are found in the work of Carlson (27), Freeman and Searcy (35), and others (36,37,38).

4. Some Practical Requirements in Effusion Studies

Whereas, the fundamental requirements listed above pertain to all Knudsen effusion experiments, there are many practical requirements which depend on the materials and techniques employed in a particular experiment. Some of these requirements are as follows:

(a) A reaction between the crucible material and the vaporizing sample may either lower the apparent vapor pressure of the condensed phase by taking it into solution or into chemical combination, or raise it due to the formation of a new, stable species. Typical examples of the former are the low vapor pressures reported for the alkali hydroxides by early workers who used nickel or other metals for crucible materials. More recent studies by Spinar and Margrave (39) have shown that in non-reactive crucibles fashioned from single crystals of magnesium oxide, the vapor pressures of the alkali hydroxides are many times higher than previously reported. Examples of the latter are the following. In studies of the vaporization of zirconium dioxide (40) and thorium dioxide (41) from tantalum crucibles, the gaseous species tantalum monoxide was found to contribute to the weight loss of the crucible (42,43). An attempt should be made to characterize the vaporization process. A change in crucible material may reveal reaction between the sample and the crucible. Chemical and X-ray diffraction analyses should be performed on all starting materials as well as on the residual substances and sublimates.

(b) The residual pressure in the vacuum system must be low enough to preclude scattering of the effusing vapor or reaction of the sample with residual gases.

(c) The effusion crucible and the sample contained therein must be at a known, uniform temperature. Winterbottom and Hirth (44) have shown that when the top of the crucible is at a higher temperature than the bottom there is a departure from molecular effusion as predicted by the cosine law with a resultant increase in the contribution of surface diffusion to the total flow. Moreover, if the top of the crucible is cooler than the bottom there is the possibility that the vapor will condense at the orifice of the crucible thus reducing the amount of sample which leaves through it.

(d) The area of the evaporating surface and its location must be such that the saturation pressure is maintained within the effusion crucible. In addition, the orifice shape and size must be such that not only is the saturation pressure maintained within the crucible, but also that the temperature uniformity within the cavity is not disturbed. Carlson (26) carefully analyzes these problems and discusses previous experimental investigations and attempts (45,46) to treat theoretically the problem of vapor saturation within the effusion crucible.

(e) The fraction of impinging molecules which stick to the target must be known, and the walls of the vacuum system must condense and retain all effusate striking them so that the target receives material only from the orifice.

(f) If the vaporization process is to be followed by weighing the crucible before and after the vaporization, the volatility of the crucible itself must be known and taken into account.

(g) The physical dimensions of the apparatus must be known accurately and allowance made for changes effected by temperature.

(h) The molecular weights and relative abundances of the vapor species must be known.

The means by which and the degree to which these various experimental requirements were met in the present investigation are discussed later in the text.

III. EXPERIMENTAL

A. Summary of the Experimental Approach

Thorium dicarbide was prepared by the reaction of graphite with either thorium metal or thorium dioxide. The total vapor pressures of gaseous species containing thorium were determined as functions of temperature by the Knudsen effusion method in which the effusing species were collected on cooled quartz targets in a system of known geometry, and the targets were assayed for thorium by neutron activation techniques. From these data, the parital pressures of $Th_{(g)}$ and $ThC_{2(g)}$ in equilibrium with $ThC_{2(s)}$ were calculated.

The vapor pressure data thus determined were combined with the data of Jackson and co-workers (21) who identified the vapor species and determined their relative abundances as a function of temperature using a mass spectrometer. Second and third law calculations were made of the enthalpy and entropy changes accompanying the reactions

$$ThC_{2(s)} = ThC_{2(g)}$$

and

$$ThC_{2(s)} = Th_{(g)} + 2C_{(graphite)}.$$

These data were combined with the measured enthalpy of vaporization of elemental thorium (22) and the standard enthalpy of formation of the solid dicarbide was determined.

B. The Preparation of Thorium Dicarbide

1. Materials

Reagent grade thorium nitrate tetrahydrate of 99.9 per cent total purity was obtained from the J. T. Baker Chemical Company, Phillipsburg,

New Jersey, and was ignited in platinum crucibles at 1000° to produce thorium dioxide. Thorium metal powder of 99.1 per cent total purity was obtained from K & K Laboratories, Inc., Jamaica, New York. Reaction crucibles were fashioned from ultra-high purity graphite obtained from the United Carbon Products Company, Inc., Bay City, Michigan. This graphite was used also in the preparation of thorium dicarbide.

2. Methods of Preparation and Apparatus

Thorium dicarbide was prepared by the reaction of thorium dioxide and graphite heated together either as a powder or in the form of pellets pressed in a die of "carborized" steel with a pellet bore of 5/16-inch. Average sample size ranged from 0.5 to 2.0 grams, and pressing at 5,000-10,000 p.s.i. resulted in pellets ranging in height from about 1/8 to 1/4-inch.

The reactant charge, powder or pellet, was loaded directly into a graphite crucible which had been outgassed previously at about 2000°. The crucible, fashioned from 3/4-inch graphite rod, was 1 1/8-inches high and was bored with a reaction well 7/16-inch in diameter and 5/8-inch deep. A graphite lid, fashioned to provide a snug fit over the tapered outer wall of the crucible was drilled with a 50 mil diameter centered orifice to allow gases to escape. A black-body hole 40 mil in diameter was drilled 1/4-inch deep into the base of the crucible. Three 40 mil tungsten legs, 3/4-inch in length, force-fitted at 120° intervals around the base into 1/4-inch deep holes, supported the crucible.

The crucible was arranged in a vacuum system shown schematically in Figure 2. The apparatus consisted essentially of a vacuum system

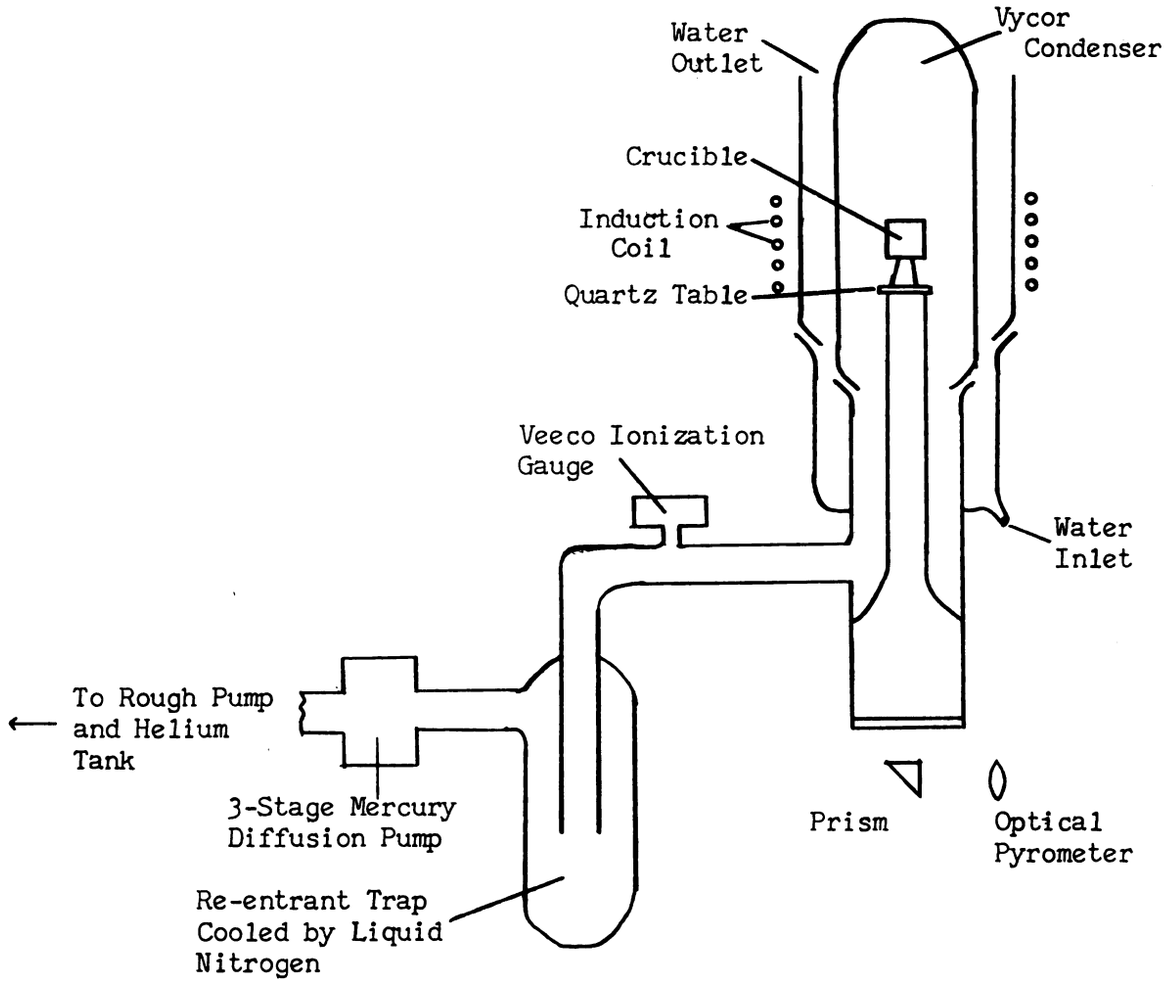


Figure 2. Schematic diagram of the apparatus used to prepare thorium dicarbide.

equipped with a Vycor water-cooled condenser, a support for the crucible and an optical window. A large diameter re-entrant trap cooled with liquid nitrogen was located between the 3-stage mercury diffusion pump and the reaction chamber. The residual pressure in the vacuum system was monitored with a Veeco ionization gauge and could be maintained at about 1×10^{-7} mm Hg with the crucible cold. The crucible stood on a fused silica table which sat on a Vycor support. The support table was provided with a 1/4-inch diameter centered hole and the temperature of the black-body hole in the base of the crucible was measured, from below, with a Leeds and Northrup model No. 8622-C optical pyrometer. The crucible was heated with a 20-kva Thermonic 250-450 kilocycle induction furnace.

Thorium dicarbide was prepared according to the reaction:

$$ThO_{2(s)} + 4C_{(graphite)} = ThC_{2(s)} + 2CO_{(g)}.$$

When the samples were heated in vacuum the pressure within the system increased due to outgassing of the reactant graphite. At about 1700°K a high pressure surge which indicated the effusion of carbon monoxide gas due to the above mentioned reaction, occurred within the system. This temperature was maintained until the pressure dropped to 1×10^{-5} mm Hg or less, whereupon it was assumed that the reaction was complete. The temperature was then increased to above 2000°K for varying lengths of time before heating was terminated. After the crucible had cooled, the vacuum system was opened to the atmosphere and the product was removed from the crucible and stored under a dry helium atmosphere until it was used for either analysis or an effusion experiment.

The reaction product, a brittle, yellow, metallic appearing, sintered mass, was proved to be thorium dicarbide by both chemical and X-ray

powder diffraction analyses. In each preparation, chemical analysis indicated the presence of trace amounts of graphite in the product. When the reactants were heated in pellet form, the sample remained intact throughout the heating process, although the pellet did expand somewhat in size.

For the reaction between thorium metal and graphite, the components were mixed in the desired mole proportions and pressed into pellets, using the technique described previously. A new graphite crucible was fashioned, identical to the one described previously, but with larger overall dimensions. The reactants were heated in vacuum to produce thorium dicarbide according to the equation:

$$Th_{(l)} + 2C_{(graphite)} = ThC_{2(s)}.$$

Since no carbon monoxide gas is given off in this reaction it was possible to heat to the desired temperature quickly without encountering gaseous discharge. This product was identical to the one prepared by the reaction between graphite and throium dioxide. Brief descriptions of the individual preparations are given in Appendix A.

C. Analysis of Thorium Dicarbide

1. X-ray Powder Diffraction Patterns

X-ray powder diffraction photographs of the samples were obtained using Cu K_α radiation ($\lambda_{\alpha u}$ = 1.5418Å) and a Debye-Scherrer X-ray powder camera of 114.59 mm diameter. The samples of thorium dicarbide were ground to a fine powder with an agate mortar and pestle in an inert atmosphere and loaded into 0.3 mm diameter Pyrex capillaries.

With the exception of one sample, P-14, which was prepared at a low temperature, the X-ray powder diffraction patterns of all samples

indicated the presence of only thorium dicarbide, and in some samples, trace amounts of graphite.

When the d values of the X-ray photographs* of the samples were checked against the values on ASTM card No. 543-DB for thorium dicarbide it was found that not all of the lines could be identified. On investigation of the d values listed on this ASTM card indicated that the values were taken from the data of von Stackelberg (6) for "tetragonal" thorium dicarbide. It was noted earlier that Hunt and Rundle (7) have shown that thorium dicarbide has a monoclinic structure, space group C2/c. Although Hunt and Rundle reported hkl values they did not list the corresponding d values. Kempter and Krikorian (12) resolved this problem by converting from the complex monoclinic lattice to the more convenient pseudo-orthorhombic lattice. Starting with the Hunt and Rundle monoclinic parameters they found the pseudo-orthorhombic parameters to be $a_0 = 10.555\mathring{A}$, $b_0 = 8.233\mathring{A}$, and $c_0 = 4.201\mathring{A}$. Using these parameters and the monoclinic hkl values reported by Hunt and Rundle, and, making use of the transformation matrix, monoclinic to orthorhombic

$$\begin{vmatrix} 1 & 0 & -1 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{vmatrix},$$

d values were calculated for each monoclinic hkl value listed by Hunt and Rundle. Because the X-ray diffraction patterns of all samples except P-14 were identical, only one has been listed in Table III.

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*In the entire text, "X-ray photograph" refers only to X-ray powder diffraction patterns.

Table III. Assigned indices for film A-1068.

Line	Intensity[a]	hkl[b]	$d_{obs.}$ (Å)	$d_{calc.}$ (Å)	Line	Intensity[a]	hkl[b]	$d_{obs.}$ (Å)	$d_{calc.}$ (Å)
1	VW	110	3.50	3.53	16	MS	311,113	1.742	1.744
2	VVW	(002)[c]	3.32	3.367	17	M	221,22$\bar{2}$	1.642	1.645
3	S	11$\bar{1}$	3.26	3.29	18	S	004,400,	1.616	1.622
4	MS	200,002	3.217	3.246			31$\bar{3}$,40$\bar{2}$		
5	VS	111	2.931	2.940			20$\bar{4}$		
6	S	20$\bar{2}$	2.698	2.639	19	VVW	11$\bar{4}$	1.558	1.555
7	VW	11$\bar{2}$	2.564	2.563	20	VW	312,023	1.509	1.512
8	W	112	2.245	2.245	21	MW	222,22$\bar{3}$	1.470	1.468
9	M	020	2.099	2.100	22	W	130	1.369	1.369
10	M	202	2.056	2.058	23	W	13$\bar{1}$	1.355	1.354
11	MW	021	1.998	1.998	24	MW	131,402	1.328	1.327
12	S	31$\bar{1}$,11$\bar{3}$	1.957	1.964			204		
13	VVW	310	1.915	1.924	25	MW	40$\bar{4}$,42$\bar{1}$	1.315	1.319
14	VVW	31$\bar{2}$	1.829	1.838	26	MW	313	1.305	1.304
15	S	002,220	1.764	1.763	27	M	132,223,	1.288	1.284
		22$\bar{1}$					024, 402, 22$\bar{4}$,42$\bar{2}$		

a. W = weak, M = medium, S = Strong, V = very.
b. Monoclinic.
c. Line 2 is the (002) line of graphite, ASTM card No. 415-HB.

Film A-1068 (sample P-12) was used because it had somewhat sharper lines than other films.

