RECENT THERMOPHYSICAL DEVELOPMENTS ON NUCLEAR MATERIALS*

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The current status of chemical thermodynamics of the actinide and lanthanide chalcogenides including high-temperature adiabatic calorimetry of these important compounds (with stress on their electronic, magnetic, order–disorder, disproportionation transitions), as well as the spin-wave magnetic contributions, is reviewed. Schottky anomalies (and the information they yield on crystal-field level splitting), definitive resolution of lattice and magnetic contributions for both first- and second-order phase transitions, and other unusual aspects of phase behavior are considered. Unpublished work on the uranium trioxides, the non-stoichiometric and metastable tetrauranium octaoxides, the uranates, etc. is included. The close parallel between actinide and lanthanide behavior evidenced by our recent unpublished thermal studies on the actinide and lanthanide trichlorides, and hexaborides is emphasized.

On passe en revue l'état actuel de la thermodynamique chimique des chalcogeniures d'actinides et de lanthanides en incluant la calorimétrie adiabatique à haute température de ces importants composés et en insistant sur leurs transitions électronique, magnéti-que, ordre–désordre aussi bien que sur les contributions magnétiques onde-spin. Les anomalies de Schottky (et l'information qu'elles fournissent sur l'écart de niveau champ-cristal), la résolution définitive des contributions réticulaire et magnétique à la fois pour les transformations de phase de premier et de second ordre et d'autres aspects inhabituels du comportement des phases sont considérés. Les recherches non publiées sur les trioxydes d'uranium, les octaoxydes d'uranium tétravalent non-stoechiométrique et métastable sont incluses. On met l'accent sur le parallélisme étroit entre le comportement des actinides et des lanthanides mis en évidence par nos études thermiques récentes non publiées sur les trichlorures d'actinide et de lanthanide et des hexaborures.

Es wird ein Überblick über den gegenwärtigen Stand der chemischen Thermodynamik der Chalkogenide der Actinoiden und Lanthanoiden einschliesslich der adiabatischen Hochtemperaturkalorimetrie mit Hinblick auf deren elektronische, magnetische, Ordnungs-Unordnungs- und Disproportionierungs-übergänge sowie magnetische Spinanteile gegeben. Es werden die Schottky-Anomalien und die Informationen, aus denen sich die Kristallfeldaufspaltung ergibt, ferner die Aufspaltung der Gitter- und mag-netischen Anteile an Phasenumwandlungen erster und zweiter Ordnung und andere ungewöhnliche Aspekte des Phasenverhaltens in Betracht gezogen. Unveröffentlichte Ergebnisse an Urantrioxiden, unstöchiometrischen und metastabilen Tetrauranoctoxiden, Uranaten, usw. ergänzen die Arbeit. Auf das sehr ähnliche Verhalten zwischen den Actinoiden und Lanthanoiden aufgrund neuerer unveröffentlichter thermischer Untersuchungen an Trichloriden und Hexaboriden der Actinoiden und Lanthanoiden wird hingewiesen.

1. Introduction

Although substantial progress has been made in approximately the last decade on the investigation of the chemical properties of the metals and compounds of the actinides, of the lanthanides, and of the transi-tion element fission products and some very interest-ing measurements have been reported, the total scope implied by the title "Nuclear Materials" is too broad to encompass in a brief presentation. Consequently, I have chosen to discuss primarily thermophysical measurements on these substances with decreasing emphasis in the order stated.

Much of the related work on other materials of nuclear import will remain uncovered for lack of time and even within the area of major emphasis some choice had to be made in the presentation of the most interesting work on these groups of materials.

Unquestionably, many important contributions

have been slighted, and emphasis has been placed on
the areas of greatest familiarity to the author. In
many instances, lacunae are pointed out but one
cannot escape the feeling that we are still overlooking
a fertile field of potential investigation spiced with
many intriguing prospects for future endeavor. On
the other hand, practical thermodynamicists cannot
be other than concerned with the fact that in this
country at least many of the most productive centers
of cryogenic and higher temperature thermophysical
research (particularly those that have a tradition of
involvement with nuclear materials) have been curtail-
ed, eliminated, or otherwise handicapped by the
present decline of scientific financing. Perhaps we
must look over the next few years with increasing
interest at the high productivity which has become
increasingly characteristic of calorimetric and thermo-
dynamic scientists in Japan, in the Soviet Union, and
perhaps soon on the Chinese mainland. In any event,
I would like to express my appreciation for the op-
portunity of the interchange which is provided by the
present Seminar. Before becoming too involved in the
aspects of the scientific problem, I should like to
suggest that it would be advantageous for thermo-
dynamicists and phase behavior scientists involved
with the several national atomic commissions, with
the International Atomic Energy Agency or within
international scientific unions to concern themselves
with the scientific and technological applications of
thermodynamic and phase behavior data on nuclear
materials. In particular, careful thought should be
taken to achieve the following goals:

