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THE VAPOUR PRESSURE OF
Th(g) ABOVE ThC₂ AS DETERMINED
BY EMISSION SPECTROSCOPY

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Norman L. Lofgren
Oscar H. Krikorian
September 20, 1963

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Norman L. Lofgren and Oscar H. Krikorian

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September 20, 1963

Abstract

Emission spectra offer a useful but relatively unexplored technique for detection of species in high temperature systems. In this work the emission intensity of atomic Th above carbon saturated ThC₂ was used as a measure of Th vapour pressure by applying the second and third laws of thermodynamics.

A King (graphite tube) furnace operated at 2100 to 2500°C was used for the emission source. The inner bore of a graphite heater tube was coated with prereacted ThC₂ to provide a region of equilibrated vapour. Spectra were detected by focusing the vapour emission onto the slit of a scanning grating spectrometer. Intensities were measured with a photo-multiplier.

Intensity measurements were made at several temperatures for Th emission to the ground state at wavelengths of 4493.33 and 5760.55Å, and for the C₂ (0 - 1) band head in the Swan system at 5635.5Å. The second law of thermodynamics was applied to the data by using the relation $p \propto IT$. Enthalpies of reaction obtained were:

By using 137.7 kcal/g. atom for the ΔH_{298}° of sublimation of Th, the data result in -26.9 ± 5 kcal/mole for the $\Delta H_{f,298}^\circ$ of ThC_2 . The value for the ΔH_{298}° of sublimation of C_2 is in agreement with previous work and lends confidence to the second law treatment.

In order to use the third law method a Th pressure calibration was necessary. Accordingly a W-foil tube lined on the inside with Th metal was supported within a graphite heater tube. The emission intensity was observed at 1950 °C and compared with the known vapour pressure of Th to obtain the calibration factor. Corrections were applied for solubility of W in the Th, and for a difference in emitting pathlength of gas in the two types of experiments. A value of < -24.9 kcal was obtained for $\Delta H_{f,298}^\circ$ of ThC_2 .

Absolute errors in the determinations are difficult to evaluate. An uncertainty in the stoichiometry of the ThC_2 phase and lack of sufficient heat capacity information complicate the situation. Precision of intensity measurements is good, however, with standard deviations ranging from 0.1 to 6%. The technique can potentially provide rapid and accurate determinations of thermodynamic data. It is well suited for actinide work in that it isolates radioactive materials from the detection system.

THE VAPOUR PRESSURE OF Th(g) ABOVE ThC₂ AS
DETERMINED BY EMISSION SPECTROSCOPY

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September 20, 1963

Introduction

Vapour pressures or enthalpies of sublimation of gaseous species have been determined by various investigators from emission and absorption of vapours produced in King (carbon-tube) furnaces.⁽¹⁻⁵⁾ Brewer, Gilles and Jenkins⁽¹⁾ originated the basic method and applied it in a study of the enthalpy of sublimation of C₂(g). They used photographic techniques to analyse the intensity of C₂ emission. In subsequent work, Brewer, Hicks, and Krikorian⁽³⁾ increased the sensitivity of the method by using photometric detection techniques, and obtained a more accurate value for the enthalpy of sublimation of C₂. They discussed problems associated with the method in some detail. Briefly, these problems are (1) self absorption of light from the emitting species, (2) development of temperature gradients in the heater tube with time, (3) a high level of blackbody radiation in the optical path, and (4) uncertainties in temperature measurement. The severity of the problems would be greatly reduced by using a third-law method for treating the data. In order to apply the third-law method, however, it is necessary to relate intensities to pressures. This can be done if absolute transition probabilities

of emission (or absolute absorption coefficients) are known for the species of interest. Very little information of this type is presently available. For certain types of reactions, however, it is possible to apply a third-law method indirectly. Thus, Vidale⁽⁵⁾, by comparing the temperatures required to give equivalent absorptions of metal vapours over pure metals and over their respective carbides, was able to determine the enthalpies of formation of the solid compounds SiC, TiC, and ZrC.

In this study the emission intensity of Th(g) above carbon-rich ThC₂ was measured as a function of temperature, and the results were treated by both second- and third-law methods. The emission intensity of C₂ was also measured and compared with previous work. A pressure calibration was made for the Th emission intensity by using Th(g) emission above Th metal as the reference standard.

