

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF CALIFORNIA, DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING AND RADIATION LABORATORY<sup>1</sup>]

## Preparation and Properties of the Sulfides of Thorium and Uranium<sup>2</sup>

BY E. D. EASTMAN,<sup>3</sup> LEO BREWER, LEROY A. BROMLEY, PAUL W. GILLES AND NORMAN L. LOFGREN

Since lattice energy calculations have indicated that the most stable sulfides of the periodic system could be expected in the neighborhood of the elements of the rare earth and actinide series, a thorough study of the sulfides of typical representatives of these elements was made. This paper describes the results of the study of the sulfides of thorium and uranium.

The earliest careful study of thorium and uranium sulfides is that of Picon<sup>4,5,6</sup> who studied methods of preparation of ThS<sub>2</sub> and US<sub>2</sub> and the properties and reactions of these compounds. Strotzer and Zumbusch<sup>7</sup> and Strotzer, Schneider and Biltz<sup>8</sup> extended the study to polysulfides above the MS<sub>2</sub> compounds and to oxidation states below the four plus state. However, due to very extensive oxygen contamination during preparation, the compositions and composition ranges given for the various phases below MS<sub>2</sub> were greatly in error.

In the present work both uranium and thorium were found to have compounds of the 2<sup>+</sup> oxidation state, US and ThS, which have the NaCl crystal structure. No compounds below the 2<sup>+</sup> oxidation state were found. The solid solution ranges for these compounds appear to be relatively small. The next phase found above the MS phase was a M<sub>2</sub>S<sub>3</sub> phase corresponding to the 3<sup>+</sup> oxidation state. Both U<sub>2</sub>S<sub>3</sub> and Th<sub>2</sub>S<sub>3</sub> were found to have the same orthorhombic structure with apparently relatively small solid solution ranges. Th<sub>2</sub>S<sub>3</sub> is an unusual thorium compound as it is the only definitely established compound observed to date which contains thorium in the 3<sup>+</sup> oxidation state. ThS<sub>2</sub> prepared by conversion of the oxide by H<sub>2</sub>S in a graphite container had the orthorhombic PbCl<sub>2</sub> structure. US<sub>2</sub> was prepared in a similar manner. Upon heating under reduced pressures, both lost sulfur through a solid solution range. US<sub>2</sub> was less stable than ThS<sub>2</sub> and lost sulfur at lower temperatures. A compound, Th<sub>7</sub>S<sub>12</sub>, of hexagonal structure, has been prepared by heating liquid ThS<sub>2</sub> above 1950° under reduced pressures. It has a homogeneity range of approximately ThS<sub>1.71-1.76</sub>. Because of the ready loss of sulfur, the study of the uranium sulfide range down

to a composition corresponding to Th<sub>7</sub>S<sub>12</sub> did not give definite results.

### Experimental

**I. Preparation of the Sulfides of Uranium and Thorium.**—Four different methods of preparation will be described below. The first three methods were also used for the preparation of the cerium sulfides and the apparatus used and details of the procedures may be obtained from the paper by Eastman, Brewer, Bromley, Gilles and Lofgren<sup>9</sup> on the cerium sulfides.

**Method 1.**—This method is suited only for ThS<sub>2</sub> and US<sub>2</sub> since it involves the treatment of the oxides with excess H<sub>2</sub>S in a carbon system. Thus one obtains the highest sulfide stable at the temperature of the preparation. The temperature of the reaction should be varied between 1200–1300°; the rate of reaction at these temperatures is fairly rapid. During the course of the reaction, the oxysulfides ThOS and UOS are first formed at lower temperature with liberation of water. As the temperature is raised to the maximum value, CO is obtained instead of water. At the higher temperatures, the H<sub>2</sub>S being introduced attacks the carbon producing CS which is believed to be an important intermediate in the reaction with ThOS and UOS to produce ThS<sub>2</sub> and US<sub>2</sub>. The last traces of oxygen are often difficult to remove even at 1300° and the temperature was often raised to 1400 or 1500° for a short time to insure complete removal of all oxygen.

