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

Preparation and Properties of the Oxide-Sulfides of Cerium, Zirconium, Thorium and Uranium[2]

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The preparation, properties and nomenclature for the oxide-sulfides of cerium, zirconium, thorium and uranium are discussed. The compounds Ce_2O_2S, ThOS, UOS and ZrOS have been prepared by the reaction of an oxide with sulfur or hydrogen sulfide. The crystal structures and lattice constants are given in Table I. The color, solubility, melting behavior, high temperature chemistry and estimated thermochemistry are described.

In the course of the work leading to the preparation of the sulfides of cerium, thorium and uranium by the reaction between the oxides and hydrogen sulfide at high temperature,[4,5] intermediate oxide-sulfide compounds were formed. It is the purpose of this paper to present the methods of preparation and the properties of these oxide-sulfides. Since an oxide-sulfide of zirconium was prepared for X-ray examination, its preparation and properties will be discussed also.

Although considerably more work has been done with cerium than with the others, in no case can the work be considered to be exhaustive. This has resulted in part from the rather limited interest in the compounds and in part from the urgency of other problems.

The apparatus and methods for all this work were the same as those used in the study of the sulfides of cerium and thorium previously reported.

Nomenclature.—One oxide-sulfide of each of the elements, zirconium, cerium, thorium and uranium exists and the nomenclature to be used for these compounds is based upon the crystal structure. If an oxide-sulfide has the same crystal structure as the pure oxide, then it is called a thio-oxide to indicate the replacement of an oxygen by a sulfur; if it has the same crystal structure as the pure sulfide, then it is called an oxy-sulfide; if it has a crystal structure different from both the oxide and sulfide, then it is named a sulfoxide. For example, Ce_2O_2S which has the same crystal structure as Ce_2O_3 is cerium(III) thio-oxide, or cerium (III) mono-thio-oxide. The latter name distinguishes it from a conceivable compound with the Ce_2O_3 structure in which more than one oxygen has been replaced by sulfur. Since ThOS has a crystal structure different from both ThO_2 and ThS_2, it is called thorium sulfoxide.

Preparation

Cerium.—Cerium(III) thio-oxide (Ce_2O_2S) has been prepared from powdered CeO_2 at about 1300° by three methods: (a) Hydrogen sulfide while being passed through an oxide refractory tube will react with CeO_2 to form the black thio-oxide according to the equation

$$4CeO_2 + 4H_2S = 2Ce_2O_2S + 4H_2O(g) + S_2(g)$$

(b) Sulfur vapor will react with CeO_2 in an oxide refractory tube according to the equation

$$2CeO_2 + S_2(g) = Ce_2O_2S + SO_2$$

(c) Hydrogen sulfide in a graphite apparatus will produce from CeO_2 either Ce_2S_3 or Ce_2O_2S, depending on the conditions. If the temperature is kept below the fusion point of the mixture and if the process is continued for a sufficiently long time, the product will be the sesqui-sulfide. The thio-oxide is formed as an intermediate product but will be the main product if the conditions requisite for the formation of the sulfide are not realized. The reaction accounting for the formation of the thio-oxide is that in (a) above.

Although conversion beyond Ce_2O_2S can be attained in method (c), it is believed that the thio-oxide is the final product in methods (a) and (b) because the partial pressure of water in an oxide refractory system arising from the reaction between H_2S and the oxide tube cannot be lowered below that of the pressure of water in equilibrium with Ce_2O_2S, Ce_2S_3 and H_2S. Presumably, as well as hydrogen sulfide, sulfur vapor in a graphite system would also produce the sesquisulfide.

Analyses were made by dissolving the sample in dilute HCl, collecting H_2 and H_2S, and calculating the oxidation state from the H_2 evolution and the sulfur content from the H_2S evolution.

Thorium, Uranium and Zirconium.—Thorium sulfoxide (ThOS) and uranium sulfoxide (UOS) have been prepared by methods similar to (a) and (c) above. Again, they are the final products in an oxide tube but intermediate products in the graphite apparatus. The compound ZrOS has been prepared by a method similar to (c). The typical reaction would be the equivalent of that in (a).