The studies were limited to a maximum temperature of 2495°C by the ThC-C eutectic.^{††} Previous work indicated that this temperature region was

^{††} Prescott and Hincke noted a "melting point" for ThC₂ in the presence of graphite. Their observed temperature, corrected to ITS-1948, gives 2490°C for the ThC₂-C eutectic. Chiotti, and Wilhelm and Chiotti⁽⁶⁾ reported a value of 2500°C, Langer, Hancock, and Kester⁽⁷⁾ found 2495 ± 40°C.

too low for accurate emission measurements⁽³⁾, but by using improved experimental techniques it was found possible to perform the measurements. The lower temperature limit of detection for both Th and C₂ above carbon-rich ThC₂ was found to be about 2000°C, and for Th above Th(l) about 1800°C. The use of low working temperatures was found to be advantageous in several ways: The self-absorption problem was alleviated because of decreased gaseous emission intensities, and problems of temperature gradients and temperature measurement were greatly reduced.

Thermodynamic Data

The enthalpy of formation of ThC_2 has been the subject of several investigations⁽⁸⁻¹¹⁾. Measurements have been made by Knudsen cell effusion using both conventional and mass spectrometric analysis, by electrolytic cell potentials, and by chemical equilibration studies. Interpretation of the results is complicated by the occurrence of high-temperature phase transformations and variable compositions in ThC_2 , and by a lack of heat capacity data.

The structure of ThC_2 at room temperature has been established by Hunt and Rundle⁽¹²⁾. It has a c-centered monoclinic unit cell with $a = 6.53$, $b = 4.24$, and $c = 6.56 \text{ \AA}$; $\beta = 104^\circ$; $Z = 4$; and space group $C2/c$. Positions of Th atoms were determined by X-ray diffraction, and of C atoms by neutron diffraction. Langer, Hancock, and Kester⁽⁷⁾, using thermogravimetric analysis, found phase transformations in ThC_2 at 1430 and at 1480°C . The structures of the high temperature forms were not identified. Chemical analyses for Th and bound carbon on a number of their samples containing excess carbon showed compositions ranging from $\text{ThC}_{1.86}$ to $\text{ThC}_{1.94}$. One sample had an approximate composition of $\text{ThC}_{2.0}$. Information on the time-temperature histories of the samples or of oxygen contents was not given. Lonsdale and Graves⁽⁹⁾ heated a sample of ThC_2 above 2000°C for more than four hours in a carbon-saturated system and obtained a composition of $\text{ThC}_{1.98}\text{O}_{0.05}$. Kempter and Krikorian⁽¹³⁾ prepared carbon-rich ThC_2 by arc-melting and obtained a composition of $\text{ThC}_{1.89}\text{O}_{0.06}$. It was not possible from the analyses to establish whether oxygen was present as a separate ThO_2 phase or in solid solution. It is apparent, however, that carbon-saturated ThC_2 has a variable carbon content that depends upon temperature and/or oxygen content. Furthermore, oxygen content may affect the transition temperature(s) of ThC_2 .

In order to present enthalpy of formation data for ThC_2 in a self-consistent manner, a selected set of thermodynamic functions is necessary. No measured values of heat capacity are available for ThC_2 , so estimations will be made. Krikorian⁽¹⁴⁾ has estimated S_{298}° values of 15.1 e.u. for ThC_2 and 17.6 e.u. for UC_2 from correlations of data on various carbides. Westrum⁽¹⁵⁾ recently measured a value of 16.18 e.u. for UC_2 . His value is somewhat uncertain because of the presence of UC and free carbon in the sample, but it indicates that Krikorian's estimates are high. A value of 14.0 ± 1.0 e.u. for S_{298}° of ThC_2 is therefore chosen. The high temperature heat capacity of ThC_2 is then estimated to be $C_p^\circ = 18.26 + 3.11 \times 10^{-3} T - 4.05 \times 10^{-5} T^{-2}$ by Krikorian's method⁽¹⁴⁾. High-temperature transitions will be ignored since the temperatures and structures are uncertain and because the heat effects are believed to be small compared with uncertainties in the thermodynamic functions.