Because of the instability of US<sub>2</sub> at high temperatures, the product of reaction at high temperatures is somewhat reduced to a lower composition. To ensure formation of US<sub>2</sub> after all oxygen has been removed, the final reaction temperature is reduced to below 1000°, thus allowing the reduced sulfide to pick up sulfur from the H<sub>2</sub>S. Since ThS<sub>2</sub> is stable in an atmosphere of H<sub>2</sub>S even above its melting point, no such precautions are necessary for its preparation in the pure state. Very pure material can be obtained by this method and samples containing less than 0.05% of either oxygen or carbon were obtained.

**Method 2.**—This method is limited to sulfide compositions between U<sub>2</sub>S<sub>3</sub> and US<sub>2</sub> and between Th<sub>7</sub>S<sub>12</sub> and ThS<sub>2</sub> which can be prepared by vacuum heating of ThS<sub>2</sub> and US<sub>2</sub> in molybdenum containers. In the case of ThS<sub>2</sub>, temperatures of 1950° are required to obtain Th<sub>7</sub>S<sub>12</sub>. US<sub>2</sub> is much more readily reduced. A sample of US<sub>2</sub> heated for 20 minutes at 1600° at 10<sup>-4</sup> mm. pressure is reduced to US<sub>1.80</sub>. A mixture of U and US<sub>2</sub> with an average composition of US<sub>1.6</sub> is found to be reduced to US<sub>1.35</sub> upon heating to 1800° for 15 minutes, but the reduction below U<sub>2</sub>S<sub>3</sub> may be due to loss of sulfur from the US<sub>2</sub> before reduction by the uranium metal. Thus we have no definite evidence to indicate whether reduction below U<sub>2</sub>S<sub>3</sub> can be obtained by vacuum heating at this temperature.

**Method 3.**—This method can be used to prepare any of the lower oxidation states of uranium and thorium by mixing ThS<sub>2</sub> or US<sub>2</sub> powders with the proper amount of metal hydride powder. The mixture is heated to 400–600° under reduced pressures to decompose the hydride to metal powder, and then heated to 2000–2200° in the cases of the thorium sulfides and US. In the case of U<sub>2</sub>S<sub>3</sub>, the final heating is not above 1800°. This method is not usually satisfactory for compositions between U<sub>2</sub>S<sub>3</sub> and US<sub>2</sub> unless carefully carried out because of sulfur loss at the high temperature. For preparing compositions above ThS or US, these lower sulfides are often used as the reducing agents instead of the metal hydrides. All the heat-

(1) This work was performed under Manhattan District Contract No. W-7405-eng-48B from 1943 to 1946.

(2) Presented at San Francisco, California meeting of American Chemical Society, March 1949.

(3) Deceased, 1945.

(4) M. Picon, *Compt. rend.*, **189**, 1989 (1929).

(5) *Ibid.*, **195**, 957 (1932).

(6) *Bull. soc. chim.*, [4] **53**, 166 (1933).

(7) E. F. Strotzer and M. Zumbusch, *Z. anorg. allgem. Chem.*, **247**, 415 (1941).

(8) E. F. Strotzer, O. Schneider and W. Biltz, *Z. anorg. allgem. Chem.*, **243**, 307 (1940).

(9) E. D. Eastman, L. Brewer, L. A. Bromley, P. W. Gilles and N. L. Lofgren, *THIS JOURNAL*, **72**, 2248 (1950).

ings are done in molybdenum containers. There is some attack due to alloying of thorium and uranium metals with the molybdenum, but the attack is not usually serious unless compositions below ThS or US which contain excess free metal are used.

**Method 4.**—This method may be used for any of the sulfides of uranium or thorium. It involves the reaction of uranium and thorium hydrides with the proper amount of  $H_2S$ . Except when the highest sulfide is prepared, a mixture of metal hydride and various sulfides is obtained which is first heated in vacuum at low temperature to remove the hydrogen and then at high temperature to obtain a homogeneous product.

The metal hydride powder used in both methods 3 and 4 helped greatly in the development of the refractory sulfides described in this paper and of the refractory cerium sulfides also described by the authors,<sup>9</sup> since the hydriding reaction converts the metal to a finely divided form. Smith<sup>10</sup> has reviewed the previous work with these hydrides and Spedding, Newton, Warf, Johnson, Nottorf, Johns and Daane<sup>11</sup> have recently reviewed the properties of uranium hydride.