(1) To extend and improve technological and
other practical applications of thermodynamic princi-
ples and data;

(2) To avoid excessive duplication of endeavor and
to outline areas where experimental research on ther-
modynamic properties might well be intensified ad-
vantageously;

(3) To extend and to streamline the compilation
of thermodynamic properties of important materials
in the nuclear energy program; and

(4) To make a concerted effort in the development
of a greater understanding of phase stability in rela-
tion to bond structure for the prime purpose of im-
proving methods for the estimation of thermo-
dynamic data.

Such an endeavor would serve the multiple pur-

poses of making potential users more aware of the
importance of thermodynamics in solving technologi-
cal problems in the nuclear area, emphasize problems
in the compilation and accessibility of such data,
and perhaps accelerate the production of the more
urgently needed items by providing potential
sponsors with a documented argument for the ur-
gency of attention to these areas. An initiatory en-
deavor to distribute such a discussion-report has al-
ready been achieved for high-temperature metallurgi-
cal systems [1].

Within the United States, the national efforts in
data evaluation, both in the public and the private
domain, seem not to be expanding; economic limita-
tions and pressures to recover operational costs are
affecting the level of operations unfavorably. How-
ever, the National Data Advisory Board attempts to
create more awareness for data evaluation needs for
research and development, to increase the involve-
ment of private industry, and — through the United
States National Committee for CODATA — to pro-
mote integration of national and international en-
deavors in all the physical sciences.

2. Significantly improved calorimetric techniques

Although calorimetric techniques generally im-
prove gradually rather than discontinuously, several
developments in recent years are of sufficient signifi-
cance to merit special attention.

One of the first of these is the laser calorimetry
developed by Professor Takahashi and his colleagues.
This is a tremendously exciting technique and one of
which I shall not say more since he is here and will
speak on the subject himself.

2.1. High-frequency relaxation method

A second method of heat-capacity measurement
which bears consideration is that of the high-fre-
quency relaxation (HFR) method for measuring the
magnetic specific heat, C. The basic method, original-
ly devised by Casimir and du Pré, uses purely magnetic
measurements to determine C without the usual un-
certainty due to the resolution of the generally much
larger lattice specific heat, and it thus allows accurate
estimates over wide ranges of temperature. The recent

development of cryogenic tunnel diode oscillators has been used to improve and extend this method by Skjeltorp and Wolf [2]. At temperatures high compared with the onset of magnetic ordering, C can be fitted to a series expansion of the form

$$C/R = C_2/T^2 + C_3/T^3 + \ldots,$$

where the parameters depend on the number of magnetic spins and in suitable cases can be related to microscopic spin–spin interaction constants. Additional information can also be obtained from the field dependence of C, which can be related to the temperature dependence of the isothermal susceptibility. Examples of materials for which this technique has been used successfully include rare earth halides, hydroxides and garnets, but many other lanthanide and actinide materials should satisfy the conditions under which this method can be applied. It has already been applied to the study of the magnetic and thermal properties of $Gd(OH)_3$, $Tb(OH)_3$ and $GdCl_3$ [3–5].

2.2. Low-temperature laser calorimetry

A ^3He calorimeter with rapid responses, useful for the measurement of small heat capacities below 1 K has also been reported by Golbrecht et al. [6]. This calorimeter employed a superconducting heat switch, achieved thermal equilibrium within 1 to 2 s with metallic samples and permitted a measurement of heat capacities as small as 30 $\mu J/K$ with a precision of 1% above 0.4 K at a rate of 80 heat capacity points per hour.