Thermodynamic functions for Th(g) have been given by several investigators⁽¹⁶⁻¹⁸⁾ based on the energy level data of Zalubas⁽¹⁹⁾. Schick, Anthrop, Dreikorn, Feber, Hanst, Panish, and Ward⁽¹⁸⁾ give thermodynamic functions for Th(s) based primarily on the low temperature data of Griffel and Skochdopole⁽²⁰⁾, and recent high temperature measurements by Wallace⁽²¹⁾. Schick et al.⁽¹⁸⁾ have also recalculated the ΔH_{298}° of sublimation of Th from the work of Darnell, McCollum and Milne⁽¹⁶⁾, and obtain 137.7 ± 1.0 kcal/g. atom. Thermodynamic functions for C(graphite) are from Stull and Sinke⁽²²⁾, for $\text{C}_2(\text{g})$ from the JANAF tables⁽²³⁾, for $\text{ThO}_2(\text{s})$ from Kelley⁽²⁴⁾, Hoch and Johnston⁽²⁵⁾, and Kelley and King⁽²⁶⁾, and for CO(g) from the JANAF tables⁽²³⁾. The $\Delta H_{f,298}^\circ$ for $\text{ThO}_2(\text{s})$ is -293.2 kcal/mol⁽²⁷⁾, and for CO(g) , -26.42 kcal/mol⁽²²⁾.

Results for $\Delta H_{f,298}^\circ$ of ThC_2 derived from various investigations are summarized in Table I. The uncertainties listed are standard deviations of the mean for indeterminate errors. Jackson, Barton, Krikorian and Newbury⁽⁸⁾ used a mass spectrometer to analyse the vapours effusing from a graphite Knudsen cell containing ThC_2 . Species detected were $\text{ThC}_2(\text{g})$ and $\text{Th}(\text{g})$. The ratio $P_{\text{ThC}_2}/P_{\text{Th}}$ was found to increase from 1.4 at 2100°C to 2.1 at 2400°C. Lonsdale and Graves⁽⁹⁾ measured vaporization rates of ThC_2 from a graphite Knudsen cell at temperatures of 2278 to 2897°K. Effusates were collected on targets and analysed radiochemically for Th. The data were treated by taking into account the vapour species reported by Jackson et al.

Prescott and Hincke⁽¹⁰⁾ investigated the reaction $\text{ThO}_2(\text{s}) + 4 \text{C}(\text{graphite}) = \text{ThC}_2(\text{s}) + 2 \text{CO}(\text{g})$, by measuring equilibrium pressures of CO. Unit activities have been assumed for the solid phases, and temperatures have been corrected to ITS-1948. Mutual solubilities of ThO_2 and ThC_2 undoubtedly occur in the reaction mixture, but the lowering of activities in the two phases will tend to cancel out in the equilibrium constant expression. A systematic difference is noted in the ΔH_{298}° values from the three highest temperatures. A second-law plot of the data shows considerable scatter.

Egan and Bracker⁽¹¹⁾ used electrolytic cells at $\sim 800^\circ\text{C}$ to study the reaction $\text{Th}(\text{s}) + 2 \text{C}(\text{graphite}) = \text{ThC}_2(\text{s})$. Of a number of cells employed, the most reproducible was one with all solid components having the arrangement: $\text{Th}, \text{ThF}_4 \mid \text{CaF}_2 \mid \text{ThF}_4, \text{ThC}_2, \text{C}$. The emf of the cell ranged from 0.328 V at 700°C to 0.308 V at 950°C. A trend of +2.6 kcal with temperature is apparent in the third-law ΔH_{298}° values and indicates systematic errors. The error limits were estimated.

With the exception of the work by Lonsdale and Graves, the third-law data are in good agreement — surprisingly good, considering the widely different techniques used. It appears that a temperature measurement error may be present in the work of Lonsdale and Graves. Temperature readings were taken by sighting through a small hole in their target into the orifice of the Knudsen cell. The hole in the target apparently limited the aperture of the cone of light required to fill the lens of the pyrometer, and gave temperature readings that were too low. Excluding the Lonsdale and Graves result, the third-law values give an average $\Delta H_{f,298}^\circ$ of -30.4 kcal/mol with an overall estimated uncertainty of ± 3.0 kcal/mol. The second law results of Jackson et al. and Lonsdale and Graves show reasonable agreement with the third-law value. If the pyrometric aperture is limited by a constant transmission factor in Lonsdale and Graves' determination, their second-law result should not be affected. Large systematic errors are present in the other second-law determinations.