The procedure used to prepare the hydride is important if one is to obtain satisfactory material. Among other difficulties, one often encounters long induction periods when hydrogen is added to the metal. One of the chief causes of a long induction period before the hydriding reaction begins is the formation of an oxide coating on the metal due to  $H_2O$  and  $O_2$  absorbed on the walls on the bulb shown in Fig. 1. These gases may be removed by preheating the evacuated bulb at  $500^\circ$ . When cool, the bulb is filled with an inert dry gas and removed for the purpose of admitting the metal sample into it. The metal previous to use is well cleaned by filling or grinding until it is quite bright and shiny. The hydrogen used should be as pure as possible.

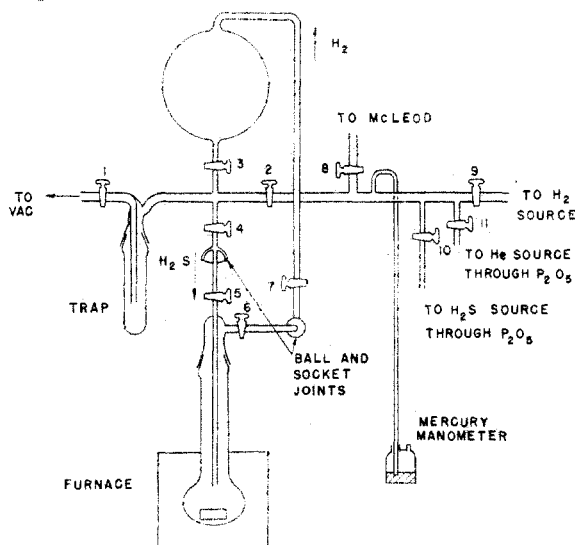


Fig. 1.—Apparatus for hydriding of metals and reaction with  $H_2S$  using circulation scheme to react fixed amounts of  $H_2S$ .

The reaction of thorium metal and hydrogen proceeds rapidly at  $300^\circ$ . In less than ten hours 300 g. is converted. The initial induction period may be reduced to only a few minutes if the temperature is first raised to  $400$ – $500^\circ$ , and then lowered to  $300^\circ$  after reaction begins. At temperatures above  $300^\circ$  and pressures of  $H_2$  below  $1/2$  atm.,  $ThH_2$  (approximately) is formed. Upon cooling to  $100^\circ$ , addi-

tional hydrogen is absorbed, forming  $ThH_{3.6}$ . The hydrogen was usually closed off before cooling so that the hydride  $ThH_2$  was obtained.

The reaction of uranium with hydrogen has been found to be very similar to that of thorium, although it proceeds directly to  $UH_3$ . A temperature of  $300^\circ$  gives satisfactory conditions for reaction.

After the hydriding of uranium or thorium has been completed and the bulb cooled, the excess hydrogen is pumped off through stopcock 1 of Fig. 1, if it is planned to use method 4 to prepare a uranium or thorium sulfide. Then  $H_2S$  dried over  $P_2O_5$  is introduced through stopcock 10, with stopcocks 1, 8, 9 and 11 closed and the other stopcocks open. From the volume of the system and the quantity of  $H_2S$  desired, the necessary pressure may be calculated and hence the correct amount added. After the addition, stopcock 10 is closed and the furnace heated to  $400$ – $500^\circ$ . The reaction proceeds according to the equations  $XH_3 + H_2S = XS + 5/2H_2$ ,  $2XH_3 + 3H_2S = X_2S_3 + 6H_2$ , etc. The  $H_2S$  in the furnace bulb is quickly converted to  $H_2$  which rises through stopcocks 6 and 7 causing the desired circulation in the system with the heavy  $H_2S$  going down through stopcocks 3, 4 and 5. After the reaction is nearly completed, the circulation of  $H_2S$  becomes very small; this requires a separate step to get its complete removal. The  $H_2$  is slowly pumped out through the liquid air trap which removes the  $H_2S$  from the  $H_2$ . It can then be returned to the bulb to complete the reaction. If the bulb is at a high enough temperature, perhaps in excess of  $550^\circ$ , complete removal of the  $H_2S$  may be obtained in one or, at the most, two steps.