Heat capacities one or two orders of magnitude smaller than those typically measured in this range were involved during study on the antiferromagnetic ordering of praseodymium hexaboride in the range 2 to 20 K. Lee et al. [7] initially used the pulse technique of Morin and Maita [8]. Lee found that the heat pulse method in the vicinity of the Néel point (near 7 K) where the heat capacity was large, required correspondingly long times to establish thermal equilibrium after application of heat pulse. In order to ascertain the possible presence of an isothermal absorption of heat on a small (30 mg) sample, a dynamical temperature relaxation method employing heating by laser beams was developed by Lee et al. [7]. This

involves the use of laser radiation to heat the sample – a technique which had been pioneered at higher temperatures [9] in Japan.

In the experimental arrangement employed, a silicon bolometer with a thin diffusion-doped layer on one side was employed as temperature sensor. At low temperatures the entire wafer except the diffused layer is insulating. The layer resistance was used as a means of indicating temperature of the sample (which was bonded to the insulating side by ultrasonic soldering). Electrical contact and mechanical support for the bolometer were established by means of fine gold wires thermally anchored to a copper block the temperature of which could be varied with a heater and sensed with a thermocouple. Both sample and bolometer were heated by a laser beam directed down a light pipe into the evacuated cryostat which was immersed in liquid helium.

In Lee's method the laser beam is switched on suddenly and the time constant of the resulting thermal relaxation is used to deduce the heat capacity. By operating a bolometer in a constant current mode, Lee was able to describe the small exponentially-saturating temperature produced by the incident radiation in terms of a time constant. A determination of the time constant then provides an absolute measurement of heat capacity provided thermal equilibrium between bolometer and sample is established in a time short compared to τ.

To verify that this was indeed the case a variant of the ac temperature technique of Sullivan and Seidel [10] in which the laser radiation is chopped at fixed frequencies and the ac component of the bolometer voltage is detected with a lock-in amplifier was used. The frequency dependence of the ac signal provides a measure of the internal time constant.

2.3. High-pressure calorimetry

One of the least popular variables among calorimetrists of all temperature persuasions seems to be pressure. However, a simple high-pressure calorimeter has been devised by Smith and Phillips [11]. This calorimeter consists of a small piston and cylinder arrangement with a mass of about 150 g constructed entirely from high-purity Cu–Be alloy (2.1 wt % Be) which was heat-treated to full hardness. The sample is placed in a close-fitting Teflon sleeve between two

Teflon discs. The cell is supported by an external screw-on collar and pressures applied to the sample at room temperature in a standard press. At the required pressure, the locking screw is tightened down onto the internal piston and the calorimeter is removed from the press and is installed in a ^{3}He cryostat. Since the heat capacity of the sample comprises typically only 3 to 5% of the total measured heat capacity, reasonably high precision is needed in the measurement of heat capacities of the cell both filled and empty. This device has been used for studies of the superconductivity of α-uranium to pressures as high as 10 kbar and on the electronic properties of a α-Ce at pressures as high as 11 kbar.

2.4. Computerization

Science, like haute couture, has its fashions. Automation these days enables you to load your calorimeter, press the button, go to lunch or to Monte Carlo — depending on the duration of the experiment and one's financial status. When you do come back to the desk you may pick up the computer output with all the relevant data transposed into a format suitable for printing the tables of data and possibly of derived thermodynamic functions. In most instances, some degree of semi-automatic and semi-manual operation seems to be the preferred solution but in some instances an on-line computer may actually be used to operate the calorimeter.

The treatment of heat capacity data by digital computers is rapidly becoming the rule rather than the exception and is typified by the methods employed by Osborne et al. [12].

3. Lanthanide compounds

Although actinide compounds have an obvious nuclear technological import, data on the corresponding lanthanide compounds provide a very useful extension of parameters as well as a basis for understanding the more complex relationships existing over truncated ranges in the actinides. For example, the five 5f–6d electronic orbital problem makes interpretation of the thermophysical, electronic, and magnetic data especially difficult. The complications introduced in both series by the conduction electrons

hinders facile interpretation. The thermal properties of the lanthanide hexaborides, for example, are shown to exhibit largely unexplained anomalies and like many of the other lanthanide compounds discussed, offer interesting possibilities for technological and possibly nuclear applications. The availability of a fairly recent summary of the thermodynamic and magnetic properties of the lanthanide chalcogenides, the pnictides and binary semi-metallic compounds [13] as well as an excellent critical assessment of the enthalpies, entropies, and Gibbs energies of formation of the lanthanide oxides compiled by Holley et al. [14] largely eliminates need for further comments. Unfortunately, to the best knowledge of the author, this interesting series of reviews under the editorship of Professor Eyring has not been continued in recent years..