The X-ray photograph of sample P-14 (film A-1077) indicated the presence of both thorium dicarbide and a dominant new phase of cubic symmetry. No ASTM card was available for thorium monocarbide, but Wilhelm and Chiotti (4) have reported a cubic (NaCl-type) structure for ThC with $a_0 = 5.34\text{Å}$. Using their data, d values were computed for thorium monocarbide and were found to be identical to those of the cubic phase on film A-1077. Table IV lists the indices assigned to the lines on this X-ray photograph.

2. Chemical Analyses

It was stated in the preceding section that the X-ray photographs of the samples indicated the presence of only thorium dicarbide, and in some cases, trace amounts of graphite. If, indeed, these are the only phases present, the problem of analysis becomes a relatively simple one.

The procedure used, in brief, was as follows. A weighed portion of the sample was dissolved in dilute hydrochloric acid, and the free graphite was collected by filtration, dried and weighed. The thorium in the filtrate was precipitated with a suitable reagent and ignited to thorium dioxide for weighing. The combined carbon originally present was calculated by difference.

At first, varying concentrations of either nitric and hydrochloric acids were used to dissolve the dicarbide samples. However, it was observed that when nitric acid was employed it was impossible to obtain reproducible graphite analyses; in all cases the amount of graphite obtained was higher than expected with a corresponding low result for the

Table IV. Assigned indices for film A-1077

Line	Intensity[a]	$d_{obs.}$ (Å)	ThC_2 hkl	$d_{calc.}$ (Å)	ThC hkl	$d_{calc.}$ (Å)
1	W	3.25	$11\bar{1}$	3.29		
2	S	3.05			111	2.068
3	W	2.93	111	2.940		
4	S	2.65			200	2.658
5	W	1.96	$31\bar{1}, 11\bar{3}$	1.964		
6	S	1.88			220	1.879
7	W	1.76	002, 220, $22\bar{1}$	1.763		
8	W	1.75	113, 311	1.744		
9	VS	1.60			311	1.603
10	MS	1.53			222	1.534
11	W	1.47	$222, 22\bar{3}$	1.468		
12	MS	1.33			400	1.329
13	S	1.22			331	1.219
14	S	1.19			420	1.189

a. W = weak, M = medium, S = strong, V = very.

combined carbon. It has been observed (47) that nitrates of the rare earths catalyze the oxidizing power of nitric acid with regard to organic compounds. Furthermore, Sasaki, Ichikawa, Imai, and Uruno (48) reported that while thorium dicarbide was completely soluble in all concentrations of hydrochloric acid, the solubility in nitric acid was dependent on the acid concentration with a minimum solubility occurring at about 6M nitric acid. For these reasons, all analyses subsequent to the first three were performed using hydrochloric acid to hydrolyze the samples.

The first method used to determine thorium involved precipitation with oxalic acid. The procedure was as follows: After the graphite had been collected by filtration, the filtrate was heated to the boiling point and an excess of a saturated solution of oxalic acid was added The precipitate was digested for 6-10 hours on a steam bath, filtered, while hot, into a tared alundum filter crucible, and ignited at 1000° to thorium dioxide for weighing.

While the precipitation with oxalic acid yielded accurate and reproducible results, a great amount of time was involved in the digestion of the precipitate. Since thorium was the only cation present, the use of ammonia as the precipitating agent yielded results which were as accurate and which could be obtained in a much shorter time.

The following procedure was adopted and used in the analysis of all samples subsequent to sample P-12.

(a) To a weighed sample (0.05 to 1.0 g) in a 250 ml beaker add 100 ml 0.5M HCl and heat for 30 minutes on a steam bath to insure the dissolution of all the thorium not present as thorium dioxide. The

combined carbon present is hydrolyzed to gaseous and condensed hydrocarbons while the free graphite remains unchanged.

(b) Filter the graphite into a tared filter crucible, dry for one hour at 105°, cool and weigh. Ignite the contents of the crucible for one hour at 1000° to drive off the carbon as carbon monoxide, cool the crucible and reweigh. In this manner any thorium dioxide originally present may be determined in addition to the free graphite.

(c) Transfer the filtrate from step (b) to a 400 ml beaker and add aqueous ammonia until a precipitate forms, about pH6. Heat the sample to the boiling point, add more ammonia to insure complete precipitation, filter the thorium hydroxide, while hot, into a tared alundum filter crucible and ignite the precipitate to thorium dioxide by heating at 1000° for one hour. Cool and weigh the crucible, determining the thorium as thorium dioxide.

(d) From the original sample weight the amount of combined carbon can be calculated by difference.

Analyses were run in duplicate whenever possible, and the precision obtained was ± 0.5 per cent. On some samples an additional thorium determination was made by direct ignition of a weighed sample to thorium dioxide. Again, agreement in results was always ± 0.5 per cent. It should be pointed out that due to the rapid hydrolysis of thorium dicarbide in moist air, care must be taken to keep moisture from the sample before the analysis is performed.

D. Effusion Experiments

1. Apparatus

The apparatus used in the effusion experiments was similar to the

one used by Ackermann, Gilles, and Thorn (49) for measuring the vapor pressure of uranium dioxide and is shown schematically in Figure 3. Essentially, the apparatus consisted of a pumping system, an evacuated Vycor condenser, a support for the effusion crucible, an optical window, and a device for presenting targets to the effusate. Below the target magazine were a magnetically operated fused silica shutter for controlling exposure times and a magnetically operated tungsten push-rod for ejecting exposed targets into the Pyrex receiver. Again, the crucible was heated with a 20-kva Thermonic high-frequency induction furnace.

Three effusion crucibles were used in this research. Crucibles No. 1 and No. 2, used in experiments A and B, were fabricated from graphite rod and with the exception of the orifice diameters were identical to the one described previously for the preparation of thorium dicarbide. Crucible No. 3, used in experiment C, was made of tungsten and was obtained from the Kulite Tungsten Company, Ridgefield, New Jersey. The crucible was 1-inch high with an inner bore of 3/4-inch diameter. Since a small amount of nickel (0.1-0.3%) was used as a binder in the fabrication of the tungsten crucible, the crucible was heated at 2300° in high vacuum to volatilize the nickel. The crucibles used will be discussed later with the individual effusion experiments.

2. Measurement of Dimensions

Equation (21) requires the measurement of three linear dimensions for calculation of the vapor pressure. These dimensions are the diameter of the orifice of the effusion crucible, the distance from the orifice to the target collimator for each experiment, and the diameter of the collimator.

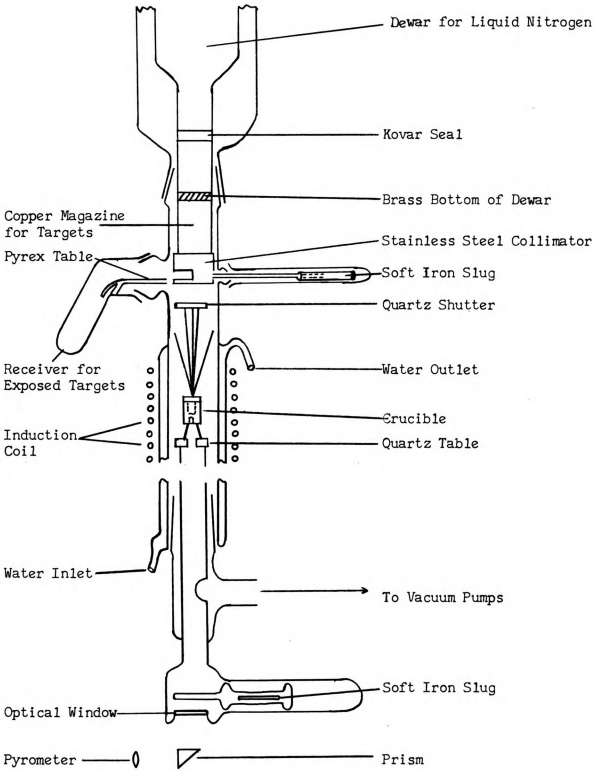


Figure 3. Schematic diagram of the apparatus used for effusion experiments.

(a) Measurement of orifice diameter

Orifice diameters of the effusion crucibles used in experiments A, B, and C were measured before and after each experiment by means of a Bausch and Lomb Model SVB-73 microscope equipped with a vernier eyepiece calibrated such that one division on the vernier scale, under high magnification (60X), equaled 0.033 mm. The effusion crucibles were mounted beneath the microscope and readings were taken along eight separate and equally spaced diameters. Standard deviations obtained were about 0.01 mm.

The arithmetic average of the eight measurements was used for the calculation of the orifice area. In those cases in which small differences were found between orifice diameters measured before and after a given experiment, the average of the two values was used. The orifice diameters are tabulated in later sections with other data for the individual experiments.

(b) Measurement of orifice-to-collimator distance

The distance from the orifice to the collimator was measured before each vaporization experiment with a cathotometer, Gaertner Scientific Company, Model No. M911, serial No. 1585a. The scale could be read directly to 0.05 mm by means of a vernier, and readings were estimated to within 0.01 mm.

The measurement was made after the apparatus had been assembled and evacuated for at least half an hour so that the greased joints were well seated. The vacuum system was then opened to the atmosphere, the shutter assembly which controlled exposure time was removed, and the height of the lip of the collimator was determined. The height of the

top of the effusion crucible was measured by sighting through the water jacketed Vycor condenser.

Each measurement was made four times and the standard deviation in the average of each measured orifice-to-collimator distance was from 0.008 to 0.010 cm. For a typical distance of 11 cm, the resulting standard deviation amounted to about 0.09 per cent.

(c) Measurement of collimator diameter

The diameter of the collimator was measured by means of a vernier caliper which could be read to 0.004 inches. Readings were taken along six separate and equally spaced diamters. The average diameter with its standard deviation was found to be 1.90754 ± 0.0049 cm.

3. Measurement of Temperature

Temperatures were measured with a Leeds and Northrup Model No. 8622-C disappearing filament optical pyrometer, serial No. 1572579. The pyrometer was calibrated at the National Bureau of Standards and scale readings together with the true temperatures, T_{NBS}, determined at the National Bureau of Standards are listed in Table V. For each of the three scale ranges of the pyrometer a graph was made of $T^{o}C_{NBS}$-$T^{o}C_{scale}$ vs. $T^{o}C_{scale}$ to obtain calibration curves which were used to correct the observed temperatures.

Before and after each series of target exposures, the transmissivity of the window and prism were measured, so that corrections could be made for the absorption of light by these objects and for any change due to coating of the window during the experiment. For this measurement the pedestal section of the vacuum system was cracked off from the pumping line and a series of measurements was made of apparent temperatures of the filament of a tungsten band lamp near 1500°, directly and

Table V. Corrections for pyrometer no. 1572579

Low Range		High Range		X High Range	
$T^{o}C_{NBS}$	$T^{o}C_{Scale}$	$T^{o}C_{NBS}$	$T^{o}C_{Scale}$	$T^{o}C_{NBS}$	$T^{o}C_{Scale}$
805	800	1107	1100	1516	1500
854	850	1204	1200	1614	1600
902	900	1304	1300	1712	1700
952	900	1405	1400	1811	1800
1001	1000	1506	1500	1911	1900
1052	1050	1606	1600	2013	2000
1102	1100	1706	1700	2217	2200
1153	1150	1757	1750	2421	2400
1203	1200			2624	2600
1228	1225			2825	2800

through the window and prism. The correction for transmissivity, $\Delta 1/T$, follows from Wien's law and is defined by the equations:

$$\Delta\frac{1}{T_W} = \frac{1}{T_W} - \frac{1}{T} \tag{23}$$

and

$$\Delta\frac{1}{T_P} = \frac{1}{T_P} - \frac{1}{T} \tag{24}$$

in which T_W and T_P are the apparent temperatures of the hot object viewed through the window and the prism, respectively, and T is the true temperature. The total correction for the window and prism is simply

$$\Delta\frac{1}{T_T} = \Delta\frac{1}{T_W} + \Delta\frac{1}{T_P} . \tag{25}$$

The quantity $\Delta 1/T_T$ is approximately constant for all temperatures, and the relationship

$$\frac{1}{T} = \frac{1}{T_o} - \Delta\frac{1}{T_T} , \tag{26}$$

in which T_o was the observed temperature, was used to calculate true temperatures from the apparent temperatures measured during the experiments. The pyrometer correction factor obtained from the data in Table V was applied before the value T_o was substituted into equation (26). The determination of $\Delta\ 1/T$ involved the measurement of relatively small temperature differences at about 1500° and extrapolation to higher temperatures. The calibration was made at 1500° because the pyrometer scale can be read most accurately at this temperature. As an example, the temperature determination for target No. 4 from effusion experiment B is shown in Appendix C.

through the window and prism. The emissivity is transmissivity, $\alpha\lambda T$, follows from Wien's law and [illegible] the upper limit

$$[illegible] \qquad (23)$$

and

$$[illegible] \qquad (24)$$

in which T_0 [illegible] (2) [illegible] and T is the temperature viewed through the window [illegible] true temperature [illegible] from the window and prism is simply

$$[illegible] \qquad (25)$$

The quantity $\alpha\lambda T$ is more strictly variant for all temperatures, and the relationship

$$[illegible] \qquad (26)$$

in which T_0 was the observed temperature, was used to calculate true temperatures from the apparent temperatures measured during the experiments. The pyrometer correction factor obtained from the data in Table V was applied before the value T_0 was substituted into equation (26).

The determination of λ & λT involved the measurement of relatively small temperature differences at about 1500° and extrapolation to higher temperatures. The calibration was made at 1500° because the pyrometer scale can be read most accurately at this temperature. As an example, the temperature determination for target No. 8 from effusion experiment B is shown in Appendix C.

Comparisons were made for the effusion crucibles between temperatures in the cavity, measured from above, and in the black body hole, measured from below. The temperature difference between the top and bottom was found to change approximately linearly with temperature and the use of a graphite radiation shield to warm the crucible lid was found to reduce greatly this difference. For crucible No. 2, the difference between the top and bottom temperatures was 18.6° at 1900°, but with the graphite shield in place, this difference was reduced to about 5°. The temperature measurement of the tungsten crucible used in experiment C will be discussed later in the text. Effusion experiments B and C were carried out with one or more graphite shields around the crucible.

The hot effusion crucibles remained at temperatures constant to ± 1° over periods up to several hours, except during experiments in which heavy deposition of graphite on the condenser walls occurred at high temperatures. Constant temperatures were attained after the deposits reached what presumably was constant reflectivity, but a downward drift of temperature tended to set in later, perhaps because of absorption of power by the now heavy deposits or because of partial shielding of the effusion crucible from the high-frequency field. Even in these cases readjustment of input power permitted maintenance of temperatures constant to within ± 3°.

In all target exposures temperatures were measured in groups of four readings to permit determination of temperature with a precision of ± 1° for each group, so that any real drift with time could be detected. The measurements were repeated frequently enough to give several

such groups during an exposure. The arithmetic average of all temperatures was taken as the temperature of the exposure.

4. Preparation of Targets

Effusate from the effusion crucibles was collected by condensation on fused silica targets. Each 1-inch diameter by 1/16-inch thick target was cleaned in boiling, concentrated nitric acid, washed in distilled water, and baked one hour at 600°. When cool, each target was mounted in a 3/8-inch thick aluminum ring (cassette) and held there by a phosphor bronze spring. The targets so mounted were stacked in the copper magazine soldered to the bottom of the liquid nitrogen container at the top of the condenser (Figure 3). The angular fraction of the total effusate impinging on a target was defined by the stainless steel collimator supporting the stack.

5. Procedure for Volatility Measurements

The procedure employed during a given series of target exposures was as follows. The sample was loaded into the effusion crucible, the targets stacked in the magazine and the apparatus shown in Figure 3 was assembled and evacuated. When the joints were well seated, the system was opened to the atmosphere, the collimator shutter assembly was removed and the orifice-to-collimator distance was measured. The system was re-evacuated, the magazine Dewar was filled with liquid nitrogen, and heating was begun when the residual pressure dropped to below 10^{-6} mm Hg. The effusion crucible was heated to the desired temperature and maintained there for at least 30 minutes to attain a steady state. Then the collimator shutter was opened, the time, read from a Precision Scientific Company "Time-It" electrical timer with the dial graduated to

0.01 minutes, was recorded and the temperature was measured. When the desired exposure time had elapsed, the shutter was closed, the target was ejected into the Pyrex receiver, the next target fell into place, the temperature was adjusted to a new value, and the cycle was repeated. When a given series was concluded, the crucible was allowed to cool in the high vacuum for several hours before the system was opened. The sample was then removed for chemical and X-ray powder diffraction analyses.