Experimental

Emission spectra were generated in a horizontal carbon tube furnace of the King type⁽²⁸⁾, similar to that used by Brewer et al.⁽¹⁾. Radiation shielding was provided for the heating element by using about 10 wraps of either thin Ta or a combination of W and Mo sheet around a graphite support tube. Power into the graphite heating element was regulated by automatic adjustment of transformers in the primary circuit of the output transformer, regulation of which was under the control of a thermo-watt meter coupled with a recording controller. The temperature variation over extended periods of time was less than $\pm 3^\circ\text{C}$, as indicated by monitoring of spectral features. Two types of heaters were used as illustrated in Fig. 1. A 1.25-cm-ID

graphite tube was employed when a system in equilibrium with carbon was desired, and a 2.5-cm-ID tube with a 1.25-cm-dia W inner liner made of 2-1/4 turns of 0.08-mm-thick sheet was used for calibration of Th emission intensities. In order to give a uniform temperature distribution along the chamber, the tubes were machined with a contour as shown in the diagram. The graphite was a fine grained material of 1.74 g/cm^3 density and 0.17 wt% ash. Principal metallic impurities determined by spectroanalysis were 0.05 wt% each of Fe and Cu, and 0.01 wt% each of Ca, Al, Mg, and Ti. The W metal was of 99.9 wt% purity.

Vacua of about 10^{-5} mm were provided for the furnace by a 720-ℓ/sec oil diffusion pump backed by a 7-ℓ/sec mechanical pump. A water cooled chevron-type baffle was used to keep the system free of oil. Temperature measurement was by optical pyrometry. Appropriate window and pyrometer corrections were applied. Pyrometer corrections were based on NBS standardized lamps and pyrometers, and a standard carbon arc⁽²⁹⁾. Temperature sightings were made either on small graphite blocks or within 15° angles in folded pieces of W foil. Furnace windows were of fused silica. They were mounted at a 5° angle from the normal to the furnace axis in order to minimize light reflections into the optical path. Shutters were used to protect the windows during vacuum heatings.

The geometry of the optics used to direct the emitted radiation is shown in Fig. 2. Baffles were used to prevent illumination from the hot chamber walls from reaching the slit. All lenses were of clear fused silica. A cylindrical lens was placed immediately in front of the spectrometer slit in order to convert the circular image of the hot chamber into a narrow rectangular line and thus increase the energy received by the detector.

Spectral intensities were detected with a Jarrell-Ash 0.5-m scanning monochromator with a 1200 lines per mm grating in an Ebert mounting, with

matched sets of replaceable entrance and exit slits of 15 to 160 microns, and with an RCA 1P28 photomultiplier tube at the exit slit. The instrument had a reciprocal dispersion of $16 \text{ \AA/mm}$ and a resolution of $0.03 \text{ \AA}$ in the visible. By one technique the output of the photomultiplier was amplified and traced out on a recording potentiometer. A relatively slow scanning speed of $5 \text{ \AA/mm}$ was used to achieve full response of the recorder. The spectral lines were found to be essentially triangular in shape and had the theoretically predicted half widths. Peak intensities of lines or band heads were used to measure intensities. Sensitivity of the output was variable by 10 steps of $2\text{-}2.5\times$ each. Conversion factors were determined for the various gains with a potentiometer and emission intensities were normalized accordingly. Calibration of the response with light from a blackbody emitter at known temperatures showed the system to be linear up to and beyond the intensities used in all measurements, including the background emissions which were quite appreciable at the higher temperatures.

Another technique used a digital multichannel analyser together with multiple scanning of a feature to enhance its signal-to-noise ratio and to allow determinations to be extended to lower temperatures. The technique has been applied previously to mass spectrometry and nuclear magnetic resonance detection as well as to other types of instrumentation⁽³⁰⁾. It is based on the principle that for successive sampling of a noisy signal, random noise increases in proportion to the square root of the number of measurements whereas a discrete signal increases directly with the number of measurements. An exact repetition of the signal and accumulation into a series of channels then allows an analysis to be made with an increase in the signal-to-noise ratio in proportion to the square root of the number of repetitions. The application to emission spectroscopy will be described

separately by Klein, Barton, Lofgren, and Krikorian⁽³¹⁾. Briefly, the exit slit of the spectrometer was modified to scan back and forth linearly with time at one cycle in 5 seconds. The drive for the scan was provided by a lever arm attached to a cam which was driven by a synchronous motor. A 6-to-1 ratio was used on the lever arm so that a 6-mm movement at the cam drove the slit 1 mm. The output of the photomultiplier was amplified and converted to a frequency proportional to its amplitude. The frequency output from each cycle of scan was then accumulated on 100 channels of the multi-channel analyser. A microswitch on the cam drive was used to address the analyser for the beginning of each scan. Channels of the analyser were triggered by a 20-cps generator. A precision of $\pm$ one channel was realized. From 100 to 3000 scans were used. The accumulated signal was printed out on paper and the data were processed with an IBM-650 computer. Intensities were measured as the area of an emission line, or as the area included within ± 5 channels of a band head peak. Backgrounds were essentially linear and were computed by a least squares solution. Standard deviations of the background curves were used to estimate the uncertainties in feature intensities.