After complete reaction, the tube is cooled and the vacuum broken with an inert, dry gas. The resulting material is transferred to a dry box and ground to get thorough mixing of the residual hydride and the sulfides. The mixture is then heated in a molybdenum crucible at  $500$ – $600^\circ$  to decompose the remaining hydride and then at  $1800$ – $1900^\circ$  for 30 minutes to obtain a uniform product. The following summary gives the method of preparation best suited for each compound:

**$ThS_2$** —Method 4 is the simplest if pure metal is available, but Method 1 will give a much purer product.

**$Th_7S_{12}$** —Method 3 is the simplest method if  $ThS_2$  is available and gives almost as pure a product as method 2 which also requires  $ThS_2$ . Method 4 which requires only metal and  $H_2S$  usually gives a less pure product.

**$ThS$  and  $Th_3S_4$** —Method 4 is simplest if  $ThS_2$  is not readily available but Method 3 gives a purer product unless very pure metal is available.

**$US_2$** —Method 4 is the simplest method although Method 1 is not difficult if equipment is available.

**$US$  and  $U_3S_4$** —Method 4 is the simplest since pure U is available although Method 3 is useful if  $US_2$  is available.

**II. Methods of Analysis.**—Some of the samples were analyzed by combustion in oxygen at  $1000^\circ$  and collection of the  $SO_2$  in alkali. From the change in weight upon combustion and the sulfur obtained, one could calculate the oxygen and sulfur contents of the sample. However, the method was not too satisfactory in that a small amount of sulfate was formed during the combustion which in the case of the thorium did not completely decompose even at  $1000^\circ$ . The sulfate residue in the combustion samples had to be determined and a correction applied. The most satisfactory method of analysis was the determination of the  $H_2S$  and  $H_2$  evolved upon solution in acid. Thus one could calculate the sulfur content and the oxidation number from which one could calculate the oxygen content of the samples. The details of the methods of analysis are described by Brewer, Bromley, Fong, Gilles, Koch and Lofgren.<sup>12</sup>

## Discussion

**Determination of Phases.**—To determine the stable phases of the thorium and uranium sulfide

(10) D. P. Smith, "Hydrogen in Metals," University of Chicago Press, Chicago, Ill., 1948.

(11) F. H. Spedding, A. S. Newton, J. C. Warf, O. Johnson, R. W. Nottorf, I. B. Johns and A. H. Daane, *Nucleonics*, 4, 4 (1949).

(12) L. Brewer, L. A. Bromley, A. D. Fong, P. W. Gilles, C. W. Koch and N. L. Lofgren, Atomic Energy Commission Declassified Paper MDDC-1654, September 22, 1945.

TABLE I  
PROPERTIES OF THE THORIUM AND URANIUM SULFIDES

Compound	Color	Melting point, °C.	Density g./cc.	Heat of formation; $\Delta H_{298}$ from S <sub>8</sub> (g)	Magnetic susceptibility
ThS	Silvery	>2200	9.57	-120 ± 5 kcal.	Not paramagnetic
Th <sub>2</sub> S <sub>3</sub>	Brown	1950 ± 50	7.88	-306 ± 3	Not paramagnetic
Th <sub>7</sub> S <sub>12</sub>	Black	1770 ± 30	7.78	-665 ± 35	Not paramagnetic
ThS <sub>2</sub>	Purple	1905 ± 30	7.36	-170 ± 20	Not paramagnetic
US	Gray metallic	>2000	10.9		4180 × 10 <sup>-6</sup> e. m. u.
U <sub>2</sub> S <sub>3</sub>			8.81		2630 × 10 <sup>-6</sup> e. m. u.
US <sub>2</sub>	Black	1850 ± 100	7.90		3050 × 10 <sup>-6</sup> e. m. u.