No other oxide-sulfides of these four elements have been found, and in fact there is not even any indirect evidence for others. An experiment designed to indicate the possible existence of Ce_2OS_2 by a maximum at this composition in the temperature-composition diagram yielded negative results. The absence of any reaction between ThO_2 and ThS or between ThO_2 and CeS indicated that probably no trivalent oxide-sulfide of thorium is stable with respect to disproportionation.

General Properties

Cerium.—Cerium thio-oxide is brown to black in color, is insoluble in water, is rapidly soluble in acids with the evolution of H_2S, and has a hexagonal crystal structure similar to that of Ce_2O_3 with constants as determined by Zachariasen[6] listed in Table I. The melting point of Ce_2O_2S is 2000 ± 200°.

A knowledge of the melting points of the sulfide-thio-oxide mixtures is necessary if one desires to sinter at high temperature sulfide objects containing some oxygen impurity. For example, if an object consisting of CeS containing a few per cent. of Ce_2O_2S and Ce_3S_4 impurities is heated to a temperature above the melting point of the Ce_2O_2S–Ce_3S_4 eutectic, the object will lose its internal strength and become distorted. Furthermore, the liquid eutectic mixture tends to segregate on the colder portions as a black film which is very hard and brittle, making parts of the product brittle and easily chipped.

The melting of mixtures of Ce_2O_2S and Ce_2S_3 and of mixtures of Ce_2O_2S and Ce_3S_4 has been observed some 200 to 400° lower than the melting points of the pure compounds. A summary of the melting data for the CeO–S system appears in Table II. Along the principal diagonal are given the melting points of the substances listed in the margins. The temperatures in the other places correspond to the eutectic points between the compound at the left of the row and the compound at the head of the column. The "x" appears in the table because the existence of Ce_3S_4, of inter-

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(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 the American Chemical Society, March, 1949.

(3) Deceased, 1945.

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

(5) Eastman, *et al.*, *ibid.*, **72**, 4019 (1950).

(6) W. H. Zachariasen, *Acta Cryst.*, **2**, 60 (1949).

TABLE I

LATTICE CONSTANTS

	Ce_2O_2S[6a]	ZrOS[11]	ThOS[10a]	UOS[10a]
Structure	Hexagonal	Cubic	Tetragonal	Tetragonal
a_1 in Å.	4.008 ± 0.01	5.696 ± 0.002	3.963 ± 0.002	3.843 ± 0.001
a_3 in Å.	6.833 ± .03	....	6.747 ± .004	6.694 ± .001
Calcd. density	5.99	4.975	8.78	9.60

[a] The lattice constants given in references (6) and (10) in kX. units have been changed to Å. units.

TABLE II

MELTING POINTS AND EUTECTIC TEMPERATURES (°C.)

	CeS	Ce_3S_4	Ce_2S_3	Ce_2O_2S
CeS	2450 ± 100	2000 ± 75	x	1900 ± 100
Ce_3S_4		2050 ± 75	Solid soln.	<1650
Ce_2S_3			1890 ± 50	<1650
Ce_2O_2S				2000 ± 200

mediate composition, does not allow eutectic formation between CeS and Ce_2S_3. These data are shown schematically in Fig. 1. This figure is consistent not only with the above data but also with qualitative observations not explicitly reported, and therefore gives some indication of the behavior of the system. But because only a few compositions have actually been studied, the location of the eutectics and contours is only approximate and for that reason temperatures have not been indicated in the figure. The figure should be used for qualitative purposes only.

It may be seen from the table and figure that the chief difficulties from low melting eutectic mixtures will be encountered when both the Ce_2O_2S phase and the Ce_3S_4 phase are present. This situation may exist when the main portion of the sulfide is either the CeS phase or the Ce_3S_4 phase, the impurity being a few per cent. of a Ce_2O_2S-Ce_3S_4 mixture in the first case or just Ce_2O_2S in the second case. Thus, to remove the possibility of formation of a low-melting compound in CeS, it is necessary to eliminate either Ce_2O_2S or Ce_3S_4, or both.