A series of targets was exposed at successively increasing temperatures over the range of a given experiment, followed by a series at successively decreasing temperatures. This procedure gave unreproducible temperature-dependent trends only in experiment A. The data from the vaporization experiments are tabulated later.

6. Analysis Targets

At the conclusion of an effusion experiment the exposed targets were removed from the receiver, taken from the aluminum cassettes and wrapped in aluminum foil. The targets, together with a set of standards, also wrapped in aluminum foil, were placed in an aluminum can and shipped to the Argonne National Laboratory where they were irradiated in the CP-5 reactor for 9 hours at a neutron flux of about 10^{12} n/cm^2/sec. The reaction of interest was:

$$Th^{232}(n,\gamma)\ Th^{233} \xrightarrow[23m]{\beta^-} Pa^{233} \xrightarrow[27.4d]{\beta^-} U^{233}(1.6 \times 10^5 y).$$

310kev. γ

The irradiated targets were returned to this laboratory and the 310 kev. gamma rays of the Pa^{233} were detected with a Model N-221 Hamner single-channel scintillation counter.

The standards for the neutron activation analyses were prepared in the following manner. Fused silica discs of the type used as targets were cleaned in boiling concentrated nitric acid, washed in distilled water, and baked at 600° for one hour. Next, a known amount of a standard solution of thorium nitrate was placed on the discs which were subsequently evaporated to dryness in a desiccator.

(a) Analysis of standard solutions

The standard solutions were prepared by aliquot dilution of another standard solution, S-I, containing approximately 1600γ of thorium per milliliter. Solution S-I was analyzed by the gravimetric method described previously and found to contain 1598 γ of thorium per milliliter. A series of solutions was prepared by aliquot from solution S-I and then were mixed for at least 30 minutes with a magnetic stirrer to insure homogeneity. These solutions were then analyzed by the spectrophotometric method described by Fletcher and Milkey (50). This method involved the formation of a 1:2 thorium-morin (5,7,2',4'-flavanol) complex. The procedure recommended by these authors was as follows:

1) To a 50 ml volumetric flask add 1.0 ml of 0.63M HCl or HNO_3.
2) Add a known amount of a solution containing 60 γ or less of thorium, free from other ions. The pH of the solution should previously be adjusted to 2.0.
3) Adjust the volume to 20 ml with distilled water.
4) Add 2.0 ml morin reagent (0.1g morin per 100 ml ethanol).
5) Mix well.
6) Adjust the volume to 50 ml with distilled water, stopper, and mix well.

7) Let stand a half hour to attain equilibrium.

8) Using water as the reference solution, measure the absorbance at 410 mμ, using a Beckman Model DU spectrophotometer.

The authors claimed the sensitivity range to be 0-60 γ thorium per milliliter of solution.

A Beer's law plot, absorbance vs. concentration was made and is shown in Figure 4. A least squares calculation allowed all points to be fitted to a straight line curve until the concentration reached about 90 γ of thorium per millimeter. At thorium concentrations greater than this the data do not follow Beer's law. The absorbance, the concentration of the samples as determined from the aliquot, and the concentration determined by the spectrophotometric technique are listed in Table VI.

(b) Activation analysis of standard discs

In order to test the accuracy of the neutron activation technique for the assay of thorium on effusion targets, a preliminary experiment was conducted. The two solutions used in preparing the standard discs were prepared by aliquot from the original standard solution, S-I, and were analyzed spectrophotometrically. The absorbances, corrected for the blank were; solution A, 0.019, solution B, 0.030. The concentrations, calculated from a least squares treatment of the data listed in Table VI, were; solution A, 3.150 γ/ml, solution B, 4.936 γ/ml.

Five standard discs were prepared:

Disc 1. 19.3×10^{-3} ml solution A (6.080×10^{-8} g thorium)

Disc 2. 22.37×10^{-3} ml solution A (7.047×10^{-8} g thorium)

Disc 3. 27.63×10^{-3} ml solution B ($13,638 \times 10^{-8}$ g thorium)

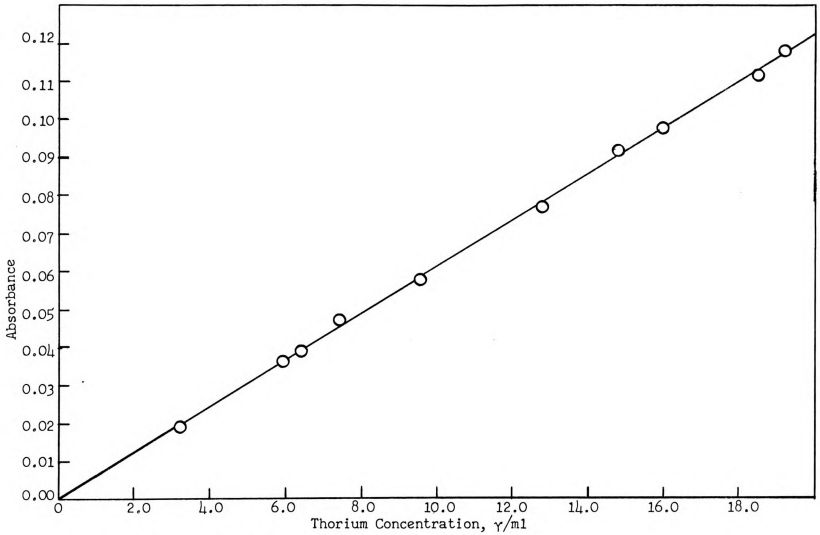


Figure 4. Beer's law plot for thorium-morin complex.

Table VI. Spectrophotometric determination of thorium

Absorbance	Thorium Concentration γ/ml (aliquot)	(calculated)
0.019	3.196	3.150
0.036	5.917	5.910
0.039	6.392	6.397
0.047	7.392	7.695
0.058	9.588	9.480
0.077	12.784	12.564
0.092	14.792	14.999
0.098	15.980	15.972
0.112	18.490	18.245
0.118	19.176	19.219
0.197	31.960	32.041

Disc 4. 27.19×10^{-3} ml solution B (13.421×10^{-8}g thorium)

Disc 5. Blank.

The standard discs were wrapped in aluminum foil, shipped to the Argonne National Laboratory for 9 hours irradiation at a neutron flux of 10^{12} n/cm^2/sec and returned to this laboratory where the gamma-activity was followed for three weeks. The activity ratios observed by counting the gamma-activity of the discs, and the standard deviations, together with the expected values are listed in Table VII.

The amount of thorium found on discs 1 and 3, based on disc 2 containing 7.047×10^{-8} g were:

Disc 1. 6.040×10^{-8} g

Disc 3. 13.551×10^{-8} g.

The differences between these amounts and the amounts expected were 0.26 and 0.64 per cent for discs 1 and 3, respectively. From these results it was concluded that this technique would yield an accurate and sensitive determination of the thorium on the effusion targets.

Deposits on the discs were thin enough so that absorption effects were negligible. It should be pointed out that the discs had to be removed from the aluminum foil wrapping before they were counted because the aluminum foil was found to have a much higher initial activity than the discs themselves.

Table VII. Activity ratios observed and expected for standard discs

No. Days Since Irradiation	Activity Ratios Corrected for Background and Blank[a] Disc 2/Disc 1	Disc 3/Disc 1	Disc 3/Disc 2
5	0.890	2.134	2.397
6	1.110	2.046	2.044
7	1.267	2.188	1.726
10	1.104	2.165	1.946
11	1.142	1.880	1.647
12	1.168	2.361	2.022
13	1.162	2.320	1.995
14	1.259	2.398	1.905
17	1.264	2.516	1.990
18	0.928	2.058	2.216
19	1.708	2.269	1.328
21	1.059	1.909	1.804
24	1.162	2.262	1.947
25	1.043	2.030	1.951
Mean Ratios	1.162 ± 0.186	2.181 ± 0.181	1.923 ± 0.241
Expected Ratios	1.159	2.243	1.935

a. Disc 4 was dropped and discarded.

IV. RESULTS AND DISCUSSION

A. Convention Chosen for the Expression of Results of Effusion Experiments

Use of the Knudsen effusion technique to determine the temperature dependence of the total volatility of a given substance when combined with the use of the mass spectrometer can provide data more reliable than that obtained from the latter alone as well as results impossible to obtain by the former alone. For example, assume that some binary compound AB evaporates by the two processes

$$AB_{(s)} = AB_{(g)}$$

and

$$AB_{(s)} = A_{(g)} + B_{(g)}.$$

A precise effusion study in which the total rate of effusion of solid AB is determined as a function of temperature would give at each temperature an "effective pressure" P_E calculated from equation (21):

$$P_E = P_{AB} + P_A \sqrt{M_{AB}/M_A} . \qquad (27)$$

Here P_{AB} and P_A represent the partial pressures of AB molecules and A atoms in the effusion crucible.

It was pointed out previously that Jackson and co-workers (21) in their mass spectrometric investigation of the vaporization of thorium dicarbide observed that the principal reactions were:

$$ThC_{2(s)} = ThC_{2(g)}$$

and

$$ThC_{2(s)} = Th_{(g)} + 2C_{(graphite)}.$$

The convention chosen here was to calculate "effective vapor pressures" P_E from the gamma-counting data for each experimental measurement by the assumption, for convenience, that the vapor had the average molecular weight 256.0603, that of thorium dicarbide. The gamma-activities of the targets were converted to the equivalent weights of thorium dicarbide that would give rise to these activities, and these weights and the above molecular weight were inserted into the effusion equation (21) to obtain values of P_E. It follows from equation (27) that the "effective pressure" P_E is related to the partial pressures P_{Th} of thorium atoms and P_{ThC_2} of thorium dicarbide molecules by the equation:

$$P_E = P_{ThC_2} + P_{Th}\sqrt{M_{ThC_2}/M_{Th}} . \qquad (28)$$

This choice of convention seemed justified for the following reasons: First, because P_E is directly related to the rate of evaporation of thorium dicarbide through equation (21); second, P_E is a function easily compared with P_{Th} and P_{ThC_2} in plots of the data; third, since P_E amounts to a fair approximation of the total pressure of vapor species in equilibrium with solid thorium dicarbide, a graph of log P_E against $10^4/T$ is a convenient reference for quick comparison of the total volatilities of thorium dicarbide and other refractory compounds The determination of P_{Th} and P_{ThC_2} from P_E will be discussed later.

B. Individual Vaporization Experiments

1. Experiment A

The thorium dicarbide used in this experiment was in the form of a 0.817 g pellet which had been annealed by heating it in a graphite crucible in vacuum at 2216°K for 90 minutes. The pellet was placed in

a graphite effusion crucible which was arranged in the vacuum system. The system was heated for 2 hours at 1945°K to aid in attaining a low initial residual pressure, 1.9×10^{-6} mm Hg.

A total of eleven targets were exposed with individual exposures ranging from 60 to 200 minutes. The first five targets were exposed at successively higher temperatures and the next five at successively lower temperatures. Target No. 11 was "exposed" at 2123°K for 60 minutes with the shutter closed to determine the efficiency of the shutter in shielding targets. Target No. 5 jammed in the collimator and it was necessary to open the vacuum system and eject it manually. It was not thought necessary to remeasure the orifice-to-collimator distance as only the shutter assembly had been moved. The system was re-evacuated to 1×10^{-6} mm Hg and the remainder of the targets were exposed.

A chemical analysis was not performed before the experiment. Analysis of the residue after the vaporization showed the stoichiometry to be $ThC_{1.989}$. The X-ray photograph of the residue (film A-1039) indicated the sample to be ThC_2.

A series of standard solutions of thorium nitrate was prepared and analyzed spectrophotometrically and standards for the neutron activation analysis were prepared as described in section D-6, Chapter III. The amount of thorium on these discs was as follows:

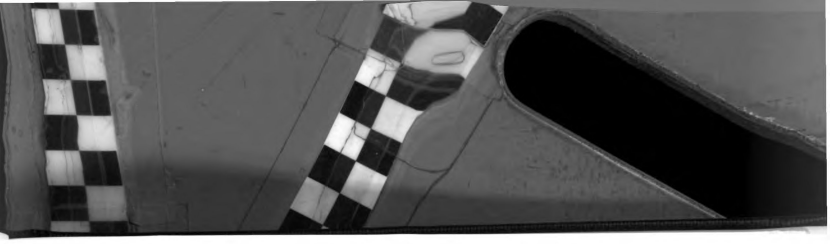
Disc 1. 13.837×10^{-8} g

Disc 2. 18.225×10^{-8} g

Disc 3. 26.971×10^{-8} g

Disc 4. 34.208×10^{-8} g

Discs 5 and 6. Blanks.



The standard discs together with the targets were wrapped in aluminum foil and sent to the Argonne National Laboratory for neutron activation. After the irradiation, the amount of thorium on the standard discs, based on disc 1 containing 13.837×10^{-8} g, was found to be:

Disc 2. $18.258 \pm 0.006 \times 10^{-8}$ g

Disc 3. $26.969 \pm 0.101 \times 10^{-8}$ g

Disc 4. $34.205 \pm 0.070 \times 10^{-8}$ g.

Target No. 11 which had been "exposed" with the shutter closed was found to have no gamma-activity above background, indicating that the shutter did indeed protect the targets from the effusate.

When the values of log P_E were graphed against $10^4/T$ for the ten effusion targets the first three points were found to lie above the curve. This was believed due to the initial formation and vaporization of the gaseous species ThO. Darnell, McCollum, and Milne (22) in their investigation of the vaporization of thorium metal observed the occurrence of initial high pressures due to the formation of this species which has a higher vapor pressure than thorium metal. They reported that as heating continued the pressure dropped because there was no longer sufficient oxygen in the system to form this species. Jackson and co-workers (21) also reported that they observed an initial occurrence of gaseous ThO and that this species disappeared with prolonged heating.

The data for targets No. 4 through No. 10 are presented in Table VIII, in which "effective pressures" P_E were calculated in accord with the previously outlined convention. A least squares equation of log P_E as a function of reciprocal temperature permitted the calculation of the following values for the heat and entropy of vaporization, from the slope

Table VIII. Data for experiment A

Exposure No.	Temperature (^{o}K)	Exposure Time (mm)	Th Collected x 10^{8}(g)	P_E (atm)
A-4	2420	120	5.240	8.580×10^{-9}
A-5	2505	120	17.900	2.983×10^{-8}
A-6	2475	120	13.136	2.185×10^{-8}
A-7	2357	120	1.934	3.126×10^{-9}
A-8	2291	120	0.397	6.327×10^{-10}
A-9	2195	121	0.133	2.051×10^{-10}
A-10	2123	188	0.032	3.114×10^{-11}

$\Delta 1/T$: 0.1123×10^{-4}

Orifice diameter : 1.04775 ± 0.0218 mm at room temperature

1.05444 mm at exposure temperature

Orifice-to-collimator distance : 11.582 cm

Collimator diameter : 1.90754 ± 0.0049 cm

and intercept, respectively:

$$\Delta H = 188.85 \text{ kcal/mole},$$

and

$$\Delta S = 41.06 \text{ e.u.}$$

2. Experiment B

This experiment was designed primarily to determine whether the composition of the condensate was time dependent by studying the volatility as a function of time at a constant temperature. For this experiment, two 1.5 g pellets were pressed from the same mixture of graphite and powdered thorium and heated together to produce thorium dicarbide. These pellets were annealed together at 2173°K for 2 hours. One pellet was analyzed before the vaporization experiment and the stoichiometry was found to be $ThC_{2.08}$. According to the data of Kempter and Krikorian (12) such a stoichiometry is unlikely. The amount of combined carbon present was calculated by difference and probably the excess weight which led to the high value for the combined carbon was due to oxygen. If the sample contained only 0.47 weight per cent oxygen, present in solid solution, the overall formula would be $ThC_{1.98}O_{0.08}$. This sample was found to contain 11.2 weight per cent excess free carbon.