The ThC_2 sample was prepared in the following manner. The inside wall of a 1.25-cm-dia tube was swabbed with a 4-to-1 diluted solution of Duco cement (an organic glue with a volatile solvent) in methyl isobutyl ketone, and a layer of Th metal powder[†] was applied to the walls.

[†]Th metal powder of -200 mesh size was supplied by Fairmont Chemical Co. ThO_2 content as determined by vacuum fusion was 0.8wt%, and principal metallic impurities were 0.03 wt% each of Ca, Al and Fe.

After an initial heating in vacuum at 2000°C, the adhesive decomposed and the metal converted to a uniformly deposited coating of ThC_2 on the wall.

To insure complete conversion, the tube was heated above 2500°C for 15 minutes under 5 cm of Ar. Since a repetition of this procedure caused no detectable change in emission intensities when the tube was cooled to a lower temperature, and also that intensities were constant with time, the system was assumed to be at equilibrium. A doubling of Ar pressure to 10 cm in a separate experiment showed no detectable effect on emission intensities. All subsequent measurements were therefore conducted with a pressure of 5 cm of Ar in the furnace.

After the chamber had reached thermal equilibrium at a particular temperature the following series of steps was conducted: (1) The temperature was observed at three points along the chamber; about 1/4 of the way from each end of the hot section and at the center, and the results were averaged. The three readings generally agreed within 20°C. (2) The background was adjusted by means of a bucking potential to allow for the maximum amplification of the feature to be studied. (3) With 100-micron slits in the monochromator the wave length was set so that about 5 Å of background radiation would be included on either side of the spectral peak, and the scan was started. (4) The temperature measurement was repeated after the last scan and in the manner described above. (5) The above procedure was repeated at the other two features until all three frequencies had been surveyed; i. e., the Th lines at 4493 and 5760 Å, and the C₂ (0 - 1) band head at 5635 Å (see Table II).

For the Th metal determination, a few tenths of a gram of Th powder were spread over the inside surfaces of a W foil tube insert (see Fig. 1). The inner surface of the tube had been roughened in order to produce as much hold-up of material as possible. The optical geometry was identical to that above except that a shorter emitting column of gas was used. A lower

temperature of operation was used because of the much greater pressure of Th. The temperature had to be raised above the melting point of Th, however, in order to have sufficient signal. Three different runs were made. With a run at 2217°K using the recorder, the Th was observed to melt and puddle along the bottom of the tube. Subsequent removal from the system showed a white coloration of the Th, indicating substantial oxidation. Two runs were made with the analyser with measurements at two temperatures for each run. On the first run about 0.1 g of Th was used. No significant puddling of material was noted. The Th intensities showed only a slight increase upon raising the temperature from 2119 to 2224°K. Visual examination of the sample showed oxidation. On the second run, about 0.4 g of Th was used. The Th intensities were up by a factor of two at 2119°K and by a factor of 10 at 2224°K as compared to the previous run. A decrease in intensities of about 25% resulted after holding for 20 minutes at 2224°K. A recheck of the lower temperature intensities showed that they had decreased similarly. The decrease in intensity is attributed to a lowering of the Th activity by dissolving of W. The sample was gray in color and indicated partial oxidation. It showed signs of having reacted with the W surface, but the Th adhered to the walls rather than puddling at the bottom of the tube. This adherence behavior is believed to be related to the rate of heating or to oxygen content.

The calibration intensities by the recorder method were 0.323 and 0.827 at 2217°K for the Th 4493- and 5760-Å lines, respectively. Using the analyser, initial intensities of 30.46 and 92.4 at 2224°K, and 1.81 and 7.53 at 2119°K were observed at the 4493- and 5760-Å lines, respectively. These intensities are in the units of Table II for the corresponding methods.

