

Lawrence Berkeley National Laboratory

Recent Work

Title

The Reaction of Uranium Oxides with Sulfur Monochlorides

Permalink

<https://escholarship.org/uc/item/1f9195vg>

Author

Brewer, Leo

Publication Date

1948-08-01

UNIVERSITY OF
CALIFORNIA

*Radiation
Laboratory*

TWO-WEEK LOAN COPY

*This is a Library Circulating Copy
which may be borrowed for two weeks.
For a personal retention copy, call
Tech. Info. Division, Ext. 5545*

BERKELEY, CALIFORNIA

UCRL-163
22

DISCLAIMER

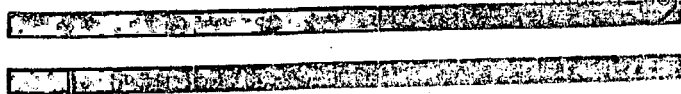
This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

UNIVERSITY OF CALIFORNIA
RADIATION LABORATORY

Cover Sheet
Do not remove

INDEX NO. UCRL-163
This document contains 8 pages
and plates of figures.
This is copy 90 of 105 Series A

Issued to: UCRL

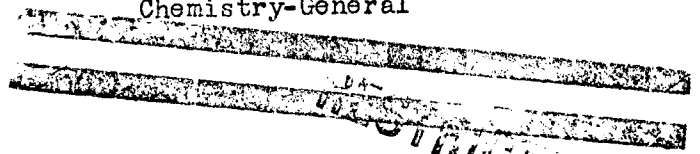


RESTRICTED
CLASSIFICATION AUTHORITY
OF THE DISTRICT ENGINEER
BY THE DECLASSIFICATION COMMITTEE

Each person who received this document must sign the cover sheet in the space below.

Route to	Noted by	Date	Route to	Noted by	Date
	<i>Wilson</i>	<i>8/17/48</i>			
	<i>J.W. J.</i>	<i>"</i>			
	<i>[Signature]</i>				

Chemistry-General



CLASSIFICATION CANCELLED BY AUTHORITY
UNIVERSITY OF CALIFORNIA OF THE DISTRICT ENGINEER
BY THE DECLASSIFICATION COMMITTEE

Radiation Laboratory

The Reaction of Uranium Oxides with Sulfur Monochlorides

by

Leo Brewer

Special Review of Declassified Reports

Authorized by USDOE JK Bratton

Unclassified TWX P182206Z May 79

REPORT PROPERLY DECLASSIFIED

<u>J N Green</u>	<u>8/16/79</u>
Authorized Derivative Classifier	Date
<u>R O N Ashunt</u>	<u>8/17/79</u>
By	Date

31 July 1948

Berkeley, California

Standard Distribution

Argonne National Laboratory	
Armed Forces Special Weapons Project	
Atomic Energy Commission, Washington	
Battelle Memorial Institute	
Brookhaven National Laboratory	
Carbide & Carbon Chemicals Corp. (K-25 Area)	
Carbide & Carbon Chemicals Corp. (Y-12 Area)	
Columbia University (Failla)	
General Electric Company	
Hanford Directed Operations	
Iowa State College	
Kellex Corporation	
Los Alamos	
Massachusetts Institute of Technology	
Monsanto Chemical Company, Dayton	
National Bureau of Standards	
Naval Radiological Defense Laboratory	
NEPA	
New York Directed Operations	
Oak Ridge National Laboratory	
Patent Advisor, Washington	
Technical Information Division, ORDO	
UCLA Medical Research Laboratory, (Warren)	
University of California Radiation Laboratory	
University of Rochester	
Western Reserve University (Friedell)	
Chicago Directed Operations	
Declassification Procedure	
Declassification Officer	
Publications Officer	
Patent Dept.	
E. O. Lawrence	
Area Manager	
Information Division	
	10-11
	12
	13-22
	23-26
	27-30
	31
	32-35
	36-42
	43
	44-45
	46-48
	49
	50-51
	52-53
	54
	55
	56-57
	58-69
	70
	71-85
	86
	87-91
	92-93
	94
	95
	96-99
	100
	101-102
	103
	104
	105

Total

105

Information Division
Radiation Laboratory
University of California
Berkeley, California

Copy Nos.