The second pellet was used for the effusion experiment. After the system had been assembled and the dimensions measured, the sample was heated at 2400°K for 2 hours in an attempt to reduce the residual oxygen activity.

Seven targets were exposed; the first four at 2333°K for times ranging from 290 to 600 minutes. The remaining targets were exposed at higher temperatures. For the first four exposures a graphite radiation

shield was placed around the crucible. After these targets had been exposed, the system was opened to the atmosphere, a second graphite radiation shield was placed over the first, the system was again evacuated, and the orifice-to-collimator distance was remeasured. At the exposure temperature for target No. 7 (2585°K) gaseous discharge occurred within the system, probably due to the volatilization of carbon monoxide gas from the crucible itself. When the system was opened the orifice of the crucible was found to have become clogged with graphite, indicating a fairly large temperature gradient across the crucible, even with two radiation shields in place. There was a very heavy deposit of graphite on the walls of the condenser. Some of this graphite may have come from the sample since analysis of the residue after the vaporization showed the stoichiometry to be $ThC_{1.90}$ with the excess graphite reduced to 0.86 weight per cent. It is more likely, however, that the deposit came from the crucible which apparently had not been outgassed at a high enough temperature. The change in the stoichiometry of the sample to $ThC_{1.90}$ was probably due to the removal of oxygen from the system and the formation of a more pure dicarbide.

X-ray photographs of both the starting material and the residue (films A-1078 and A-1079, respectively) were identified as being characteristic of the phase ThC_2.

A series of standards for the activation analysis was prepared as described for experiment A. The amount of thorium on these discs was as follows:

Disc 1.	40.183×10^{-8} g
Disc 2.	40.183×10^{-8} g
Disc 3.	73.703×10^{-8} g

Disc 4. 77.550×10^{-8} g

Discs 5 and 6. Blanks.

As before, these standard discs were wrapped in aluminum foil and irradiated together with the effusion targets for this experiment. Standard disc 3 was broken and discarded. The amount of thorium on standard discs 2 and 4, based on disc 1 containing 40.183×10^{-8}g was found to be:

Disc 2. $40.136 \pm 0.24 \times 10^{-8}$ g

Disc 4. $77.666 \pm 0.46 \times 10^{-8}$ g.

When the values of log P_E were graphed against 1/T it was observed that three of the exposures at 2333°K resulted in virtually the same measured "effective pressures" while the value for the fourth exposure was somewhat lower. A least squares calculation of log P_E as a function of reciprocal temperature indicated the heat and entropy of vaporization to be:

$$\Delta H = 176.20 \text{ kcal/mole},$$

and

$$\Delta S = 35.62 \text{ e.u.}$$

These values were lower than those calculated for experiment A. It was pointed out above that the orifice was found to be clogged with graphite after exposure No. 7. It is probable that this clogging of the orifice was a gradual process, and if so, failure to take into account the reduced orifice area in equation (21) would indeed lead to low calculated pressures, and hence, a lowering of the values of the slope and intercept of the curve. With this thought in mind it was decided that the composition of the condensate probably did not change with time at a given temperature.

The data for this experiment are presented in Table IX. When these data are compared with those for experiment A it is apparent that the initial heating at 2400°K had eliminated or at least reduced the problem of formation and vaporization of the species $ThO_{(g)}$. However, the heavy deposition of graphite on the walls of the condenser and the gaseous discharge which occurred at 2585°K indicated the need for a different crucible material if the temperature range was to be extended beyond 2500°K.

3. Experiment C

For this experiment it was decided to use a tungsten crucible in an attempt to extend the temperature range. The crucible was described previously, in Section D, Chapter III. Although the crucible was provided with a tungsten lid, the lid did not fit snugly and a new one was fashioned from molybdenum. The crucible and lid were outgassed in vacuum at 2000° for 2 hours to volatilize the nickel binder. A heavy deposit of nickel formed on the condenser walls and the orifice in the lid clogged. The crucible was further heated in vacuum, with no lid in place, at 2200° until no more deposit was observed to form on the condenser walls. Another lid was fashioned, this time of tantalum, and the crucible was heated at 2000° for one hour with the tantalum lid in place. Only a slight deposit formed on the walls of the condenser and the orifice appeared to remain unchanged.

A graphite cup, with the same inner bore as the pellet press, 5/16-inch, was machined so that it fit snugly into the crucible, and the crucible with tantalum lid and graphite cup in place, was heated in vacuum at 2100° for one hour. Again, no change in the orifice was apparent.

Table IX. Data for experiment B

Exposure No.	Temperature (^{o}K)	Exposure Time (min)	Th Collected x 10^{8} (g)	P_E (atm)
B-1	2333	600	2.407	2.082×10^{-9}
B-2	2334	300	1.205	2.084×10^{-9}
B-3	2334	300	1.141	1.974×10^{-9}
B-4	2334	290	0.900	1.610×10^{-9}
B-5	2486	180	6.907	2.069×10^{-8}
B-6	2516	270	14.522	2.917×10^{-8}

$\Delta 1/T$: 0.0901×10^{-4}

Orifice diameter : 0.63525 ± 0.0142 mm at room temperature

0.63931 mm at exposure temperature

Orifice-to-collimator distance : 11.515 ± 0.007 cm for targets 1 to 4

11.533 ± 0.011 cm for targets 5 and 6

Collimator diameter : 1.90754 ± 0.0049 cm.

Because the crucible was not fitted with leg holes in its base it was placed on a stand fashioned from 15 mil sheet tantalum with three 60 mil tantalum legs spot-welded to the base at about 120° intervals. However, because of the weight of the crucible, this assembly proved to be unstable, the crucible falling off the stand if too large a voltage increase was applied to the coil.

A new support assembly was fashioned and is shown schematically in in Figure 5. Both the graphite block and the boron nitride table were provided with 1/4-inch holes drilled through the centers to allow measurement of the temperature of the crucible base with an optical pyrometer. The graphite block stood on three 60 mil tantalum legs, 1 1/4-inches long, force-fitted at 120° intervals into 1/4-inch deep holes drilled into the base. These legs were in turn force-fitted into three identical holes in the top of the boron nitride table. This assembly proved to be stable regardless of the power increases applied to the coil.

Because there was no black body hole in the base of the crucible the vacuum system was provided with both top and bottom optical window and prism assemblies and a temperature calibration experiment was conducted in which the temperatures measured for the crucible orifice (black body hole) were compared with the apparent base-temperatures. The difference between top and bottom temperatures was found to vary linearly with the temperature and a least squares fit of the data showed the slope and intercept to be 1.00811 and -1.64955°C, respectively. The graph of top temperature against bottom temperature is shown in Figure 6.

During the effusion experiment the apparent temperature of the crucible base was measured and corrected to the cavity temperature.

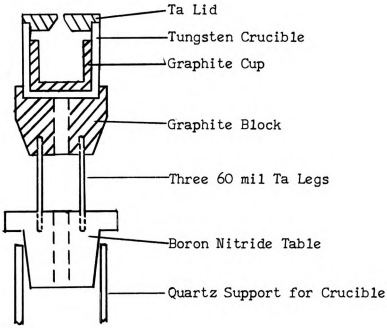


Figure 5. Schematic diagram of crucible support assembly for experiment C.

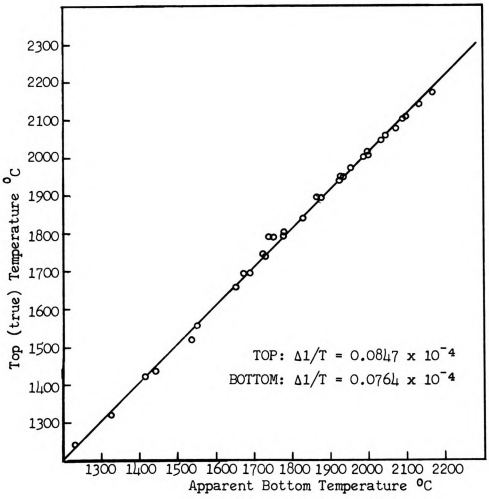


Figure 6. Temperature calibration curve for experiment C.

Two 2.0 g pellets were pressed from the same mixture of thorium and graphite powders and were heated together to prepare thorium dicarbide. The pellets were annealed at 2275°K for 2 hours. One pellet was analyzed chemically before the vaporization experiment and the stoichiometry was found to be $ThC_{1.993}$ with 0.87 weight per cent excess free carbon. The second pellet was used for the experiment.

After the system had been assembled the crucible was heated at 2400°K for 3 hours to reduce the residual oxygen activity. A graphite radiation shield, which had been used during the temperature calibration experiment, was placed over the crucible lid.

Twelve targets were exposed with individual exposure times ranging from 111 to 300 minutes. Targets were exposed at successively higher temperatures until the maximum temperature was attained, and then at successively lower temperatures until the target magazine was empty. Four of the targets were used to test for total condensation of the effusate on the targets. The results of these "bounce check" experiments are discussed later in the text.

Although a deposit of graphite formed on the walls of the condenser, it was not as heavy as those formed when graphite crucibles were used.

Analysis of the residue indicated the stoichiometry $ThC_{2.00}$ with 0.71 weight per cent free carbon. X-ray photographs of both the starting material and residue (films A-1203 and A-1204, respectively) were identified as being characteristic of thorium dicarbide.

A series of standards for the activation analysis was prepared and the amount of thorium on these discs was:

Disc 1. 1.327×10^{-8} g

Disc 2. 2.221×10^{-8} g

Disc 3. 2.496×10^{-8} g

Disc 4. Blank.

These standards together with the targets were irradiated as before. The amount of thorium on discs 1 and 2, based on disc 3 containing 2.496×10^{-8} g was found to be:

Disc 1. $1.332 \pm 0.067 \times 10^{-8}$ g

Disc 2. $2.287 \pm 0.116 \times 10^{-8}$ g.

The data for this experiment are listed in Table X and a least squares treatment of the values of log P_E graphed against reciprocal temperature indicated the heat and entropy of vaporization to be:

$$\Delta H = 188.41 \text{ kcal/mole}$$

and

$$\Delta S = 40.93 \text{ e.u.}$$

4. Summary of the Determination of Effective Pressures

The graph of the values of log P_E against $10^4/T$ for the three vaporization experiments is shown in Figure 7. A least squares treatment of the data leads to an "effective heat of vaporization" of 185.40 ± 3.15 kcal/mole, and the log of the "effective pressure" P_E as a function of temperature is given by the equation:

$$\log P_{E(atm)} = -\frac{40,736(\pm 717)}{T} \times 10^4 + 8.742(\pm 0.304). \quad (29)$$

The determination of the values of the partial pressures P_{Th} and P_{ThC_2} in equilibrium with solid thorium dicarbide is discussed later, in Section C.

Table X. Data for experiment C

Exposure[a] No.	Temperature (^{o}K)	Exposure Time (min)	Th Collected x 10^8 (g)	P_E (atm)
C-3	2240	180	0.326	3.652×10^{-10}
C-4	2321	180	1.418	1.618×10^{-9}
C-5	2359	180	2.687	3.092×10^{-9}
C-6	2454	180	12.391	1.454×10^{-8}
C-7	2498	120	16.206	2.878×10^{-8}
C-8	2430	120	5.670	9.932×10^{-9}
C-9	2368	120	2.074	3.587×10^{-9}
C-12	2257	120	0.303	5.000×10^{-10}

Δ 1/T : 0.0764×10^{-4}

Orifice diameter : 0.93555 ± 0.013 mm at room temperature

0.93658 mm at exposure temperature

Orifice-to-Collimator distance : 10.62375 ± 0.0096 cm

Collimator diameter : 1.90754 ± 0.0049 cm

[a]Exposures 1, 2, 10 and 11 were used in testing for total condensation of the effusate on targets and the results are described elsewhere.

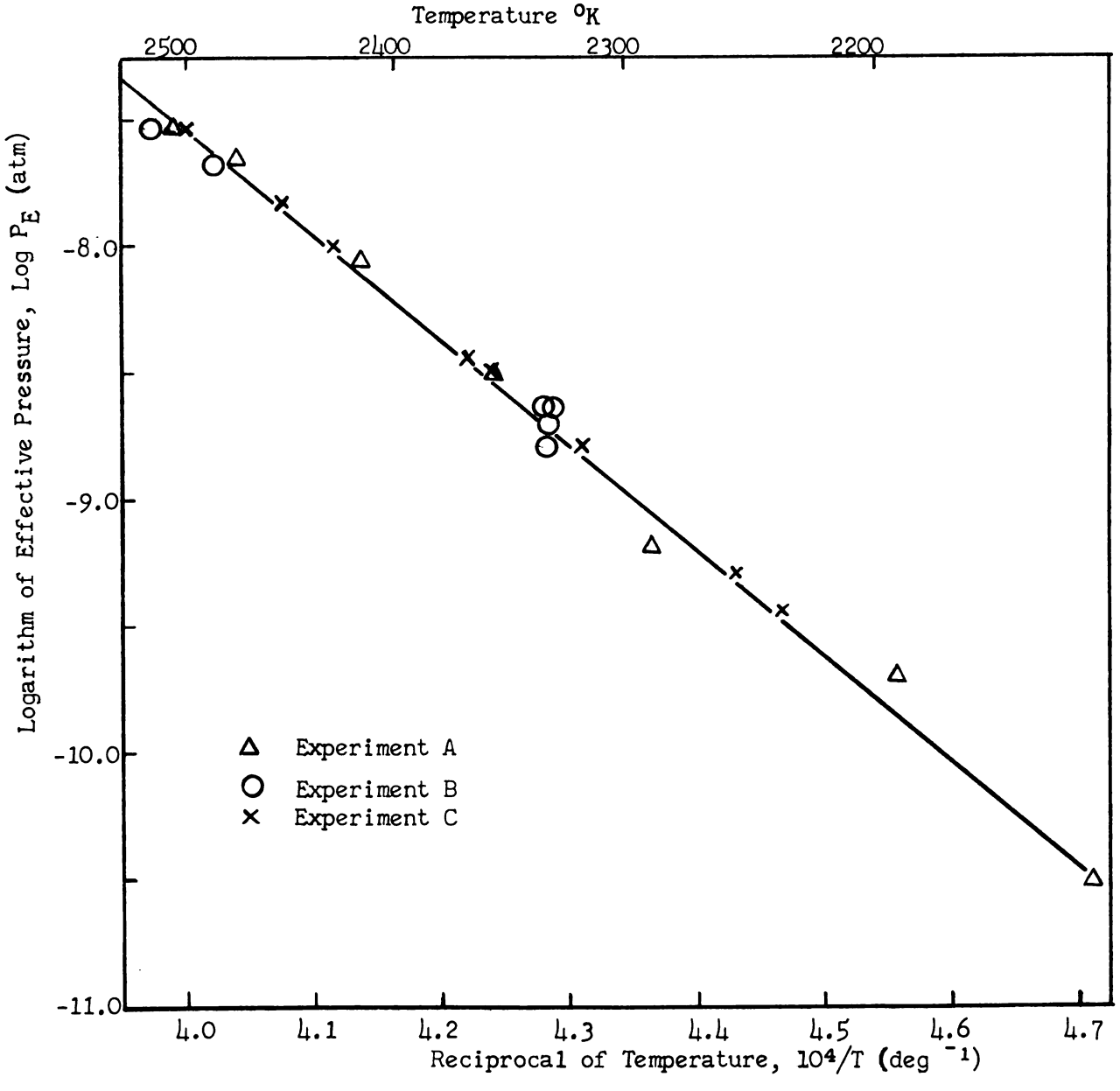


Figure 7. The effective vapor pressure of thorium dicarbide as a function of reciprocal temperature.