Results

The equilibria of principal interest may be described by the reactions

In these equations, the Th^* and Th^{**} represent gaseous states of electronically excited atoms, which according to Zalubas⁽¹⁹⁾, are unclassified odd states that decay to the $^3\text{F}_2$ ground state of $\text{Th}(\text{g})$ at wavelengths of 5760.55 and 4493.33 Å, and have excitation energies of 49.64 and 63.63 kcal/mol, respectively. The $\text{C}(\text{graphite})$ represents graphite saturated with ThC_2 , but can probably be considered to be essentially pure graphite in its reference state. Similarly $\text{ThC}_2(\text{s})$ is saturated with graphite, but may have a composition different from stoichiometric ThC_2 . The extent of departure from stoichiometry is presently unknown, however, and ThC_2 of unit activity will be assumed for purposes of thermodynamic calculations.

The second-law relation may be expressed as,

$$\Delta F_T^\circ / T = - R \ln(p_i) = \int \Delta H_T^\circ d(1/T),$$

where p_i refers to the equilibrium partial pressure of $\text{Th}^*(\text{g})$ or $\text{Th}^{**}(\text{g})$.

The data do not give directly a measure of p_i , but an intensity of emission I , which is proportional to concentration, n/V . Thus, we may substitute for p_i ,

$p_i = (n/V)RT = k_i I_i T$. ΔH_T° is obtained from integration of the heat capacity equation, $\Delta C_p^\circ = \Delta a + \Delta bT + \Delta c/T^2$, with the result $\Delta H_T^\circ = A + \Delta aT + (\Delta b/2)T^2$

$- (\Delta c)/T$. The C_p° relation for ThC_2 has been given previously, for graphite: $C_p^\circ = 4.03 + 1.14 \times 10^{-3}T - 2.04 \times 10^{-5}T^{-2}$ (given by Kelley⁽²⁴⁾), and the C_p° of a single

excited state of atomic Th is taken as $(5/2)R$. Integration of the second-law expression gives the final form for treating the data:

$$\Sigma = R \ln (I_1 T) + \Delta a \ln (T) + (\Delta b/2)T + (\Delta c/2)/T^2 = A/T + \text{const.}$$

When Σ is plotted against $1/T$, the resulting slope gives the constant A , which is used to determine ΔH_{2500}° from the ΔH_T° equation. Values of ΔH_T° outside the experimental range are calculated by using tabular data.

The $\Delta H_{f,298}^\circ$ of ThC_2 is also calculated from the thermodynamic data given. Results are summarized in Table III.

Another set of equilibria studied was

where C_2^* refers to the $(0-1)$ band head emission for the C_2 Swan (${}^3\Pi_g - {}^3\Pi_u$) system. The above method of calculation can be repeated, but with the following modifications: $\Delta F_T^\circ/T = -R \ln (I_{\text{Th}} I_{\text{C}_2} T^2)$, and C_2^* is assumed to emit from a single excited energy state with $C_p^\circ = (5/2)R$. The total C_2^* excitation energy is taken as 58.02 kcal/mol. Electronic excitation consists of 1.74 kcal/mol for the ${}^3\Pi_u$ state above the ground ${}^1\Sigma_g^+$ state, and 55.40 kcal/mol of excitation for the ${}^3\Pi_g$ state above ${}^3\Pi_u$. A rotational excitation of 0.88 kcal/mol, corresponding to an effective rotational quantum number of $J = 12.8$, is calculated by considering the contributions of 31 triplet components that lie within 5.0 cm^{-1} of the head. The $\Delta H_{f,298}^\circ$ of ThC_2 may also be derived if the enthalpy of formation of $\text{C}_2(\text{g})$ is known. Using the value of Brewer *et al.*⁽³⁾ of 195 ± 5 kcal/mol for ΔH_0° of sublimation of C_2 gives the results listed in Table III.

Data for the equilibria

were also treated by the foregoing methods, and provided a useful check of the second-law method (see Table III).

The difference method of Brewer et al.⁽³⁾ may also be used to obtain the $\Delta H_{f,298}^\circ$ of ThC_2 . The difference in ΔH_T° for reactions (5) and (1) or (5) and (2) is obtained by combining Σ functions. Thus,

$$\Sigma(5) - \Sigma(1) = R \ln \frac{I(C_2)}{I(\text{Th})} + f(T) = \frac{A(5) - A(1)}{T} + \text{const.},$$

where $f(T)$ is obtained from the appropriate C_p° values, and the A values are related to ΔH_T° as before. This method has the advantage of minimizing systematic errors that affect $C_2(g)$ and $\text{Th}(g)$ in a similar fashion.

