

1975

A thermodynamic study of phase stability in the thorium - copper equilibrium system

Donald Max Bailey
Iowa State University

Follow this and additional works at: <https://lib.dr.iastate.edu/rtd>

 Part of the [Metallurgy Commons](#)

Recommended Citation

Bailey, Donald Max, "A thermodynamic study of phase stability in the thorium - copper equilibrium system " (1975). *Retrospective Theses and Dissertations*. 5185.
<https://lib.dr.iastate.edu/rtd/5185>

This Dissertation is brought to you for free and open access by the Iowa State University Capstones, Theses and Dissertations at Iowa State University Digital Repository. It has been accepted for inclusion in Retrospective Theses and Dissertations by an authorized administrator of Iowa State University Digital Repository. For more information, please contact digirep@iastate.edu.

INFORMATION TO USERS

This material was produced from a microfilm copy of the original document. While the most advanced technological means to photograph and reproduce this document have been used, the quality is heavily dependent upon the quality of the original submitted.

The following explanation of techniques is provided to help you understand markings or patterns which may appear on this reproduction.

1. The sign or "target" for pages apparently lacking from the document photographed is "Missing Page(s)". If it was possible to obtain the missing page(s) or section, they are spliced into the film along with adjacent pages. This may have necessitated cutting thru an image and duplicating adjacent pages to insure you complete continuity.
2. When an image on the film is obliterated with a large round black mark, it is an indication that the photographer suspected that the copy may have moved during exposure and thus cause a blurred image. You will find a good image of the page in the adjacent frame.
3. When a map, drawing or chart, etc., was part of the material being photographed the photographer followed a definite method in "sectioning" the material. It is customary to begin photoing at the upper left hand corner of a large sheet and to continue photoing from left to right in equal sections with a small overlap. If necessary, sectioning is continued again — beginning below the first row and continuing on until complete.
4. The majority of users indicate that the textual content is of greatest value, however, a somewhat higher quality reproduction could be made from "photographs" if essential to the understanding of the dissertation. Silver prints of "photographs" may be ordered at additional charge by writing the Order Department, giving the catalog number, title, author and specific pages you wish reproduced.
5. PLEASE NOTE: Some pages may have indistinct print. Filmed as received.

Xerox University Microfilms

300 North Zeeb Road
Ann Arbor, Michigan 48106

75-17,378

BAILEY, Donald Max: 1932-
A THERMODYNAMIC STUDY OF PHASE STABILITY IN
THE THORIUM - COPPER EQUILIBRIUM SYSTEM.

Iowa State University, Ph.D., 1975
Engineering, metallurgy

Xerox University Microfilms, Ann Arbor, Michigan 48106

**A thermodynamic study of phase stability in the
thorium - copper equilibrium system**

by

Donald Max Bailey

**A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY**

Major: Metallurgy

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

For the Major Department

Signature was redacted for privacy.

For the Graduate College

**Iowa State University
Ames, Iowa**

1975

TABLE OF CONTENTS

| | Page |
|--|------|
| INTRODUCTION | 1 |
| Purpose | 1 |
| Phase Relations | 1 |
| Direct Determination of Gibbs Free Energies | 3 |
| Choice of Electrolyte | 5 |
| Thermochemical Considerations | 7 |
| EXPERIMENTAL DETAILS | 10 |
| Apparatus | 10 |
| Sample Materials and Preparation | 13 |
| Experimental Procedure | 15 |
| RESULTS | 18 |
| DISCUSSION | 23 |
| SUMMARY | 35 |
| ACKNOWLEDGEMENTS | 36 |
| LITERATURE CITED | 37 |

INTRODUCTION

Purpose

Since thorium is a fertile material, thermodynamic data on its binary alloy systems are relevant to nuclear technology. The increased interest in thorium as a potential breeder material is evidenced in part by the more than five-fold increase in these data within the past ten years (Smith, 1974). Preceding the present work, thermodynamic data were available in part for slightly more than 50 of 160 known thorium binary alloy phases. The present work is the fourth in a series at this laboratory; the previous three were of Th-Ni, Th-Co, and Th-Fe alloys (Skelton et al., 1970, 1971, 1973). The present work was undertaken to bridge the gap between these alloys and the Th-Zn alloy system (Chiotti and Gill, 1961) and to allow a comparison of the relative phase stabilities in the series.

Phase Relations

The thorium-copper equilibrium system has been examined by several investigators (Guertler, 1940; Grube and Botzenhardt, 1942; Raub and Engel, 1943; Schiltz et al., 1971; Berlin, 1972). The two most recent investigations agree that four intermediate phases exist and further agree in regard to the stoichiometries of the phases ThCu_6 , ThCu_2 ,

and Th_2Cu . The crystallographic investigation of Buschow and van der Goot (1970) has shown ThCu_6 to be isostructural with CeCu_6 , and Baenziger et al. (1956) and Murray (1955-56) have similarly shown ThCu_2 and Th_2Cu to be isostructural with AlB_2 and CuAl_2 , respectively. Schiltz et al. (1971) reported the remaining phase to be $\text{ThCu}_{3.6}$, while Berlin (1972) reported ThCu_3 . Berlin indicated that ThCu_3 was likely isostructural with ThAu_3 and with rare-earth silver phases (Steeb et al., 1968). Steeb et al. suggested, on the basis of the similarity of lattice parameters and space group, that these phases are isostructural with PuAg_3 (Runnals, 1956). McMasters et al. (1970) reported the stoichiometry RE_2Ag_7 for these rare-earth phases with silver. The crystallographic work of Bailey and Kline (1971) established the stoichiometry $\text{REAg}_{3.6}$ for the gadolinium-silver phase and by implication for the phases reported by Steeb et al., by McMasters et al., and by Berlin. By comparison of powder diffractometer data for the silver-rich phase in the plutonium-silver system with data calculated assuming the $\text{GdAg}_{3.6}$ structure of Bailey and Kline, Wood et al. (1970) confirmed the stoichiometry $\text{PuAg}_{3.6}$ for this phase. As an adjunct to the present thermodynamic investigation, Bailey (1973) determined by powder diffraction data that $\text{ThCu}_{3.6}$ is isostructural with $\text{GdAg}_{3.6}$. On these bases and on the further basis of the close comparison of the lattice parameters for the phase reported by Berlin and by

Bailey (1973), the phase relationships of Schiltz et al. (1971) are corroborated and their phase diagram appears in Fig. 1.

Direct Determination of Gibbs Free Energies

Gibbs free energies of reaction may be measured directly by vapor pressure techniques and by electromotive force (emf) methods. The choice of method is usually based on the characteristics of the system to be studied, with the emf cell offering advantages in systems with low vapor pressures. The emf method offers the experimentalist a "feel" for the cell operation in that a drift in potential with time is indicative of an experimental problem. The use of galvanic cells with solid electrolytes for directly measuring the free energies of formation of phases of metallurgical interest has recently been gaining in popularity. Although the use of solid electrolytes such as glass, porcelain, and other ceramic materials dates to the beginning of the century, systematic investigation of solid electrolyte materials began only after the pioneering studies of transport processes in ionic materials by Frenkel (1926), Wagner and Schottky (1930), and Jost (1933). The primary impetus for the recent application of the technique originated with Kiukkola and Wagner (1957), who outlined the potential use of galvanic cells with solid and liquid electrolytes for determining the

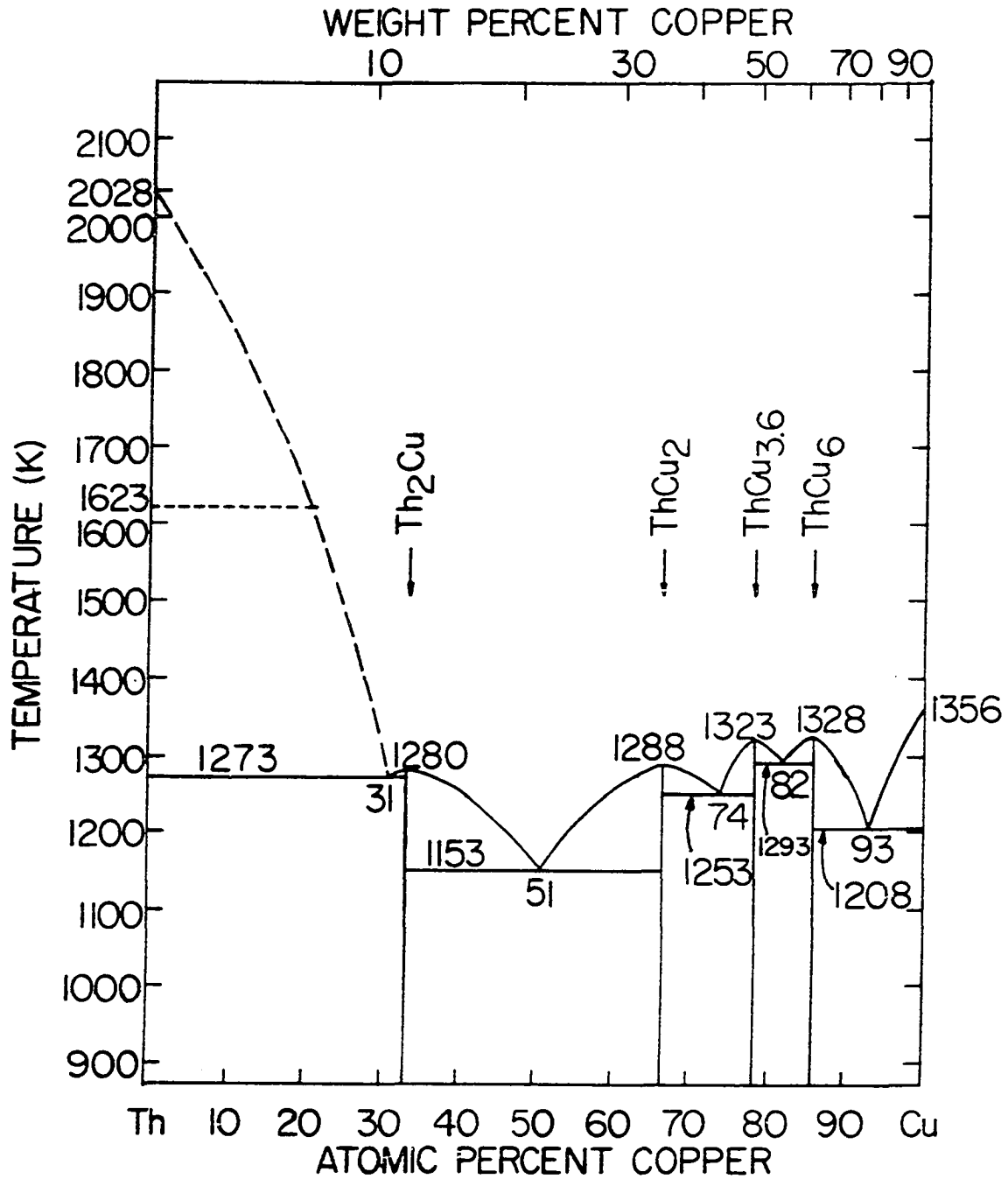


Fig. 1. The Th-Cu temperature-composition diagram (after Schiltz *et al.*)

free energies of formation of compounds of metallurgical interest at elevated temperatures.

