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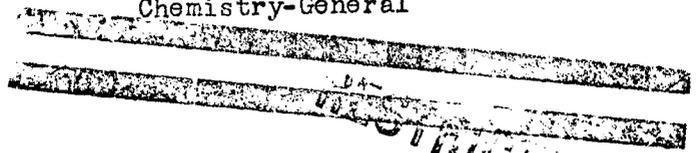
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Chemistry-General



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Radiation Laboratory

The Reaction of Uranium Oxides with Sulfur Monochlorides

by

Leo Brewer

Special Review of Declassified Reports

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The Reaction of Uranium Oxides with Sulfur Monochloride

Leo Brewer

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Abstract

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

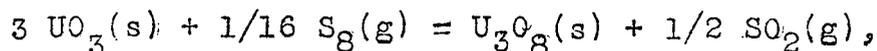
The Reaction of Uranium Oxides with Sulfur Monochloride

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.

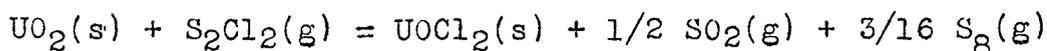
With the Cl_2 partial pressure or the $(S_2Cl_2)/(S_2Cl_2)$ ratio and with the $(SO_2)/(S_8)$ ratio fixed, one can calculate what oxidation state of uranium we will obtain. Using the data for uranium compounds given by Brewer, Bromley, Gilles and Lofgren⁽⁶⁾, one can show first that for a pure oxide phase,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

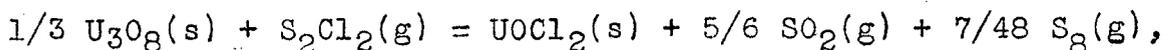
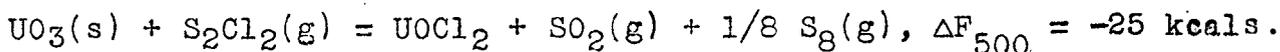
$(SO_2)^{1/2}/(S_8)^{1/16} = 10^{13}$. At 500°K, one would have around 10^{-2} atm S_8 present in $S_2Cl_2(g)$ at one atmosphere pressure. Thus one would have to maintain a SO_2 partial pressure of 10^{26} atm to prevent reduction. Further calculations of this sort show that the reduction must take place 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

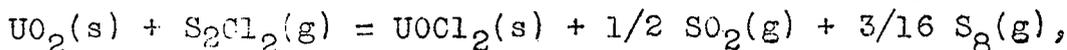


takes place quite readily, and as in the case of the pure oxides, one can show that the higher oxy-chlorides will be reduced under these conditions to $UOCl_2$ or the tetravalent state.

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:



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

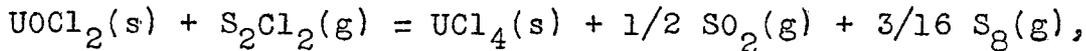


$$\Delta F_{500} = -12 \text{ kcal.}$$

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.