5. Conditions Related to the Measurement of Vapor Pressures

(a) Crucible Materials

The materials used for the construction of effusion crucibles must have certain characteristics before good measurements can be made with them. Among the necessary properties are low volatility, tightness with respect to leaking, and chemical inertness to the sample. Both graphite and tungsten can be heated inductively and both retain their mechanical strength over the temperature range of this study.

In all three vaporization experiments, chemical analyses and X-ray photographs of both starting materials and residues indicated no reaction between the crucible and the sample. The only change detected in the sample, whether heated in graphite or tungsten crucibles, was that the percentage of free carbon in the sample was lower in the residue, as would be expected. While a more complete study would be required to prove noninteraction, it was concluded that the effect of chemical interaction between the sample and the crucible, if any, was within the limits of experimental precision.

The heating of the thorium dicarbide samples in graphite crucibles quite often resulted in a heavy deposit on the walls of the condenser below the level of the effusion crucible orifices. When this deposit could be identified it was found to be graphite. This deposit severely limited the temperatures which could be attained because with the accumlation of a large deposit, there was a corresponding danger of breaking the condenser. In all experiments a light deposit, presumed to be graphite, formed on the targets. It is not known whether this deposit came from the surface of the lid or diffused through it (or the orifice) from the interior of the crucible. It is unlikely that it came from the surface of the lid since such a phenomenon would lead to

an increase in the orifice size and in those instances in which the orifice size did change it was observed to become smaller. If the graphite diffused through the lid, it would seem possible that this material flow could disturb the equilibrium conditions within the crucible. However, the agreement between the results of experiment A, without a radiation shield, and experiment B, with radiation shields, shows any effect to have been outside experimental prescision and hence undetected.

The heavy deposition which formed on the walls of the condenser when graphite crucibles were used led to the use of a tungsten crucible in experiment C. Unfortunately, the induction furnace was not operating properly and it was impossible to appreciably extend the temperature range studied.

(b) Test for total condensation

It is necessary, in the calculation of vapor pressures from amounts of effusate collected on targets, that any departure from total condensation be taken into account. At the outset of this research, quantitative condensation was expected because of the use of well-cleaned target surfaces and the relatively low target temperatures, especially since the backless cassettes would permit radiation of heat in the vertical direction.

The procedure used to test for incomplete condensation was as follows: A hole was drilled through the centers of both a fused silica target and a circular 5 mil platinum disc of the same diameter, and both were placed in the aluminum cassette with the platinum disc below the fused silica target. By this arrangement, some of the effusate could pass through these targets and strike the target next above in

the magazine. If reflection occurred, some of the reflected molecules would strike and stick to the lower fused silica target. The platinum disc protected the lower fused silica target from receiving effusate directly. Two such condensation tests were performed in the course of experiment C. The first was conducted at 2235°K and the lower targets had 0.096-inch diameter holes. The second was conducted at 2364°K and the holes in the lower targets were 0.037-inch in diameter. In both cases, activity was detected on the lower target. At 2235°K this activity was 1.93 per cent that of the upper target, and at 2364°K, 2.22 per cent.

The conclusion was that, although "bouncing" of effusate from the targets occurred to a detectable extent, and therefore constituted a small systematic error in the calculated vapor pressures, allowance for this in the final calculations did not seem to be justified.

(c) Change in dimensions with temperature

Orifice diameters measured at room temperature were corrected for the expansion due to temperature by use of the values (28) 5.33×10^{-6} deg^{-1} for the mean linear expansion of tungsten and 3.1×10^{-6} deg^{-1} for graphite between 0 and 2000°.

Increase in the length of the effusion crucibles was calculated to be 0.16 and 0.3 mm for graphite and tungsten, respectively. Shrinkage of the copper magazine when the Dewar was filled with liquid nitrogen was calculated to be about 0.5 mm with the effusion cell cold. This effect must have been less with the effusion crucible hot since radiation from the crucible may have raised the target temperatures several hundred degrees.

For the calculation of P_E, the room temperature orifice-to-collimator distances tabulated with the other experimental data were used. The resultant error is a small systematic one tending to raise the measured pressures of high temperatures more than those at low temperatures. The uncertainty in the orifice-to-collimator distance was estimated to be about ± 0.02 cm, an error of about ± 0.2 per cent.

At liquid nitrogen temperature the decrease in the diameter of the stainless steel collimator was calculated to be about 0.6 mm, and at 800° the increase was calculated to be about 0.2 mm. The actual temperature was probably nearer room temperature than either of these and the room temperature value was used in the calculation of pressures. The estimated uncertainty due to this systematic error was ± 0.1 mm, approximately 0.5 per cent.

C. Treatment of the Data

1. Calculation of P_{Th} and P_{ThC_2} from P_E

Jackson and co-workers (21) who studied the vaporization of thorium dicarbide mass spectrometrically observed that the two principal reactions are

$$ThC_{2(s)} = ThC_{2(g)}$$

and

$$ThC_{2(s)} = Th_{(g)} + 2C_{(graphite)}.$$

It is necessary that we have some method of converting the measured "effective pressures" P_E into the partial pressures of $ThC_{2(g)}$ and $Th_{(g)}$, respectively.

The use of the mass spectrometer as a detector for the molecular beam effusing from a Knudsen crucible is basically as follows. The

effusing molecules pass through collimating slits and some are ionized, usually by collision with an electron beam. The resulting ions are accelerated electrostatically as an ion beam from the ionization region into an evacuated space where the beam is resolved by magnetic deflection or drift time into components whose ions are characterized by different charge-to-mass rations. Assume, for simplicity, that all ions are singly charged molecules or atoms which are formed in the effusate without changes in formula. Then the ion current I_i^+ due to the species of molecular weight M_i is related (51) to the partial pressure p_i of the corresponding molecules of kind i in the effusion crucible at temperature T by the equation:

$$I_i^+T = GD_i\sigma_i p_i. \tag{30}$$

Here G_i is a constant determined by the physical dimensions of the system and the ionizing beam intensity. D_i is the efficiency of the ion detector for ions of molecular weight M_i and σ_i is the cross section or efficiency of ionization for molecules i when bombarded with electrons of the particular energies used.

From equation (30) it follows that at any temperature

$$\frac{P_{ThC_2}}{P_{Th}} \cdot \frac{\sigma_{ThC_2}}{\sigma_{Th}} = \frac{I^+_{ThC_2}}{I^+_{Th}}. \tag{31}$$

Rearrangement and substitution into equation (28) gives,

$$P_{Th} = \frac{\dfrac{\sigma_{ThC_2}}{\sigma_{Th}} \cdot P_E}{\dfrac{I^+_{ThC_2}}{I^+_{Th}} + \dfrac{\sigma_{ThC_2}}{\sigma_{Th}}\sqrt{M_{ThC_2}/M_{Th}}}. \tag{32}$$

Hence,

$$\log P_{Th} = \log P_E + \log \frac{\sigma_{ThC_2}}{\sigma_{Th}} - \log\left[\frac{I^+_{ThC_2}}{I^+_{Th}} + \frac{\sigma_{ThC_2}}{\sigma_{Th}}\sqrt{\frac{M_{ThC_2}}{M_{Th}}}\right] \quad (33)$$

and

$$\log P_{ThC_2} = \log P_{Th} + \log \frac{I^+_{ThC_2}}{I^+_{Th}} - \log \frac{\sigma_{ThC_2}}{\sigma_{Th}} . \quad (34)$$

Jackson and co-workers reported values of $\log (I^+_{ThC_2}/I^+_{Th})$ as a function of temperature and a least squares treatment of their data allowed the calculation of $I^+_{ThC_2}/I^+_{Th}$ at any temperature in the range studied. These authors reported the values of σ_{Th} and σ_{ThC_2} as 89.5 and 97.8, respectively. The values of $I^+_{ThC_2}/I^+_{Th}$ and $\sigma_{ThC_2}/\sigma_{Th}$ so obtained and the values of P_E determined in experiments A, B, and C were substituted into equations (33) and (34) and the values for P_{Th} and P_{ThC_2} were obtained for these experiments and are listed in Table XI.

When the values of $\log P_{Th}$ and $\log P_{ThC_2}$ are graphed against $10^4/T$, equation (6) relates the slope and the intercept to the heats and the entropies of the vaporization processes, respectively. The graph of $\log P_{Th}$ against $10^4/T$ for the reaction

$$ThC_{2(s)} = Th_{(g)} + 2C_{(graphite)}$$

is shown in Figure 8. The graph of $\log P_{ThC_2}$ against $10^4/T$ for the reaction

$$ThC_{2(s)} = ThC_{2(g)}$$

is shown in Figure 9.

The results of a least squares treatment are:

For the reaction

Table XI. P_{Th} and P_{ThC_2} from experiments A, B, and C.

Exposure No.	Temperature (°K)	$10^4/T°K$	P_{Th} (atm)	P_{ThC_2} (atm)
A-10	2123	4.710	1.803×10^{-11}	1.218×10^{-11}
A-9	2195	4.556	1.120×10^{-10}	8.793×10^{-11}
C-3	2240	4.464	1.914×10^{-10}	1.639×10^{-10}
C-12	2257	4.431	2.581×10^{-10}	2.288×10^{-10}
A-8	2291	4.364	3.168×10^{-10}	2.997×10^{-10}
C-4	2321	4.309	7.898×10^{-10}	7.882×10^{-10}
B-1	2333	4.286	9.964×10^{-10}	1.017×10^{-9}
B-2	2334	4.284	9.965×10^{-10}	1.019×10^{-9}
B-3	2334	4.285	9.443×10^{-10}	9.646×10^{-10}
B-4	2334	4.284	7.443×10^{-10}	7.610×10^{-10}
A-7	2357	4.242	1.447×10^{-9}	1.573×10^{-9}
C-5	2359	4.240	1.460×10^{-9}	1.559×10^{-9}
C-9	2368	4.222	1.679×10^{-9}	1.823×10^{-9}
A-4	2420	4.133	3.839×10^{-9}	4.546×10^{-9}
C-8	2430	4.116	4.406×10^{-9}	5.304×10^{-9}
C-6	2454	4.076	6.316×10^{-9}	7.906×10^{-9}
A-6	2474	4.041	9.314×10^{-9}	1.206×10^{-8}
B-5	2486	4.023	8.658×10^{-9}	1.147×10^{-8}
C-7	2498	4.004	1.203×10^{-8}	1.615×10^{-8}
A-5	2505	3.992	1.238×10^{-8}	1.681×10^{-8}
B-6	2516	3.974	1.188×10^{-8}	1.642×10^{-8}

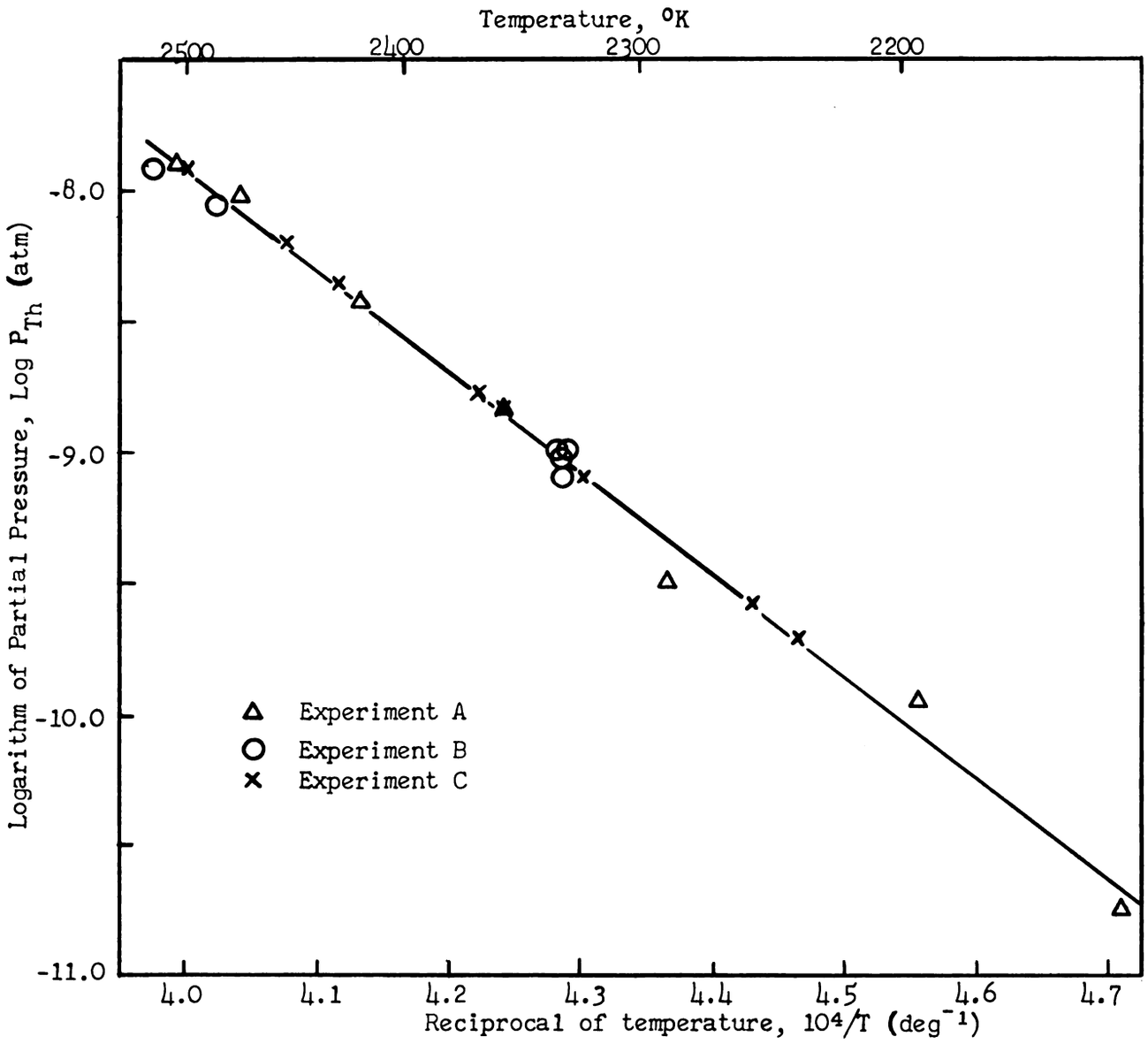


Figure 8. The temperature-dependence of the partial pressure of thorium vapor in equilibrium with solid thorium dicarbide.