There is some evidence that in addition to lowering the melting points of CeS and Ce_3S_4, the presence of a small amount of oxygen in solid solution in Ce_2S_3 will change it from its normal $Ce_3S_4(Th_3P_4)$ type crystal structure to another unknown structure, possibly the $Th_2S_3(Sb_2S_3)$ type crystal structure. The Ce_3S_4 structure is obtained for the Ce_2S_3 composition because of the vacancy of some of the metal sites of the Ce_3S_4 structure. The Th_2S_3 crystal structure is obtained with pure trivalent sulfides with a sufficiently high cation to anion ratio as for thorium, uranium and neptunium. The cation to anion ratio in Ce_2S_3 is not great enough to obtain the Th_2S_3 type crystal structure, but replacement of some of the sulfur atoms by oxygen atoms is believed to increase the ratio sufficiently to possibly stabilize the Th_2S_3 type structure over the normal Ce_3S_4 type structure that is observed for smaller cation–anion ratios.

The evidence for the above conclusion is that Zachariasen[7] reported that samples submitted to him consisting by analysis of 25 mole % of Ce_2O_2S and 75 mole % of Ce_2S_3 as well as a mixture of 50 mole % of Ce_2O_2S and of Ce_2S_3 gave the X-ray pattern of Ce_2O_2S, but that neither mixture gave the pattern corresponding to the normal Ce_3S_4 crystal structure of Ce_2S_3. Instead, the other pattern in addition to the Ce_2O_2S pattern was a complex one which could be similar to the Th_2S_3 pattern. The X-ray examination of a single crystal will be necessary before a definite identification can be made. Templeton and Dauben[8] also report that Ce_2S_3 samples submitted to them containing by analysis 10 mole % Ce_2O_2S and 20 mole % Ce_2O_2S gave a complex pattern similar to that observed by Zachariasen. The compound Ce_3S_4 is not changed in structure by the presence of oxide since a sample analyzing $Ce_2O_2S{\cdot}2.7Ce_3S_4$ gave the cubic Ce_3S_4 pattern. A sample analyzing $Ce_2O_2S{\cdot}38CeS_{1.47}$ also gave the normal cubic pattern. It is not known whether this is due to the very small oxygen content or to the partial reduction of the Ce_2S_3. Thus, it is seen that less than 10 mole % of Ce_2O_2S can change the Ce_2S_3 to a new crystal type. Further experiments would be necessary to determine the minimum amount of oxygen required for the conversion and for the definite identification of the new phase. The melting point, heat of formation, and other properties are apparently very similar to those of the normal form. It is interesting to note that Klemm, Meisel and Vogel[9] have reported that Pr_2S_3 is converted to a new crystal structure by the presence of 5 mole % of oxygen. The change is undoubtedly the same as in the case of cerium. The lower right corner of Fig. 1 schematically expresses the formation of this different phase.

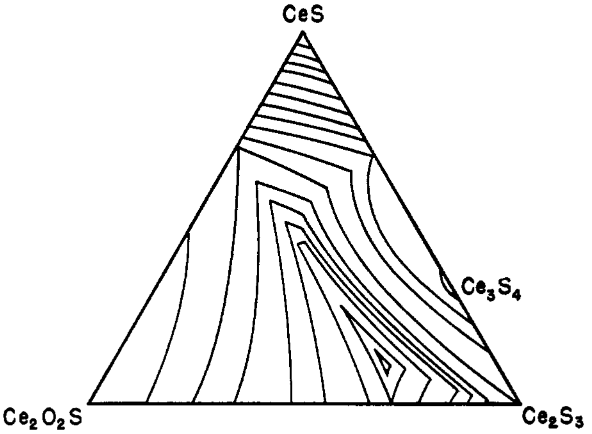

Fig. 1.—Schematic representation of the temperature-composition diagram of part of the system Ce–O–S. This diagram should not be used for quantitative purposes.