3.1. Lanthanide sesquioxides

Although resolution of the levels resulting from splitting of the ionic ground state by the crystal fields is usually achieved by spectroscopists, on occasion the cryogenic calorimeter can do yeoman service, especially in the absence of optical grade samples.

Subsequent to earlier heat capacity measurements on La(III) and on Nd(III) oxides and deduced crystal field splitting of the ground electronic level of the former sesquioxide, the spectrum of Nd(III) ion in a La(III) oxide host was observed by Henderson et al. [15]. They report five crystal field lines for the ground state ($^4I_{9/2}$) at 0, 23, 84, 253, and 496 cm^{-1}. The first two excited levels are in excellent accord with corresponding values deduced from heat capacity data alone (0, 21, 81 and 400 cm^{-1}), and the center of density of the higher levels also corresponds. However, the interpretation of the electronic heat capacity data of the cubic Gd(III), Dy(III), Ho(III), and Er(III) oxides was hampered by the lack of spectral data. These cubic lattices have two non-equivalent types of cation sites. Three-fourths of the cations have C_2 symmetry. The remaining cations possess C_{3i} symmetry. The spectra reported for Dy(III) [16], Er(III) [17, 18], and Tm(III) ions [18] with C_2 symmetry in Yt(III) oxide or in single crystal Ln(III) oxides together with heat capacity data permitted derivation of the lattice heat capacity for the cubic oxides from Gd_2O_3 to Lu_2O_3
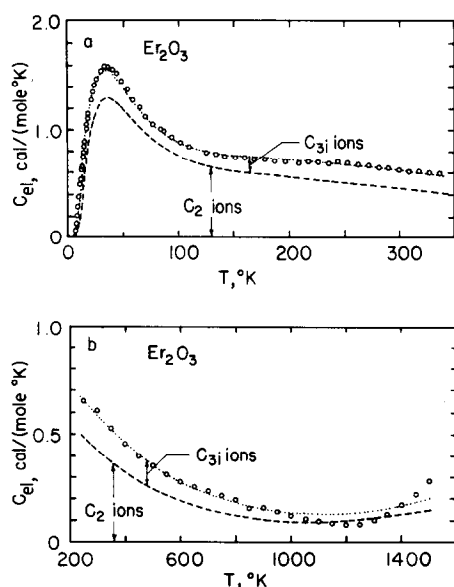
Fig. 1. Schottky (excess) heat capacity of Er_2O_3 [19]. In fig. 1a the circles represent data from this laboratory. The dashed curves represent the calculated electronic heat capacity of the C_2 ions based on the spectroscopic data of Kisliuk et al. [17], and Gruber et al. [18]; the dotted curve shows total electronic heat capacity by adding the contribution for the C_{3i} levels. In fig. 1b the circles represent heat capacities from enthalpy increment determinations of Pankratz and King, and the curves have the same significance.

and energy levels for the C_{3i} ions in Dy_2O_3, Er_2O_3 and Tm_2O_3 [19]. As an example of the success of the method consider Er_2O_3 [19] as represented in fig. 1. Contributions to the electronic heat capacity, C_{el}, based on spectroscopic levels reported for the C_2-type ions in Er(III) oxide [17, 18] consisting of doublets at O, 39, 76, 89, 158, 258, 495, and 500 cm^{-1}, are represented by dashed curves in fig. 1 which depicts C_{el} for the low-temperature region. These values were derived by subtracting the lattice contribution from the apparent heat capacities. The C_{el} remaining after removal of the contributions of the C_2 ions is attributed to the levels in the C_{3i} ions. The levels and their degeneracies are deduced in part from the position and magnitude of the Schottky peaks in the observed C_{el} (for separations of less than 100 cm^{-1}) and in part from the splittings of the ground state term by fourth- and sixth-order terms of cubic crystal fields. The levels thus derived are doublets at 0, 12, 50, 55, 150, and 450 cm^{-1} and a quar-

tet at 550 cm^{-1}. These correspond most closely to the levels in a cubic field with a ratio of sixth- to fourth-order terms (V_6/V_4) of -0.25. The Γ_8 level is split to 12 and 50 (or 55) cm^{-1}, and the second Γ_8 level is split to 150 and 450 cm^{-1}. The C_{el} data require levels at 12, 50, and 55 cm^{-1} ($\pm$ 10% of ΔE).