Choice of Electrolyte

Schmalzried (1972) states that in order to build up and maintain a stable potential difference on the order of one volt in a galvanic cell, the minimum conductivity of the electrolyte must exceed about $10^{-6} \Omega^{-1} \text{cm}^{-1}$, which is achieved only at high temperatures for most solid electrolytes. Further, since the transference numbers of electrons or holes must be low, solid compounds have been found useful as electrolytes generally only if the difference between the anion and the cation on Pauling's (1960) electronegativity scale is more than two. This thumb rule permits solid oxide and solid halide electrolytes, but holds little promise for solid sulfide, nitride, or carbide electrolytes. Steele (1968) has shown that the open circuit voltage for an electrolyte (MX_2) which conducts by both ionic and electron transfer is given by

$$E = \frac{1}{zF} \int_{\mu_{\text{X}_2}'}^{\mu_{\text{X}_2}''} t_{\text{ion}} d\mu(\text{X}_2), \quad [1]$$

where $\mu'(\text{X}_2)$ and $\mu''(\text{X}_2)$ are the chemical potentials of the anionic species in the left and right half-cells, respectively, F is Faraday's constant, $23062 \text{ cal volt}^{-1}(\text{gram equivalent})^{-1}$ and z is the number of equivalents of charge passed through the cell. Hinze and Patterson (1973) have demon-

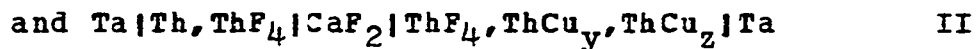
strated that CaF_2 has an ionic transference number essentially of unity over the temperature range 400 - 800 C at fluorine partial pressures ranging down to its stability limit, and hence is a useful solid electrolyte within this range of experimental conditions. Given an ionic transference number of unity, equation [1] simplifies to

$$E = 1/z_f (\mu''(x_2) - \mu'(x_2)). \quad [2]$$

Markin (1968) cited successful applications of CaF_2 as a solid electrolyte in galvanic cells spanning a wide range of temperatures and fluorine activities and emphasized that the use of single crystalline CaF_2 results in more stable emf's than are achieved with sintered compacts due to reduced penetration of the electrode materials into the electrolyte. Thorium binary systems for which this electrolyte has been employed include Th-Ru (Kleykamp and Murabayashi, 1974a), Th-Rh (Kleykamp and Murabayashi, 1974b), Th-Re (Rezukhina and Pokarev, 1971), Th-C (Aronson, 1964; Aronson and Sadofsky, 1965), Th-S (Aronson, 1967), Th-B (Aronson and Auskern, 1966), and the Th-Fe, Th-Co, and Th-Ni systems (Skelton et al., 1970, 1971, 1973). Flengas (1973) observed that mixed potentials arising from impurities in the inert gas atmosphere are less likely to occur for halide and sulfide systems than for oxide systems. On these bases CaF_2 was chosen as the electrolyte for the present investigation.

Thermochemical Considerations

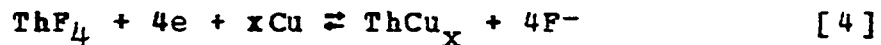
The experiments were conducted with displacement cells of the type



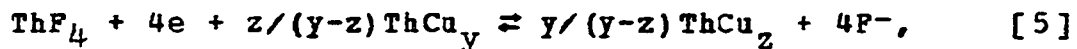
The reaction for the left half-cell is



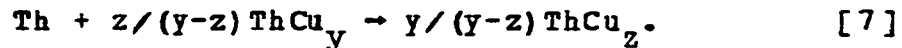
For the right side, the half-cell reactions are



and



resulting in the following cell reactions:



If a galvanic cell is operated reversibly at constant temperature, the Gibbs free energy for the cell reaction is

$$\Delta G^\circ = -zE. \quad [8]$$

If, further, the pure solid phases are chosen as the standard states and the limited solid solubilities are neglected, the open circuit emf data are convertible to standard free energies of formation.

The electrochemical potential of a cell component, η , is given by

$$\eta = \mu + z\phi, \quad [9]$$

where z is the ionic charge and ϕ is the galvanic voltage.

For a cell such as I above,

$$E\gamma = [\phi_e(\text{Ta}') - \phi_e(\text{Ta}'')] \gamma \quad [10]$$

where the prime again designates components in the left half-cell and the double prime those in the right and ϕ is the potential of the electrons at the tantalum leads.

Equating the chemical potentials of the mobile electrons leads to

$$E\gamma = \eta_e(\text{Ta}') - \eta_e(\text{Ta}''). \quad [11]$$

The potential of the electrons in the tantalum leads is that of the electrons in the respective half-cell, thus

$$\eta_e(\text{Ta}') = \eta_e' \quad [12]$$

$$\text{and } \eta_e(\text{Ta}'') = \eta_e'' \quad [13]$$

and, at equilibrium,

$$\eta_{F^-}' = \eta_{F^-}'' \quad [14]$$

On each side of the cell

$$\mu_F = \eta_{F^-} - \eta_e \quad [15]$$

Substitution into equation [11] leads to

$$E\gamma = \eta_{F^-}' - \mu_F' - \eta_{F^-}'' + \mu_F'' \quad [16a]$$

$$= \mu_F'' - \mu_F' \quad [16b]$$

consistent with equation [2] above. From the Gibbs - Duhem relation,

$$\mu_{\text{Th}} + 4\mu_F = \mu_{\text{ThF}_4} = \text{const} \quad [17a]$$

$$\mu_{\text{Th}}' + 4\mu_F' = \mu_{\text{Th}}'' + 4\mu_F'' = \mu_{\text{ThF}_4} \quad [17b]$$

Combining equations [16b] and [17b],

$$\mu_{\text{Th}}'' - \mu_{\text{Th}}' = 4(\mu_F' - \mu_F'') = -4\gamma E. \quad [18]$$

At equilibrium in the left half-cell, and choosing pure solid thorium as the standard state,

$$\mu_{\text{Th}}^{\text{I}} = \mu_{\text{Th}}^{\circ}, \quad [19a]$$

and similarly, at equilibrium in the right half-cell, choosing the solid phases as the standard states and ignoring any slight solid solubility among the phases,

$$\mu_{\text{Th}}^{\text{II}} + x\mu_{\text{Cu}}^{\circ} = \mu_{\text{ThCu}_x}^{\circ} \quad [19b]$$

$$\text{and } \mu_{\text{Th}}^{\text{II}} + z/(Y-z)\mu_{\text{ThCu}_y}^{\circ} = Y/(Y-z)\mu_{\text{ThCu}_z}^{\circ} \quad [19c]$$

For cell I,

$$\mu_{\text{Th}}^{\text{II}} - \mu_{\text{Th}}^{\text{I}} = \mu_{\text{ThCu}_x}^{\circ} - x\mu_{\text{Cu}}^{\circ} - \mu_{\text{Th}}^{\circ} \quad [20a]$$

$$= f_{\Delta G_{\text{ThCu}_x}^{\circ}}, \quad [20b]$$

where $f_{\Delta G_{\text{ThCu}_x}^{\circ}}$ is the standard free energy of formation of ThCu_x . Thus

$$f_{\Delta G_{\text{ThCu}_x}^{\circ}} = -47E_{\text{I}}. \quad [21]$$

Similarly, for cell II,

$$\begin{aligned} \mu_{\text{Th}}^{\text{II}} - \mu_{\text{Th}}^{\text{I}} + z/(Y-z)\mu_{\text{ThCu}_y}^{\circ} - z/(Y-z)\mu_{\text{Th}}^{\circ} - Yz/(Y-z)\mu_{\text{Cu}}^{\circ} \\ = Y/(Y-z)\mu_{\text{ThCu}_z}^{\circ} - \mu_{\text{Th}}^{\circ} - z/(Y-z)\mu_{\text{Th}}^{\circ} - Yz/(Y-z)\mu_{\text{Cu}}^{\circ}. \end{aligned} \quad [22]$$

$$\mu_{\text{Th}}^{\text{II}} - \mu_{\text{Th}}^{\text{I}} = r_{\Delta G^{\circ}} = Y/(Y-z)f_{\Delta G_{\text{ThCu}_z}^{\circ}} - z/(Y-z)f_{\Delta G_{\text{ThCu}_y}^{\circ}} \quad [23]$$

Thus

$$f_{\Delta G_{\text{ThCu}_z}^{\circ}} = -47((Y-z)/Y E_{\text{II}} + z/Y E_{\text{I}}). \quad [24]$$

EXPERIMENTAL DETAILS

Apparatus

The experimental apparatus is shown schematically in Fig. 2. A multilead glass-to-metal pass-through for the electrical connections to the cell is soldered to the brass lid. The tantalum cell leads and the Chromel-Alumel thermocouple are soldered to the pass-through leads on the inside of the cell chamber. On the outside, the thermocouple circuit is continued by Chromel and Alumel wires to an ice-bath reference junction with copper wires which then lead to the measuring potentiometer, while copper conductors are soldered directly to the exterior pass-through leads for the electrode circuits. The thermocouple wire was calibrated by the manufacturer against National Bureau of Standards platinum wire, and calibration of the assembled thermocouple with the melting points of aluminum, silver, and copper confirmed that standard tables of thermocouple emf vs. temperature could be used without introduction of significant error (<0.1%). Tantalum wafers connected the tantalum electrical leads to the electrodes of the open-stacked double cell. The suitability of tantalum for this purpose was established by Magnani et al. (1969), who found that tantalum did not contaminate the electrode materials in this alloy system. The external positive leads were shielded to the