systems, various compositions were prepared and submitted to Dr. Zachariasen of the Manhattan District Metallurgical Laboratory at Chicago. For example, a sample analyzing ThS<sub>0.93</sub>·0.10 ThO<sub>2</sub> was found by X-ray analysis to consist of 5–10 mole % Th, 10 mole % ThO<sub>2</sub>, and 80–85 mole % ThS. Other similar samples with S/Th ratios appreciably below unity showed the presence of free thorium metal while a sample analyzing ThS<sub>0.97</sub>·0.06ThO<sub>2</sub> contained no free metal and consisted almost entirely of ThS with a trace of Th<sub>2</sub>S<sub>3</sub>. A sample analyzing ThS<sub>1.31</sub>·0.06ThO<sub>2</sub> contained 70% Th<sub>2</sub>S<sub>3</sub> and 30% ThS with a trace of ThO<sub>2</sub>. A sample analyzing ThS<sub>1.622</sub>·0.011ThO<sub>2</sub> consisted almost entirely of the Th<sub>7</sub>S<sub>12</sub> phase with a small amount of Th<sub>2</sub>S<sub>3</sub>. Samples analyzing ThS<sub>1.77</sub> consisted of only the Th<sub>7</sub>S<sub>12</sub> phase. These results and other similar ones allow one to conclude that phases of compositions in the vicinity of ThS and Th<sub>2</sub>S<sub>3</sub> exist with no other phases between Th and ThS or Th<sub>2</sub>S<sub>3</sub> and ThS. Apparently there is a solid solution range around Th<sub>7</sub>S<sub>12</sub> with no other phases between Th<sub>2</sub>S<sub>3</sub> and Th<sub>7</sub>S<sub>12</sub>. Finally there is a phase at ThS<sub>2</sub>. The ThS phase may have a solid solution range of several atomic per cent. since the lattice constant of ThS in the presence of Th metal varied from 5.669 kX. to 5.671 kX. while ThS in the presence of Th<sub>2</sub>S<sub>3</sub> was observed to have a lattice constant of 5.662 kX. However one apparently erratic determination of 5.679 kX. for ThS in the presence of Th<sub>2</sub>S<sub>3</sub> makes it difficult to draw definite conclusions. It might be pointed out that all the samples of the ThS and Th<sub>2</sub>S<sub>3</sub> phases which were studied were saturated with ThO<sub>2</sub> as oxygen-free thorium metal was not available for the preparations. Apparently ThOS is not stable in the presence of ThS and will react with it to form ThO<sub>2</sub> and Th<sub>2</sub>S<sub>3</sub>. The uranium system was studied in a similar manner but not as completely. Compositions between U<sub>2</sub>S<sub>3</sub> and US<sub>2</sub> gave complicated X-ray powder patterns and the phase relations have not yet been worked out. The US<sub>2</sub> was not found to be isomorphous with ThS<sub>2</sub>. The details of the structures of the various phases have been reported separately by Zachariasen.<sup>13</sup>

In addition to studying sulfides of various oxidation states, mixtures of sulfides of thorium and uranium and thorium and cerium were made.

(13) W. H. Zachariasen, *Acta Cryst.*, **2**, 288, 291 (1949), and ANL-FWHZ-161 (1946).

The MS phases appear to be completely miscible in one another. For example, Th<sub>0.33</sub>U<sub>0.61</sub>S consisted of only one cubic phase with a lattice constant of 5.575 kX. which is intermediate between the constants for US and ThS. Likewise mixtures of CeS and ThS gave solid solutions with intermediate lattice constants. An attempt was made to stabilize the thorium analog of Ce<sub>3</sub>S<sub>4</sub> by preparing Th<sub>2</sub>Ce<sub>3</sub>S<sub>4</sub>, but a mixture containing the ThS and Th<sub>2</sub>S<sub>3</sub> phases was obtained with the lattice constants of both phases altered due to the presence of Ce.

**Properties of the Sulfides of Thorium and Uranium.**—Many of the properties of these sulfides are summarized in Table I.

ThS has a specific electrical resistance at room temperature of less than 10<sup>-4</sup> ohm-cm. Th<sub>2</sub>S<sub>3</sub> and Th<sub>7</sub>S<sub>12</sub> have specific resistances of 10<sup>-4</sup> to 10<sup>-3</sup> ohm-cm. although Th<sub>2</sub>S<sub>3</sub> appears to be the slightly better conductor. ThS<sub>2</sub> and US<sub>2</sub> are essentially insulators at room temperatures.