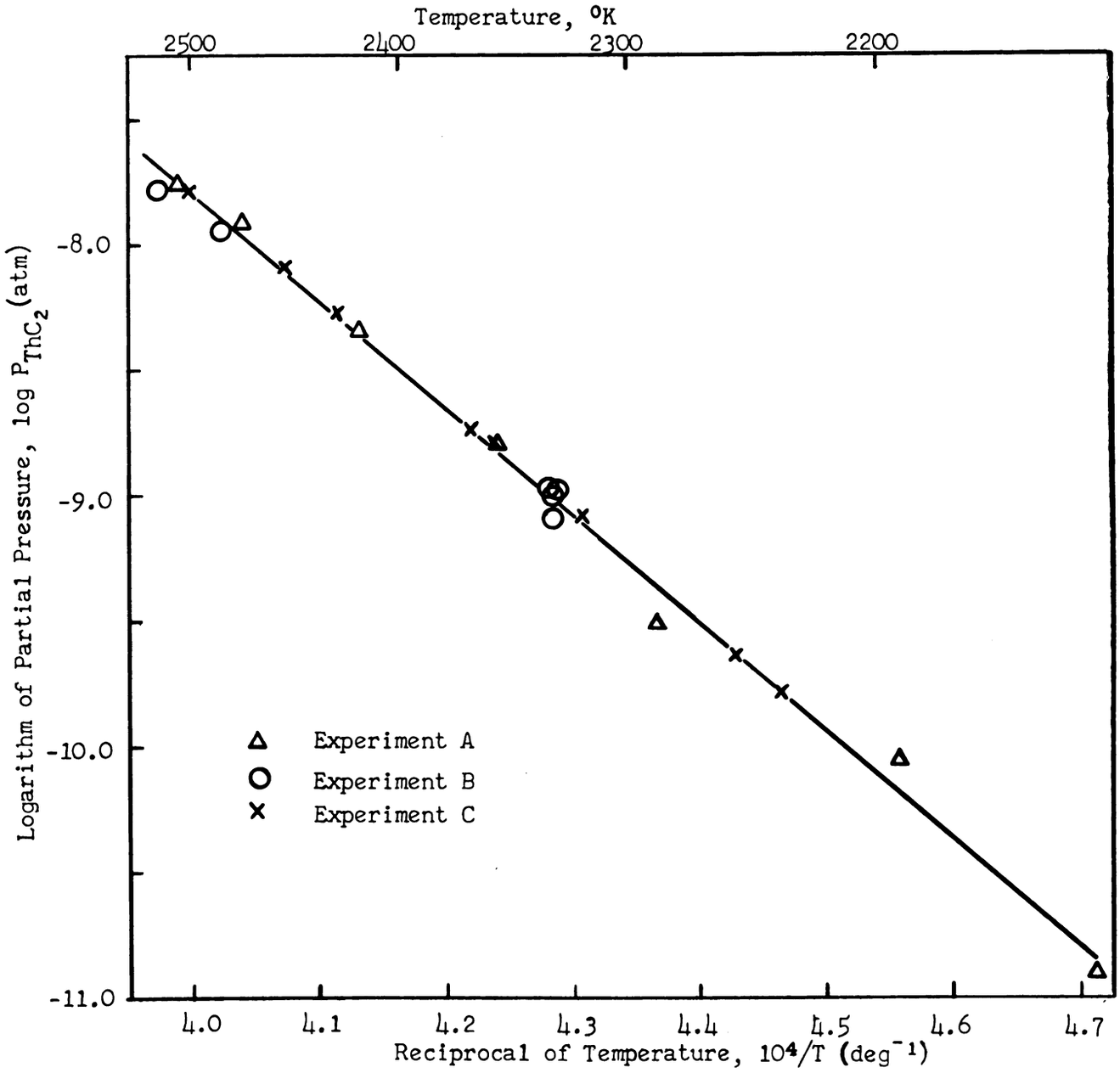


Figure 9. The temperature-dependence of the partial pressure of thorium dicarbide vapor in equilibrium with solid thorium dicarbide.

$$ThC_{2(s)} = Th_{(g)} + 2C_{(graphite)}$$

$$\Delta H^{o}_{298} = 176.92 \pm 3.30 \text{ kcal/mole},$$

$$\Delta S^{o}_{298} = 34.49 \pm 0.64 \text{ e.u.}$$

For the reaction

$$ThC_{2(s)} = ThC_{2(g)}$$

$$\Delta H^{o}_{298} = 196.24 \pm 3.30 \text{ kcal/mole},$$

$$\Delta S^{o}_{298} = 42.81 \pm 0.72 \text{ e.u.}$$

A least squares solution for the two vaporization reactions, assuming that $\Delta C_p = 0$, leads to the following expression for the vapor pressure of each species in equilibrium with solid thorium dicarbide:

$$\text{For } Th_{(g)}, \quad \log P_{(atm)} = -\frac{38,664(\pm 721.5)}{T} + 7.537(\pm 0.3062), \quad (35)$$

$$\text{For } ThC_2(g), \quad \log P_{(atm)} = -\frac{42,887(\pm 721.7)}{T} + 9.355(\pm 0.3063). \quad (36)$$

From the reported (22) value for the enthalpy of vaporization of thorium metal and the enthalpy listed above for the dissociation reaction, the standard enthalpy of formation of solid thorium dicarbide was determined to be $\Delta H^{o}_{298} = -40.32 \pm 3.33$ kcal/mole.

2. Calculation of Free Energy Functions

It was shown in the preceding section that the principal reactions involved in the vaporization of thorium dicarbide are

$$ThC_{2(s)} = ThC_{2(g)}$$

and

$$ThC_{2(s)} = Th_{(g)} + 2C_{(graphite)}.$$

We can check the second law values of the enthalpies of vaporization and dissociation obtained from the slope of a graph of log P against 1/T by means of a third law calculation based on the equation

$$\Delta H^{o}_{298} = - T \left[\Delta\left(\frac{F^{o}_{T} - H^{o}_{298}}{T}\right) \right] - RT \ln P. \qquad (37)$$

The necessary free energy functions for $Th_{(g)}$, $ThC_{2(g)}$, $ThC_{2(s)}$, and $C_{(graphite)}$ are tabulated in Table XII. The thermodynamic functions $H^{o}_{T} - H^{o}_{298}$ are listed in Table XIII, and the values of S^{o}_{T} for these species are listed in Table XIV. These functions were obtained as described below.

(a) $Th_{(g)}$

The thermodynamic functions were interpolated from the tabulation of Darnell, McCollum, and Milne (22).

(b) Graphite

Thermodynamic functions were taken from Stull and Sinke (24).

(c) $ThC_{2(s)}$

The following values of S^{o}_{298} and C^{o}_{p} used in calculating thermodynamic functions for $ThC_{2(s)}$ have been estimated by Krikorian (52):

$$S^{o}_{298} = 15.1 \pm 3 \text{ e.u.},$$

and

$$C^{o}_{p} = 12.60 \pm 1.16 + (2.00 \pm 0.18) \times 10^{-3} T - (2.62 \pm 0.20) \times 10^{5}/T^{2} \text{ cal/deg-mole.}$$

The calculations of the thermodynamic functions follow from the relationships:

$$H^{o}_{T} - H^{o}_{298} = \int_{298}^{T} C_{p}\, dT, \qquad (38)$$

$$S^{o}_{T} = S^{o}_{298} + \int_{298}^{T} C_{p}\, d\ln T, \qquad (39)$$

and

$$\left(\frac{F^{o}_{T} - H^{o}_{298}}{T}\right) = \left(\frac{H^{o}_{T} - H^{o}_{298}}{T}\right) - S^{o}_{T}. \qquad (40)$$

Table XII. Free energy functions, cal/deg-mole

Temperature (°K)	$-\left(\frac{F_T^o-H_o^o}{T}\right)_{trans}$ $ThC_2(g)$	$-\left(\frac{F_T^o-H_o^o}{T}\right)_{vib}$ $ThC_2(g)$	$-\left(\frac{F_T^o-H_o^o}{T}\right)_{rot}$ $ThC_2(s)$	$-\left(\frac{F_T^o-H_{298}^o}{T}\right)_{total}$ $ThC_2(g)$	$-\left(\frac{F_T^o-H_{298}^o}{T}\right)$ $ThC_2(s)$	$-\left(\frac{F_T^o-H_{298}^o}{T}\right)$ $Th(g)$	$-\left(\frac{F_T^o-H_{298}^o}{T}\right)$ $C(graphite)$
2200	47.48	8.83	19.00	76.48	29.94	51.94	5.93
2300	47.70	9.11	19.09	77.02	30.51	52.20	6.13
2400	47.92	9.38	19.14	77.53	31.06	52.47	6.32
2500	48.12	9.64	19.25	78.04	31.60	52.71	6.50
2600	48.31	9.89	19.33	78.52	32.12	52.98	6.69
2700	48.50	10.13	19.41	78.98	32.63	53.24	6.87
2800	48.68	10.36	19.48	79.43	33.13	53.48	7.04

Table XIII. Thermodynamic functions, $H_T^o - H_{298}^o$, cal/mole

Temperature (°K)	$ThC_2(g)$	$ThC_2(s)$	$Th(g)$	$C(graphite)$
2200	26284	27956	13332	9745
2300	27752	29661	14191	10360
2400	29217	31386	15048	10980
2500	30686	33132	15900	11600
2600	32160	34898	16640	12230
2700	33631	36684	17388	12860
2800	35105	38491	18200	13500

Table XIV. Values of S_T^o, cal/deg-mole.

Temperature (°K)	$ThC_2(g)$	$ThC_2(s)$	$Th(g)$	$C(graphite)$
2200	88.42	42.65	58.00	10.35
2300	89.09	43.40	58.37	10.63
2400	89.70	44.14	58.74	10.89
2500	90.31	44.85	59.07	11.14
2600	90.89	45.54	59.38	11.39
2700	91.44	46.22	59.68	11.63
2800	91.97	46.87	59.98	11.86

(d) $ThC_{2(g)}$

(1) Translational

The translational contributions were calculated in the usual manner using the following equations (53,54):

$$-\left(\frac{F_T^o - H_o^o}{T}\right) = R(1.5\ \ln M + 2.5\ \ln T) - 7.283\ \text{cal/deg}, \quad (41)$$

$$S_T^o = R(1.5\ \ln M + 2.5\ \ln T) - 2.315\ \text{cal/deg}, \quad (42)$$

$$(H_T^o - H_o^o) = 2.5\ RT, \quad (43)$$

and

$$C_p^o = 2.5\ R. \quad (44)$$

Here M is the molecular weight of the gas, T the temperature in degrees Kelvin, and R is the molar gas constant.

(2) Vibrational

For estimating vibrational contributions a set of assumptions was employed similar to those used by Chupka (20) for LaC_2. He assumed a linear assymetric molecule which preserved the $C_2^=$ group. This assumption was based partly on the observation that metallic dicarbides appeared to be the predominant species in the gas phase. Also the alkaline earth and lanthanon dicarbides, as well as thorium dicarbide, appear to have $C_2^=$ groups in the solid phase. This suggests that a gaseous metallic dicarbide is likely to have a strong ionic contribution to its bond. This is further borne out by the work of Honig (51) on the electron affinities of gaseous carbon species in which he observed that C_2 has by far the highest electron affinity.

The Th-C bond distance was taken to be that of Th-O in $ThO_{(g)}$ (22), 1.93Å, and the C-C bond distance was taken as 1.31Å (55). The

force constants were calculated from Badger's rule (56,57):

$$k(r_e - d_{ij})^3 = C_{ij} \tag{45}$$

where k is the stretching force constant in dynes/cm, r_e is the equilibrium internuclear distance, and d_{ij} and C_{ij} are constants. Taking C_{ij} as 1.86×10^5 and d_{ij} as 0.73 for the C-C bond, and C_{ij} as 1.14×10^5, d_{ij} as 1.33 for the Th-C bond, the C-C stretching force constant was determined to be 9.533×10^5 dynes/cm and the Th-C stretching force constant 5.27×10^5 dynes/cm. The bending force constant was taken as 0.20×10^5 dynes/cm.

The vibrational frequencies in sec^{-1} were calculated according to the following equations (58):

$$4\pi (\nu_1^2 + \nu_3^2) = k_1 \left(\frac{M_{Th} + M_C}{M_{Th} M_C}\right) + k_2 \left(\frac{2}{M_C}\right), \tag{46}$$

$$16\pi \nu_1^2 \nu_3^2 = k_1 k_2 \cdot \frac{M_{Th} + 2M_C}{M_{Th} M_C^2}, \tag{47}$$

and

$$4\pi^2 \nu_2^2 = \frac{k_\delta}{l_1^2 l_2^2} \left(\frac{l_1^2}{M_C} + \frac{l_2^2}{M_{Th}} + \frac{(l_1 + l_2)^2}{M_C}\right), \tag{48}$$

where k_1 is 5.278×10^5 dynes/cm, k_2 is 9.533×10^5 dynes/cm, k_δ is 0.20×10^5 dynes/cm, M_{Th} is 385.134×10^{-24} g, M_C is 19.936×10^{-24} g, and l_1 and l_2 are 1.93Å and 1.31Å, respectively. The fundamental frequencies ($\omega = \nu/c$) were then calculated to be

$$\omega_1 = 595.9 \text{ cm}^{-1}$$

$$\omega_2 = 400.0 \text{ cm}^{-1} \text{ (doubly degenerate)}$$

$$\omega_3 = 1767.8 \text{ cm}^{-1}$$

If we define a dimensionless quantity u such that (54)

$$u = \frac{h\nu}{kT} = \frac{hc\omega}{kT} = \frac{1.4388\omega}{T}, \tag{49}$$

the thermodynamic functions are given by the following relationships:

$$-\left(\frac{F_T^o - H_o^o}{T}\right) = -R \ln(1-e^{-u}), \tag{50}$$

$$S_T^o = R\left(\frac{u}{e^u-1} - \ln(1-e^{-u}\right), \tag{51}$$

$$(H_T^o - H_o^o) = RT \frac{u}{e^u-1}, \tag{52}$$

and

$$C_p^o = R \frac{u^2 e^u}{(e^u-1)^2} . \tag{53}$$

(3) Rotational

On the basis of the linear assymetric model used in the calculation of the vibrational contributions the rotational contributions were calculated as follows.

The displacement of atoms from the center of gravity is given by

$$\sum_i m_i x_i = 0 \tag{54}$$

where m_i is the atomic weight expressed in grams and x_i is the distance in Å of a given atom from the center of gravity. The values of m_i for thorium and carbon are 385.134×10^{-24} and 19.936×10^{-24} g, respectively. The values of x_i were taken as a, 1.93Å - a, and (1.93 + 1.31)Å - a, for the thorium and the two carbon atoms, respectively, where a represents the distance of the thorium atom from the center of gravity. The solution of equation (54) gives

$$a = 0.298 Å.$$

The moment of inertia is given by

$$I = \sum_i m_i d_i^2 \tag{55}$$

where d_i is the corrected value for x_i in equation (54). The values of d_i were calculated to be:

$$d_{Th} = 0.298\text{Å},$$
$$d_{C_1} = 1.632\text{Å},$$
$$d_{C_2} = 2.942\text{Å}.$$

The corresponding moments of inertia were calculated to be

$$I_{Th} = 34.32 \times 10^{-40} \text{ g cm}^2$$
$$I_{C_1} = 53.06 \times 10^{-40} \text{ g cm}^2$$
$$I_{C_2} = 172.49 \times 10^{-40} \text{ g cm}^2.$$

The moment of inertia of the molecule was calculated to be

$$I = 259.87 \times 10^{-40} \text{ g cm}^2. \tag{56}$$

The rotational partition function is given by

$$Q = 1/\sigma y \tag{57}$$

where σ, the symmetry number, is unity for an assymetric linear molecule, and the dimensionless quantity y is given by

$$y = \frac{h^2}{8\pi^2 IkT}. \tag{58}$$

When h was taken as 6.6252×10^{-27} erg sec and k as 1.38045×10^{-16} erg/deg, y was calculated to be 0.15496/T.

When T is large and σ is unity, the rotational contributions to the thermodynamic functions are given by the equations (54):

$$-\left(\frac{F_T^o - H_o^o}{T}\right) = -R \ln y, \tag{59}$$

$$S_T^o = R(1 - \ln y), \tag{60}$$

$$(H_T^o - H_o^o) = RT, \tag{61}$$

and

$$c^0 = R. \tag{62}$$

(4) Electronic

The electronic partition function is given by

$$q_e = w_e \, e^{-\epsilon_e/kT} . \tag{63}$$

Generally, there is a large separation in electronic energy levels and we need only be concerned with the ground electronic state (53) hence,

$$q_e = w_{e_1} \, e^{-\epsilon_{e_1}/kT} \tag{64}$$

where w_{e_1} is the degeneracy of the electronic ground state and ϵ_{e_1} is the energy of that state. If we make the assumption that the ground state for thorium dicarbide gas is $^1\Sigma$ then equation (64) reduces to

$$q_e = 1. \tag{65}$$

The value of the free energy function is then given by the relation

$$-\left(\frac{F_T^o - H_o^o}{T}\right) = R \ln q_e = 0. \tag{66}$$

The electronic contribution to the other thermodynamic functions are also found to be zero, hence there is no electronic contribution to the values tabulated in Table XII.