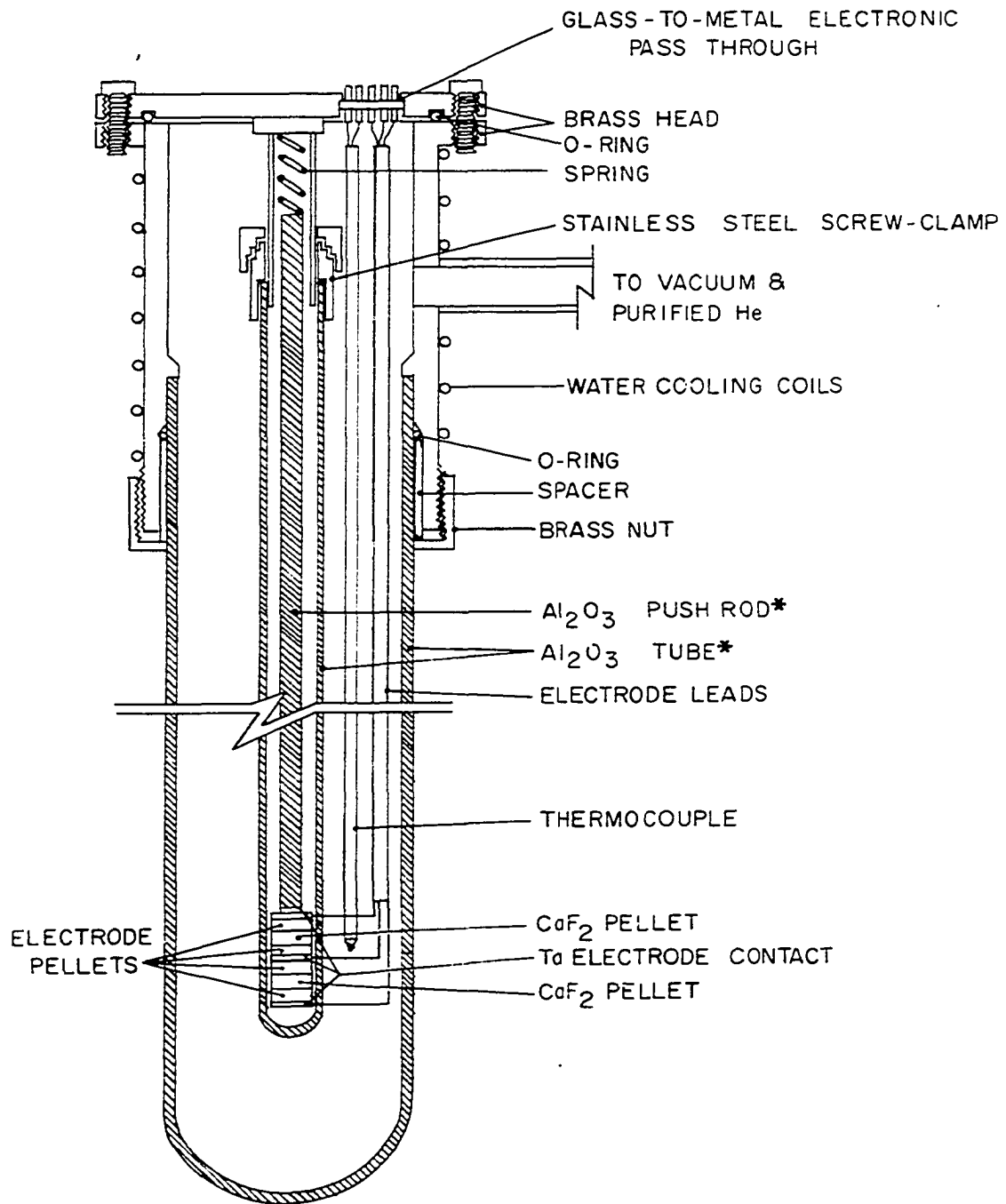


Fig. 2. Electromotive force apparatus. *Impervious alumina, McDanel Refractory Porcelain Company

guard potential of the measuring potentiometer, while the negative leads were connected to ground. All emf measurements were made with a Leeds and Northrup model K-3 potentiometer with an electronic DC nullmeter connected between the positive emf source and the potentiometer with the high-impedance side of the nullmeter toward the emf cell. The selection of emf source for measurement was made with a Leeds and Northrup rotary selector switch, which also allowed the connection of the nullmeter across the positive and negative leads of the potentiometer for standardizing the potentiometer slidewire. A spring loaded Al_2O_3 push rod held the cell assembly in firm contact. The system was assembled with O-ring seals to provide a gas-tight assembly. The entire cell envelope was mounted to the rear of a vacuum glove box so that access for assembly of the stacked cell could be made through the box, affording the protection of an inert gas atmosphere to the reactive cell components.

The cell was heated by a Lindberg Hevi-Duty non-inductively wound split-tube furnace. Power was supplied by a West stepless transformer controlled by a West set point controller which monitored the furnace temperature with a centrally located thermocouple. Temperatures were controllable to within one degree C for several days. A grounded stainless steel tube surrounded the outer Al_2O_3 cell envelope to screen external electrical noise from the experi-

ment.

The experiments were run at a positive pressure of about 2 psi in a purified helium atmosphere derived from the glove box. The purification was accomplished by circulating the helium gas through a molecular sieve and through copper wool which was periodically heated to 400 C. The moisture content of the glove box atmosphere was monitored from time - to - time and after each entry into the box with a MEECO model W electrolytic water analyzer. Moisture levels were maintained to 2ppm or less. The oxygen level was not quantitatively measured, but was indicated to be small by the ability of the glove box atmosphere to maintain the operation of an unprotected 25-watt tungsten lamp filament for several hours.

Sample Materials and Preparation

Optical quality high purity CaF_2 single crystals, purchased from Harshaw Chemical Company, were used as electrolytes. The 1/8 inch thick discs were cut from 1/2 inch diameter rods whose axes were parallel to the $\langle 111 \rangle$ crystallographic direction. The copper used in this investigation was obtained from the American Smelting and Refining Company and the thorium metal and thorium fluoride were prepared in the Ames Laboratory. The results of the impurity analyses for these electrode materials are given in Table I.

Table I. Impurity Analysis of Alloying Elements and ThF₄ in ppm

| Impurity | Th | Cu | ThF ₄ |
|----------|-----|------|------------------|
| H | <1 | - | - |
| B | - | - | <0.5 |
| N | 20 | - | - |
| C | 30 | - | - |
| O | 85 | - | - |
| Na | <10 | - | - |
| Mg | <20 | - | 55-120 |
| Al | 20 | - | <25 |
| Si | <20 | <0.1 | 50-100 |
| S | -0 | <1 | - |
| Ca | <20 | - | 150-500 |
| Cr | <20 | - | - |
| Mn | <20 | <0.5 | <20 |
| Fe | <20 | <0.7 | - |
| Ni | <20 | <1 | - |
| Se | - | <1 | - |
| Ag | 0.2 | <1 | - |
| Cd | - | <1 | 0.2 |
| In | - | - | 35-45 |
| Sn | - | <1 | - |
| Sb | - | <1 | - |
| Te | - | <2 | - |
| Au | - | <2 | - |
| Pb | - | <1 | - |
| Bi | - | <0.1 | - |

The alloys were prepared by arc-melting together the appropriate amounts of thorium and copper in an atmosphere of purified argon. Homogenization was enhanced by successively inverting and remelting each alloy eight times. X-ray powder diffraction patterns were taken of all alloys, and were in all cases consistent with the phase diagram of Schiltz *et al.* (1971), though it should be noted that in the region between ThCu₆ and ThCu_{3.6} the very large number of lines present precluded resolution in some angular regions. The electrodes

were obtained by mixing pulverized metal or alloy with approximately 20 wt% ThF_4 powder and compacting the aggregate in a press. The pulverized metal was prepared from brittle alloys by crushing in a diamond mortar and from non-brittle alloys by filing with a tungsten carbide file. Strain energy in the pulverized material was relieved by annealing the compacted pellets for an hour or more in_situ in the electrochemical cell at elevated temperature before beginning the measurements. All operations were conducted in the glove box atmosphere except in the case of the initial three alloys, 3 at% Th, 10 at% Th, and 15.5 at% Th. In these three cases the material, loaded in the pellet press, was removed from the glove box for a short period of time while enclosed in a plastic bag for protection from the atmosphere, compacted in an external press, and returned to the glove box for subsequent operations. Data from a 15.5 at% Th alloy compacted with a mechanical press in the glove box yielded results in good agreement with the alloy compacted externally, and this procedure was adopted for all subsequent alloys. Compaction was at approximately 12,000 psi.

Experimental Procedure

A procedure was initiated for the initial specimens which were pressed externally to remove any gases which may have been adsorbed in the process. The electrochemical cell

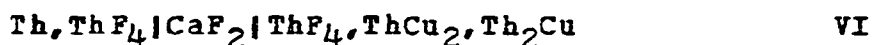
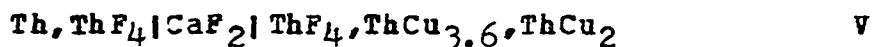
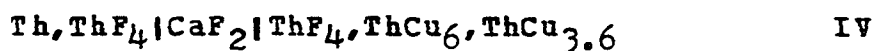
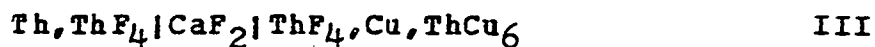
was evacuated to about 0.05 Torr, heated to near 100 C for an hour or more, heated to 200 C for several hours, then filled with helium from the glove box and heated to the initial test temperature. Although this procedure was likely not required for those specimens for which all operations were performed in the glove box, it was retained as a useful precaution against moisture which may have diffused through the gloves during sample manipulation. The glove box atmosphere was verified dry to within 2 ppm H₂O by the moisture analyzer before filling the electrochemical cell with helium.

Emf measurements were recorded at each temperature when the emf no longer changed with time, normally within one or two hours of attaining the higher test temperatures and within several hours for the lower temperatures. Frequently a larger voltage than the measured emf was impressed on the cell to perturb it away from equilibrium by titration. Reestablishment of the emf at the original value supported the validity of the datum point. One run was made with all electrodes made of the Th, ThF₄ mixture to demonstrate that no thermal emf of significance was developed within the cell. The symmetric double cell configuration provided a continued indication of the absence of thermal emf's during the subsequent runs through a comparison of the data from the chemically equivalent members of the double cell. In those few cases where the data compared unfavorably the data were

discarded. Data were collected when the experimental temperatures were approached both from higher and lower temperatures. Thus the criteria for evaluating the reversibility of the electrochemical cell as outlined by Oriani (1956) (stable emf, emf recoverable after perturbation by an impressed voltage, and emf reproducible regardless of the approach from higher or lower temperature) were met.