CLASSIFICATION CANCELLED BY AUTHORITY
OF 1-8
BY THE D9 CLASSIFICATION COMMITTEE
10-11

The Reaction of Uranium Oxides with Sulfur Monochloride

Leo Brewer

CLASSIFICATION CANCELLED BY AUTHORITY
OF THE DISTRICT ENGINEER
BY THE DECLASSIFICATION COMMITTEE

Abstract

Thermodynamic calculations are made to determine the
result of reacting uranium oxides with S_2Cl_2 .

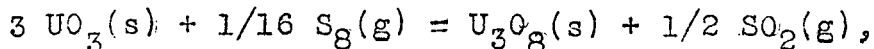
The Reaction of Uranium Oxides with Sulfur Monochloride

Leó Brewer

It is desired to use available thermodynamic data to calculate the result of the reaction of S_2Cl_2 with uranium oxides at 400-500°K.

One must first establish the sulfur and sulfur compound species which will be of importance. Brewer⁽¹⁾ states that S_2Cl_2 vapor is largely undecomposed below 1000°K. Using the data given by Brewer⁽¹⁾, Brewer, Bromley, Gilles and Lofgren⁽²⁾, Yost and Russell⁽³⁾, the National Bureau of Standards⁽⁴⁾ and Kelley⁽⁵⁾, one can calculate that S_2Cl_2 vapor at its atmospheric boiling point of 411°K contains about 10^{-1} atm $S_2Cl_2(g)$, 10^{-2} atm $S_8(g)$, $10^{-5.5}$ atm $Cl_2(g)$ and 10^{-3} atm $S_6(g)$. If oxygen is introduced into the system in small amounts, one can show that SO_2 is the main species with the $SOCl_2$ partial pressure being about 1 percent of the SO_2 partial pressure under these conditions. The SO_2Cl_2 partial pressure would be less than 0.1 percent of the SO_2 partial pressure. The SO partial pressure can not be accurately calculated, but it undoubtedly would be a minor species under these conditions.

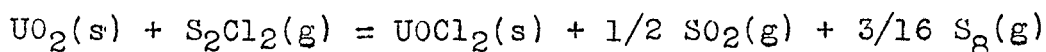
With the Cl_2 partial pressure or the $(S_2Cl_2)/(S_2Cl_2)$ ratio and with the $(SO_2)/(S_8)$ ratio fixed, one can calculate what oxidation state of uranium we will obtain. Using the data for uranium compounds given by Brewer, Bromley, Gilles and Lofgren⁽⁶⁾, one can show first that for a pure oxide phase, reduction will occur to the UO_2 phase. Thus for the reaction



one calculates at 500°K that $\Delta F_{500} = -29.9$ kilocalories or

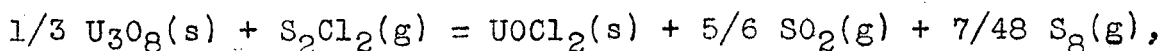
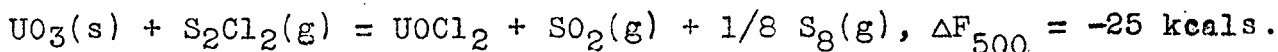
$(SO_2)^{1/2}/(S_8)^{1/16} = 10^{13}$. At 500°K, one would have around 10^{-2} atm S_8 present in $S_2Cl_2(g)$ at one atmosphere pressure. Thus one would have to maintain a SO_2 partial pressure of 10^{26} atm to prevent reduction. Further calculations of this sort show that the reduction must take place even further. Thus with 10^{-2} atm S_8 at 500°K, more than 4 atm SO_2 would be required to prevent reduction from the lower end of the U_3O_8 solid solution range to the upper end of the UO_2 solid solution range at $UO_{2.25}$. Thus, it is quite clear that with an excess of S_2Cl_2 present, one would definitely get reduction to the UO_2 solid solution range if one had a pure oxide phase.

However, one might expect the oxide to be converted to an oxy-chloride phase. Again using the data given for uranium compounds by Brewer, Bromley, Gilles and Lofgren⁽⁶⁾, one can show that the reaction

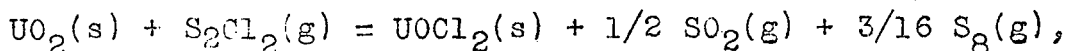


takes place quite readily, and as in the case of the pure oxides, one can show that the higher oxy-chlorides will be reduced under these conditions to $UOCl_2$ or the tetravalent state.