The assumption made above is a valid approximation at low temperatures; however, at high temperatures a contribution can be expected from the excited states. It may even be that at sufficiently high temperatures the ground state is $^3\pi$ not $^1\Sigma$. Because no data on the electronic spectra of thorium dicarbide or related compounds were available, it was believed that the assumption made above was as good as any that could be drawn and that at temperatures up to 2500°K the contributions from excited states were negligible.

3. Calculation of the Enthalpies of Vaporization for Experiments A, B, and C.

The values of the free energy functions listed in Table XII were used to calculate the changes in the free energy functions accompanying the reactions

$$ThC_{2(s)} = ThC_{2(g)}$$

and

$$ThC_{2(s)} = Th_{(g)} + 2C_{(graphite)}.$$

A least squares treatment of these values as a function of temperature was performed and changes in the free energy functions for the two reactions were determined for all experimental temperatures. These values and the values of P_{Th} and P_{ThC_2} listed in Table XI were substituted into equation (37) and the enthalpy changes accompanying the two vaporization reactions were determined. These third law enthalpy values are presented in Table XV.

Finally, the mean values of the heats of dissociation and vaporization determined by second and third law treatments of the data for experiments A, B, and C are:

For the reaction

$$ThC_{2(s)} = Th_{(g)} + 2C_{(graphite)}$$

Second law, $\Delta H^{o}_{298} = 176.92 \pm 3.30$ kcal/mole,

Third law, $\Delta H^{o}_{298} = 175.82 \pm 0.68$ kcal/mole;

For the reaction

$$ThC_{2(s)} = ThC_{2(g)}$$

Second law, $\Delta H^{o}_{298} = 196.24 \pm 3.30$ kcal/mole,

Third law, $\Delta H^{o}_{298} = 204.96 \pm 1.25$ kcal/mole.

Table XV. Third law values of the enthalpies of vaporization of ThC_2

Temperature (°K)	$ThC_{2(s)} = Th_{(g)} + 2C_{(graphite)}$ ΔH^o_{298} kcal/mole	$ThC_{2(s)} = ThC_{2(g)}$ ΔH^o_{298} kcal/mole
2123	176.06	204.97
2195	174.22	203.20
2240	175.55	204.55
2257	175.50	204.57
2291	177.38	206.43
2321	175.51	205.74
2333	175.38	204.46
2334	175.43	204.51
2334	175.66	204.74
2334	176.63	204.71
2357	175.42	204.60
2359	175.60	204.70
2368	175.69	204.80
2420	175.62	204.77
2430	175.72	204.87
2454	175.74	204.71
2474	175.39	204.59
2486	176.52	205.72
2498	175.81	205.02
2505	176.19	204.81
2516	177.17	206.39
Mean Value	175.82 ± 0.68	204.96 ± 1.25

The standard enthalpy of formation of solid thorium dicarbide was calculated to be - 40.32 ± 3.33 kcal/mole and - 39.22 ± 0.84 kcal/mole from the second and third law results, respectively.

D. Analysis of Errors in the Measured "Effective Pressures"

One should be able to show from the errors in the various experimentally determined quantities whether or not the scatter in the data plotted in Figure 7 can be ascribed solely to random errors in the measurements, or whether or not there were other factors involved. This evaluation may best be done by considering the errors involved in one representative datum, and that chosen for treatment was exposure No. 5 from Series C at 2359°K, for which $10^4/T = 4.240$.

The observed scatter arises from two sources. One is the random errors in the quantities expressed in second term in the equation for P_E;

$$P_E = (\text{constants}) \quad [(\frac{w\sqrt{T}}{\rho^2 t})(\frac{r^2 + d^2}{r^2})]$$

in which w represents the amount of thorium on the target, ρ the orifice diameter, r the collimator radius, d the orifice-to-collimator distance, and T and t represent the temperature and the time of the exposure, respectively. The second source of scatter is the displacement of the experimental points above and below the log P_E vs. $10^4/T$ curve due to errors $\Delta 10^4/T$ in the reciprocal temperature.

Consider the first effect. The various values and measured or estimated standard deviations for the experimental quantities for exposure C-5 are the following: $w = 2.687 \pm 0.136$; $\sqrt{T} = 48.535 \pm 0.021$; $\rho^2 = 0.877 \pm 0.024$; $t = 180 \pm 0.02$; $(r^2 + d^2/r^2) = 125.070 \pm 0.123$.

From the theory of the propagation of errors it was calcualted that P_E = (constants) x (103.32 ± 2.536). The contribution of random errors is thus 2.455 per cent and the expected standard deviation in log P_E is log (1.02445) = 0.0105.

The contribution of the second effect is as follows. For an error ΔT in the measured temperature the corresponding displacement amounts to $\Delta 10^4/T$ x slope $\cong$ slope x $(\Delta T/T^2)\ 10^4$. The estimated standard deviation in measured termperatures is ± 2 degrees, as was discussed previously. From the slope of equation (29) we find, at the exposure temperature, 2359°K, for target C-5, an expected uncertainty in log P_E of ± 0.017. The corresponding multiplicative uncertainty in P_E is 1.040; the expected standard deviation in P_E resulting from the uncertainty in $10^4/T$ is thus ± 4.0 per cent.

Combining the two parts of the calculated standard deviation, we have for exposure C-5,

$$\text{Std. dev. in } \log P_E = \pm\sqrt{(0.017)^2 + (0.0105)^2} = \pm\ 0.01997.$$

The corresponding estimated standard deviation in the measurement of the absolute value of the "effective pressure" of thorium dicarbide was ± 4.7 per cent.

In the neighborhood of $10^4/T$ = 4.24, about three-fourths of the points may be expected to lie within ± 0.02 of the value of log P_E obtained from equation (29). Examination of Figure 7 shows this criterion is satisfied for the points from experiment C, but that some of the data from experiments A and B have larger residuals than expected. In the discussion of experiment B it was pointed out that the orifice size decreased during the course of that experiment. This phenomenon would

account for the apparent low values obtained for exposures B-4, B-5, and B-6. The scatter at the lowest temperatures, specifically points A-7 and A-8, is not understood.

It is concluded that there are no random experimental errors unaccounted for in the measurement of the total rate of effusion except at the extremes of the temperature range.

E. Other Investigations

1. The Results of Lonsdale and Graves

Lonsdale and Graves (19) who studied the vaporization of thorium dicarbide over the temperature range 2300 to 2900°K obtained a second law enthalpy of vaporization of 172.0 ± 4.6 kcal/mole. From this, they calculated the heat of formation of the solid dicarbide to be ΔH^{o}_{298} = - 46 ± 6 kcal/mole.

However, they based their calculations on the assumption that the only reaction occurring was

$$ThC_{2(s)} = Th_{(g)} + 2C_{(graphite)}.$$

From the study of Jackson and co-workers (21) it is obvious that the reaction

$$ThC_{2(s)} = ThC_{2(g)}$$

must also be taken into account. The data of Lonsdale and Graves were converted to values of P_{Th} and P_{ThC_2} by assuming that their reported values for the vapor pressure of $Th_{(g)}$ in equilibrium with $ThC_{2(s)}$ were actually "effective pressures" p_0 calculated from equation (21) based on an effusing species of molecular weight 232.038. In order to compare the "effective pressures" determined by these authors with those measured in this investigation the values determined by Lonsdale and Graves were

multiplied by the factor $(M_{Th}/M_{ThC_2})^{1/2}$ to convert the data to "effective pressures" P_E based on the average molecular weight of the effusing species being 256.0603. From these values of P_E, the values of P_{Th} and P_{ThC_2} were calculated in the manner described above in Section C. The values of P_E, P_{Th}, and P_{ThC_2} calculated from the data of Lonsdale and Graves are presented in Table XVI. Third law values of the enthalpies of dissociation and vaporization of $ThC_{2(s)}$ were calculated from these partial pressures and are listed in Table XVII. For the sake of comparison, the values of P_E calculated from the data of Lonsdale and Graves, together with the values determined in experiments A, B, and C are graphed against $10^4/T$ in Figure 10. In this figure, the straight line was obtained from a least squares treatment of the data from experiments A, B, and C.

The enthalpy values listed in Table XVII show a temperature-dependence and Figure 10 shows that the values of P_E calculated from the data of Lonsdale and Graves do not increase linearly with temperature. There are several possible explanations for this behavior.

(a) One explanation could be that the values calculated for the changes in the free energy functions were in error. However, the failure of the third law heats calculated from the data obtained in experiments A, B, and C to exhibit this dependence indicates that the changes in the free energy functions vary linearly with temperature and that the temperature dependence was related to the measured values of the vapor pressure.

(b) A heat capacity effect could cause the value of the slope of the curve in Figure 10 to decrease at higher temperatures. When vapor

Table XVI. Vapor pressures calculated from the data of Lonsdale and Graves.

Temperature (^{o}K)	$10^4/T^{o}K$	P_E (atm)	P_{Th} (atm)	P_{ThC_2} (atm)
2278	4.390	7.1×10^{-10}	3.6×10^{-10}	3.3×10^{-10}
2355	4.246	3.0×10^{-9}	1.4×10^{-9}	1.5×10^{-9}
2426	4.122	7.4×10^{-9}	3.3×10^{-9}	4.0×10^{-9}
2471	4.047	1.7×10^{-8}	7.3×10^{-9}	9.4×10^{-9}
2531	3.951	3.6×10^{-8}	1.5×10^{-8}	2.1×10^{-8}
2583	3.871	4.7×10^{-8}	1.8×10^{-8}	2.8×10^{-8}
2617	3.821	7.5×10^{-8}	3.6×10^{-8}	5.8×10^{-8}
2673	3.741	1.5×10^{-7}	5.5×10^{-8}	9.5×10^{-8}
2673	3.741	3.0×10^{-7}	1.1×10^{-7}	1.9×10^{-7}
2723	3.672	6.8×10^{-7}	2.4×10^{-7}	4.4×10^{-7}
2745	3.643	4.3×10^{-7}	1.4×10^{-7}	2.8×10^{-7}
2750	3.636	6.3×10^{-7}	2.1×10^{-7}	4.1×10^{-7}
2779	3.598	8.6×10^{-7}	2.8×10^{-7}	5.6×10^{-7}
2815	3.552	1.3×10^{-6}	4.2×10^{-7}	8.8×10^{-7}
2858	3.499	2.0×10^{-6}	6.2×10^{-7}	1.4×10^{-6}
2897	3.452	2.4×10^{-6}	7.1×10^{-7}	1.6×10^{-6}

Table XVII. Third law values of the enthalpies of vaporization of $ThC_{2(s)}$ calculated from the data of Lonsdale and Graves

Temperature (°K)	$ThC_{2(s)} = Th_{(g)} + 2C_{(graphite)}$ ΔH^{o}_{298} kcal/ mole	$ThC_{2(s)} = ThC_{2(g)}$ ΔH^{o}_{298}, kcal/mole
2278	175.71	204.75
2355	175.36	204.46
2426	176.83	205.98
2471	176.31	205.50
2531	177.21	206.45
2583	179.91	209.17
2617	178.78	208.09
2673	180.50	209.84
2673	176.98	206.32
2723	177.20	205.39
2745	180.19	209.60
2750	178.45	207.86
2779	178.81	208.24
2815	178.91	208.37
2858	179.61	209.10
2897	181.31	210.83
Mean Values	178.25 ± 1.58	207.50 ± 1.98

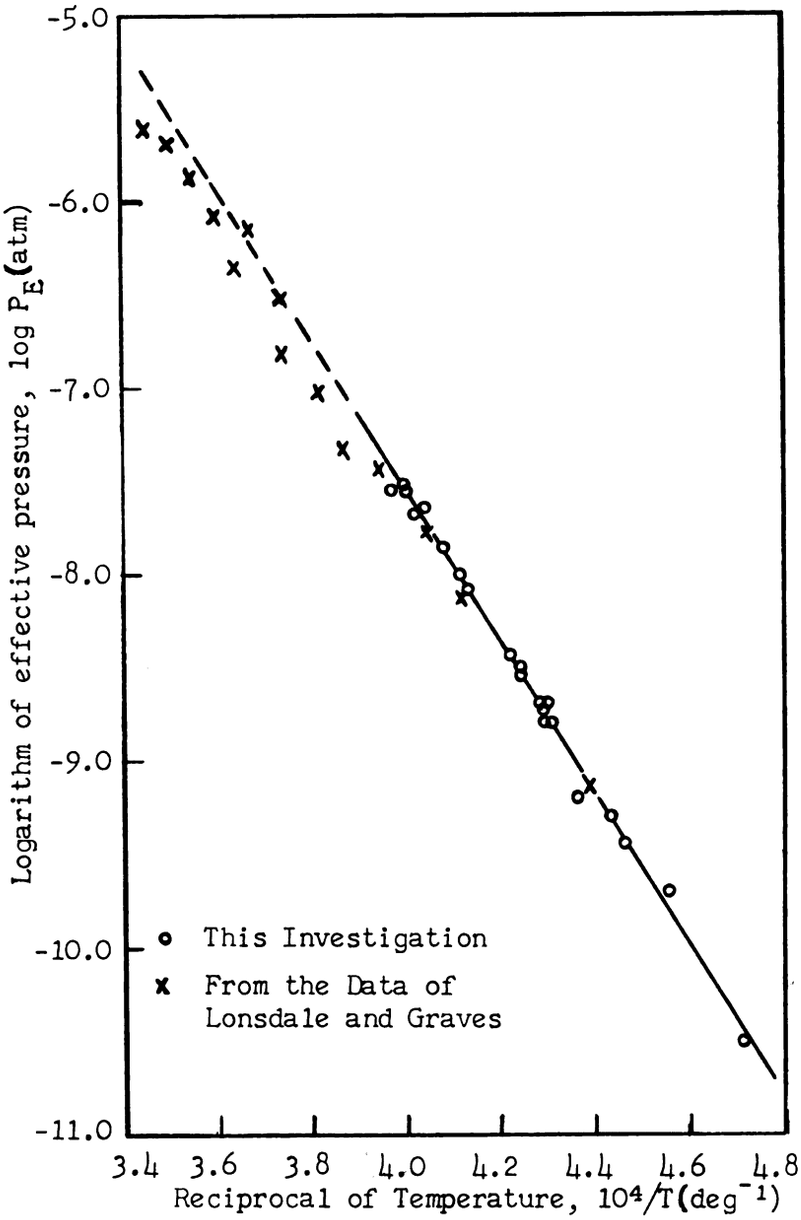


Figure 10. The temperature-dependence of the effective vapor pressure of thorium dicarbide.

pressures are calculated from equation (6) the tacit assumption is made that the difference in the heat capacities of the solid and gaseous phases is constant in the temperature range studied. The fact that the data for experiments A, B, and C do not show this effect and the fact that Lonsdale and Graves did not attain the melting temperature of $ThC_{2(s)}$ (2928°K) would seem to indicate that the assumption that ΔC_p is zero in the temperature range studied is valid. Nevertheless, a phase change in which thorium dicarbide attains a new structure may occur and the possibility of a heat capacity effect cannot be ruled out.

(c) At the highest temperatures attained the vapor pressure of graphite is appreciable and the effusion process could be changing from molecular to viscous flow. Such a phenomenon, however, should cause a positive change in the slope of the curve in Figure 10.

(d) Considering the rather large scatter in the points at high temperatures it is probable that the cause of the decrease of the slope lies in experimental errors. It was demonstrated in experiment C of this investigation that complete condensation of effusate on the targets is not attained and that the amount of "bouncing" increases as the temperature is increased. Because Lonsdale and Graves used graphite rather than fused silica targets it is probable that the temperatures of their targets were higher than those for the targets used in this investigation. These authors did not test for total condensation of the effusate on the targets and the effect of "bouncing" is not known.