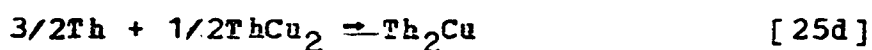
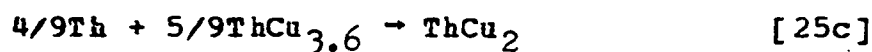
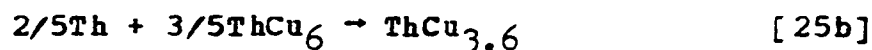
RESULTS

Data were accumulated over the temperature range 729 - 1219 K with electrochemical cells of the type



with all phases remaining solid throughout the experiments.

The cell reactions for the above cells are, respectively,



The experimental data are tabulated in Table II. Linear least squares fits to the experimental emf's as functions of temperature are presented both analytically and graphically in Fig. 3. Also shown in Fig. 3 are the experimental data of Magnani et al. (1969) for Cu - 5 at% Th and Cu - 7 at% Th alloys.

The phase diagram of Schiltz et al. (1971) indicates negligible solid solubility of thorium in copper. The $\text{GdAg}_{3.6}$ structure found for $\text{ThCu}_{3.6}$ allows, in principle, for a maximum solubility of 2 at% Cu for this phase, but Bailey and Kline (1971) argue for $\text{GdAg}_{3.6}$ on the basis of

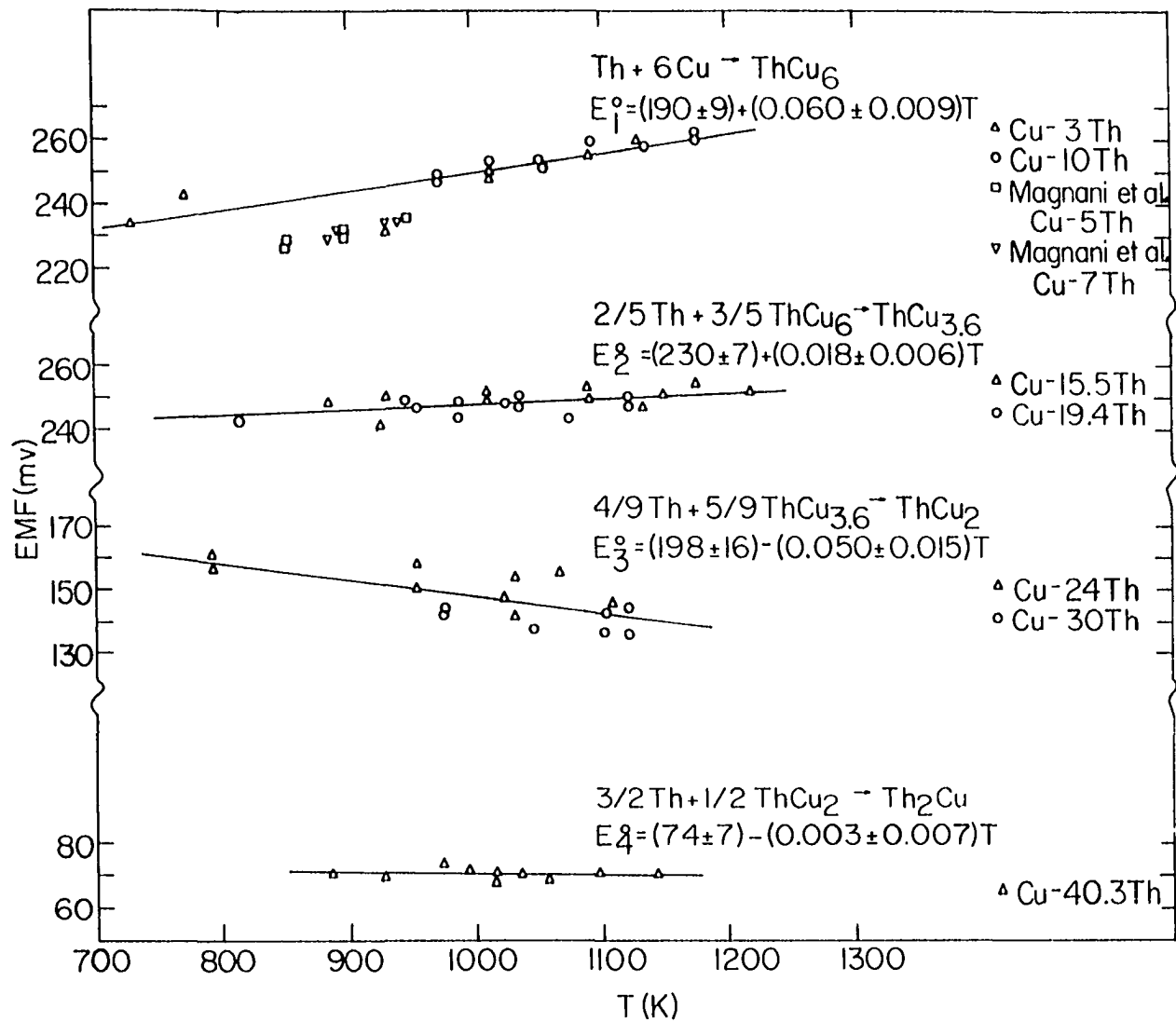


Fig. 3. Electromotive force data as functions of temperature for various alloys and reactions

Table II. Experimental Values for Electromotive Forces at Measured Temperatures for Various Th-Cu Compositions

| Comp. at. % | Temp. K | Electro- motive force, mV | Comp. at. % | Temp. K | Electro- motive force, mV | |
|----------------|------------|---------------------------------|----------------|------------|---------------------------------|------|
| Cu-3 Th | 729 | 234.5 | Cu-24 Th | 1065 | 155.5 | |
| | 773 | 242.9 | | 1021 | 146.8 | |
| | 931 | 232.4 | | 1030 | 141.8 | |
| | 1012 | 248.5 | | 952 | 150.3 | |
| Cu-10Th | 1052 | 253.2 | 792 | 156.3 | | |
| | 1012 | 252.4 | 952 | 158.1 | | |
| | 972 | 249.2 | 791 | 160.3 | | |
| | 1092 | 259.1 | 1106 | 145.6 | | |
| | 971 | 245.3 | 1031 | 154.1 | | |
| | 1053 | 253.7 | Cu-30 Th | 1120 | 144.7 | |
| | 1133 | 259.7 | | 1046 | 137.3 | |
| | 1175 | 261.1 | | 1101 | 142.8 | |
| 1012 | 249.8 | 974 | | 142.8 | | |
| Cu-15.5 Th | 1175 | 260.0 | 1100 | 136.1 | | |
| | 1091 | 255.8 | 973 | 142.6 | | |
| | 1134 | 257.9 | 1118 | 135.5 | | |
| | Cu-15.5 Th | 1176 | 254.8 | Cu-40.3 Th | 1096 | 70.3 |
| | | 1010 | 251.7 | | 1056 | 68.4 |
| | | 884 | 248.5 | | 1015 | 67.9 |
| | | 927 | 250.0 | | 972 | 73.5 |
| | | 1089 | 253.6 | | 992 | 71.1 |
| | | 1219 | 251.7 | | 1035 | 70.0 |
| | | 1149 | 250.9 | | 927 | 69.4 |
| | | 1011 | 248.9 | | 1014 | 70.6 |
| | | 1131 | 246.5 | | 1141 | 70.5 |
| 926 | | 241.0 | 886 | | 70.6 | |
| 1088 | 249.8 | | | | | |
| Cu-19.4 Th | 1120 | 250.1 | | | | |
| | 1024 | 248.2 | | | | |
| | 1035 | 250.3 | | | | |
| | 987 | 248.6 | | | | |
| | 1074 | 243.4 | | | | |
| | 1121 | 247.5 | | | | |
| | 1036 | 247.5 | | | | |
| | 791 | 242.8 | | | | |
| | 988 | 243.3 | | | | |
| | 946 | 249.0 | | | | |
| | 954 | 247.0 | | | | |
| | 1035 | 245.0 | | | | |

atomic sizes and experience with several crystals, that the solubility range is likely much smaller. Schiltz et al. (1971) reported no indication of a significant range of homogeneity in any of the four intermediate phases. The emf data were therefore analyzed with the pure solid phases as standard states and it was assumed that no significant deviation from unit activities occurred in the alloys. With these assumptions, the emf data yield standard free energies as follows, with E_{III} through E_{VI} the open circuit emf values for cells III through VI, respectively:

$$\begin{aligned} r_{\Delta G_{III}^{\circ}} &= -47E_{III} = f_{\Delta G^{\circ}}(\text{ThCu}_6) \\ &= -17520 \pm 830 - (5.53 \pm 0.92)T \text{ cal/mol,} \quad [26] \end{aligned}$$

$$\begin{aligned} r_{\Delta G_{IV}^{\circ}} &= -(2/5)47E_{IV} = f_{\Delta G^{\circ}}(\text{ThCu}_{3.6}) - 3/5f_{\Delta G^{\circ}}(\text{ThCu}_6) \\ f_{\Delta G^{\circ}}(\text{ThCu}_{3.6}) &= -47(2/5E_{IV} + 3/5E_{III}) \\ &= -18990 \pm 740 - (4.06 \pm 0.92)T \text{ cal/mol,} \quad [27] \end{aligned}$$

$$\begin{aligned} r_{\Delta G_{V}^{\circ}} &= -(4/9)47E_{V} = f_{\Delta G^{\circ}}(\text{ThCu}_2) - 5/9f_{\Delta G^{\circ}}(\text{ThCu}_{3.6}) \\ f_{\Delta G^{\circ}}(\text{ThCu}_2) &= -47(4/9E_{V} + 2/9E_{IV} + 1/3E_{III}) \\ &= -18700 \pm 1000 - (0.2 \pm 1.3)T \text{ cal/mol,} \quad [28] \end{aligned}$$

$$\begin{aligned} r_{\Delta G_{VI}^{\circ}} &= -(3/2)47E_{VI} = f_{\Delta G^{\circ}}(\text{Th}_2\text{Cu}) - 1/2f_{\Delta G^{\circ}}(\text{ThCu}_2) \\ f_{\Delta G^{\circ}}(\text{Th}_2\text{Cu}) &= -47(3/2E_{VI} + 2/9E_{V} + 1/9E_{IV} + 1/3E_{III}) \\ &= -19500 \pm 1500 + (0.3 \pm 1.5)T \text{ cal/mol.} \quad [29] \end{aligned}$$

Values for the Gibbs free energies of formation at 973 K, which is near the mean of the temperature range of measurement, are listed in Table III.