On the high-temperature aspects, the enthalpy determinations of Tsagareisheili are of considerable interest. Many of these extend up to 1600 K and they include the sesquioxides of lanthanum, lutetium [20], yttrium and cerium (dioxide) [21], scandium [22], gadolinium [23], samarium and europium [24], and erbium [25].

Enthalpies of formation of lanthanide sesquioxides have also been determined recently at the Los Alamos Scientific Laboratory under the direction of Drs. C.E. Holley, Jr. and E.J. Huber. Because Dr. Holley is at this meeting, he will present this work himself, and since much of it has already been reviewed [14], I will make no further comments on it except to say that the data have been of great utility in ascertaining the relative stabilities of the B and C forms of some of the sesquioxides [26].

3.2. Lanthanide chalcogenides

Cryogenic heat capacities have been reported for NdS, LaSe, LaTe and for lanthanide sesquichalcogenides [27–31] and for lanthanide chalcogenides of the formula Ln_3Ch_4 [32]. High-temperature enthalpies of the europium chalcogenides have been determined to 1725 K [33].

3.3. Lanthanide halides

Thomas Deline has completed measurements between 5 and 350 K on europium tribromide in collaboration with Professor John Haschke and the present author [34]. No anomalous behavior was observed over the temperature region in question although there is every expectation that transitions will occur at lower temperatures. James Sommers is undertaking a study of an extensive series of the lighter lanthanide trichlorides over the same range of temperature. Preparation of the compounds is well underway, but no actual measurements have as yet been made. Except for measurements made in the vicinity of 1–2 K by Colwell [35] together with

high-temperature enthalpy-type measurements by
Bredig [36] and his colleagues, little thermophysical
work has been done on the lanthanide halides. It is true
that some heat capacity measurements have been on
hydrated materials [37] and these have been analyzed
by Cobble for estimates of the thermodynamic prop-
erties [38].

Recent magnetic studies have revealed canted
antiferromagnetic ordering of the gadolinium tri-
chloride moments below 2 K [39] as well as some
correlation (and lack thereof) between the magnetic
and thermal properties of the trihalides [40]. Ther-
mal studies of entropies and crystal field splittings
have been reported for four of the trichloride hexa-
hydrates [37]. Higher temperature studies include
vaporization behavior, phase equilibria and thermo-
dynamic properties [41], enthalpy of fusion of SmF_3
[42], enthalpies of seven trifluorides [43], of the
vapor formation of several trichlorides [44] and
oxychlorides [45] as well as high-temperature ther-
modynamic properties of fluorides [46] and en-
thalpies of formation of fluorides [47].

3.4. Lanthanide hexaborides

These electrically conducting substances pose
significant problems in the interpretation of their
thermal anomalies and consequently of their thermo-
dynamics. The heat capacity of LaB_6 is of normal
sigmate behavior without thermal anomalies; the
other hexaborides studied all show cooperative, anti-
to paramagnetic λ-type transitions near 10 K fol-
lowed by complex Schottky transitions with maxima
between 20 and 80 K [48]. The resolution of the
magnetic and electronic contributions for the LnB_6's
was achieved by means of the heat capacity of
diamagnetic LaB_6 as an estimate of the lattice vibra-
tional heat capacity. For NdB_6, the Schottky anoma-
lies were resolved in terms of energy levels (2, 4, 4 at
230 and 640 cal/mole K) [49] generated by the crys-
tal field splitting of the ten-fold degenerate ground
state of the assumed Nd(III) ions [4]. The data on
PrB_6 and CeB_6 (λ-transition at 7 K, Schottky at
35 K) appear to be interpretable on a basis similar to
that for NdB_6 [48].

However, the results for GdB_6 (λ-anomaly at
16 K, Schottky maximum at 30 K corresponding to a
splitting of 61.3 cm^{-1}) are inconsistent with the
much smaller expected crystal field splitting of an
$^8S_{7/2}$ ground state. No cogent explanation of the
anomaly has yet been postulated. The total transi-
tional entropy in GdB_6 and other properties (lattice
parameters, Mössbauer and adsorption spectra, mag-
netic susceptibility, etc.) cast considerable doubt that
lanthanide metals are in fact in III oxidation states in
some of the hexaborides. Since EuB_6, Yb_6, SmB_6,
and the alkaline earth hexaborides all contain divalent
metal ions, this state may obtain at low temperatures
in other lanthanide hexaborides [50].