Thorium, Uranium and Zirconium.—Thorium sulfoxide is yellow in color, very slowly soluble in dilute acids and only somewhat more rapidly soluble in hot concentrated nitric acid, and has a tetragonal crystal structure with constants as determined by Zachariasen[10] listed in Table I. No low melting eutectics between ThOS and the thorium sulfides have been observed. Uranium sulfoxide is a black material, soluble in concentrated nitric acid, and has a tetragonal crystal structure isomorphous with ThOS and with constants as determined by Zachariasen[10] listed in Table I. Zirconium sulfoxide is a yellow material relatively insoluble, and has a simple cubic structure with constants as determined by McCullough, Brewer and Bromley[11] listed in Table I.

High Temperature Reactions

Cerium.—The high temperature chemistry of cerium thio-oxide may be discussed in terms of its reactions with carbon, hydrogen sulfide, metals and other sulfides. At 1500° Ce_2O_2S does not react with carbon although some reduction seems to take place at about 1600°. As pointed out above H_2S will not produce the sesqui-sulfide from the thio-oxide in an oxide tube. The combined action of carbon and hydrogen sulfide will, however, cause complete conversion to the sesqui-sulfide as discussed in a previous paper.[4]

At low temperatures metallic cerium will not react with Ce_2O_2S but above about 1700° reaction appears to form CeO(g) according to the equation

$$Ce_2O_2S + Ce(l) = CeS + 2CeO(g)$$

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(7) W. H. Zachariasen, University of Chicago, private communication, 1945.

(8) D. H. Templeton and C. H. Dauben, University of California, private communication, 1949.

(9) W. Klemm, K. Meisel and H. U. Vogel, *Z. anorg. allgem. Chem.*, **190**, 123 (1930).

(10) W. H. Zachariasen, *Acta Cryst.*, **2**, 291 (1949).

(11) J. D. McCullough, L. Brewer and L. A. Bromley, *ibid.*, **1**, 287 (1948).

since the oxygen content of CeS is reduced by heating with excess cerium. However, since cerium metal usually contains appreciable amounts of cerium carbide, the removal of the oxide impurity might be due to CO formation.

If CeS with a very low Ce_3S_4 content is heated with a small amount of Ce_2O_2S above 1700° in a vacuum, CeO should be evolved as a gas and Ce_3S_4 should be produced as a liquid or solid. This reaction should proceed until the activity of the Ce_2O_2S has been reduced to a low value, by virtue of its solution in the Ce_3S_4 produced in the reaction. Experimentally it has been found necessary to add metallic cerium in order to obtain any appreciable reduction of oxygen content in CeS through volatilization of CeO.

Except for the previously mentioned change of crystal structure of Ce_2S_3 by the presence of Ce_2O_2S, there appears to be no reaction of the thio-oxide with Ce_3S_4 or Ce_2S_3.

Thorium, Uranium and Zirconium.—As with cerium, the oxide-sulfides of these elements can be completely converted to the highest sulfides by H_2S in a graphite system at about 1500°. It has been reported[12] that ThOS reacts with carbon at about 1900° producing ThS and CO and although no other products were noted, the resulting material undoubtedly contained thorium carbide and oxide in addition to the sulfide. Metallic thorium reacts with ThOS forming ThS and ThO_2.

From the experimental evidence that ThO_2 is stable when heated with ThS, the most probable reaction of ThS with ThOS is the formation ThO_2 and Th_2S_3. With the higher sulfides, Th_4S_7 and ThS_2, the sulfoxide does not react. The stability of ThOS in the presence of Th_2S_3 is not known but it is suspected that it exists under such conditions.

Thermochemistry

Cerium.—Although the heat of solution has not been determined for the thio-oxide and, therefore, the heat of formation has not been directly determined, some estimates of this latter quantity can be made from the following considerations. In a transpiration experiment during the course of the work, nitrogen was bubbled through liquid sulfur at a temperature for which the vapor pressure of sulfur is about 0.1 atm. and then was passed over powdered CeO_2 in a furnace at a temperature of about 1500°. In about two hours with a nitrogen flow of about one ml./sec. essentially complete conversion to Ce_2O_2S had occurred but conversion to the sesqui-sulfide was not attained. In a graphite apparatus conversion to Ce_2S_3 has been obtained in long runs as low as 1300°K. and in four hours at about 1600°K. These experiments allow estimation of equilibrium constants which when combined with estimated entropies give limits on the heat of formation of the thio-oxide. If the heat of formation of Ce_2S_3 from rhombic sulfur is taken as $\Delta H_{298} = -300.5$ kcal./mole and if the heat of formation of CeO_2 is taken as $\Delta H_{298} = -448$ kcal./mole, our estimate for the heat of formation of Ce_2O_2S is $\Delta H_{298} = -430 \pm 15$ kcal./mole from rhombic sulfur.