Table III. Thermodynamic Functions for the Formation of the Four Th-Cu Intermediate Phases

| Phase | $-AG^\circ$ | $-\Delta H^\circ$ | ΔS° |
|---------------------|-------------|-------------------|------------------|
| ThCu ₆ | 3.27 ± 0.01 | 2.50 ± 0.12 | 0.79 ± 0.13 |
| ThCu _{3.6} | 4.99 ± 0.02 | 4.12 ± 0.16 | 0.88 ± 0.20 |
| ThCu ₂ | 6.30 ± 0.04 | 6.21 ± 0.35 | 0.07 ± 0.44 |
| Th ₂ Cu | 6.40 ± 0.05 | 6.51 ± 0.51 | -0.11 ± 0.49 |

Also listed in Table III are the mean entropies of formation and mean enthalpies of formation evaluated from the slopes and intercepts of the temperature dependencies of the free energies of formation. The cumulative nature of the errors causes the experimental uncertainties to increase from ThCu₆ to Th₂Cu.

DISCUSSION

The data of Magnani et al. (1969) indicate $-\Delta G_{973}^{\circ} = 3.13$ kcal/g-atom, $-\Delta H_{850-949}^{\circ} = 2.09$ kcal/g-atom, and $\Delta S_{850-949}^{\circ} = 1.06$ cal/g-atom-deg for the phase ThCu_6 . Corresponding values in Table III show that the free energy of formation is reproduced in the present work to approximately 4% and that the enthalpy and entropy of formation are reproducible to about 20%. The greater number of experimental points and the extended temperature range of measurement make the present values preferable.

Figure 4 compares the values of $-\Delta G_{973}^{\circ}$ for the Th-Fe, Th-Co, Th-Ni, Th-Cu, and Th-Zn systems. For the phases less rich in thorium than $X_{\text{Th}} = 0.25$, the crystal structures are, with the exception of ThZn_4 , related to the Laves phases and to the CaZn_5 structure. The Th-M bonds, where M is Fe, Co, Ni, Cu, or Zn, play a dominant role in the phase stability. For these two or three phases within a given system, ΔG° is nearly constant when expressed in terms of kcal/g-atom Th (Fig. 5) and increases in magnitude from -16.5 for M = Fe through -22.7 for M = Cu, -30.2 for M = Co, to -52.2 for M = Ni. The value for the structurally related zinc phase, $\text{Th}_2\text{Zn}_{17}$, is -37.5. The mean values of ΔH are shown in Fig. 6. As in Fig. 4 for ΔG , the curves are nearly linear in the thorium-poor portion. When converted to kcal/g-atom Th (Fig. 7) the enthalpy values for the thorium-poor phases are nearly

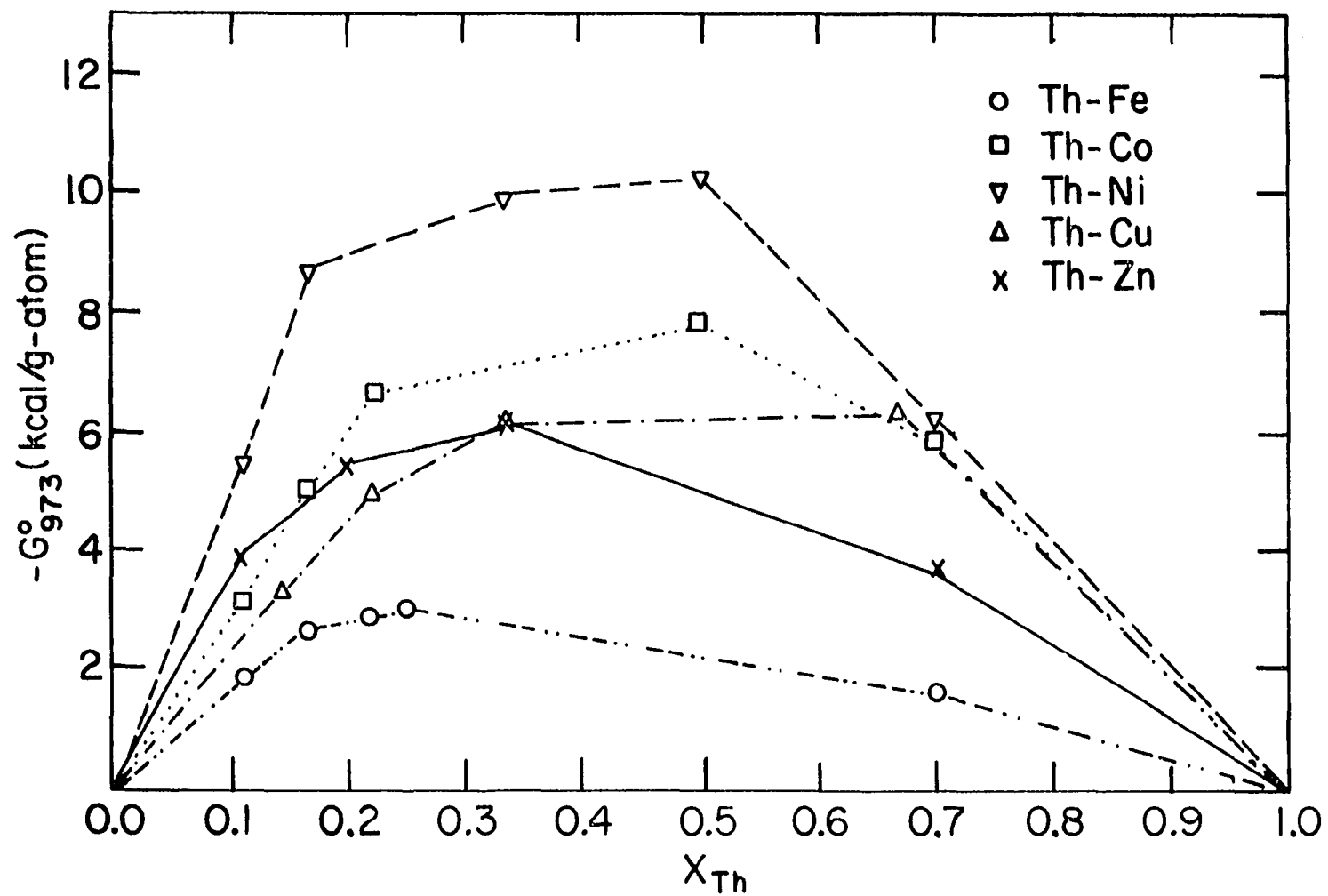


Fig. 4. Comparison of free energies of formation as functions of composition for the phases in the Th-Fe, Th-Co, Th-Ni (Skelton et al., 1970, 1971, 1973), Th-Zn (Chiotti and Gill, 1961), and Th-Cu systems (this work)

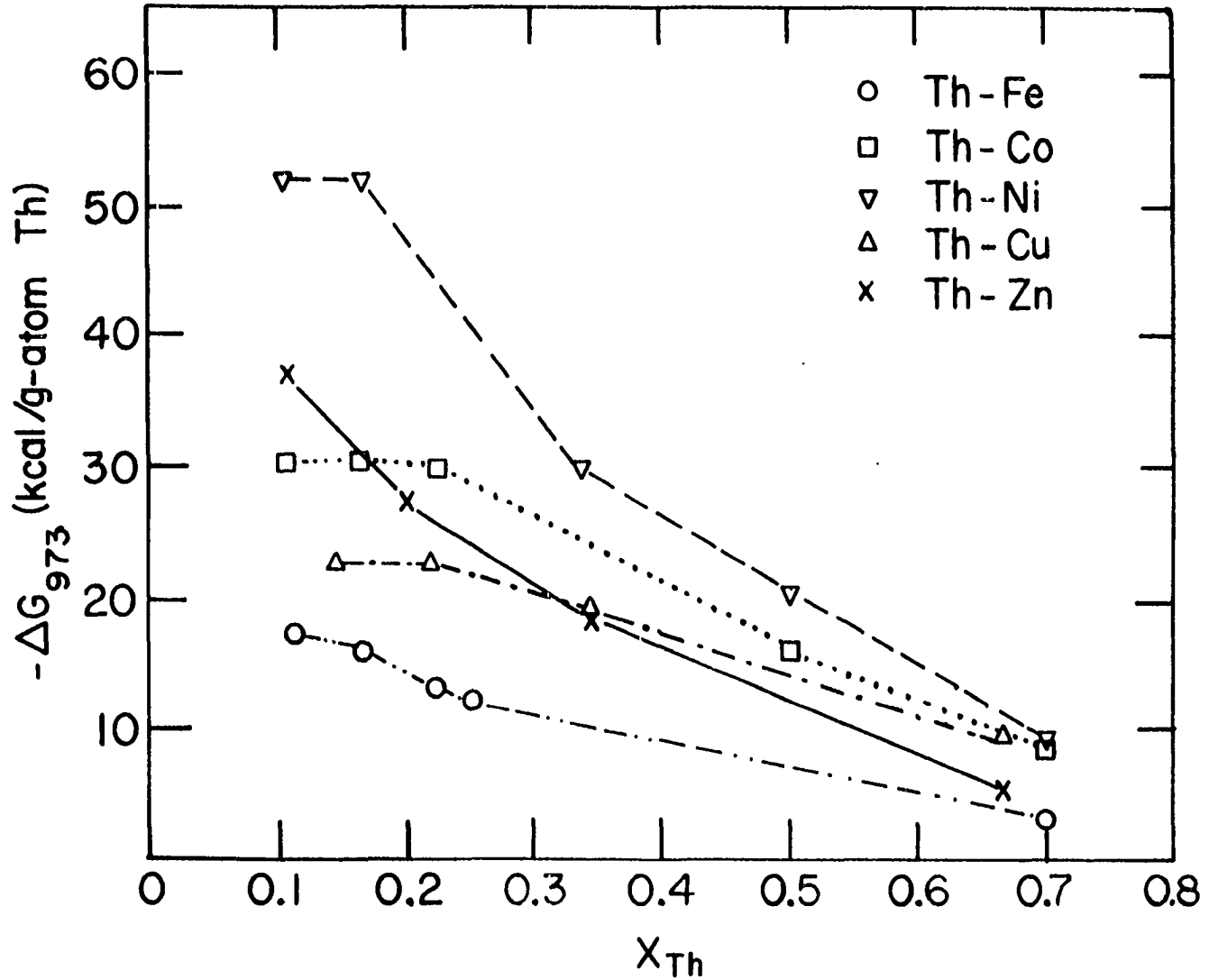


Fig. 5. Comparison of free energies of formation (kcal/g-atom Th) as functions of composition for the phases in the Th-Fe, Th-Co, Th-Ni (Skelton *et al.*, 1970, 1971, 1973), Th-Zn (Chiotti and Gill, 1961), and Th-Cu systems (this work)