Further interesting work on these materials in-
cludes the unpublished data of Westrum et al. [34],
the low-temperature heat capacities determined at
Talence [51] as well as the less quantitative work
reported by Geballe et al. [52] and by Matthias
[53].

3.5. Lanthanide pnictides

Among the most interesting studies reported on
these substances are the low-temperature heat capac-
ities which exhibit Schottky-type thermal anomalies
in some of the lanthanide bismuthides and anti-
monides; these anomalies are among the crystal field
effects reported by Wallace [54]. From low-tempera-
ture studies on the electrical and magnetic properties
of lanthanide nitrides [55] and the heat capacity
from 1.7 to 270 K [56], the spontaneous magnetiza-
tion and the magnetic heat capacity below the order-
ing temperatures have been evaluated as well as the
splitting of the ground-state multiplet. Thermo-
dynamic functions have been evaluated [34] from
these data.

3.6. Miscellaneous

Developments in the chemical thermodynamics of
the lanthanides have been discussed [57] and the
estimation and the evaluation of the entropies for
related compounds provided. Optical spectral studies
of low 4f levels of the lanthanides have been sum-
marized by (the late) G.H. Dieke [58].

The status of thermal and thermochemical data
has been evaluated for the semi-metallic compounds
of both lanthanides and actinides [59].

4. Thermodynamics of the actinides

4.1. Metals

Data on the heat capacity of uranium [60–62], on neptunium [63], and on plutonium-242 [64–66] have been reviewed by Mendelssohn [67] and the values for thorium and protactinium included.

4.2. Oxides

The definitive paper on low-temperature heat capacity of uranium dioxide establishes the λ-type anomaly at 30.44 K [68]. The data are compared with neutron scattering results. A number of recent studies extend high-temperature enthalpies to the melting point [69–72]. Two high-precision studies by different techniques [73, 74] are remarkable in their close accord although done independently by different techniques. Enthalpy data on the gaseous phase have been fit to a theoretically derived equation [75].

Among the several studies dealing with the interesting thermodynamic properties of U_4O_9 are the three indicated here [76–78]. High-temperature transformations in lanthanide oxides and related thermophysical information have been summarized

and reviewed by others [79–81]. High-temperature thermodynamic properties of some uranium oxides have been ascertained from EMF cell measurements in Rumania [82]. The same laboratory has reported high-temperature enthalpy and related thermodynamic functions on stoichiometric and non-stoichiometric uranium oxides [83] but it is difficult to correlate these results with other data reported in the literature.

High-temperature enthalpy data to 1000 K on U_3O_8 [84] to supplement the earlier cryogenic values [85] have been obtained. The α-, β-, and γ-UO_3 phases have been investigated over both high- and cryogenic-temperature ranges by Cordefunke and Westrum [86]. The results are especially interesting at low temperatures as shown in fig. 2.

The thermodynamics of hypostoichiometric uranium dioxides have been investigated from the study of oxygen partial pressures in two laboratories [87, 88]. At the same time a new technique of gas equilibration in a sealed silica system has been developed to obtain thermodynamic data for both the hypo- and hyperstoichiometric dioxide [89]. A definitive study by Grønvold et al. [90] permits an interesting resolution of the electronic energy levels and other contributions. Marchidan [91] also studied non-stoichiometric oxides at high temperatures. A most exciting pioneer study involving the direct determination of specific enthalpies of oxygen in UO_{2+x} by Gerdanian and Dodé has been reported [92].

The gas phase properties of uranium dioxide have been evaluated from spectral data [93].

For PuO_2, the low-temperature data of Sandenaw and of Kruger have been supplemented by enthalpy data between 192 and 1400 K [94] and from 1500 to 2715 K [95] and interpreted by Manes [96]. Unfortunately the stored energy matter is problematical in [239]Pu; recent results from the Argonne National Laboratory indicate that the long awaited availability of [244]Pu will provide better, more reliable data—especially in the cryogenic region.

Data on PuO_2–UO_2 solid solutions are also available [97–99].