ThS was not melted at 2200° and probably melts around 2500°. US was not melted at 2000°. Picon's<sup>6</sup> value for ThS<sub>2</sub> was checked. The Th-ThS eutectic is above 2050° and the ThS-Th<sub>2</sub>S<sub>3</sub> eutectic is around 1800°.

Except for US<sub>2</sub> which begins to lose sulfur under reduced pressures above 1200° and for ThS<sub>2</sub> which begins to lose sulfur above 1900°, none of the other sulfides show any appreciable volatilities except at higher temperatures. There is no evidence for any volatility except by decomposition to the gaseous atoms. ThS has a decomposition pressure of less than 10<sup>-3</sup> mm. of at 2200°. Th<sub>2</sub>S<sub>3</sub> and Th<sub>7</sub>S<sub>12</sub> had no observable volatility at 1700°. The method used to determine the melting points and volatilities are the same as those used for the cerium sulfides.<sup>9</sup>

The densities given in Table I were obtained from the following lattice constants obtained by Zachariasen:<sup>13</sup> ThS,  $a = 5.67$  kX.; Th<sub>2</sub>S<sub>3</sub>,  $a_1 = 10.97 \pm 0.05$ ,  $a_2 = 10.83 \pm 0.05$ ,  $a_3 = 3.95 \pm 0.03$  kX.; Th<sub>7</sub>S<sub>12</sub>,  $a_1 = 11.041 \pm 0.001$ ,  $a_2 = 3.983 \pm 0.001$  kX.; ThS<sub>2</sub>,  $a = 4.259 \pm 0.002$ ,  $a_2 = 7.249 \pm 0.003$ ,  $a_3 = 8.600 \pm 0.003$  kX.; US,  $a = 5.47$  kX.; U<sub>2</sub>S<sub>3</sub>,  $a_1 = 10.39 \pm 0.02$ ,  $a_2 = 10.63 \pm 0.02$ , and  $a_3 = 3.88 \pm 0.01$  kX. Th<sub>7</sub>S<sub>12</sub> density was obtained by displacement.

In contrast to the cerium sulfides<sup>9</sup> which dissolved readily in dilute acid, all of the thorium and uranium sulfides dissolved only slowly in di-

lute acids at room temperatures. They were all quite stable toward air at room temperature and even toward boiling water if well sintered. In regard to mechanical properties, ThS and US were very similar to CeS.<sup>9</sup> Th<sub>2</sub>S<sub>3</sub> and U<sub>2</sub>S<sub>3</sub> were rather similar to Ce<sub>3</sub>S<sub>4</sub>.<sup>9</sup>

Westrum and Eyring<sup>14</sup> have determined the heat of formation of Th<sub>2</sub>S<sub>3</sub>. From this heat and the observed high temperature physical and chemical behavior of the sulfides of thorium such as vapor pressures, reactions with metals, and other high temperature equilibria, the heats per mole were estimated for formation from the gaseous S<sub>2</sub> standard state and are tabulated in Table I. These may be corrected to the rhombic sulfur standard state by using 31 kilocal. for the heat of sublimation of S<sub>2</sub>. The methods used to obtain heats of formation from semi-quantitative high temperature equilibria data are illustrated by Evans<sup>15</sup> using the cerium sulfides as examples and by Brewer, Bromley, Gilles and Lofgren<sup>16</sup> using the molybdenum halides as examples.

**Discussion of Bonding of Semi-metallic Sulfides.**—During the course of study of the refractory sulfides of uranium, thorium, cerium and barium, considerable thought was devoted to the reasons for the differences in properties found for the various sulfides in terms of the bonding existing in the solid lattices. The dipositive sulfides are especially interesting to compare since all have the sodium chloride structure and differences in behavior could not be attributed to differences in structure. A knowledge of the magnetic susceptibilities of these compounds would be particularly useful in order to determine the extent of contribution of the available electrons to the bonding. Professor M. Calvin kindly determined the magnetic susceptibilities of our samples. The results for the cerium sulfides have been given previously by the authors.<sup>9</sup> The results obtained for the uranium and thorium sulfides are given in Table I.