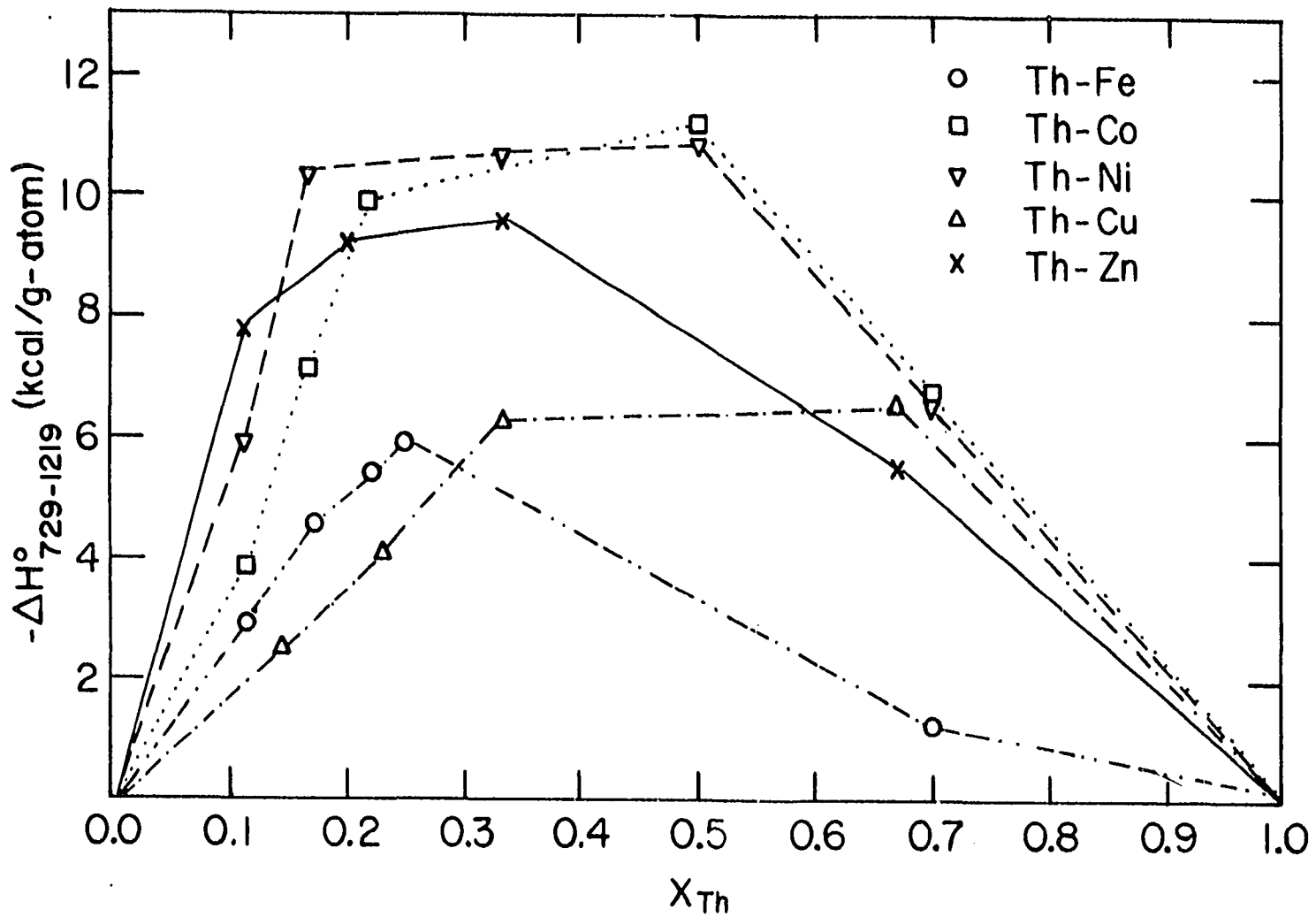


Fig. 6. Comparison of enthalpies of formation as functions of composition for the phases in the Th-Fe, Th-Co, Th-Ni (Skelton *et al.*, 1970, 1971, 1973), Th-Zn (Chiotti and Gill, 1961), and Th-Cu systems (this work)

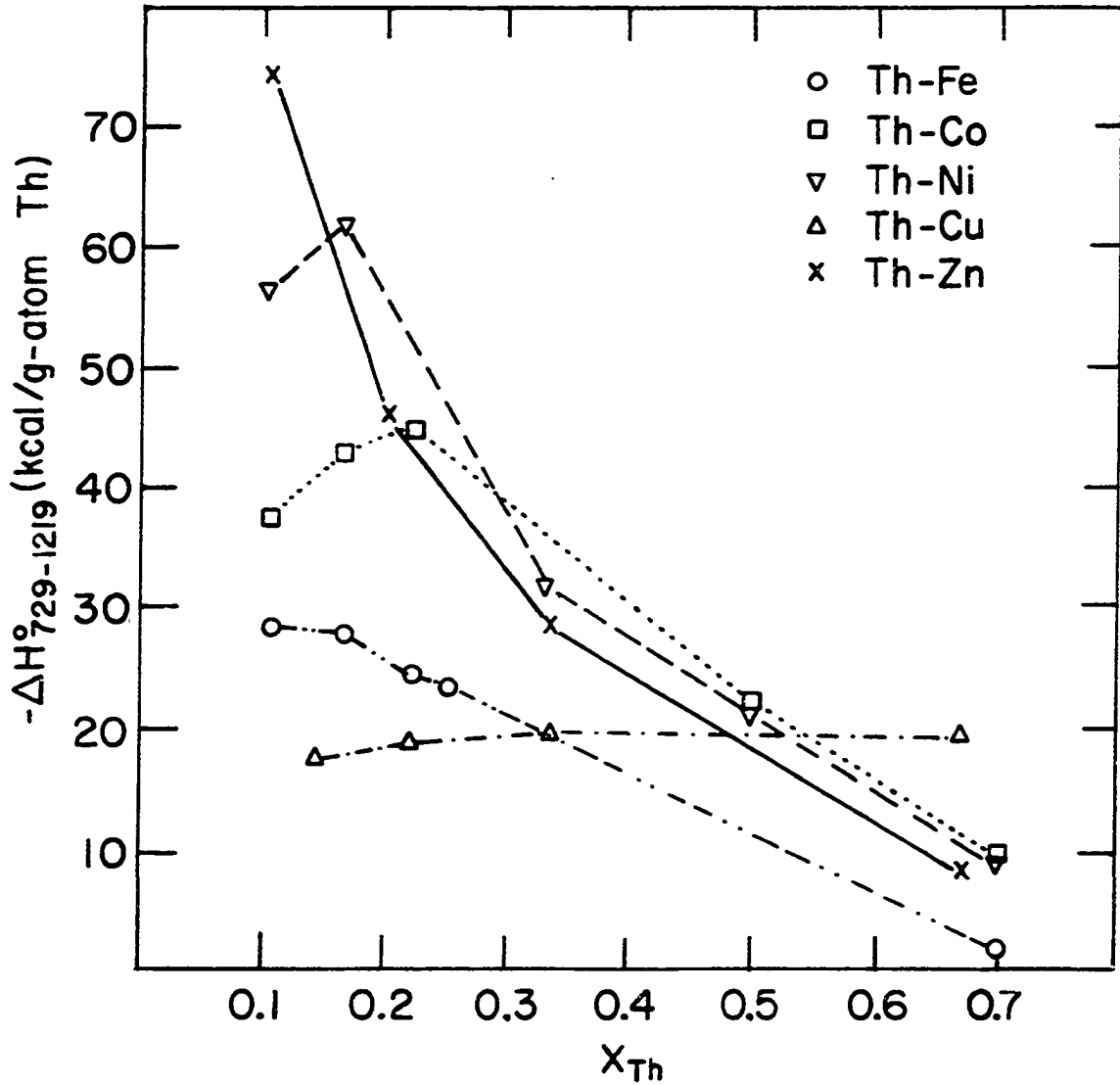


Fig. 7. Comparison of enthalpies of formation (kcal/g-atom Th) as functions of composition for the phases in the Th-Fe, Th-Co, Th-Ni (Skelton *et al.*, 1970, 1971, 1973), Th-Zn (Chiotti and Gill, 1961), and Th-Cu systems (this work)

constant within a given system, with values -18, -28, -41, -86, and -74 for the systems of Cu, Fe, Co, Ni, and Zn, respectively. The reversal of the Fe and Cu positions in the two series is likely associated with the small positive entropies of formation of ThCu_6 and $\text{ThCu}_{3.6}$. Only these phases and Th_7Fe_3 have positive entropies of formation, with the value for ThCu being essentially zero. Data for the Th-Rh, Th-Ru, and Th-Re systems show small negative entropies of formation are also the rule for these systems, and thus the positive values for Th_7Fe_3 , ThCu_6 , and $\text{ThCu}_{3.6}$ are atypical for thorium alloys.

Fig. 8 shows the mean ΔH values for thorium poor phases of constant thorium content as a function of the atomic number of the second element of the binary system. These values tend negative at Cr, and slightly positive at Mn. The Th-Cr system is reported to be a simple eutectic system (Carlson and Stevens, 1968) consistent with this trend. Although the Th-Mn system is not well established, Carlson and Stevens report the existence of the thorium-poor phases ThMn_{12} , $\text{Th}_4\text{Mn}_{23}$, and ThMn_2 . An investigation of the thermodynamics of formation of these phases to establish whether they complete the observed trends for the transition metals would be interesting.