A third-law treatment may also be used for reactions (1) and (2), based on calibrations with $\text{Th}(g)$ emission above $\text{Th}(l)$. The calibration reactions are

with $\Delta F_{T_c}^\circ / T_c = -R \ln k_{ij} I_{ij} T_c$ where T_c is the calibration temperature.

Intensity data from reactions (1) and (2) may be extrapolated to T_c by means of free energy functions. Thus,

$$\frac{\Delta F_{T_c}^\circ}{T_c} = -R \ln k_{ij} I_{ij} T - \left(\frac{\Delta F_T^\circ - \Delta H_{298}^\circ}{T} + \frac{\Delta H_{298}^\circ}{T} \right) + \left(\frac{\Delta F_{T_c}^\circ - \Delta H_{298}^\circ}{T_c} + \frac{\Delta H_{298}^\circ}{T_c} \right).$$

Combination of reaction (7) or (8) with (1) or (2) gives $\text{Th}(s) + 2\text{C}(\text{graphite}) = \text{ThC}_2(s)$. Combining and rearranging the associated $\Delta F_{T_c}^\circ$ expressions gives

$$\begin{aligned} \Delta H_{f,298}^\circ(\text{ThC}_2) = & -RT \ln \left(\frac{k_{ij} I_{ij} T_c}{k_{ii} I_{ii} T} \right) - T \left(\frac{\Delta F_{T_c}^\circ - \Delta H_{298}^\circ}{T_c} \right)_j + T \left(\frac{\Delta F_T^\circ - \Delta H_{298}^\circ}{T} \right)_i \\ & - \Delta H_{j,298}^\circ \left(\frac{T - T_c}{T_c} \right) \end{aligned}$$

where j refers to reactions (7) or (8), and i refers to reactions (1) or (2). The free energy function for (7) or (8) is calculated by using $C_p^\circ = (5/2)R$ and the Sackur-Tetrode relation for $\text{Th}^*(g)$ or $\text{Th}^{**}(g)$ together with data for condensed-phase Th. $\Delta H_{j,298}^\circ$ is the sum of the ΔH_{298}° of sublimation of Th(s) to ground state Th(g) plus the excitation energy to Th^* or Th^{**} . Since Th(g) is essentially all in the ground state at room temperature, the ΔH_{298}° of sublimation of Th(s) is used directly.

The ratio k_j/k_i may be replaced by the reciprocal ratios of emitting pathlengths, since identical optics were used throughout the experiments. Pathlengths for the recorder detection experiments were 14 cm for the ThC_2 -C system and 9 cm for elemental Th. For the analyser detection experiments, pathlengths were 13 cm and 10.5 cm, respectively. The $\Delta H_{f,298}^\circ$ of ThC_2 was found to be -21.3 ± 0.1 kcal/mol based on the recorder data, and -24.9 ± 0.1 kcal/mol by the analyser technique, where the uncertainties are standard deviations of the mean for indeterminate errors.

Discussion

The various second-law determinations with the recorder show a better consistency than with the analyser. This results in part from fewer data points being taken with the analyser. Reactions (1) and (2) give the most direct result for $\Delta H_{f,298}^\circ$ of ThC_2 . Using half weights for the analyser results gives an average value of -26.9 kcal/mol with an overall estimated uncertainty of ± 5 kcal. This is taken then as the most reliable second-law value.

The values obtained for the heat of sublimation of C_2 as given by reaction (5), become 198.2 and 201.9 kcal/mol at 0°K for ground state C_2 . These values are somewhat higher than the 195 ± 5 kcal/mol reported by Brewer et al. (3). The differences in energy between the two states of Th are given

by reaction (6), and may be compared with the theoretical value of 13.99 kcal/mol. The remainder of the reactions depend upon the somewhat uncertain value for the enthalpy of sublimation of C_2 and so cannot be given much weight. It is apparent, however, that the analyser data are in error for these reactions. The results improve by combining the least squares ΔH_{2500}° values directly. Thus, from reactions (3) and (4) one obtains ~ -36 , and from (5) - (1) and (5) - (2), ~ -23 kcal/mol for $\Delta H_{f,298}^\circ$ of ThC_2 from the analyser data.