4.3. Other uranium chalcogenides

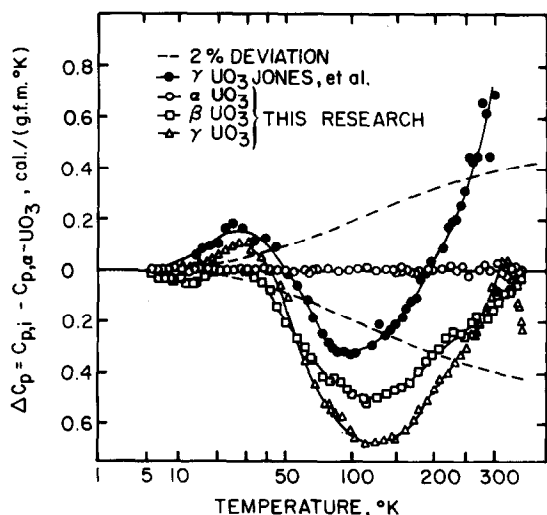Here data are sparser. Cryogenic data on ThS

Fig. 2. Low temperature relative heat capacities of UO_3 [86].

[100], US [101], and USe [102], are representative. Enthalpy data extend to 1800 K [103]. Other chalcogenides recently studied are US_2 and US_3 [104] as well as $US_{1.9}$ and USe_2 [105]. Heat capacities of solid solutions of US–UP have been studied over the cryogenic region [106].

4.4. Carbides

Cryogenic heat capacity data on UC [107, 108], $UC_{1.91}$ [108], $ThC_{2\pm x}$ [109], and U_2C_3 [108] are supplemented by enthalpy data to 925 K [110, 111]. $NpC_{0.91}$ [112], $PuC_{0.81}$ [113], and Pu_2C_3 [114] have been studied also.

4.5. Pnictides

Low-temperature C_p on UN [115–117], higher temperature enthalpy data [107, 118–120], and thermochemical and phase equilibrium data have been reviewed [121, 122]. Tagawa has considered the equilibrium nitrogen pressure data for U_2N_3 [123]. Cryogenic heat capacities exist for $UN_{1.91}$, $Un_{1.59}$, and $UN_{1.73}$ [108]

4.6. Borides

Uranium diboride's heat capacity has been studied from 1 to 350 K [124], from 600 to 1500 K [125], and from 1300 to 2300 K [126].

4.7. Halides

Little recent work exists, but enthalpies of fusion for UF_4 [127] are revealing in comparison with that of ZrF_4.

4.8. Miscellaneous

The chemical thermodynamic properties of plutonium have been compiled by Oetting [128] and by Rand et al. [129].

5. Thermodynamics of fission products

5.1. Molybdenum compounds

Over the past several years Mr. Harmas Kiwia (of

Tanzania) has been undertaking an intensive investigation of the thermodynamics of important molybdenum compounds on which thermophysical data are virtually totally lacking. This endeavor [34] is timely in the sense that the Soviet compilers have just completed an analysis of the recently available thermochemical Russian data on the enthalpies of formation of many of these materials. At the present time, studies on the $MoSe_2$ and $MoTe_2$ have been completed. These supplement the (still) unpublished data [130] on MoS_2. These data are of considerable interest from another point of view since the limiting law behavior of the heat capacity of essentially the lamellar lattices has been claimed to follow a T^2 dependence. I think that we have largely laid this ghost to rest and established by our earlier work in boron nitride and other substances that a T^3 behavior obtains and that the interaction between parallel layers is by no means totally negligible. However, the data on these three molybdenum chalcogenides which form a sandwich-layer-lattice should remove any remaining doubt. In addition to these three compounds, we have studied enthalpies at low temperatures on MoO_2Cl_2, $MoOCl_3$ and $MoOCl_4$ and should very soon be in a position to define the relative stabilities of these materials. In addition, heat capacities have been measured on $MoCl_3$ and $MoCl_4$ while those on $MoCl_5$ are in progress. Although gaps still exist in thermophysical properties of molybdenum compounds it is believed that this increment of nine compounds combined with the thermochemical data recently obtained in the USSR will do much to set this region of the periodic table in order from the point of view of thermodynamic stability.

5.2. Molten salts

Although this area is one of acknowledged relevance and spice insofar as actinide thermodynamics are concerned, it has not been incorporated within the scope of this review. It can be expected, however, to be an area of enhanced importance over the next decade insofar as nuclear thermodynamics are concerned.

Acknowledgements

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