Kubaschewski and Evans (1958) correlated the volume contraction which occurs on compound formation with the

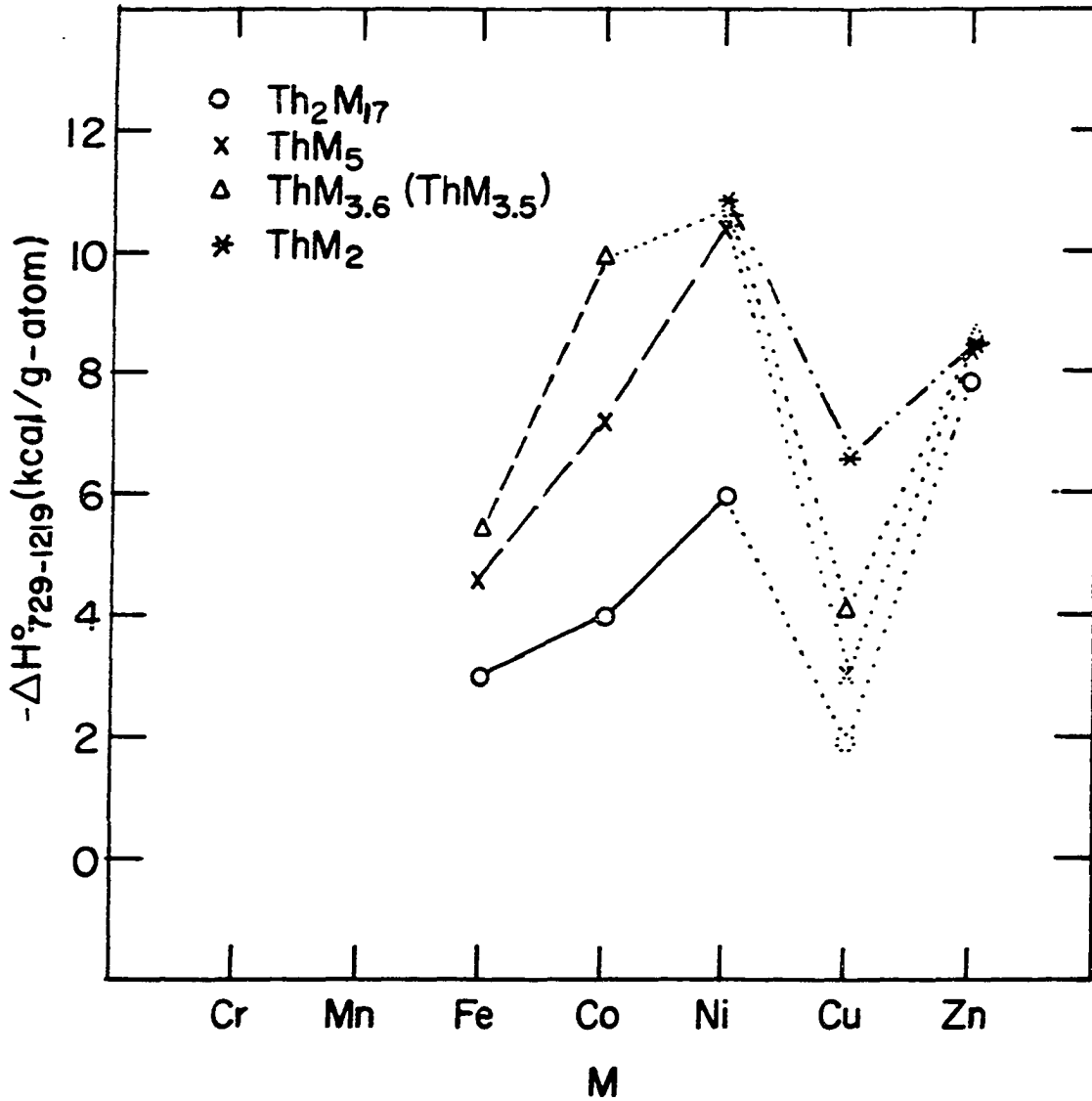


Fig. 8. Mean enthalpies of formation for thorium-poor phases Th-M as a function of the element M. Dotted datum points represent most negative limits for unstable phases

enthalpies of formation for many compounds. The data in Table IV indicate that the correlation fails to hold in the systems discussed here. Kubaschewski (1959) has since suggested that for many compounds, including CaCu_5 , the enthalpy of formation may be well approximated by assuming that the energy of attraction between atoms of the pure metals, represented by their heats of sublimation, is equally distributed over all interatomic bonds up to a distance of $2\sqrt{2}$ times the atomic radius and is inversely proportional to the bond distance. He further assumes that this energy is independent of whether the metal is pure or alloyed, and that the energy of attraction between two unlike atoms is the arithmetic mean of that obtained from their heats of sublimation. Effective coordination numbers, C^* , and enthalpies of formation are evaluated from the equations

$$C_A^* = \frac{\sum C_A (\sqrt{2} (2r_A) - d_A) / (\sqrt{2} - 1) 2r_A}{\sum C_{AB} (\sqrt{2} (r_A + r_B) - d_{AB}) / (\sqrt{2} - 1) (r_A + r_B)}, \quad (30)$$

and

$$-\Delta H = N_A L_A (C_A^*(\text{alloy}) - C_A^*(\text{metal})) / C_A^*(\text{metal}) + N_B L_B (C_B^*(\text{alloy}) - C_B^*(\text{metal})) / C_B^*(\text{metal}). \quad (31)$$

The results of these calculations for the phases of the Th-Fe, Th-Co, Th-Fe, Th-Co, Th-Ni, Th-Cu, and Th-Zn systems are tabulated in Table IV and are plotted as functions of thorium content in Fig. 9. Although errors on the order of 1 kcal/mole are to be expected in the calculated values due to

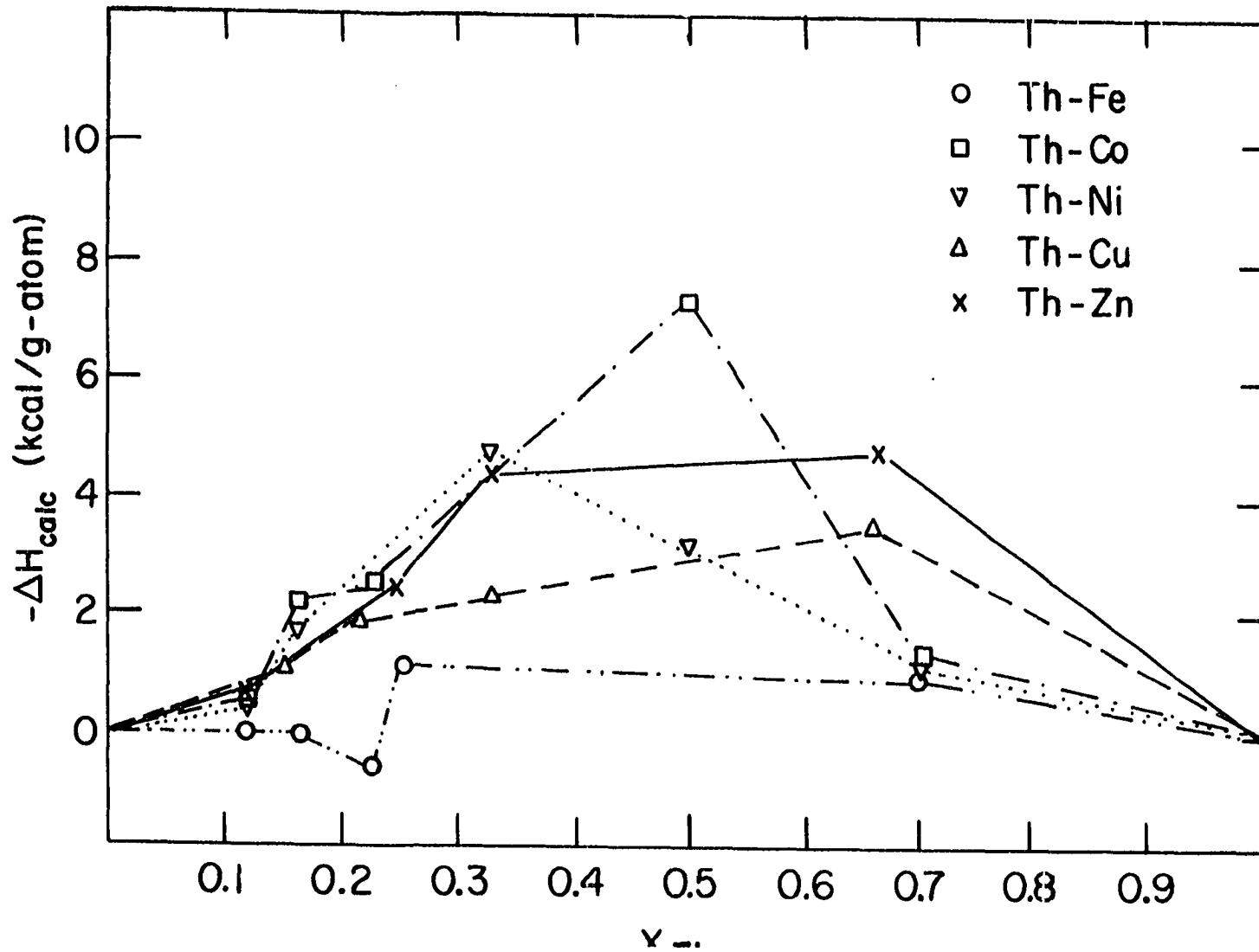


Fig. 9. Calculated enthalpies of formation for the phases in the Th-Fe, Th-Co, Th-Ni, Th-Cu, and Th-Zn systems