The third-law results depend markedly upon the degree of saturation of the W tube with Th vapour in equilibrium with pure Th liquid. Oxidation is believed to have reduced the pressure of emitting gas in the recorder experiment and in the first analyser experiment. The second analyser experiment, although showing a higher Th intensity, also appears not to have reached saturation. A second-law plot shows the ΔH_{2170}° of sublimation of $Th(g)$ to be high by 65 ± 8 kcal/mol. The value for $\Delta H_{f,298}^\circ$ of ThC_2 is therefore considered to be more negative than the calculated value of -24.9 kcal/mol.

These experiments demonstrate the applicability of spectroscopic detection methods for determining enthalpies of reaction. Further refinement is necessary, however, for results of higher accuracy. Spectroscopic detection has two important advantages over detection by mass spectrometry in that, (1) higher gas pressures can be used and (2) the detection system can be isolated from the source of material. The latter advantage is important for work with highly radioactive or other hazardous materials.

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Table I. The $\Delta H_{f,298}^{\circ}$ of the $\text{ThC}_2(\text{s})$ from various investigations.

Method of investigation	$\Delta H_{f,298}^{\circ}$, kcal/mol, by second law	$\Delta H_{f,298}^{\circ}$, kcal/mol, by third law	Investi- gators
Knudsen cell, mass spectrometer	-35.9 ± 2.8 -31.4 ± 6.5	-30.7 ± 0.6	Ref. (8)
Knudsen cell, target	-36.8 ± 4.6	-23.1 ± 0.4	Ref. (9)
High temperature equilibria	-59.5 ± 12.9	-31.6 ± 1.2	Ref. (10)
Electrolytic cell	-39.9 ± 8	-28.9 ± 0.8	Ref. (11)

Table II. Emission intensity data for Th(g) and C₂(g). Data are presented in the order of measurement.

T(°K)	Th*, 5760 Å	Th**, 4493 Å	C ₂ *, 5635 Å
<u>Part A: Recorder Technique</u>			
2679	6.92	3.951	22.05
2485	0.391	0.188	0.618
2716	10.73	6.28	37.39
2528	0.766	0.372	1.361
2599	2.385	1.216	5.41
2519	0.747	0.353	1.318
2711	10.81	6.29	37.44
2440	0.207	0.0904	0.292
2639	4.017	2.244	10.75
2562	1.336	0.693	2.769
2483	0.455	0.191	0.636
2705	10.55	6.16	36.90
2703	10.22	5.85	34.80
<u>Part B: Analyser Technique</u>			
2585	132.8	74.08	253.9
2502	38.07	21.12	49.81
2410	--	--	10.24
2666	448.5	268.0	1132.4
2556	87.02	49.99	148.8
2732	1094.6	718.9	3628
2434	--	6.41	--
2706	784.0	477.2	2234
2474	24.67 ^a	10.21 ^a	24.04
2333	--	--	1.603 ^a
2693	--	--	1707

^a These values are given 1/2 weight in treatment of the data since they showed standard deviations of 3 to 6% compared to less than 2% for intensities of the other points.

Table III. Summary of second-law enthalpies of reaction for the $\text{ThC}_2\text{-C}$ system.

Reaction (see text)	ΔH_{2500}° (kcal/mol)		$\Delta H_{f,298}^\circ (\text{ThC}_2)$ (kcal/mol)	
	Recorder	Analyser	Recorder	Analyser
(1)	196.9 ± 2.0	205.0 ± 1.1	-24.0	-32.1
(2)	213.2 ± 1.3	215.8 ± 3.1	-26.3	-28.9
(3)	441.7 ± 4.4	464.3 ± 1.2	-27.1	-49.6
(4)	458.6 ± 3.1	473.3 ± 2.8	-30.0	-44.7
(5)	244.9 ± 2.5	248.6 ± 6.0	--	--
(6)	15.4 ± 1.5	4.6 ± 0.9	--	--
(5)-(1)	47.9 ± 1.7	55.9 ± 3.2	-21.0	-12.9
(5)-(2)	33.2 ± 1.3	41.8 ± 1.9	-21.7	-12.4

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Fig. 1. Heater tubes. All material is of graphite with the exception of the W tube insert.

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Fig. 2. Schematic drawing of the optical arrangement. The spectrometer grating rotates for normal scanning by the instrument. The scanning slit is used for repetitive scanning over short wavelength intervals.

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