Both cerium and thorium have four electrons available in the outer electron shells. ThS is not paramagnetic. Since unbonded electrons would remain unpaired in the incompleated shells available to them, all four electrons must be participating in bonds. Since CeS has one unpaired electron, only three electrons have been paired in bonds. These compounds are all highly reducing and one would certainly expect that the sulfur atoms have taken up two electrons apiece to complete their octets. Thus we have two additional electrons available of which both are paired through bonding in ThS, but of which only one is paired in CeS. We know from the fact that the

transition metals do not exhibit any appreciable paramagnetism that "d" electrons will pair to form metallic bonds or resonating covalent bonds when the atoms are close enough.

Pauling<sup>17</sup> and Engel<sup>18</sup> review the concept of metallic bonding in terms of resonating covalent bonding. The metal ions in these sulfides are almost as close together as the atoms in the free metal. Therefore, it is very unlikely that the paramagnetism could be due to unpaired "d" electrons. Therefore it is quite reasonable to assume that the paramagnetism of the sulfides of the rare earth and actinide metals is due to unpaired "f" electrons. It is noteworthy that all of the cerium sulfides have one free "f" electron, the same as is observed for cerous ion. None of the thorium sulfides are paramagnetic and therefore even the extra electrons not taken up by the sulfur atoms are bonded. The bonding must be between the thorium ions in the NaCl lattice just as one obtains bonding between the thorium atoms in the metal lattice.

US has a magnetic susceptibility corresponding to two "f" electrons while U<sub>2</sub>S<sub>3</sub> has one "f" electron. Thus US and U<sub>2</sub>S<sub>3</sub> have two "d" electrons which are involved in metallic bonding between the metal ions. While ThS has two "d" electrons involved in metallic bonding, Th<sub>2</sub>S<sub>3</sub> has only one and ThS<sub>2</sub> no "d" electrons involved in metallic bonding. The properties of the compounds are in agreement with this. US<sub>2</sub> has a magnetic susceptibility which would correspond to very little contribution of "d" electrons to metallic bonding. It is interesting to note how the relative stabilities of the "d" and "f" electrons not only vary from element to element but from one oxidation state to another of the same element.

From the heats of formation of BaS, CeS and ThS, one can calculate lattice energies using estimated ionization potentials where necessary. These calculations confirm the extent of metallic bonding since the lattice energies decrease in the order ThS, CeS, BaS or in the order of number of metallicly bonded "d" electrons even after correcting for differences in ionic radii. Thus we visualize these dipositive sulfides to be a simple arrangement of dipositive and dinegative ions in a sodium chloride lattice with the coulombic energy of such a lattice being a major contribution to the lattice energy. However, the sulfides which have "d" electrons involved in metallic bondings display a much higher stability or greater lattice energy than could be expected from coulombic interaction alone and the difference is attributed to the bonding between the dipositive cations involving the available "d" electrons, but not the "f" electrons.

CeS and ThS afford the most clear-cut demon-

(14) E. F. Westrum and L. Eyring, private communication from Univ. of Michigan, Ann Arbor, and Univ. of Calif., Berkeley, 1948.

(15) M. W. Evans, National Nuclear Energy Series, "Plutonium Project Record," Vol. 14B, Paper 9 (1950) McGraw-Hill Book Co., New York, N. Y.

(16) L. Brewer, L. A. Bromley, P. W. Gilles and N. L. Lofgren, *ibid.*, Vol. 14B, Paper 8.

(17) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940.

(18) Niels N. Engel, *Ingeniøren*: M101 (1939); M.1 (1940) *Haandbogi Metallare: Selskabet for Metalforskning, Copenhagen, 1945 and unpublished work (1949).*

stration of this since they both have the same number of valence electrons and the lattice constants are very close. Yet CeS which has one unbonded and unpaired "f" electron has a much lower lattice energy than ThS which has no "f" electrons and can contribute both of its extra electrons to metallic bonding.