Table IV. Effective Coordination Numbers, Calculated Enthalpies of Formation, and Volume Contractions for the Intermediate Phases in the Th-Fe, Th-Co, Th-Ni, Th-Cu, and Th-Zn Systems

| Phase | C_A^* | C_B^* | $-\Delta H_{\text{calc}}$ | $-\Delta H_{\text{meas}}$ | $-\Delta V(\%)$ |
|----------------------------------|---------|---------|---------------------------|---------------------------|-----------------|
| Th ₂ Fe ₁₇ | 18.2 | 11.2 | 0.0 | 2.98 | -0.1 |
| ThFe ₅ | 17.7 | 10.8 | 0.1 | 4.59 | -1.4 |
| Th ₂ Fe ₇ | 15.8 | 9.9 | -0.6 | 5.46 | 0.2 |
| ThFe ₃ | 17.0 | 10.7 | 1.2 | 5.92 | 3.2 |
| Th ₇ Fe ₃ | 14.2 | 8.6 | 0.9 | 1.20 | -0.1 |
| Th ₂ Co ₁₇ | 19.4 | 11.9 | 0.4 | 3.94 | 0.1 |
| ThCo ₅ | 19.6 | 11.8 | 2.2 | 7.14 | 2.9 |
| Th ₂ Co ₇ | 18.4 | 10.9 | 2.5 | 9.98 | 4.7 |
| ThCo | 16.7 | 9.1 | 7.3 | 11.88 | 1.8 |
| Th ₇ Co ₃ | 14.7 | 8.6 | 1.3 | 6.71 | -2.0 |
| Th ₂ Ni ₁₇ | 19.6 | 11.7 | 0.4 | 5.93 | 1.2 |
| ThNi ₅ | 19.4 | 11.5 | 1.7 | 10.35 | 1.0 |
| ThNi ₂ | 19.0 | 9.8 | 4.8 | 10.68 | 3.1 |
| ThNi | 16.0 | 8.1 | 3.1 | 10.82 | -4.3 |
| Th ₇ Ni ₃ | 14.6 | 8.5 | 1.2 | 6.59 | -2.6 |
| ThCu ₆ | 18.5 | 11.5 | 1.1 | 2.50 | - .2 |
| ThCu _{3.6} | 18.1 | 10.7 | 1.8 | 4.09 | -1.8 |
| ThCu ₂ | 17.0 | 9.3 | 2.3 | 6.62 | -4.6 |
| Th ₂ Cu | 14.2 | 9.2 | 3.6 | 6.51 | -1.9 |
| Th ₂ Zn ₁₇ | 17.2 | 14.8 | 0.7 | 7.84 | 14.3 |
| ThZn ₄ | 17.3 | 12.3 | 2.5 | 9.20 | 7.6 |
| ThZn ₂ | 16.0 | 10.8 | 4.4 | 9.61 | 3.0 |
| Th ₂ Zn | 14.1 | 10.2 | 4.8 | 5.50 | 0.2 |

uncertainties in the parameters used in the computation, the disparity between the calculated and measured data attributes little validity to the application of these assumptions to the systems discussed here, particularly in the thorium-poor region where geometric factors were expected to dominate the bonding. For the thorium-rich phases, where there are few, if any, bonds between the transition metals, the agreement is quite acceptable for Th₂Zn and within a factor of two for Th₂Cu. The lack of agreement between the experimental data

and estimates based on geometric factors for those thorium-poor phases where the transition metal interactions with themselves and with thorium dominate the bonding suggests that perhaps the d-levels contribute strongly to the bonding.

Brewer (1967) has advanced an approach to the stability of transition metal structures which is founded on the so-called Engel correlation. This approach is basically a valence-bond model wherein a body-centered cubic structure is correlated with an electron configuration $d^{n-1}s$, the hexagonal close-packed structure with one s and one p electron ($d^{n-2}sp$), and the face-centered cubic structure is correlated with one s and two p electrons ($d^{n-3}sp^2$). Brewer has calculated effective bonding enthalpies for d and for s,p bonding electrons from sublimation enthalpies and from promotion energies derived from spectrographic data. The s,p bonding enthalpies increase as one moves to the right through the periodic table. The bonding enthalpies of the d electrons for the first transition series are much weaker than those of the s,p electrons. Further, the bonding effectiveness of a d electron decreases as the number of d bonds increases, reaching a minimum at five d bonds per atom, apparently owing to interference between the d bonds themselves. Fractional promotions are allowed, with the number of promoted d electrons chosen to optimize the bond energy gained with respect to the cost in terms of promotion energy.

Brewer (1967) has tabulated bond energies for transition elements in simple cubic and in hexagonal close-packed structures: the lack of data for promotional energies precluded such calculations for face-centered cubic structures. The valencies and bond energies calculated for Fe, Co, Ni, Cu, and Zn are presented in Table V. The trends in the measured enthalpies (Fig. 8) are, with the exception of Cu, in general accord with the bonding energies in Table V. If Cu is considered to behave as a monovalent metal and

Table V. Bonding Energies of the $d^{n-2}sp$ Valence State in the Hexagonal Close-packed Structure (after Brewer, 1967)

| | Fe | Co | Ni | Cu* | Zn |
|-----------------------------------|-----|-----|-----|-----|-----|
| Number of bonding electrons/atom | 6 | 5 | 4 | 2.4 | 2 |
| Bonding energy (kcal/mole) | 154 | 169 | 171 | 135 | 124 |
| * $d^{9.3}sp^{0.7}$ valence state | | | | | |

retain the ground state $d^{10}s$, the bond energy calculated by Brewer is 61 kcal/mole, which is more in accord with the trends in Fig. 8. Thus the thorium-poor phases in these systems seem to be stabilized by the interactions of d electrons rather than by geometric factors.

SUMMARY

The thermodynamics of formation of the four intermediate phases in the Th-Cu system, ThCu_6 , $\text{ThCu}_{3.6}$, ThCu_2 , and Th_2Cu , have been evaluated from electromotive force measurements. Measurements were made in the temperature range 729-1219 K with a solid-state emf cell employing CaF_2 as the electrolyte. The free energies and enthalpies of formation are essentially constant, in units of kcal/g-atom Th, for the thorium-poor phases in this system, a feature shared with the Th-Fe, Th-Co, and Th-Ni systems. The measured enthalpy values do not coordinate well with volume contractions on phase formation or with calculations based upon effective coordination numbers in these phases where the interatomic bonds are between thorium and the transition metal or between the transition metal atoms themselves. The trend in magnitude of the enthalpies of formation in the thorium-poor phases in the Th-Fe, Th-Co, Th-Ni, and Th-Zn phases is in accord with the bonding energies for the $d^{n-2}sp$ valence states for the respective transition metals (and for zinc): the value for the Th-Cu system is lower, corresponding more closely to the bonding energy of the monovalent $d^{10}s$ state for copper. The structures of these phases thus appear to be stabilized by the interaction of the d electrons in bonding rather than by geometric factors, with the d electron contribution being less pronounced for copper.

ACKNOWLEDGEMENTS

The author sincerely appreciates the guidance and counsel of Dr. J. F. Smith, who suggested the research topic. The thorium metal which was used in this investigation was kindly supplied by Dr. D. T. Peterson and Mr. F. A. Schmidt. The alloys were arc-melted by Mr. E. J. Ritland.

LITERATURE CITED

- Aronson, S. (1964), Nuclear Metallurgy, 10, 247.
- Aronson, S. (1967), J. Inorg. Nucl. Chem., 29, 1611.
- Aronson, S. and Auskern, A. (1966), Proceedings of the Symposium on Thermodynamics, Vienna, 22-27 July 1965, Vol 1, International Atomic Energy Agency, Vienna, p 165.
- Aronson, S. and Sadofsky, J. (1965), J. Inorg. Nucl. Chem., 27, 1769.
- Baenziger, N. C., Rundle, R. E., and Snow, A. I. (1956), Acta Crystallogr., 9, 93.
- Bailey, D. M. (1973), J. Less-Common Metals, 30, 164.
- Bailey, D. M. and Kline, G. R. (1971), Acta Crystallogr., B27, 650.
- Berlin, B. (1972), J. Less-Common Metals, 29, 337.
- Brewer, L. (1967), in Phase Stability in Metals and Alloys, Rudman, P. S., Stringer, J., and Jaffe, R. I., Eds., New York, McGraw-Hill, pp39-61.
- Buschow, K. H. J. and van der Goot, A. S. (1970), J. Less-Common Metals, 20, 309.
- Carlson, O. N. and Stevens, E. R. (1968), AEC Report IS-1752, Ames, Ia.
- Chiotti, P. and Gill, K. J. (1961), Met. Soc. AIME Trans., 221, 573.
- Flengas, S. M. (1973), High Temp. - High Press., 5, 551.

Frenkel, J. (1926), Z. Phys., 35, 652.

Grube, G. and Botzenhardt, L. (1942), Z. Elektrochem., 48, 418.

Guertler, W. (1940), Metallwirtschaft, 19, 435.

Hinze, J. W. and Patterson, J. W. (1973), J. Electrochem. Soc., 120, 96.

Jost, W. (1933), J. Chem. Phys., 1, 466.

Kiukkola, K. and Wagner, C. (1957), J. Electrochem. Soc., 104, 308 and 379.

Kleykamp, H. and Murabayashi, M. (1974a), J. Less-Common Metals, 35, 227.

Kleykamp, H. and Murabayashi, M. (1974b), J. Less-Common Metals, in press.

Kubaschewski, O. (1959), in The Physical Chemistry of Metallic Solutions and Intermetallic Compounds, London, Her Majesty's Stationery Office, paper 3C.

Kubaschewski, O. and Evans, E. L. (1958), Metallurgical Thermochemistry, New York, Pergamon, p 204.

Magnani, N. J., Skelton, W. H., and Smith, J. F. (1969), Nuclear Metallurgy, 15, 727.

Markin, T. L. (1968), in Electromotive Force Measurements in High Temperature Systems, Alcock, C. B., Ed., New York, American Elsevier, pp 91-97.

McMasters, O. D., Gschneidner, K. A., and Venteicher, R. F. (1970), Acta Crystallogr., B26, 1224.

- Murray, J. R. (1955-56), J. Inst. Metals, 84, 91.
- Oriani, R. A. (1956), J. Electrochem. Soc., 103, 194.
- Pauling, L. (1960), The Nature of the Chemical Bond, 3rd ed., Ithaca, N. Y., Cornell University Press, p 93.
- Raub, E. and Engel, M. (1943), Z. Elektrochem., 49, 487.
- Rezukhina, T. N. and Pokarev, B. S. (1971), J. Chem. Thermodynamics, 3, 369.
- Runnals, O. J. C. (1956), Can. J. Chem., 34, 142.
- Schiltz, R. J., Jr., Stevens, E. R., and Carlson, O. N. (1971), J. Less-Common Metals, 25, 175.
- Schmalzried, H. (1972), in Metallurgical Chemistry, Kubaschewski, O., Ed., London, Her Majesty's Stationery Office, paper 1.4.
- Skelton, W. H., Magnani, N. J., and Smith, J. F. (1970), Met. Trans., 1, 1833.
- Skelton, W. H., Magnani, N. J., and Smith, J. F. (1971), Met. Trans., 2, 473.
- Skelton, W. H., Magnani, N. J., and Smith, J. F. (1973), Met. Trans., 4, 917.
- Smith, J. F. (1974), J. Nucl. Mater, 51, 136.
- Steeb, S., Godel, D., and Lohr, C. (1968), J. Less-Common Metals, 15, 137.

Steele, B. C. H. (1968), in Electromotive Force Measurements in High Temperature Systems, Alcock., C. B., Ed., New York, American Elsevier, pp 3-27.

Wagner, C. and Schottky, W. (1930), Z. Phys. Chem., B11, 163.

Wood, D. H., Cramer, E. M., and Wallace, P. L. (1970), AEC Report UCRL-72225, Livermore, Calif.