2. <u>The Results of Jackson and Co-workers</u>

Despite the lack of precision in the values of the vapor pressures determined at the higher temperatures, the data of Lonsdale and Graves are in much closer agreement with the data from experiments A, B, and C

than are those of Jackson and co-workers. The second and third law values of the enthalpies determined by these authors are (21):

For the reaction

$$ThC_{2(s)} = Th_{(g)} + 2C_{(graphite)}$$

Second law, $\Delta H^{o}_{298} = 160.3 \pm 3.2$ kcal/mole,

Third law, $\Delta H^{o}_{298} = 184.7 \pm 1.5$ kcal/mole;

For the reaction

$$ThC_{2(s)} = ThC_{2(g)}$$

Second law, $\Delta H^{o}_{298} = 188.1 \pm 3.4$ kcal/mole,

Third law, $\Delta H^{o}_{298} = 212.8 \pm 1.5$ kcal/mole.

The standard enthalpy of formation of $ThC_{2(s)}$ was calculated to be - 23.7 ± 3.5 kcal/mole, and - 48.1 ± 2.0 kcal/mole from the second and third law results, respectively.

This discrepancy between the second and third law enthalpies is disturbing. Upon examination of these author's data it was found that they had made an arithmetic error in the calculations of the free energy functions for the $ThC_{2(g)}$, but this error was not large enough to account for the large difference in enthalpies. Also, this error would not affect the calculation of the enthalpy change in the dissociation reaction in which $Th_{(g)}$ is formed. When the values of P_{Th} and P_{ThC_2} were compared with those obtained in the current investigation and those calculated from the data of Lonsdale and Graves, they were found to be lower by a factor of about 5. Because the sensitivity calibration of the mass spectrometer for absolute pressure measurements involves the use of secondary standards, the pressures determined by this technique are more likely to be in error than are those determined by the

effusion method. Another possible cause for the discrepancy lies in the measurement of temperatures. The standard technique in mass spectrometric investigations is to graph IT against 1/T. Here I is the relative intensity of the gaseous species and the quantity IT is related to the vapor pressures. Possible uncertainties in the temperature scale are accentuated in this method. It whould be noted that while errors in the measurement of temperature will greatly affect the calculation of the partial pressures of the vapor species, the effect on the measured ion intensity ratio, $I^+_{ThC_2}/I^+_{Th}$, is much less and the values listed by Jackson and co-workers should probably be considered as reliable.

In summary, considering the lack of precision in the data of Lonsdale and Graves and the low vapor pressures determined by Jackson and co-workers, it is believed that the partial pressures of $Th_{(g)}$ and $ThC_{2(g)}$, in equilibrium with $ThC_{2(s)}$, are best characterized by the present investigation.

F. Suggestions for Further Research

1. The Thorium-Carbon System

The phase diagram shown in Figure 1 is only a tentative one and a more complete study of the system should be made. One method of accomplishing this end would be to prepare samples of ThC_x with varying mole ratios of carbon-to-thorium in an arc melter and studying the composition as a function of temperature by X-ray diffraction techniques, including the use of a camera designed to operate at high temperatures.

A calorimetric study should be made and the heat capacity of solid thorium dicarbide determined as a function of temperature.

The mass spectrometric investigation of the vaporization process should be repeated and the temperature range covered should be extended. This study would involve problems basic to mass specrometric investigations, i.e., the calibration of the mass spectrometer for absolute pressure measurements, and the theoretical calculation of the ionization cross sections of individual gaseous species.

The Knudsen effusion study should be extended to higher temperatures, and the effusion from non-carbon crucibles investigated; in the present study, the crucibles used led to an excess of carbon being present at all times.

Finally, the system thorium-oxygen-carbon has not been studied and the effect of oxygen on the vaporization process and on the stabilities of the solid phases should be investigated.

2. Determination of Thermodynamic Functions for Vapor Species

At the present time the literature contains little information pertaining to the spectroscopic data for the vapor species of refractory inorganic compounds. The thermodynamic functions, such as the free energy functions and the entropies, are usually viewed as being separable in the following manners:

$$S_T^o = S_t^o + S_r^o + S_v^o + S_e^o,$$

where t, r, v, and e refer to the translational, rotational, vibrational, and electronic contributions, respectively. The translational contribution can be unambiguously calculated for any gaesous molecule provided that its molecular weight is known. The rotational and vibrational contributions may be estimated with fair accuracy if the molecular structure is known. This may be determined in many cases by electron

diffraction techniques. Micro-wave studies can yield very precise structural information if the molecule has a permanent dipole. In some instances it may be possible to determine the rotational and vibrational spectra by means of matrix isolation techniques. However, the determination of the structure of triatomic and more complex gaseous molecules remains a difficult problem and much remains to be done in this area.

Perhaps the most difficult to assess are the electronic contributions. In the first place, there are few, if any, spectroscopic data for most triatomic molecules and the investigator must make use of an assumed ground state. In the second place, the idea that excited electronic states make negligible contributions is based on the tacit premise that only moderate temperatures will be of interest. At temperatures of 2000°K and greater, excited electronic states may contribute significantly to the thermodynamic functions. Compilation of electronic energy levels would be of great value in calculating thermodynamic functions for gaseous molecules, but the determination of these data remains a formidable problem.

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APPENDICES

APPENDIX A

SUPPLEMENTARY EXPERIMENTAL DATA

Individual Preparations of Thorium Dicarbide

1. First Attempt

Powdered graphite and thorium dioxide in the molar ratio 5.6:1 graphite to thorium dioxide were mixed and loaded into a graphite crucible which was placed in the vacuum system and heated for one hour at about 2260°K. After heating was terminated, the system was opened to helium, and then to the atmosphere and a small portion of the brittle, sintered product was ground to a powder, loaded into a 0.3 mm diameter capillary, and an X-ray powder diffraction photograph was taken (film A-949). Because only two lines showed on the film, the sample was reheated for one hour at 1870°K, then for one hour at 2500°K. During this heating a graphite radiation shield was placed around the crucible to decrease the deposition of graphite on the walls of the condenser. The sample did not change in appearance during this second heating. Another X-ray powder diffraction photograph was taken (film A-960) and, although the film was of poor quality, the sample was identified as thorium dicarbide.

2. Series P-1 to P-9

This series consisted of nine preparations in which varying amounts of graphite were heated with thorium dioxide. After the product had been formed, the temperature was raised and the samples were annealed for varying lengths of time. Sample sizes ranged from 0.1 to 2.0 grams and the samples were used either to test analytical methods or for effusion experiments. In all analyses performed on this series of samples,

the thorium was precipitated with oxalic acid. The data for this series are summarized in Table AI and each preparation is discussed briefly below.

P-1. Nitric acid was used to hydrolyze the sample and the amount of free graphite found was higher than expected. The empirical formula determined by the chemical analysis was $ThC_{1.47}$, but the X-ray diffraction pattern indicated that the sample was ThC_2. It was decided to use hydrochloric acid in the hydrolysis of sample P-2 to see if more consistent analytical results could be obtained.

P-2. In this, and in all subsequent preparations in this series, a graphite radiation shield was employed to decrease the deposition of graphite on the walls of the condenser. Hydrochloric acid was used to hydrolyze the sample and the empirical formula was found to be $ThC_{1.98}$. The X-ray powder diffraction pattern indicated the sample to be ThC_2.

P-3. Nitric acid was used in the hydrolysis and the analysis indicated the unrealistic stoichiometry, $ThC_{0.65}$, however, the X-ray powder diffraction pattern was that of ThC_2. The amount of free carbon found was far in excess of that expected and it was decided that nitric acid oxidized some of the combined carbon to free graphite. Hydrochloric acid was used in all subsequent hydrolyses.

P-4. No X-ray powder diffraction pattern was taken, The analysis indicated the stoichiometry to be $ThC_{2.07}$.

P-5. Since this sample was used in a preliminary effusion experiment E-1, no analysis was performed and no X-ray powder diffraction pattern was taken.

P-6. The chemical analysis indicated the empirical formula, $Thc_{2.06}$ and the X-ray powder diffraction pattern was that of ThC_2. To test the

Table AI. Data for series P-1 to P-9

Sample No.	Mole Ratio c/ThO_2	Annealing Conditions T(^{o}K)	Time(min)	Formula (analysis)	X-ray Results Film No.	Phases
P-1	5:1	2190	75	$ThC_{1.47}$	A-922	ThC_2
P-2	5:1	2400	70	$ThC_{1.58}$	A-993	ThC_2
P-3	5:1	2358	240	$ThC_{0.65}$	A-994	ThC_2
P-4	5:1	2366	120	$ThC_{2.07}$	None	---
P-5	5:1	2353	60	---	None	---
P-6	4.4:1	2367	210	$ThC_{2.06}$	A-1005	ThC_2
P-7	4.5:1	---	240	---	None	---
P-8	4.5:1	2216	90	---	None	---
P-9	4.5:1	2218	45	---	A-1066	ThC_2

determination of thorium by precipitation with oxalic acid, a portion of the sample was ignited directly to thorium dioxide to determine the thorium content. The weight percentages of thorium found by precipitation and by direct ignition were 85.81 and 85.02, respectively.

P-7. In the last three preparations in this series the reactants were heated in the form of pellets which had been pressed for ten minutes at 10,000 p.s.i. During the preparation the Veeco ionization gauge on the vacuum system failed to function, and the sample was discarded.

P-8. This sample was used for effusion experiment E-2 and analysis and X-ray diffraction pattern of the sample are described in the discussion of this experiment.

P-9. The X-ray diffraction pattern was that of ThC_2, however, due to a sample spill during filtration, no chemical analysis was obtained.

3. Series P-10 to P-15

This series consisted of six preparations in which varying amounts of graphite were heated with thorium metal to produce throium dicarbide. Because no carbon monoxide was produced as a reaction product it was possible to attain the desired temperatures quickly. Sample sizes ranged from 1.2 to 2.8 grams. The analysis of samples P-10 and P-11 involved the use of oxalic acid to precipitate the thorium; in all other analyses the thorium was precipitated with aqueous ammonia. The data for this series are summarized in Table AII. And each preparation is discussed briefly below.

Table AII. Data for series P-10 to P-15

Sample No.	Mole Ratio c/Th	Annealing Conditions T(°K)	Time(min)	Formula (analysis)	X-ray Results Film No.	Phases
P-10	2.46:1	2313	180	$ThC_{2.01}$	A-1046	ThC_2
P-11	2.14:1	2400	60	$ThC_{2.00}$	A-1050	ThC_2
P-12	2.36:1	1970	120	$ThC_{1.91}$	A-1068	ThC_2
		2000	60	$ThC_{1.93}$		
P-13A	1.90:1	2000	90	$ThC_{1.82}$	A-1074	ThC_2
P-13B		1890	240	$ThC_{1.81}$		
P-14	1.96:1	1850	300	$ThC_{1.30}$	A-1077	ThC_2 and ThC
P-15	2.50:1	1950	80	$ThC_{2.07}$	A-1078	ThC_2

P-10. The X-ray powder diffraction pattern was that of ThC_2 and the chemical analysis were as follows: Expected, thorium 88.69%, graphite 2.13%, and combined carbon 9.18%; found, thorium 88.71%, graphite 2.07%, and combined carbon 9.22%.

P-11. This sample was prepared at a somewhat higher temperature than the others and there was a very heavy deposit of graphite on the walls of the condenser. The X-ray powder diffraction pattern (film A-1050) was that of ThC_2 and the analysis indicated the formula to be $ThC_{2.00}$. A portion of the sample was exposed to the air for one hour and an X-ray powder diffraction pattern (film A-1051) which indicated the presence of two phases, ThC_2 and ThO_2 was taken.

P-12. This was the only preparation in this series in which the reactants were heated in powder form, in the others the samples were heated as pellets which had been pressed for ten minutes at 10,000 p.s.i. After the sample had been heated for two hours at 1970°K a portion was taken for analysis, which indicated the stoichiometry $ThC_{1.91}$. The remainder of the sample was heated for another hour at 2000°K and the analysis indicated the empirical formula to be $ThC_{1.93}$. The X-ray powder diffraction pattern was that of ThC_2

P-13. In most previous preparations the amount of excess graphite in the product was greater than that desired. Therefore, it was decided to attempt a preparation in which an excess of thorium was used. Two pellets were pressed from the same reactant mixture and heated together for ninety minutes at 2000°K. One pellet was analyzed and the stoichiometry found to be $ThC_{1.82}$ with 3.61% excess graphite. The X-ray powder diffraction pattern was that of ThC_2. The second pellet was reheated for four hours at 1890°K and analyzed. Although the stoichiometry was

found to be nearly the same, $ThC_{1.81}$, the amount of excess graphite had been reduced to 1.29%.

P-14. In this preparation the reactants were heated at a lower temperature than usual and the chemical analyses indicated the empirical formula to be $ThC_{1.30}$. The X-ray powder diffraction pattern revealed that the sample consisted of both ThC_2 and a new phase of cubic symmetry which was identified as ThC.

P-15. Two pellets were pressed from the same reactant mixture and heated together. One pellet was used for effusion experiment E-3. The other was analyzed and the empirical formula was found to be $ThC_{2.07}$. The X-ray powder diffraction pattern, as usual, was that of ThC_2.

4. Series P-16 to P-24

This series consisted of nine preparations in which thorium and graphite were heated together to produce thorium dicarbide samples to be used in calorimetry experiments by E. F. Westrum at the University of Michigan, Ann Arbor, Michigan. In sample P-16 the reactants were heated in powder form, in all others the reactants were heated as pellets which had been pressed at 10,000 p.s.i. After each preparation the sample was stored in a dry box under a helium atmosphere. Samples P-18 and P-19 were inadvertently exposed to the atmosphere and discarded. The remaining samples were ground together with an agate mortar and pestle in an inert atmosphere and the entire product was heated in vacuum for five hours at 2400°K. A portion of this resultant product was taken for an X-ray powder diffraction pattern (film A-1132) which indicated the sample to be ThC_2. Since any excess graphite would interfere in calorimetry measurements, the sample was twice more ground

under an inert atmosphere and heated in vacuum for five hours at 2400°K. The final product consisted of sintered yellow chunks and chemical analysis indicated the empirical formula to be $ThC_{1.998}$ and another X-ray powder diffraction pattern (film A-1133) again showed the product to be ThC_2.

A 26.7 gram portion of the sample was loaded into a sealed container, in a drybox and taken to Ann Arbor, Michigan for heat capacity measurements.

5. Preparation P-25

This sample was used in effusion experiment E-4 and is described in the discussion of this experiment.

APPENDIX B

TABULATION OF PHYSICAL CONSTANTS

$R = 1.98726$ cal/deg-mole

$h = 6.6252 \times 10^{-27}$ erg sec

$k = 1.38045 \times 10^{-16}$ erg/deg

$c = 2.99793 \times 10^{10}$ cm/sec

$hc/k = 1.4388$ cm deg

$R \ln x = 4.5758 \log_{10} x$ cal/deg-mole

Mass of atom of unit atomic weight $= 1.65979 \times 10^{-24}$ g

Atomic weight of thorium = 232.038

Atomic weight of carbon = 12.01115

Atomic weight of oxygen = 15.9994

Mass of thorium atom $= 385.134 \times 10^{-24}$ g

Mass of carbon atom $= 19.936 \times 10^{-24}$ g

APPENDIX C

Table AIII. Temperature measurement for exposure no. 4, experiment B

T^oC (observed)	T^oC (Corrected for Pyrometer)	T^oK	$10^4/T^oK$	$-\Delta 10^4/T^oK$	T^oK (true)
2001.0	2014.00	2287.16	4.3722	4.2821	2335.30
1999.75	2012.75	2285.91	4.3746	4.2845	2333.99
1999.20	2012.20	2285.36	4.3756	4.2855	2333.45
2000.50	2013.50	2286.66	4.3731	4.2830	2334.81
1999.25	2012.25	2285.41	4.3755	4.2854	2333.50
2000.50	2013.50	2286.66	4.3731	4.2830	2334.81
1998.80	2011.80	2284.96	4.3764	4.2863	2333.01
1999.50	2012.50	2285.66	4.3751	4.2850	2333.72
2000.00	2013.00	2286.16	4.3741	4.2840	2334.27
					2334.10 ± 0.87