From the above one can definitely say that the first step upon adding S_2Cl_2 to uranium oxides at 500°K is given by the following equations:



$$\Delta F_{500} = -13 \text{ kcal.}$$

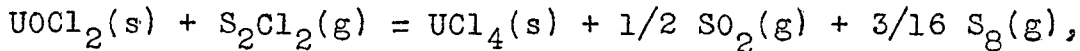


$$\Delta F_{500} = -12 \text{ kcal.}$$

Thus if only one mole of S_2Cl_2 is added per gram atom of

uranium, one will obtain UOCl_2 . If an excess of S_2Cl_2 is present, one can expect conversion of the UOCl_2 to a pure uranium chloride.

For example, for the reaction



one calculates $\Delta F_{500} = -9$ kcal. With S_8 and SO_2 maintained each at one atmosphere, UOCl_2 will still be completely converted to UCl_4 unless the S_2Cl_2 partial pressure falls below about 10^{-4} atm at around 500°K . We must now check the possibility of the formation of higher chlorides of uranium. This will be determined by the chlorine partial pressure. We have noted above that about $10^{-5.5}$ atm Cl_2 are found in equilibrium with 1 atm S_2Cl_2 at 411°K and this is raised to about 10^{-5} atm around 500°K .

Heats of formation are available for UCl_4 , UCl_5 and UCl_6 , but entropies are available only for UCl_4 and UCl_6 . If we, for a moment, neglect UCl_5 , we calculate for the equilibrium

$\text{UCl}_6(\text{s}) = \text{Cl}_2(\text{g}) + \text{UCl}_4(\text{s})$, $\Delta F_{500} = 5.6$ kcal or a chlorine partial pressure of $10^{-2.5}$ atm required to convert $\text{UCl}_4(\text{s})$ to $\text{UCl}_6(\text{s})$. Obviously, the chlorine partial pressure in S_2Cl_2 vapor is much too small to result in the formation of $\text{UCl}_6(\text{s})$. Even the partial pressure of UCl_6 vapor will be small in the presence of $\text{S}_2\text{Cl}_2(\text{g})$ and $\text{UCl}_4(\text{s})$. It would be around 10^{-3} atm at 500°K .

Since the entropy of UCl_5 is not known, it is not possible to make a very precise calculation, but using the estimate given by Brewer, Bromley, Gilles and Lofgren⁽⁶⁾, gives one $\Delta F = 5.8$ kcal for $\text{UCl}_5(\text{s}) = \text{UCl}_4(\text{s}) + 1/2 \text{Cl}_2(\text{g})$. This would indicate that a chlorine partial pressure of 10^{-5} atm would produce UCl_5 from UCl_4 . Since this corresponds to the Cl_2 partial pressure in $\text{S}_2\text{Cl}_2(\text{g})$ at one atmosphere, S_2Cl_2 is almost capable of producing UCl_5 . If there

is not a large excess of S_2Cl_2 present, the S_8 formed in the conversion of the oxide to $UOCl_2$ would reduce the Cl_2 partial pressure sufficiently to prevent possibility of formation of UCl_5 . The only possibility of formation of UCl_5 is in the case of the use of a very large excess of S_2Cl_2 over that required for conversion of the uranium oxide to UCl_4 with the temperature as low as possible and even in that case, it appears very unlikely that the oxidizing power of the S_2Cl_2 is quite high enough to produce UCl_5 .

In conclusion, thermodynamic calculations indicate that the treatment of uranium oxides with S_2Cl_2 at 400-500°K will produce $UOCl_2$ if there is an excess of oxide and it will produce UCl_4 if there is an excess of S_2Cl_2 . There is no possibility of production of UCl_6 although there is a slight possibility that UCl_5 might be formed if a very large excess of S_2Cl_2 were used at temperatures considerably below 500°K.

References

- (1) L. Brewer, Declassified AEC Paper MDDC-438-G.
- (2) L. Brewer, L. A. Bromley, P. W. Gilles and N. L. Lofgren, Declassified AEC Paper MDDC-438-F.
- (3) D. M. Yost and H. Russell, "Systematic Inorganic Chemistry" Prentice-Hall, New York, 1944.
- (4) National Bureau of Standards Selected Values of Chemical Thermodynamic Properties, December 31, 1947.
- (5) K. K. Kelley, Bureau of Mines Bulletin, 406 (1937).
- (6) L. Brewer, L. A. Bromley, P. W. Gilles and N. L. Lofgren, Declassified AEC Paper MDDC-1543 (BC-82), April 1, 1947.