The above consideration of bonding not only explains the relative stabilities of the sulfides, electrical properties, etc., but it also explains the abnormal behavior of the bond distances. Thus the bond distance in Å. between the metal ion and sulfide ion is as follows: BaS, 3.2; CeS, 2.88; ThS, 2.84; US, 2.74. The influence of the extra bonding due to the "d" electrons is clearly seen. In spite of the fact that Th is larger than Ce in normal compounds, the extra "d" electron available in ThS reduces the bond distance compared to CeS. A similar effect is seen when the bond distances for the tripositive sulfides are compared:

La<sub>2</sub>S<sub>3</sub>, 3.01; Ce<sub>2</sub>S<sub>3</sub>, 2.98; Th<sub>2</sub>S<sub>3</sub>, 2.90; U<sub>2</sub>S<sub>3</sub>, 2.82. Comparison of these values with the crystal radii observed in compounds with no metallic bonding as given by Zachariasen<sup>19</sup> will emphasize the effect of metallic bonding.

### Summary

The stable phase regions of the uranium and thorium sulfides have been determined. Methods of preparation of the pure compounds have been found. Many of the properties of these sulfides have been studied. Several of the sulfide phases show considerable promise for use as refractory containers. The distribution of "d" and "f" electrons is discussed and the types of bonding in the semi-metallic sulfides of two and three oxidation states are discussed.

(19) W. H. Zachariasen, *Phys. Rev.*, **73**, 1104 (1948).

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## The Correct Application of the Gibbs-Helmholtz Equation to Reversible Galvanic Cells in which Several Phases Are in Equilibrium at One of the Electrodes

BY R. E. BARRIEAU<sup>1</sup>

Some confusion exists in the literature concerning the application of the Gibbs-Helmholtz equation to reversible galvanic cells in which several phases are in equilibrium at the electrodes.

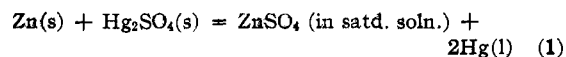
As Brickwedde and Brickwedde<sup>2</sup> have pointed out, saturated cells involving hydrated salts are either ignored or incorrectly treated in modern texts on thermodynamics. However, in the brief abstract of their correct application of the Gibbs-Helmholtz equation they state, "The Gibbs-Helmholtz equation relating the heat of the cell reaction to the free energy changes is not directly applicable to the electromotive force of cells in which the concentration of a solution entering the cell reaction changes with temperature." This statement is apt to leave the impression the Gibbs-Helmholtz equation is limited in its application. Such an interpretation would be unfortunate. The Gibbs-Helmholtz equation is derivable from very general principles, since it involves the relationship of the temperature coefficient of reversible work and the corresponding isothermal entropy change. For this reason, it may be stated with confidence that the Gibbs-Helmholtz equation is directly applicable to any reversible galvanic cell.

Confusion has arisen because of the failure to write correct cell reactions. As Lewis and Randall<sup>3</sup> have stated, "We cannot too strongly em-

phasize the importance of considering the electromotive force as a property, not of the cell, but of the reaction which occurs within the cell. Until that reaction is definitely known, measurements of electromotive force have no meaning. This is not a point of mere academic interest." It may be stated with confidence that one of the criteria that must be met, if the cell reaction presumably is known, is that the Gibbs-Helmholtz equation must be directly satisfied. If a reaction is written to represent a certain reversible cell reaction and it is then found that the Gibbs-Helmholtz equation is not applicable, this means that an incorrect cell reaction has been written.

The principle for writing complete cell reactions where several phases are in equilibrium at each electrode is the following: The processes that will take place between the phases in equilibrium are those that will maintain the phases in equilibrium. The application of this principle will be illustrated by developing the complete cell reaction for the Clark cell.

In the Clark cell, one electrode consists of mercury, mercurous sulfate, zinc sulfate heptahydrate and an aqueous solution saturated with respect to zinc sulfate heptahydrate and mercurous sulfate. The other electrode consists of zinc, saturated zinc amalgam, zinc sulfate heptahydrate and an aqueous solution saturated with zinc sulfate heptahydrate. We may start by writing the reaction



Here the reaction of zinc and mercurous sulfate

(1) California Research Corporation, Richmond, California.

(2) Brickwedde and Brickwedde, *Phys. Rev.*, [II] **60**, 172 (1941).

(3) Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, N. Y., 1923, p. 400.