Thorium.—Our estimate for the heat of formation of ThOS at 1500°K. based upon similar considerations is $\Delta H = -210 \pm 20$ kcal./mole.

It is interesting to note that sulfides of both the two and three oxidation states are quite stable for all the elements discussed in this paper while except for the tripositive oxide and thio-oxide of cerium, none of these elements has stable oxides or oxide-sulfides of the two and three oxidation states. This difference is general for most metallic elements and appears to be due mainly to the greater decrease in stability of lattices of higher oxidation number than of the lattices of lower oxidation number when the oxide ions are replaced by sulfide ions. This is due to the considerable anion–anion repulsion introduced when one tries to crowd the large sulfide ions around a small metallic ion.

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[12] B. M. Abraham and N. R. Davidson, Manhattan District Paper CN-3001, May, 1945.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

α-Halo Ketones. III. Solid–Liquid Equilibrium in the System 2-Chloro-3-heptanone and 4-Chloro-3-heptanone[1]

BY J. D. NEWKIRK AND J. G. ASTON

The solid–liquid equilibrium diagram for the system 2-chloro-3-heptenone (B) and 4-chloro-3-heptanone (A) has been determined. Compounds A_3B_2 and AB are formed, the former, being unstable, giving a peritectic point.

In the present paper is presented the solid–liquid equilibrium phase diagram for the system 4-chloro-3-heptanone and 2-chloro-3-heptanone which has been determined experimentally for later use in ascertaining the composition of the product resulting from the direct chlorination of 3-heptanone.

Experimental

Preparation of Materials.—Both chloroketones were prepared by the method of Cason[2a,2b] whereby a chloroacid chloride is coupled with a cadmium alkyl. The compounds were fractionated through a column of about 20 theoretical plates. Purities and heats of fusion for both isomers were determined in a calorimeter type melting point apparatus developed by Aston and co-workers.[3]

The calorimetric data thus obtained assuming solid insolubility of the impurity, indicated that for 4-chloro-3-heptanone $\Delta H_f = 3092$ cal./mole, $T_0 = 212.05$°K. and 96.02% purity, while for 2-chloro-3-heptanone $\Delta H_f = 3613$ cal./mole, $T_0 = 225.90$°K. and 95.19% purity, where ΔH is the heat of fusion and T_0 the melting point of the pure compound calculated from the data.

Although the purities were low in both cases, lack of material and difficulty in crystallization prevented further purification by fractional crystallization.[3]

Apparatus and Method.—The phase diagram is shown in Fig. 1 and the data from which it was constructed in Table I.

TABLE I

COMPOSITION AND TEMPERATURE OF POINTS ON PHASE DIAGRAM

Point	Composition, mole % B	Liquidus point, °C.
1	0	210.22
2	9.09	207.67
3	23.1	203.18
4	33.3	205.95
5	41.2	210.06
6	47.4	210.58
7	53.5	210.58
8	62.2	213.72
9	50.0	210.87
10	55.6	210.99
11	62.5	213.71
12	71.5	216.61
13	83.4	219.92
14	100	224.21

The data assembled for the phase diagram were deter-

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[1] The first two papers were: I, Aston and Greenburg, THIS JOURNAL, **62**, 2590 (1940); II, Greenburg and Aston, *ibid.*, **62**, 3135 (1940).

[2] (a) Cason, *ibid.*, **68**, 2078 (1946); (b) Aston and Newkirk, *ibid.*, **73**, 3900 (1951).

[3] Aston, Fink, Tooke and Cines, *Ind. Eng. Chem., Anal. Ed.*, **19**, 218 (1947).